March 20, 1956 P. PAWLYK 2,738,762

APPARATUS FOR THE DEPOSITION OF NON-CONDUCTIVE COPPER COATINGS FROM VAPOR PHASE

Original Filed Oct. 8, 1951 2 Sheets-Sheet 1

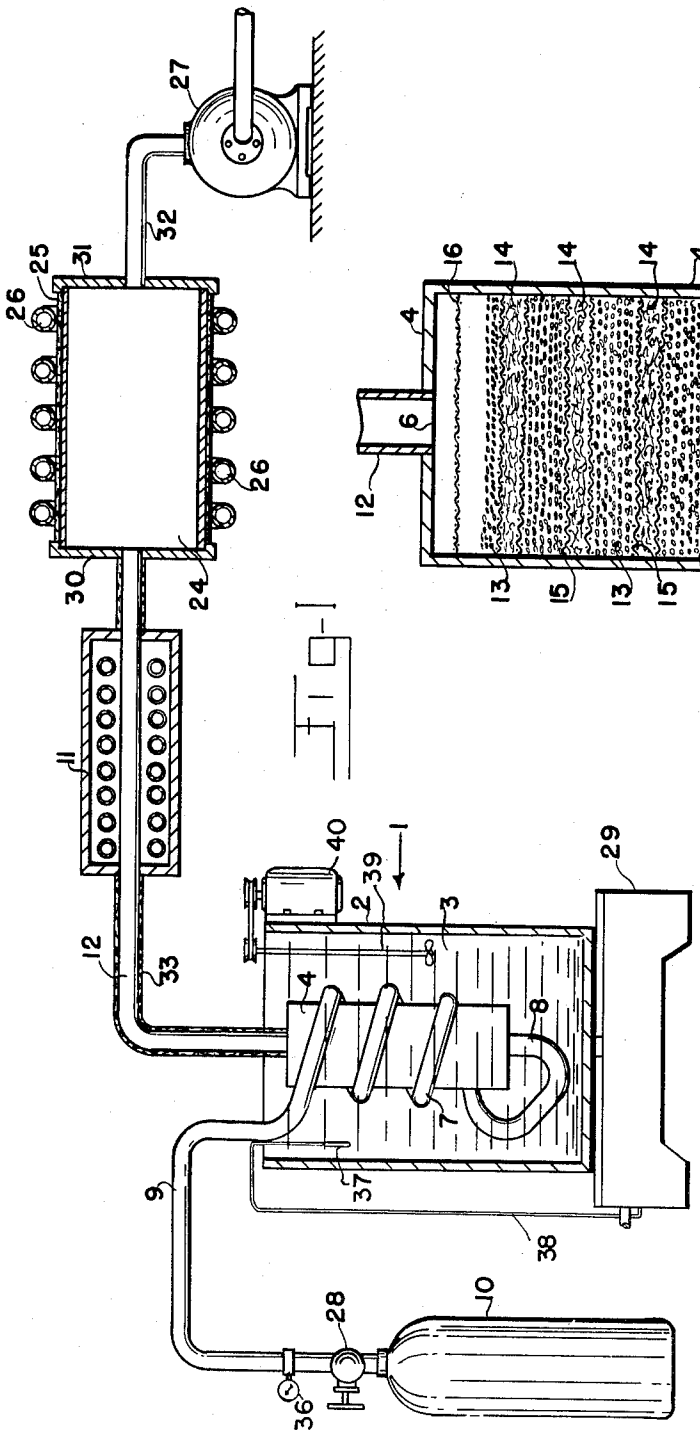


FIG-1

FIG-2

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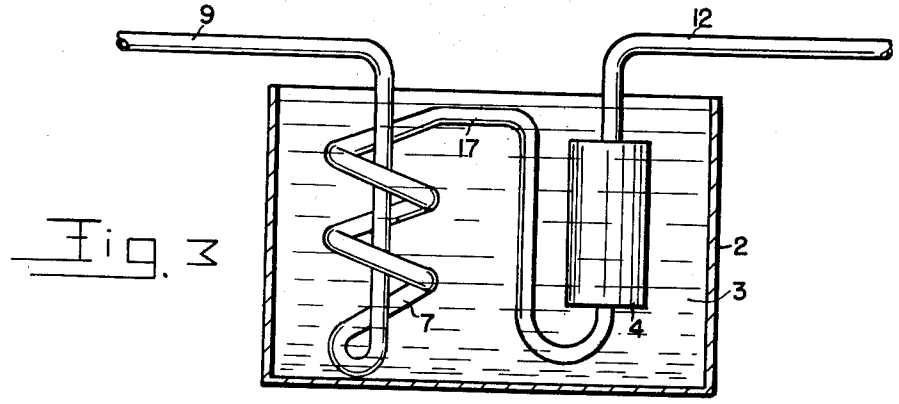


Fig. 3

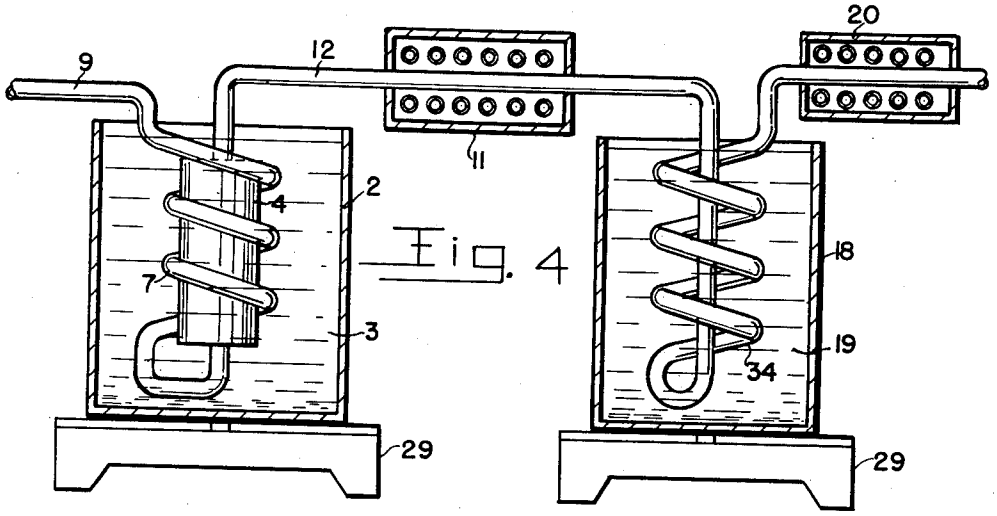


Fig. 4

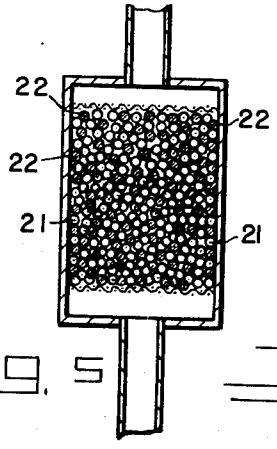


Fig. 5

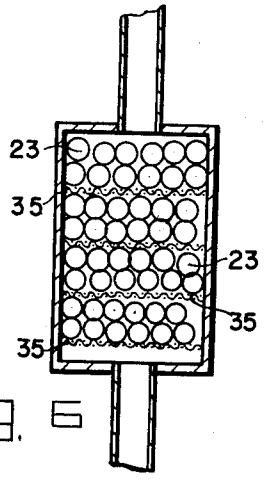


Fig. 6

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2,738,762

APPARATUS FOR THE DEPOSITION OF NON-CONDUCTIVE COPPER COATINGS FROM VAPOR PHASE

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Original application October 8, 1951, Serial No. 250,302. Divided and this application July 20, 1953, Serial No. 389,663

4 Claims. (Cl. 118—49)

This invention relates to means and methods of obtaining uniform concentrations of mixed gases at constant temperatures. More particularly the invention relates to the control of gaseous mixtures, one of the gases of which is a metal-bearing compound decomposable under the influence of heat to deposit metal.

This application is a division of co-pending application Serial No. 250,302, filed October 8, 1951, and assigned to the same assignee as the present invention.

This application is related to co-pending applications, Serial Nos. 250,301; 250,303; 250,304; 250,305; 250,306 and 250,307; all filed October 8, 1951, and by the same inventor as the present application.

The efficient plating of objects with metals, by the pyrolysis of gaseous metal-bearing compounds and the deposition of the metallic component of the gas requires close control of decomposition conditions in order that a fine uniform deposit may be obtained. Premature heating of the metal-bearing gas above the decomposition point induces uncontrolled decomposition in the gas plating apparatus, and thus deprives the process of efficiency, since the concentration of metal in the gas striking the object to be plated will then be uncontrolled and in some cases insufficient to provide a uniform, adherent coat on the workpiece.

An inert carrier gas may be used together with the metal-bearing gas and serves as an effective diluent affording means of control of the concentration of the metal-bearing gas. Such inert gases are carbon dioxide, nitrogen, helium and argon.

This invention contemplates subjecting the metal-bearing compound in the liquid or solid state to the action of a carrier gas under controlled conditions of temperature, and effecting vaporization of the metal-bearing compound under the controlled conditions to provide a plating gas mixture uniform in concentration and of predetermined temperature characteristics.

The invention also contemplates particular structural arrangements for the handling of the solid or liquid metal-bearing compound, which arrangements facilitate the contact with the carrier gases to accomplish intimate contact between these primary components. Thus, for example, fusing together of the solid particles of metal-bearing compound may be prevented by the arrangements of the invention.

The invention further contemplates the provision of novel procedural steps to assist in the attainment of the desired plating gas of uniform characteristics.

These and other allied purposes of the invention are attained by providing apparatus for the passage of the inert carrier gas through a pre-heating coil, maintained at a constant temperature, immediately prior to contacting the solid or liquid metal-bearing component with the carrier gas, the metal-bearing component itself being held at constant temperature conditions. The contact of the carrier gas with the metal-bearing component is facilitated by dispersing the particles of metal-bearing solid in a carburetor or gas mixing chamber in layers, and interspersing glass beads or ceramic material with the metal-bearing solid to facilitate the dispersement. Glass wool and/or metal screening may be employed to support the metal-bearing solid compounds, and both are effective to cleanse the gases as well as to assist in contact thereof with the solid compound.

Where the metal-bearing compound is in the liquid state the inert carrier gases may be bubbled through the material, a procedure which is facilitated by the employment of horizontal screens spaced along the vertical axis of the carburetor. The screens are in this instance effective to prevent the entraining of the gas in restricted paths, and the minor turbulence created by the screen is sufficient to insure of adequate liquid contact by the gas.

In accordance with the process of this invention the passage of the carrier gas under controlled conditions to the similarly controlled metal-bearing compound results in controlled temperature conditions in the gas mixture flowing from the carburetor to the plating chamber. This gas mixture may be subjected to a further heating step before entering the plating chamber and such a step is particularly effective where the desired gas temperature in the chamber is higher than the temperature which may be effectively employed in the carburetor.

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

Figure 1 is a schematic view of one embodiment of the invention;

Figure 2 is a longitudinal sectional view of the carburetor of the embodiment of Figure 1;

Figure 3 illustrates a modification of the carburetor system of Figure 1;

Figure 4 illustrates another embodiment of the invention;

Figure 5 illustrates a method of packing the carburetor with solids; and

Figure 6 illustrates a modification of the structure of Figure 5.

Referring to Figure 1 there is shown at **10** a tank of liquified carbon dioxide provided with a valve **28** and from which extends a short copper conduit **9** having therein a gauge **36** which measures gas flow. The inner end of conduit **9** is formed into a coil **7** which surrounds the carburetor **4**, the lower end of the coil being secured in the opening **5** (Figure 2) of the carburetor. The coil **7** and carburetor **4** are immersed in oil **3** contained in tank **2** and this assembly, indicated generally at **1**, is adapted to be maintained at an elevated temperature by electric heater element **29** secured beneath container **2**. Heater element **29** may be provided with thermostatic means, including element **37** secured to the heater by conductor **38**, for automatically controlling the temperature of the oil **3** but where the volume of the oil is relatively large in comparison with the carburetor volume, and the temperature of the oil not greater than about 150° C. manual control is fully effective since electric heaters are readily obtainable which supply a substantially constant heat input.

At the upper opening **6** (Figure 2) of the carburetor **4** there is secured a conduit **12** which connects with plating chamber **24**. Conduit **12** is provided with asbestos or other heat insulating material **33** and may in given instances be itself of a heat insulation material. Interposed between the carburetor **4** and the plating chamber, and surrounding conduit **12** is a heater **11**.

The plating chamber **24** may be adapted to contain an object to be plated or may itself be the object which is to be plated. The latter arrangement is shown in Figure 1 wherein the internal walls of the chamber are to be coated with metal, and to effect this the hollow tube or pipe member **24** is provided with end flanges **30, 31.**

Flange 30 secures the member 24 to conduit 12 while flange 31 secures the chamber to an outlet line 32 provided with a vacuum 27 which exhausts to the atmosphere or a recovery apparatus as desired.

Chamber 24 is surrounded with a thin layer of asbestos 25 surmounted by an electric heating coil 26 powered from a source (not shown).

In Figure 2 the carburetor 4 is shown provided with vertically arranged layers 13 of chromium carbonyl, supported on screens 15 which are separated by layers of glass wool 14. As shown in Figure 2 the screens are in pairs spaced apart and the glass wool is between adjacent pairs, each pair being adapted for supporting therebetween the chromium carbonyl. Metal screens 16 are positioned adjacent the inlet 5 and outlet 6 to provide a thoroughly dispersed gas flow. The metal screens 15 and 16 are approximately 100 mesh and the powder particles thereon vary from about 2 to 5 times the size of the screen openings.

In the modification of Figure 3 the coil 7 and carburetor 4 are each immersed in oil 3 but the carburetor is not enclosed by the coil as in Figure 1 but is separated from it by a short length of connecting coil 17 which is also immersed in the bath. Such an arrangement is particularly useful where the temperature variation throughout the bath is negligible and the arrangement is desirable due to the simplified mechanical connections. This structure is particularly useful in connection with liquid metal-bearing compounds as the carburetor may be readily recharged.

Figure 4 illustrates an embodiment of the invention in which the mixture of gases emanating from the carburetor 4 and heat jacket 11, as in the embodiment of Figure 1, are passed through a second coil 34, maintained in a constant temperature bath 18 containing oil 19 heated by element 29. This arrangement is particularly suited for complete stabilization of the temperature of the gases, the mixture emanating from this constant temperature bath then being subject to the heat of heating jacket 20 prior to entry to the plating chamber. This mode of raising the temperature in controlled steps is particularly effective where the temperature of decomposition of the metal bearing gases is relatively high.

Figures 5 and 6 set forth arrangements of solid metal-bearing compounds which are particularly suited for establishing good contact with the carrier gases. Numeral 21 of Figure 5 indicates glass beads interspersed with fragments 22 of solid chromium carbonyl. Numeral 23 in Figure 6 indicates beads of chromium carbonyl supported by screens 35.

In the operation of the apparatus the usual precautions are observed of providing a clean workpiece and flushing of the apparatus free of air prior to entry of the plating gases. Referring particularly to Figure 1, carbon dioxide gas is bled from cylinder 10 into coil 7 through end 9 and attains a temperature substantially equal to that of the oil bath before entering the carbureting chamber 4 at 5. The carburetor is, as noted, packed with chromium carbonyl fragments which also are at substantially the temperature of the oil bath, in the present case 170° C. Preferably the temperature of the oil bath and gases entering the carburetor is between about 10 to 40° C. higher than that required for vaporization of the carbonyl. Thus the slight tendency of the gases to cool as they expand into the carburetor is not a serious factor in the operation of the equipment.

It will be clear that the particular temperature of the entering gases is a variable factor depending upon the physical dimensions of the carburetor and coil, the method of packing the carburetor and the particular compound to be volatilized. However, it will not generally be necessary to raise the temperature of the incoming gases more than 40° C. above that required for vaporization of the carbonyl.

The hot carrier gas contacting the carbonyl vaporizes the same and the mixture of gases flows upwardly, under the influence of the pressure of the carrier gas, to the heating jacket 11, where additional heat is supplied to the gases, the temperature of which however is still below the decomposition point of the chromium carbonyl.

The packing of the carburetor in the indicated manner tends to eliminate any tendency of the metal bearing compounds to fuse together and consequently uniform gas flow to the plating chamber is secured with the apparatus of invention.

The metal-bearing gas entering the plating chamber 24, at flow rates of the carbon dioxide measured at the tank 10 of between about 1 liter to 8 liters per minute, will fill the chamber uniformly with plating gas which decomposes under the influence of the heat of the chamber depositing chromium on the interior walls of the chamber. The pressure of the gases in the chamber may be maintained by the vacuum pump 27 at a pressure of 5 to 7 pounds absolute, although this pressure may be varied upwardly to speed the plating time, or lowered to achieve deposits of very fine metal. The temperature of the chamber wall in the present instance is about 600° F. and may be varied between about 550–700° F. to change the rate of deposition of metal. However, under the conditions noted, and a pressure of 5–7 pounds, a uniform plating having a thickness of approximately .003 may be obtained in about 50 to 60 minutes over the interior length of a 5" tube.

The attainment of a uniform mixture of carrier and metal-bearing gas at the entrance to the plating chamber is essential to the uniform deposition of the metal and leads to the result noted above. However, in instances where the temperature of the carburetor is considerably below that desired for optimum plating of the workpiece, the uniform gas mixture emanating from the carburetor may be additionally heated with the apparatus of Figure 4 while maintaining uniformity in the gas mix.

The feature of pre-heating above the vaporization point of the metal-bearing compound insures of maximum and uniform vaporization at a given internal temperature of the carburetor. Where the carburetor and coil are exposed to the same oil bath a vapor pressure of carbonyl will of course exist over the fragments but the physical arrangement of the system is such that little carbonyl will flow until the carrier gas sweeps away the carbonyl allowing more of the material to vaporize.

All metal-bearing gases which are subject to decomposition by heat to result in the deposition of the metallic component may be suitably employed in the process and apparatus of invention. Thus the solid metal-bearing compounds such as molybdenum carbonyl, tungsten carbonyl and cobalt carbonyl, as well as liquids, for example, the nickel carbonyl and iron penta carbonyl, may be employed. The hydrides of antimony and tin, chromyl chloride, copper nitroxyl and cobalt nitrosyl carbonyl are other effective agents.

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.

I claim:

1. In apparatus for gas plating, the structure comprising a plating chamber having an inlet and outlet, a hollow conduit secured at one end to said inlet, a heater element surrounding said conduit, a constant temperature source of plating gas secured to the other end of said conduit, and means including a source of vacuum connected to the outlet of said plating chamber for the passing of plating gases through said apparatus.

2. In apparatus for gas plating with heat decomposable gaseous metal-bearing compounds, the combination of a gas plating chamber having an inlet and an outlet, with a gas mixing chamber communicating with the inlet of said gas plating chamber for intermixing the gaseous

metal-bearing compound with inert carrier gas, and means comprising solid discrete particles in said gas mixing chamber to facilitate intimate contact of the inert carrier gas with the gaseous metal-bearing compound.

3. In apparatus for gas plating with heat decomposable gaseous metal-bearing compounds, the combination of a gas plating chamber having an inlet and an outlet, with a gas mixing chamber communicating with the inlet of said gas plating chamber for intermixing the gaseous metal-bearing compound with inert carrier gas, and means comprising multiple layers of solid discrete particles supported on foraminous material disposed in said mixing chamber to facilitate intimate contact of the inert carrier gas with the gaseous metal-bearing compound.

4. In apparatus for gas plating with heat decomposable gaseous metal-bearing compounds, a gas plating

chamber having an inlet and an outlet, a gas mixing chamber communicating with said inlet, said gas mixing chamber containing spaced screens for supporting a solid gasifiable metal-bearing compound, means for heating said gas mixing chamber to a substantially uniform temperature throughout, and means including a source of vacuum connected to the outlet of said plating chamber for withdrawing the gaseous mixture from said gas mixing chamber and into said plating chamber.

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