May 21, 1957 B. OSTROFSKY ET AL 2,793,140

METHOD OF GAS PLATING WITH A CHROMIUM COMPOUND AND PRODUCTS OF THE METHOD

Filed Oct. 20, 1953 2 Sheets-Sheet 1

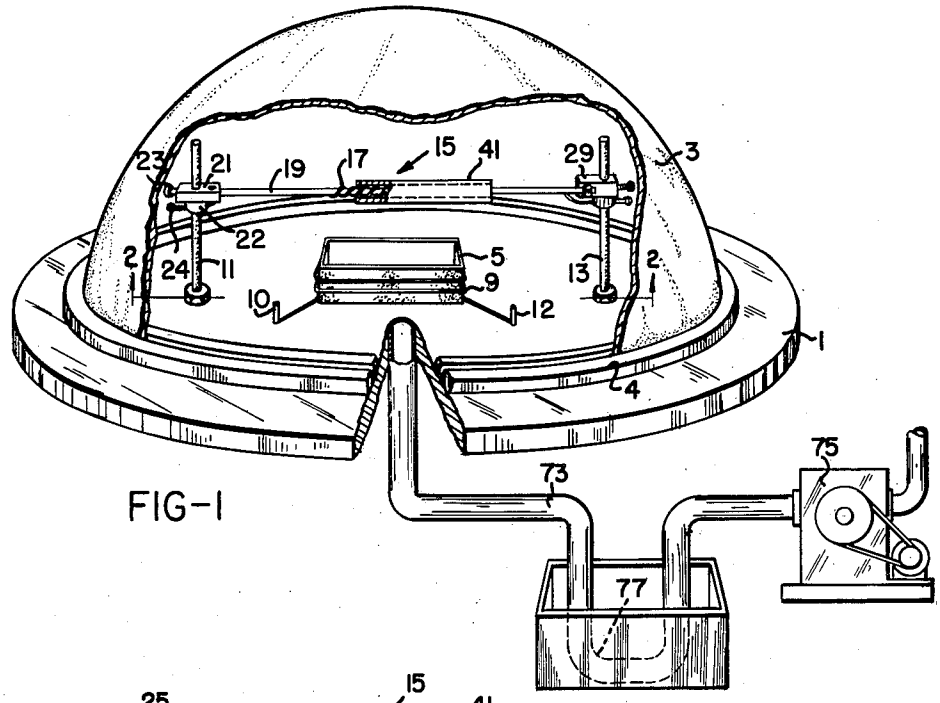


FIG-1

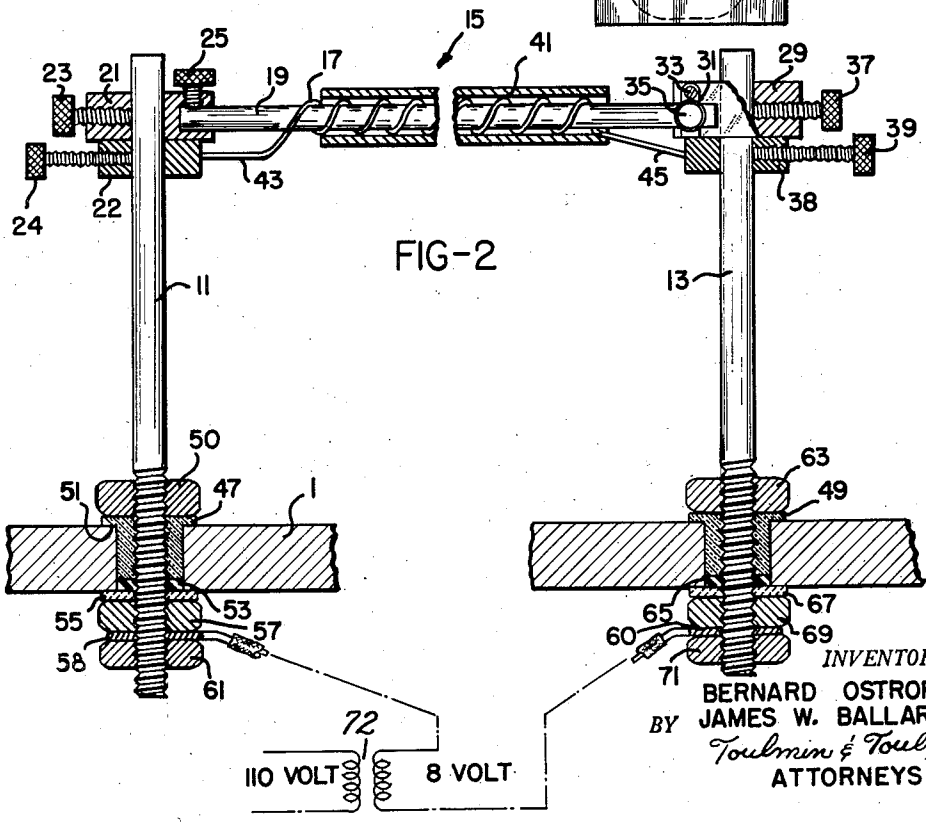


FIG-2

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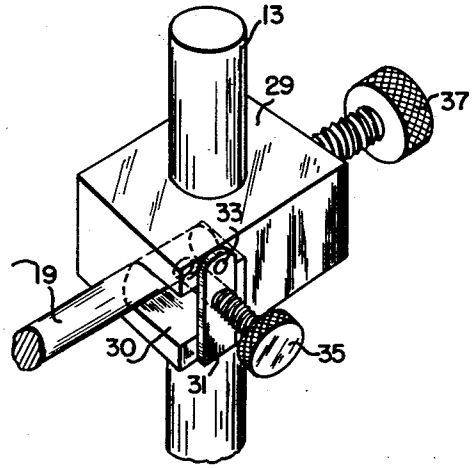


FIG.-3

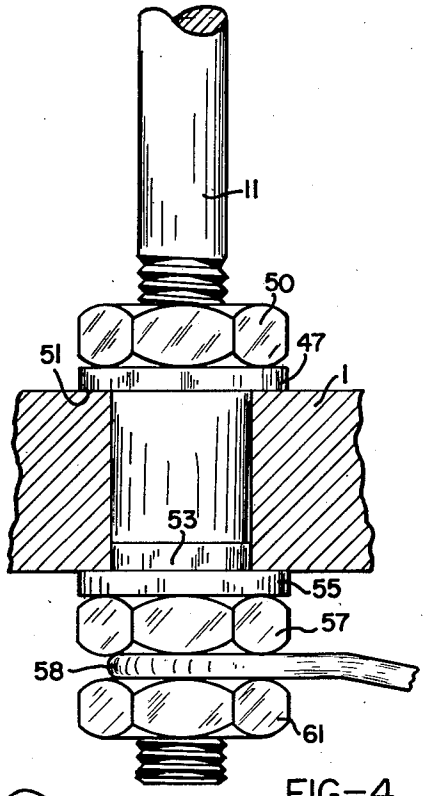


FIG.-4

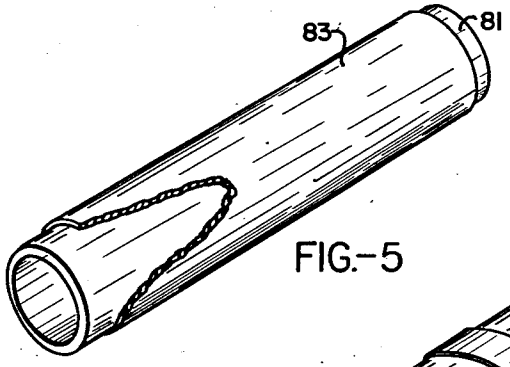


FIG.-5

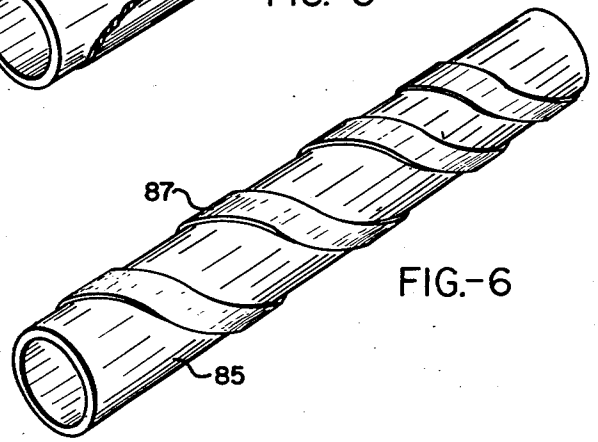


FIG.-6

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METHOD OF GAS PLATING WITH A CHROMIUM COMPOUND AND PRODUCTS OF THE METHOD

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15 Claims. (Cl. 117—107)

This invention relates to the production of electrical resistance elements and particularly to a method of manufacturing the resistance elements by deposition from a gaseous state of an electrically conductive strata on a nonconductive material.

Chromium hexacarbonyl is a colorless crystalline material which is readily sublimed; when sufficiently heated the sublimed or gaseous carbonyl normally decomposes into the metal and oxides of carbon. Accordingly chromium hexacarbonyl has heretofore been considered as of some utility in the gas plating of articles of manufacture.

In prior art processes it has been customary to employ the chromium hexacarbonyl with carrier gases and to effect the heat decomposition of the carbonyl at relatively low temperatures—that is on the order of about 300° F.

It is a primary object of the present invention to describe a novel process for the gas plating of electrical insulating materials with chromium hexacarbonyl.

It is an important object of this invention to describe a novel coating material deposited by the thermal decomposition of chromium hexacarbonyl.

It is a particular object of this invention to describe a novel resistor element attained by the thermal decomposition of chromium hexacarbonyl on a ceramic material.

It is a further object of this invention to describe apparatus useful in the process of invention.

These and other allied objectives are attained by volatilizing chromium hexacarbonyl at low pressures and contacting an electrical insulating material maintained at a temperature of at least 200° C. (392° F.) with the vapors.

In the preferred procedure the chamber in which the deposition is effected is maintained at a very low pressure, preferably about one millimeter of mercury, and the atmosphere of the chamber is substantially completely an atmosphere of chromium hexacarbonyl and decomposed gaseous products of the carbonyl.

Under the conditions outlined above the material deposited from the gaseous state appears shiny and metallic during the actual deposit, but upon cooling the coating on the ceramic workpiece is a dull gray-black in color and is not metallic appearing.

The coating on the ceramic or other insulating material is electrically conductive and the product of the invention—that is the ceramic with the coating material thereon—is highly useful as an electrical resistance element. The conductivity of the material increases with the depth of coating and by controlling the depth any degree of conductivity may be achieved.

The depth of the coating is controllable by controlling the time of exposure of the workpiece to the atmosphere of the hexacarbonyl. A longer time of exposure at any given temperature of the workpiece results in a greater thickness of coating and consequently a lower resistance value of the resistance elements produced; a very short time of coating may result in a substantially

monomolecular layer of the deposited material, and consequently a relatively thin coat is occasioned and an element of relatively high electrical resistance is thereby produced. The resistance of the product may also be adjusted by providing the deposited coat in a spiral form as will be noted more particularly hereinafter.

Increasing the temperature of the workpiece above 200° C. increases the rate of deposition and a temperature of 350–450° C. (662–842° F.) is preferred as the action at lower temperatures is relatively slow. At about 400° C. a coating, on a hollow ceramic cylinder 1 inch in length and about 5/16 inch outside diameter, having a resistance of about 5 ohms is attained in about 2 to 3 minutes plating time in the process of invention.

The reactions which occur under the conditions set forth above are apparently, at the relatively high temperature and low pressure of the carbonyl employed, productive of mixtures of some nitrides in chromium metal, and these films are deposited on the workpiece and form the electrically conductive coating thereof. To exclude nitride formation as much as possible the plating apparatus is maintained substantially free of air.

The apparatus most useful for the process of invention involves an arrangement in which the volatilization of the carbonyl is carried out in close proximity to the ceramic base material. Thus the possibility of contamination of the carbonyl is substantially excluded and close control of the operation is facilitated.

The equipment includes apparatus for the continuous application of vacuum to the plating chamber and the exhaust gases of the decomposition of the carbonyl as well as any undecomposed carbonyl are withdrawn from the plating area constantly—the undecomposed gas is preferably trapped out for reuse.

In the apparatus a plating chamber is defined by a support and a closure member thereon; the source of the carbonyl is preferably mounted on the support and the object to be plated is mounted thereabove in spaced relation with the support and closure member. Most suitably only one conduit is provided, that being for the passage outwardly of the chamber of exhaust gases.

The invention will be more fully understood by reference to the following detailed description and accompanying drawings wherein:

Figure 1 is a perspective view partially in section of the apparatus of invention;

Figure 2 is a sectional view taken on line 2—2 of Figure 1;

Figure 3 is a perspective view of a portion of the structure of Figure 2;

Figure 4 is an enlarged view partially in section of a portion of the structure of Figure 2;

Figure 5 is a perspective view partially in section illustrating one embodiment of the product of invention; and

Figure 6 illustrates in perspective another embodiment of the product of invention.

Referring to the drawings there is shown at 1 a support in the form of a metal plate of iron or steel over which a dome 3 extends to define with the plate a plating chamber. The plate 1 is preferably of steel as it must have sufficient strength to resist the high stresses applied thereto; and the dome 3 which is preferably transparent and of heavy glass or plastic material such as Lucite, rests on a rubber sealing ring 4 and is adapted to air tightly seal the interior from the atmosphere and to itself resist the heavy pressures exerted by the atmosphere when the interior is evacuated.

Positioned on the plate 1 is a glass receptacle 5 adapted to contain chromium hexacarbonyl which is volatilizable when subjected to heat; the particular mode of supplying heat to receptacle 5 is not critical but that method which exposes the least apparatus to the plating chamber

is preferred. As shown receptacle **5** has a resistance heating coil **9** preferably of Nichrome wound therearound and the opposite ends thereof are secured in an electrically conductive manner to rods **10, 12** which pass in an insulated manner through plate **1** and are connected across a source of voltage (not shown). A six volt source of supply is adequate in conjunction with a few turns of Nichrome to permit raising the hexacarbonyl to the sublimation temperature (about 100° C.).

Also passing through the plate **1** are a pair of brass rods **11, 13** which are supported by the plate in opposed and insulated relation. Passing between the rods and removably secured thereto is a support for objects to be plated as indicated generally at **15**; the Nichrome resistance heating wire **17** is supported on an insulating or ceramic member **19** and the turns of the wire may be spaced or touching as desired. The member **19** is secured in an adjustably mounted block or electrically conductive securing member **21** fixed on rod **11** and screw **23** passes through the block to secure the same to the rod. Screw **25** secures the member **19** to the block; a collar **22** supports the block **21** and is itself retained by screw **24** on rod **11**.

The other end of the insulating member **19** is removably secured in electrically conductive block **29** which for purpose of removal is provided (Figure 3) with an opening **30** having a gate member **31** connected at **33** by a flange screw to the block; in the closed position a screw **35** engages the member **19** to retain the same in position. This block **29** is movably retained on rod **13** by screw **37** and a supporting collar **38** is retained by screw **39**.

Secured centrally of the member **19** and over the resistance heating wires **17** is a hollow cylindrical ceramic tube or body **41**, the external surface of which is to be contacted by the volatilized carbonyl from the receptacle **5**. The resistor wires contact the interior of the ceramic tube **41** directly and are supplied with current at 6–8 volts through leads **43, 45** attached respectively to blocks **21, 29** by screws or other suitable means to insure quick heating of the tube.

The rods **11, 13** where they pass through the plate **1** are insulated therefrom. For the purpose of insulation the plate is apertured to receive Bakelite or other suitable insulating plugs or bushings **47, 49**.

The bushing **47** is flanged at **51** and is retained against the surface of the plate **1** by the nut **50**; this bushing terminates within the lower end of the plate and is surrounded by a rubber ring **53** which is abutted and retained by a washer **55** of electrical insulating material such as Bakelite. The washer **55** is secured in position by metal nut **57** which is threaded on the lower portion of rod **11**. Packing nut **61** locks the nut **57** securely in place and secures the metal washer **58** through which current passes from the 8 volt source. The construction of the lower end of rod **13** is similar to that of rod **11** and includes the Bakelite plug **49** retained by nut **63**, rubber ring **65**, Bakelite washer **67** and nuts **69, 71**, and metal washer **60**.

The invention thus described provides that rods **11, 13** may be employed as conductors by connection across the secondary of transformer **72** which is fed from any suitable 110 volt source; plugs **47, 49** insulate the rods from the plate and avoid the possibility of short circuits.

As shown in Figure 1 conduit **73** is connected between the plate **1** and a vacuum pump **75**; trap **77** provides for the collection of undecomposed carbonyl while the exhaust gases of the thermal decomposition pass through the pump to the atmosphere.

Referring now to Figures 5 and 6 products of invention are illustrated. Thus ceramic body **81** has a conductive coating **83** thereon and this coating is adherent and extends over the whole outer surface. The conductivity of the structure of Figure 5 is determined and controlled by the depth or thickness of the coating.

The structure of Figure 6 includes a ceramic hollow body **85** which has thereon a continuous stripe of deposited coating **87** which stripe may be of any desired width; the pitch may also be varied as desired and accordingly control of the resistance is readily achieved. The stripe itself may be produced in any suitable manner as by masking off other adjacent areas to permit stripe formation.

In the production of the resistors or resistance elements with the apparatus arranged as in Figure 1 the chamber within the dome **3** is first evacuated to a pressure not greater than about 4 mm. of mercury. Higher pressures give rise to formation of chromium nitrides which are non-conductive and should be avoided.

When the evacuation is satisfactorily completed heat is applied to the glass vessel **5** and the temperature brought up to about 100° C. by means of the resistance heating arrangement already described and the carbonyl volatilizes to substantially fill the chamber. During this procedure the pump **75** is preferably operated to insure of maintaining the required vacuum conditions; while this may give rise to some loss of carbonyl the procedure is preferred to assure of optimum conditions and if properly trapped most of the carbonyl will be recovered.

Voltage is meanwhile applied to the transformer and the temperature of the ceramic body **41** raised to at least 200° C.; some deposition may occur at lower temperatures but it is generally spotty and does not result in a satisfactory product.

The gases of chromium hexacarbonyl which substantially fill the interior of the chamber may suitably exert a pressure of about one centimeter of mercury or slightly higher. An undue rise in pressure of the carbonyl occasions deposition in the dome and plate, causes loss of material and may yield a non-uniform deposit. Accordingly the pressure as decomposition takes place may vary slightly it is preferable to maintain the pressure in the chamber at about one centimeter of mercury during deposition.

The thickness of deposit is dependent upon the time of exposure and the temperature of the body being coated as well as the pressure of the plating gas. These are correlative factors and may be controlled to produce a desired coating thickness.

At thicknesses on a ceramic cylinder 1" in length and 5/16" outside diameter sufficient to give a resistance of greater than about 80 ohms the resistor has a positive coefficient of resistance; at resistances of less than about 70 ohms the temperature coefficient is definitely negative; between resistance values of about 70 and 80 ohms resistors having a substantially zero coefficient of resistance are obtained.

It will be understood that this invention is susceptible to modification in order to adopt it to different usages and conditions and accordingly it is desired to comprehend such modifications within this invention as may fall within the scope of the appended claims.

We claim:

1. In gas plating apparatus, a metallic support, a dome thereon defining therewith a plating chamber, a pair of rods passing through the metallic support in spaced relation and insulated from the support, an electrically non-conductive member connecting the rods together within the chamber and constructed and arranged to support an object to be plated, means to heat an object supported on the non-conductive member, and means to supply to an object within the chamber a heat decomposable metal bearing gas.

2. In gas plating apparatus, a metallic support, a dome thereon defining therewith a plating chamber, a pair of electrically conductive rods passing through the metal support in spaced insulated relation, means to supply an electric current to said rods, an electrically non-conductive member within the chamber extending between the rods and supported thereby, a resistance heating element

electrically connected between the rods and supported on the non-conductive member within the chamber, said non-conductive member and heating element being constructed and arranged to support and heat an object to be plated, and means to supply to an object to be plated a heat-decomposable metal bearing gas.

3. In gas plating apparatus, a metallic support, a dome thereon defining therewith a plating chamber, a pair of electrically conductive rods passing through the metal support in spaced insulated relation, means to supply an electric current to said rods, a ceramic tube member within the chamber extending between and supported by the rods, a resistance heating element connecting the rods and supported on the ceramic tube, said heating element and ceramic tube being constructed and arranged to receive thereover a tubular object to be plated, and means to supply to an object to be plated a heat decomposable metal-bearing gas.

4. In combination, in gas plating apparatus, a ceramic member, a resistance coil wound around the ceramic member, a pair of electrically conductive rods each in electrical contact with an end of said coil and in supporting relation with the ceramic member, and a dome-shaped plating chamber housing the ceramic member, coil and rods and having the rods extending to the outer side thereof.

5. In combination, in gas plating apparatus, a metal plate, metal rods passing through the plate in spaced relation, insulation means surrounding each of the rods and insulating the same from the plate, a dome defining with the plate a plating chamber, an electrically non-conductive member within the chamber supported between the rods, and resistance-heating means within the chamber wound around the non-conductive member and connecting the rods interiorly of the chamber.

6. In combination, in gas plating apparatus, a metal plate, a dome, means on the plate sealing the dome and plate to define a plating chamber, means to support an object to be plated within the chamber in spaced relation with the plate and dome, said means including a non-conductive member and a pair of electrically conductive rods supporting the member, and a source of a heat decomposable metal bearing plating gas within the chamber constructed and arranged on the plate and below the support means to supply the gas to an object to be plated.

7. In combination, in gas plating apparatus, a plate and a dome defining a plating chamber, means to support an object to be plated within the chamber said means including a non-conductive member and a pair of electrically conductive rods supporting the member, a source of a heat decomposable metal bearing compound within the chamber below the non-conductive member, means to heat said source to supply an atmosphere of plating gas within the chamber, and means to exhaust said gas from said chamber continuously to maintain said atmosphere at a low pressure.

8. The method which involves contacting a heated, electrically non-conductive body in a chamber with gaseous chromium hexacarbonyl, the temperature of the heated body being at least about 200° C. the pressure within the chamber being of a low value and not greater than about 4 millimeters of mercury and the chamber being free of air.

9. The method which involves contacting a heated, electrically non-conductive body in a chamber with gaseous chromium hexacarbonyl, the temperature of the heated body being in the range of between about 350°–450° C. the pressure within the chamber being of a low value and not greater than about 4 millimeters of mercury and the chamber being free of air.

10. The method which involves heating an electrically non-conductive body in a chamber to a temperature of between about 200° C. and 450° C., and exposing the heated body to chromium hexacarbonyl gas at a pressure of less than about one millimeter of mercury.

11. The method which involves exhausting a spacing of air to a pressure of not greater than 4 mm. of mercury, volatilizing chromium hexacarbonyl in said spacing, and heating a ceramic body to a temperature of at least about 200° C. in said spacing in contact with the chromium hexacarbonyl to effect thermal decomposition thereof in contact with the ceramic body.

12. The method which involves exhausting a spacing of air to a pressure of not greater than 4 mm. of mercury, volatilizing chromium hexacarbonyl in said spacing, and heating a ceramic body to a temperature of between about 350° C. and 450° C. in said spacing in contact with the chromium hexacarbonyl to effect thermal decomposition thereof in contact with the ceramic body.

13. As an article of manufacture, an electrical resistance element comprising a ceramic body having a coating film thereover of chromium metal, said resistance element having a resistance of between about 70–80 ohms.

14. As an article of manufacture, an electrical resistance element comprising a hollow ceramic cylinder having a coating film of metal, said resistance element having a resistance of between about 70–80 ohms.

15. As an article of manufacture, an electrical resistance element comprising a hollow ceramic cylinder having a coating film of chromium metal, said resistance element having a resistance of between about 70–80 ohms.

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