United States Patent Office

2,859,132

Patented Nov. 4, 1958

2,859,132

GAS PLATING USING NITROUS OXIDE

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No Drawing. Application May 9, 1956
Serial No. 583,637

16 Claims. (Cl. 117—107)

This invention relates to the art of deposition of metals. More particularly the invention appertains to gas plating of metals using heat-decomposable gaseous metal compounds.

Deposition of protective metal coatings has been accomplished heretofore by pyrolitic gas plating methods but a mat or dull finish is usually obtained; for many purposes, however, it is desired that the metal deposit have a high luster.

It is accordingly a principal object of this invention to provide a method of gas plating whereby bright metal deposits having a high luster are produced.

Another object is to provide a method of gas plating materials to metallize them wherein the plating is carried out in the presence of a brightener which alters the physical characteristic of the deposit whereby the metal coating is smooth and bright.

A further object is to provide a method of gas plating which produces metal deposits having increased light reflectance as compared to that exhibited by ordinary gas plating methods and which produce dull, non-reflective metal deposits.

Another object is to produce a smooth, even metal coating, e. g. nickel, that can be subsequently electroplated with copper without the necessity of first abrading the surface.

Still another object of the invention is to provide metal coatings which exhibit a mirror-like reflectance by gas plating using metal compounds such as metal carbonyls and the like, which are heat-decomposed in contact with the heated surface to be metal coated, the surface being heated to a temperature sufficient to cause the gaseous metal compound to decompose and the metal constituent to deposit on the heated surface.

These and other objects and advantages will be apparent to those skilled in the art from the following description.

Briefly, in accordance with this invention, it has been discovered that by carrying out gas plating employing a heat-decomposable metal compound, e. g., metal carbonyl and a volatile compound containing nitrogen, that metal deposits which are smooth and mirror-like are produced. The method has been found to be particularly useful in gas plating nickel from nickel carbonyl to produce smooth, bright metal deposits.

Gaseous nitrogen compounds found to be effective brighteners in gas plating metal deposits are the volatile amines, for example ammonia, or compounds which release NH_3 on being heated such as methanamine (hexamethylene tetramine). Nitrous oxide (N_2O) gas also has been found to produce bright metal deposits. Small quantities of these compounds need only be used. For example 0.5 to 15% by volume of the brightener in the gaseous plating mixture has been found to be effective.

Bright metal deposits may be obtained using from 0.5 to 15% by volume of the brightener but the best results are obtained with nickel carbonyl when the gaseous nickel carbonyl plating gas contains about 10% by volume of brightener such as nitrous oxide or sublimed methenamine or ammonia.

While the reason for the enhanced results obtained using metal carbonyl containing these gaseous compounds as brighteners has not been established it is believed that the presence of nitrogen as NH_3 or N_2O provides a reducing and deposition-modifying atmosphere during gas plating which results in the production of bright metal deposit. It is also believed that the presence of the brightener compound produces a grain refining effect. Any one or all of these factors may account for the production of the highly reflective metal deposits using metal carbonyl and the gaseous nitrogenous brightener. The bright metal gas plating deposit may be produced on various materials, e. g., fibers made of glass, wire or the like inorganic material as well as synthetic fibers, filaments or fabrics made of rayon, nylon and the like.

Metals to be deposited may be introduced as gaseous metal carbonyls or vaporized solutions of certain of the metal carbonyls in readily vaporizable solvents (e. g. petroleum ether) also nitroxyl compounds, nitrosyl carbonyls, metal hydrides, metal alkyls, aryls or aralkyls, metal halides, and the like. Illustrative compounds of the carbonyl type are carbonyls of nickel, iron, chromium, molybdenum, tungsten, cobalt, and ruthenium.

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; and halides 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 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 range of from 375° F. to 425° F.

Heating of objects to temperatures in the above range may be accomplished in many ways depending upon the type of object being plated. If the object is stationary, the object may be set on a resistance heater or so-called hot plate. If the object is moving, it may be heated by passing over resistance heaters, or by infra-red light, or by passage of electricity therethrough either of standard or high frequency or like means.

The material to be coated, where necessary, is cleaned of foreign matter prior to gas plating, this may be effected mechanically or chemically, or by employing both, depending upon the material being gas plated. Where refractory fibers, such as glass are to be gas plated with metal, the same may be effected by subjecting the hot glass fiber as it is continuously drawn from a molten batch of glass into fibers. In the gas plating or organic fibers or material made of such fibers, it, of course, is

necessary to control the temperature and time of heating the fibers whereby the gas plating can be attained without injuring the material.

Inert carrier gas such as carbon dioxide helium, nitrogen and hydrogen which is free of oxygen preferably is used as a carrier gas, generally making up from about 25% to 70% of the gaseous medium of the gas plating chamber, the remainder being gaseous metal carbonyl and nitrous oxide.

The invention is further illustrated by the following examples.

Example I

Copper discs were wire brushed to clean the surface. The discs were positioned on the hot plate and heated to a temperature of approximately 400° F. Into the housing was fed a mixture of vaporous nickel carbonyl admixed with nitrous oxide (10% by volume being nitrous oxide), and argon gas, the carbonyl being present in the proportions of approximately 5 ozs. of carbonyl per cubic foot of argon.

The copper discs were plated in accordance with standard operating procedure of passing approximately 3 cubic feet of gas mixture per hour through the housing, for a period of 2 minutes, at the end of which time a plating of 0.0012 inch of nickel was obtained which was bright and light reflective.

Example II

Glass fiber treated as in the previous operation is positioned on the hot plate and an identical gas mixture fed to the chamber. Inside the chamber the gas was maintained at a temperature of approximately 125° F. by the coolant. However, the gas circulated in the housing at a rate of about 60 feet per second due to the operation of the fan. The plating time was 2 minutes, as in Example I, and a smooth bright nickel deposit is produced.

Example III

Rayon fiber is treated as described in Example II, but maintaining the temperature of plating at between 180–190° F., and a nickel plated fiber is thereby produced.

Example IV

The process of Example I is repeated using molybdenum carbonyl gas in place of nickel cabonyl and gas plating in the presence of nitrous oxide to produce a bright smooth deposit of the metal.

Example V

The process of Example I is repeated using chromium carbonyl instead of nickel carbonyl and gas plating concurrently in an atmosphere containing nitrous oxide to produce a bright deposit of chromium.

Example VI

In this example the gas plating of nickel on glass fibers was carried out as described in Example I, except in place of nitrous oxide, there was substituted sublimed or gaseous methenamine.

Example VII

In this example a sheet or panel (2" x 4") made of plastic material (Bakelite sheet) was gas plated with nickel using nickel carbonyl as described in Example I. The brightener in this instance was brushed on the panel surface using an aqueous solution of formaldehyde (39% formaldehyde) and ammonia such as when heated during gas plating produced methenamine.

The nickel deposit obtained had a high luster and was uniformly bright.

Example VIII

The gas plating was carried out as described in Example I except instead of nitrous oxide ammonia gas (NH_3) was used as the brightening agent to produce a bright nickel deposit.

Example IX

In this example a panel or board molded from synthetic resin condensation product of ethylene glycol and terephthalic acid (Du Pont Mylar) is sandblasted and then vapor degreased by the application of trichlorethylene. The thus cleaned surface is sprayed lightly with a solution consisting (by weight) of 15 parts concentrated ammonium hydroxide (NH_4OH), 15 parts formalin (27% formaldehyde solution) and 80 parts ethyl alcohol. Thereafter the panel was placed in the gas plating chamber and heated to 280° F. and the chamber purged with carbon dioxide. The heated panel was then gas plated for six minutes with nickel carbonyl, the latter flowing at 2140 cubic centimeters per minute into the plating chamber.

The plated panel had a bright reflective surface finish.

Example X

A resin board was sandblasted and cleaned and gas plated using nickel carbonyl and brightener solution spray of formalin and ammonia in ethyl alcohol as described in Example IX. In this instance the plating gas mixture was diluted 50/50 by volume with carbon dioxide.

A bright metal deposit was obtained after six minutes gas plating similarly as in Example IX.

Example XI

Gas plating of nickel on resin board was carried out as described in Example IX, using a plating gas mixture consisting of 23 cc. of gaseous ammonia per minute and 3000 cc. carbon dioxide per minute. After gas plating for five minutes with panel heated to 285° F. a bright silvery coating deposit of nickel was obtained.

Example XII

In this example, a resin panel was cleaned and gas plated as described in Example IX, utilizing a plating temperature of 300° F. The plating gas consisted of a mixture flowing into the plating chamber per minute of

4800 cc. argon gas
23 cc. ammonia gas (NH_3)

After gas plating with the above mixture for five minutes the plated resin board was removed and exhibited a bright mirror-like deposit of nickel.

Although exhaustive tests have not been made, there is an indication that the compounds which function best as brightening agent in gas plating are those containing nitrogen and which have an affinity for oxygen, e. g. reducing compounds. A synergistic effect is believed to be produced by such nitrogen compounds, the same functioning both as a grain refining agent and deoxidizing agent to thus prevent darkening of the uniformly fine grain deposit. This effect is further substantiated by test runs made wherein hydrogen gas was used to provide a reducing atmosphere during gas plating, but this failed to produce bright mirror-like metal deposits, and such as produced using NH_3 and N_2O as brightening agents. Tests also have shown that the use of inert gases such as argon, helium, nitrogen, carbon dioxide, etc. are not effective as brighteners. These gases are, however, useful as carrier gases for the metal bearing gases. Further experimental runs have indicated that a mixture of inert gas with a deoxidizer or reducing gas, such as the brightening compounds of nitrogen aforementioned work best where a bright smooth deposit of metal is desired.

When gas plating with heavy metals, e. g. carbonyls of nickel, chromium, copper, molybdenum, etc., it is not necessary to have the plating chamber free of water vapor and in some instances the presence of a small amount of

water vapor is beneficial. In the case of gas plating of light metals, such as aluminum, magnesium or lithium which readily react with water, it is necessary to provide a moisture free atmosphere in the gas plating chamber.

As a carrier gas, argon is better than nitrogen because of the tendency of nitrogen to form nitrides. Argon is also a conductor of electricity and thus assists in ionizing the gaseous metal compound during gas plating. Other relatively inert gases which may be used are neon, krypton and xenon.

It will be understood that while there have been given herein certain specific examples of the practice of this invention, it is not intended thereby to have this invention limited to or circumscribed by the specific details of materials, proportions, or conditions herein specified, in view of the fact that this invention may be modified according to individual preference or conditions without necessarily departing from the spirit of the disclosure and the scope of the appended claims.

What is claimed is:

1. The method of gas plating bright, smooth metal coatings which comprises bringing a mixture of metal-bearing vapor and a gaseous brightener compound containing nitrogen into contact with the article to be plated, and heating the gaseous mixture to a temperature sufficient to cause decomposition of the metal bearing vapor and deposition of the metal constituent onto the surface of the article, said nitrogen-containing compound being selected from the group consisting of ammonia, methenamine, nitrous oxide, and ammonium hydroxide.

2. The method of gas plating bright, smooth metal coatings which comprises bringing a mixture of gaseous metal carbonyl and a gaseous brightener compound containing nitrogen into contact with the article to be plated, and heating the gaseous mixture to a temperature sufficient to cause decomposition of the gaseous metal carbonyl and deposition of the metal constituent onto the surface of the article, said nitrogen-containing compound being selected from the group consisting of ammonia, methenamine, nitrous oxide, and ammonium hydroxide.

3. The method of gas plating surfaces of material to provide the same with a light reflective coating of metal which comprises the steps of heating said surface to be plated to a temperature sufficient to cause decomposition of a heat-decomposable metal-bearing gaseous compound brought in contact therewith, and while thus heated contacting said heated surface with a heat-decomposable metal-bearing gaseous compound in the presence of a brightening agent, said brightening agent being a gaseous compound containing nitrogen and selected from the group consisting of gaseous ammonia and nitrous oxide.

4. The method of gas plating metal onto surfaces of material to provide the same with a light reflective coating of metal which comprises the improvement step of heating the material to be plated and contacting the same while heated with vaporizable metal carbonyl admixed with nitrous oxide, said heating being sufficient to cause decomposition of the metal carbonyl and deposition of the metal onto the surface of the material.

5. The method of gas plating metal onto surfaces of material to provide the same with a light reflective coating of metal which comprises the improvement step of heating the material to be plated and contacting the same while heated with vaporizable metal carbonyl admixed with methenamine, said heating being sufficient to cause decomposition of the metal carbonyl and deposition of the metal onto the surface of the material.

6. The method of gas plating nickel onto surfaces of rayon fiber to provide the same with a light reflective coating of metal which comprises the improvement step of heating the rayon fibers to be plated and contacting the same while heated with vaporizable nickel carbonyl admixed with a brightener, said brightener comprising a compound of nitrogen, and said heating being sufficient to cause decomposition of the nickel carbonyl and deposition of the nickel onto the surface of the rayon fibers, said nitrogen compound being selected from the group consisting of ammonia, methenamine, nitrous oxide, and ammonium hydroxide.

7. The method of gas plating molybdenum carbonyl onto surface of material to provide the same with a light reflective coating of metal which comprises the improvement step of heating the material to be plated and contacting the same while heated with vaporizable molybdenum carbonyl admixed with nitrous oxide, said heating being sufficient to cause decomposition of the molybdenum carbonyl and deposition of the molybdenum carbonyl onto the surface of the material.

8. The method of gas plating chromium carbonyl onto surfaces of material to provide the same with a light reflective coating of metal which comprises the improvement step of heating the material to be plated and contacting the same while heated with vaporizable chromium carbonyl admixed with nitrous oxide, said heating being sufficient to cause decomposition of the chromium carbonyl and deposition of the chromium carbonyl onto the surface of the material.

9. In the method of gas plating metals onto surfaces by bringing metal bearing gaseous compound into contact with the surface to be plated and heating said metal bearing gaseous compound to a temperature sufficient to cause it to decompose and deposit the metal constituent onto the surface to be plated, and carrying out said deposition in the presence of nitrous oxide.

10. The method of gas plating metal onto surfaces of material to provide the same with a light reflective coating of metal which comprises the improvement step of heating the material to be plated and contacting the same while heated with vaporizable metal carbonyl admixed with methenamine, said heating being sufficient to cause decomposition of the metal carbonyl and deposition of the metal onto the surface of the material, said methenamine being introduced as an aqueous solution of formaldehyde and ammonia which upon heating releases methenamine.

11. In the method of gas plating metals onto surfaces by bringing metal bearing gaseous compound into contact with the surface to be plated and heating said metal bearing gaseous compound to a temperature sufficient to cause it to decompose and deposit the metal constituent onto the surface to be plated, and carrying out said deposition in the presence of ammonia gas.

12. In the method of gas plating metals onto surfaces bringing metal bearing gaseous compound into contact with the surface to be plated and heating said metal bearing gaseous compound to a temperature sufficient to cause it to decompose and deposit the metal constituent onto the surface to be plated, and carrying out said deposition in the presence of a gaseous compound of nitrogen which has an affinity for oxygen, said nitrogen compound being selected from the group consisting of ammonia, methenamine, nitrous oxide and ammonium hydroxide.

13. In the method of gas plating metals onto surfaces by bringing metal bearing gaseous compound into contact with the surface to be plated and heating said metal bearing gaseous compound to a temperature sufficient to cause it to decompose and deposit the metal constituent onto the surface to be plated, and carrying out said deposition in the presence of a mixture of ammonium hydroxide and formaldehyde.

14. In the method of gas plating metals onto surfaces by bringing metal bearing gaseous compound into contact with the surface to be plated and heating said metal bearing gaseous compound to a temperature sufficient to cause it to decompose and deposit the metal constituent onto the surface to be plated, and carrying out said deposition in the presence of a spray solution consisting of a mixture by weight of 15 parts concentrated ammonium hydroxide, 15 parts formalin and 80 parts ethyl alcohol.

15. In the method of gas plating metals onto surfaces by bringing metal bearing gaseous compound into contact with the surface to be plated and heating said metal bearing gaseous compound to a temperature sufficient to cause it to decompose and deposit the metal constituent onto the surface to be plated, and carrying out said deposition in the presence of ammonia and argon gases.

16. As an article of manufacture having a bright metal coating and made in accordance with the method of claim 1.

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