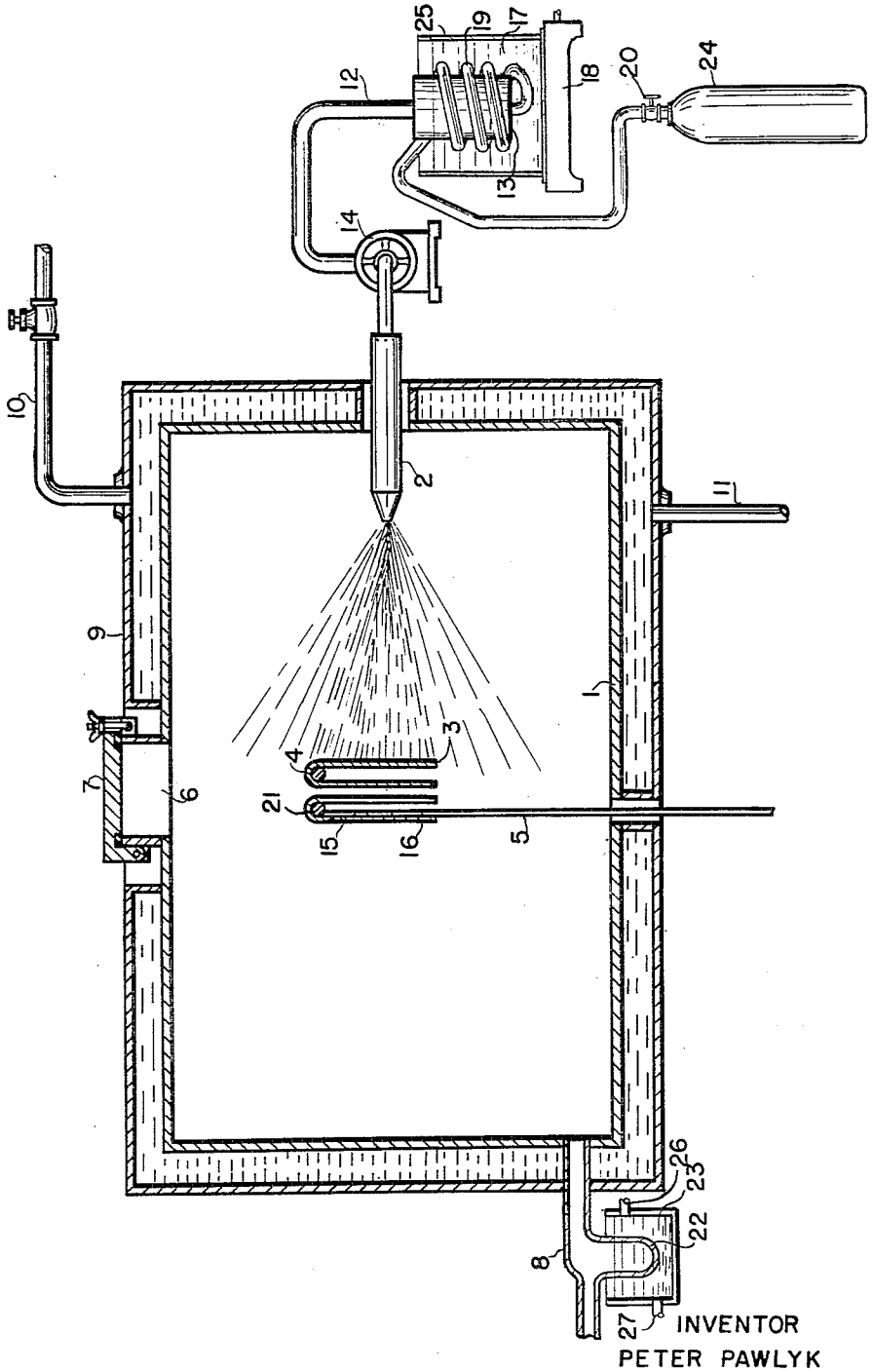
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GAS PLATING METAL OBJECTS WITH COPPER ACETYLACETONATE

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# GAS PLATING METAL OBJECTS WITH COPPER ACETYLACETONATE

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This invention relates to the plating of metallic objects with copper by the thermal decomposition of gaseous copper acetylacetonate.

Normally, in the plating of articles by the thermal decomposition of metal-bearing compounds, it is essential for satisfactory operation that the plating be performed under reduced pressure conditions. The low pressure conditions increase the length of the mean free path between gas molecules and it has been considered that such a condition is necessary for the securing of adequate metallic deposits. However it has been discovered that copper acetylacetonate is particularly suitable for the plating of objects at atmospheric pressures and that the above noted requirement may be eliminated when this copper compound is employed with an inert carrier gas.

It is accordingly a primary object of this invention to provide a new and novel process of plating objects using copper acetylacetonate as the source of the metallic coating.

It is a particular object of this invention to set forth particular conditions for the plating of objects with copper from copper acetylacetonate.

It is another object of this invention to provide a plating process involving the thermal decomposition of a gaseous metal-bearing compound which may be carried out at atmospheric pressures.

In the process of invention copper acetylacetonate is vaporized, mixed with a carrier gas and directed onto a heated workpiece which is to be copper plated whereupon the gaseous compound decomposes depositing copper on the workpiece or object. The copper acetylacetonate exhibits optimum effectiveness when employed in a plating atmosphere having a temperature in the range of 300° F. to 450° F., with the workpiece at a temperature of between about 500° F. to 650° F., and when the flow rate of the gases is high, that is in excess of one liter per minute on a workpiece having an area of about 8 square inches.

The invention will be more fully understood by reference to the following specific examples and accompanying drawing wherein the single figure illustrates apparatus particularly suitable for the practice of the invention.

Referring to the drawing there is shown an apparatus for the metallic coating of small workpieces of metallic character. The reference numeral **1** indicates a chamber having a nozzle **2** sealed in one wall thereof, the nozzle being connected through pump **14** and insulated conduit **12** to a carburetor **13** containing the granules of copper acetylacetonate. Carburetor **13** is immersed in an oil bath comprising tank **25** and oil **17** which bath may be maintained at a substantially constant temperature by electric heater **18**. Surrounding the carburetor **13** is a hollow coil **19** having one end thereof opening into the lower side of the carburetor and the other end opening to valve **20** on tank **24** of carbon dioxide.

Positioned centrally of chamber **1** a metal workpiece **3**, to be plated, is suspended from a permanent support **4** secured in a side wall of the chamber. Also secured in the chamber, closely adjacent the workpiece **3**, is a resistance heating element **16** mounted on plate **15**, the complete unit being secured on support **21**. This resistance heating element supplied through conductor **5** from a source (not shown) and plate **15** are effective to heat, by radiation and conduction, metallic workpieces suspended from support **4**. It will be understood that the workpieces may be of substantially any shape and the invention is not to be considered as limited to the particular arrangement shown.



The chamber **1** is also provided with an exhaust port **8** which may be open directly to the atmosphere, but is preferably provided as at **22** with a trap for recovery of metal-bearing vapors. The trap may be surrounded with cooling water **23** for condensation of the vapors.

The chamber **1** is also provided with an opening **6** for the entry of workpiece **3**, the opening being closed by cover **7** when the equipment is in operation.

A cooling water jacket **9** having an inlet **10** and outlet **11** surrounds chamber **1** and is adapted to pass sufficient cooling water to maintain the temperature of the chamber walls between about 80 to 100° F.

In the practice of the process of invention the metallic workpiece is first cleansed by any suitable means known to the art. For example, metallic pieces may be treated with an acid to remove scale, etc., and then washed free of the acid with alcohol.

Also as a preliminary step the apparatus may be flushed free of air by the passage of an inert carrier gas through the chamber prior to insertion of the object.

After the cleaned workpiece has been fixedly secured in the chamber **1** and brought up to a temperature in the range of 500 to 650° F. the valve **20** on tank **24** is opened and vapors of carbon dioxide pass to the coil **19** submerged in the oil maintained at a temperature of about 300 to 450° F., whereby the carbon dioxide vapors attain a temperature in the same range. These heated vapors then pass into carburetor **13** and assist in the vaporization of the copper acetylacetonate, which then, thoroughly mixed with carbon dioxide, flows under the pressure thereof to the pump **14** and nozzle **2**. Pump **14** is not generally necessary but should be employed if the length of conduit **12** is excessive or the diameter thereof exceedingly small.

The gases, which under the conditions noted and a carbon dioxide flow from tank **24** of one liter per minute, may contain less than about 10% of metal bearing gas, expand into chamber **1** filling the same. In most cases it will be desirable to direct the gas flow directly to workpiece **3** but such will not be necessary for the copper acetylacetonate gas molecules in their random motion will upon striking the heated object decompose depositing the copper metal thereon.

The metal plate **15** will of course also receive a coating of copper but this is not detrimental since the coat will radiate heat well to the object **3** and such metal is of course recoverable. The inner walls of the chamber, as they are maintained at a relatively low temperature by the passage of the water through the cooling jacket, will receive substantially no metallic deposit.

The metal workpiece under the conditions stated will receive a deposit of copper of about .001 inch in approximately 3 to 60 minutes.

The copper acetylacetonate as it decomposes will, due to the gaseous products of decomposition formed, create a pressure towards the opening **8** and the waste gases will exhaust therethrough. At the high flow rates employed some copper acetylacetonate may pass through the exhaust line with the waste gases; as this compound is relatively expensive it will generally be desirable to conduct the vapors through a trap, depositing the copper acetylacetonate therein while the other waste gases pass to the atmosphere. Such a procedure will not affect the pressure in the chamber materially if the trap is itself vented to the atmosphere.

The following specific examples set forth optimum plating conditions for the use of copper acetylacetonate. Such conditions are not to be considered as limited to the specific apparatus set out hereinbefore, and are to be taken as illustrative only of the conditions under which the process is operable.

*Example I*

| | |
|---|---|
| 1. Temperature of workpiece (steel) | 650° F. |
| 2. Temperature of carburetor | 350° F. |
| 3. Flow rate of carrier gas | 1.0 liter per minute. |
| 4. Carrier gas | $CO_2$. |
| 5. Time for deposition of .001" of copper | 5 minutes. |

*Example II*

1. Temperature of workpiece (cast iron) ---------- 500° F.
2. Temperature of carburetor---- 300° F.
3. Flow rate of carrier gas------ 1.0 liter per minute.
4. Carrier gas---------- $CO_2$.
5. Time for deposition of .001" of copper ---------- 60 minutes.

(This example represents threshhold conditions for deposition of copper.)

*Example III*

1. Temperature of workpiece (steel) ---------- 650° F.
2. Temperature of carburetor---- 450° F.
3. Flow rate of carrier gas------ 2 liters per minute.
4. Carrier gas---------- $CO_2$.
5. Time for deposition of .001" of copper ---------- 3 minutes.

*Example IV*

1. Temperature of workpiece (steel) ---------- 650° F.
2. Temperature of carburetor---- 400° F.
3. Flow rate of carrier gas------ 2 liters per minute.
4. Carrier gas---------- Nitrogen.
5. Time for deposition of .001" of copper ---------- 4 minutes.

Preferably in the practice of this invention the temperature of the workpiece is maintained between about 500 to 850° F., and the plating atmosphere at about 300 to 450° F., the flow rate of the gases providing the atmosphere being in the range of about one liter per minute to 8 liters per minute.

The ratio of inert carrier gas to copper acetylacetonate in the plating gas is not critical at the flow rates set forth, the more dilute gases merely requiring a longer plating time for a given thickness of deposited copper. The carrier gas itself may be any of the inert gases such as nitrogen, argon or helium.

This application is related to copending applications, Serial Nos. 250,301; 250,302; 250,303; 250,304: 250,306; and 250,307; all filed October 8, 1951, and all by the same inventor as the present application.

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. A process of plating a metallic object with copper comprising the steps of heating the object to be plated to a temperature in the range of 500 to 650° F., and contacting the heated object with gaseous copper acetylacetonate in an atmosphere containing an inert carrier gas at substantially atmospheric pressure and a temperature range of between about 300 to 450° F., and for a time sufficient to cause decomposition of said copper acetylacetonate and deposition of the copper metal onto said object.

2. A process of plating a steel object with copper comprising the steps of heating the object to a temperature of about 650° F., vaporizing copper acetylacetonate at a temperature of about 350° F., contacting the vaporized copper compound with carbon dioxide gas at a temperature of about 350° F. to form a flowing mixture of the gases, and subjecting the heated object to the action of said flowing mixture of gases at substantially atmospheric pressures.

3. A process of plating a cast iron object with copper comprising the steps of heating the object to a temperature of about 500° F., vaporizing copper acetylacetonate at a temperature of about 300° F., contacting the vaporized copper compound with carbon dioxide gas at a temperature of about 300° F. to form a flowing mixture of the gases, and subjecting the heated object to the action of said flowing mixture of gases at substantially atmospheric pressures.

4. A process of plating a steel object with copper comprising the steps of heating the object to a temperature of 650° F., vaporizing copper acetylactonate at a temperature of 450° F., contacting the vaporized copper compound with carbon dioxide at a temperature of 450° F. to form a flowing mixture of the gases, and subjecting the heated object to said action of the flowing mixture of gases at substantially atmospheric pressures.



5. A process of plating a steel object with copper comprising the steps of heating the object to a temperature of 650° F., vaporizing copper acetylacetonate at a temperature of 450° F., contacting the vaporized copper compound with nitrogen at a temperature of 450° F. to form a flowing mixture of the gases, and subjecting the heated object to the action of said flowing mixture of gases at substantially atmospheric pressures.

6. A process of depositing approximately .001" of copper on a metallic object comprising the steps of heating the object to be plated to a temperature in the range of 500 to 600° F., and contacting the heated object with a mixture of the gases of copper acetylacetonate and carbon dioxide at a temperature in the range of about 300 to 450° F. under substantially atmospheric pressure conditions and for a period of about 3 to 60 minutes.

7. A process of depositing approximately .001" of copper on a metallic object comprising the steps of heating the object to a temperature of about 650° F., vaporizing copper acetylacetonate at a temperature of about 350° F., contacting the vaporized copper compound with carbon dioxide gas at a temperature of about 350° F. to form a flowing mixture of the gases, and subjecting the heated object to the action of said flowing mixture of gases at substantially atmospheric pressures for a period of about 5 minutes.

8. A process of depositing approximately .001" of copper on a metallic object comprising the steps of heating the object to a temperature of about 500° F., vaporizing copper acetylacetonate at a temperature of about 300° F., contacting the vaporized copper compound with carbon dioxide gas to form a flowing mixture of the gases, and subjecting the heated object to the action of said flowing mixture of gases at substantially atmospheric pressures for a period of about 60 minutes.

9. A process of depositing approximately .001" of copper on a metallic object comprising the steps of heating the object to a temperature of 650° F., vaporizing copper acetylacetonate at a temperature of 450° F., contacting the vaporized copper compound with carbon dioxide at a temperature of 450° F. to form a flowing mixture of the gases, and subjecting the heated object to the action of said flowing mixture of gases at substantially atmospheric pressures for a period of about 3 minutes.

10. A process of depositing approximately .001" of copper on a metallic object comprising the steps of heating the object to a temperature of 650° F., vaporizing copper acetylacetonate at a temperature of 450° F., contacting the vaporized copper compound with nitrogen at a temperature of 450° F. to form a flowing mixture of the gases, and subjecting the heated object to the action of said flowing mixture of gases at substantially atmospheric pressures for a period of about 4 minutes.

11. A process of plating a metallic object with copper comprising the steps of heating the object to be plated to a temperature in the range of about 500–650° F., and contacting the heated object with gaseous copper acetylacetonate in an atmosphere containing an inert carrier gas at substantially atmospheric pressure and at a temperature range of between about 300–450° F. and for a time between 3 to 60 minutes to cause decomposition of said gaseous copper acetylacetonate and deposition of the copper metal constituent onto said object.


**References Cited in the file of this patent**

UNITED STATES PATENTS

| | | |
|---|---|---|
| 1,675,120 | Marden et al. | June 26, 1928 |
| 2,304,182 | Lang | Dec. 8, 1942 |
| 2,344,138 | Drummond | Mar. 14, 1944 |
| 2,430,520 | Marboe | Nov. 11, 1947 |
| 2,468,825 | Jernstedt | May 3, 1949 |
| 2,474,038 | Davignon | June 21, 1949 |
| 2,576,289 | Fink | Nov. 27, 1951 |

OTHER REFERENCES

Preprint No. 8 presented to American Society of Metals at the 32nd Annual Convention, Molybdenum Plating by Reduction of Penta-Chloride Vapor, by W. J. Childs et al. (only page 3 relied upon).