Nov. 16, 1954 P. PAWLYK 2,694,651

DEPOSITION OF COPPER OXIDES ON HEAT INSULATING MATERIAL

Filed Oct. 8, 1951 2 Sheets-Sheet 1

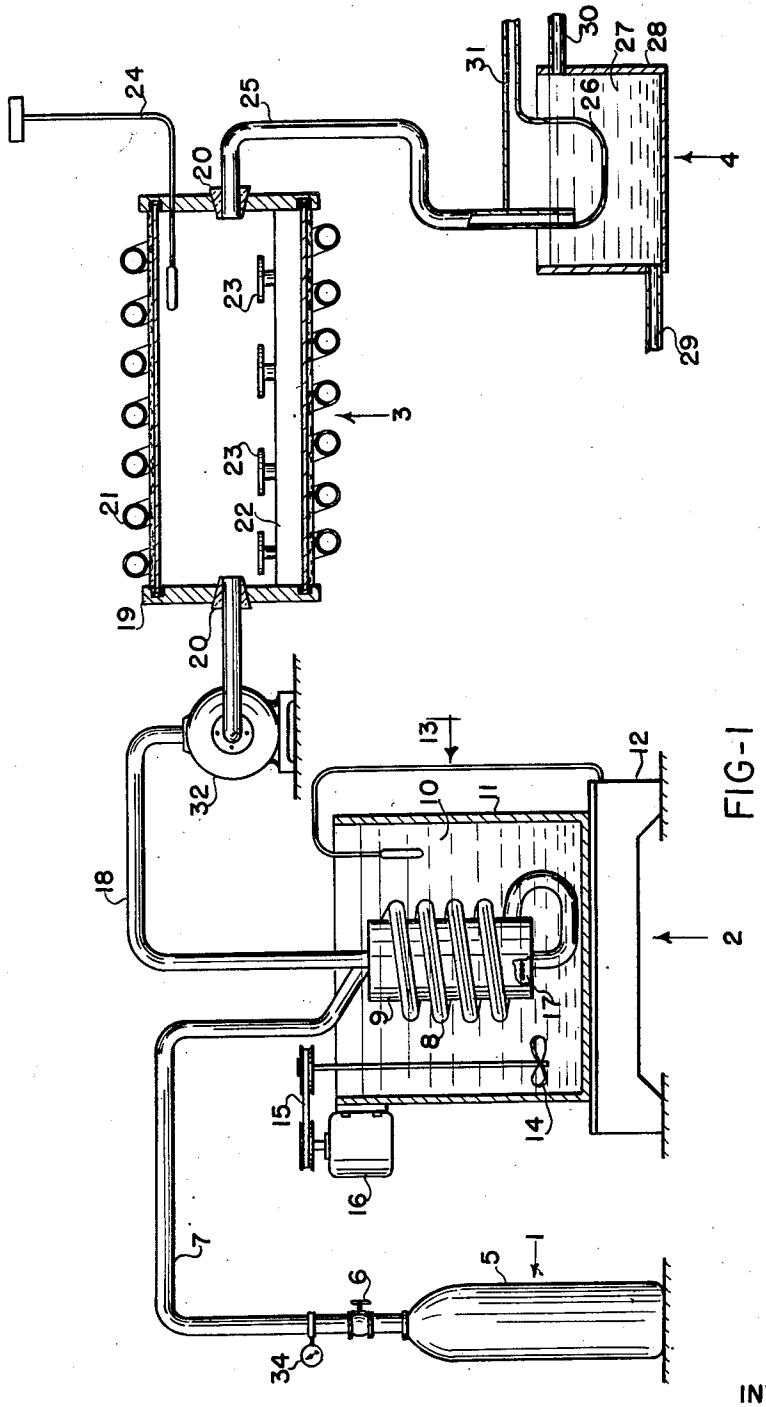


FIG-1

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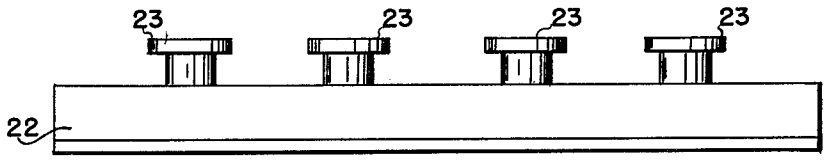


FIG-2

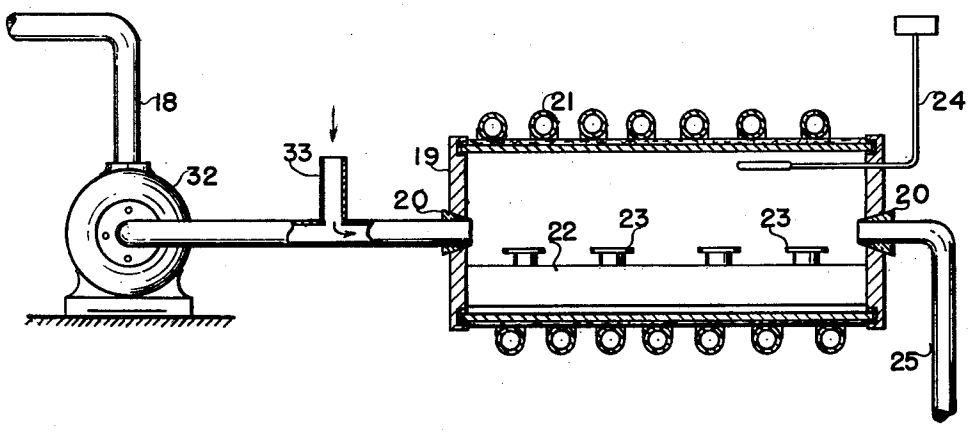


FIG-3

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2,694,651

DEPOSITION OF COPPER OXIDES ON HEAT INSULATING MATERIAL

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Application October 8, 1951, Serial No. 250,303

7 Claims. (Cl. 117—106)

This invention relates to a gas plating system and process for the production of semi-conductive and non-conductive coatings on insulating materials and to the products produced by the process.

It has been found that electrically resistant layers of high quality may be produced by the formation of the mixed copper oxides, particularly cuprous oxide, on metallic and non-metallic bases by contacting the base under carefully controlled conditions, to be more particularly discussed hereinafter, with copper acetylacetonate in the gaseous state to effect decomposition thereof. The process of formation of the oxides may be facilitated by carrying out the decomposition in an oxidizing atmosphere to achieve selective oxidation of any deposited metallic component present as decomposition of the copper acetylacetonate occurs.

This invention accordingly contemplates the provision of a unique method for the attainment of films of mixed oxides of copper on non-conductive materials.

The invention also contemplates the provision of unique resistive elements attained by depositing from the gaseous state mixed oxides of copper on non-conductive base materials.

The method of invention is practiced by heating a dielectric base material to a temperature range below that at which copper acetylacetonate will decompose to copper metal and contacting the base material with heated vapors of copper acetylacetonate at a rate sufficient to maintain the temperature of the material below the said range and at a pressure substantially equal to that of the atmosphere. Under these conditions the plating deposited on the insulating base will comprise essentially the mixed oxides of copper.

The resistance characteristics of the deposited layer, for a given concentration of metal-bearing gas in the plating chamber, will vary with the velocity of gas flow, the higher flow rates contributing to the formation of a greater proportion of the cupric oxide, although some cuprous oxide will always be present. Similarly lower flow rates may contribute to the formation of more cuprous oxide but the cupric phase will exist in the coating.

In the preferred embodiment of the invention the copper acetylacetonate is vaporized from the solid compound by contacting the heated solid with a heated inert gas, which gas carries the metal-bearing vapors to a plating chamber. The copper acetylacetonate decomposes at approximately 455° F. and accordingly the temperature of the solid compound and the inert carrier gas must be maintained considerably below this temperature point.

The plating chamber to which the heated gas mixture is carried is itself heated, and the arrangement thereof is such that the workpiece therein which is to be plated is at a lower temperature than the atmosphere surrounding it. This is accomplished by exposing the workpiece in the chamber only to the heat of the flowing gases and to radiation from the element which heats the chamber; the workpiece is thus heated by radiation to a temperature below that of the atmosphere and is maintained in this condition by the heated flowing gases; the temperature of the material is maintained above 450–455° F. however which is adapted to cause copper oxides to deposit on the workpiece. The object to be plated is not itself heated directly as is normally the custom in the gas plating art. Preferably control is achieved by regulating the temperature of the flowing gases at a point,

spaced slightly from the workpiece, and between the workpiece and plating chamber heater.

The hot gases when they strike the workpiece of lower temperature than the surrounding atmosphere will only partially decompose, and depending upon the exact conditions of the system, a mixture of cuprous oxide and cupric oxide, or a mix containing the oxides, plus a small amount of copper metal will be attained. For example, films may be obtained on ½ inch diameter ceramic discs with resistances varying from 10 ohms to substantially infinity. The control of the resistance is attained primarily by controlling the rate of gas flow over the discs in the plating chamber.

Control of the oxide formation may also be influenced by the bleeding into the system of small amounts of oxygen which tends to develop cupric oxide formation. As the system will contain both carbon dioxide and the carbon monoxide decomposition product, care must be exercised to prevent water vapor or any appreciable amounts of hydrogen bearing carbon compounds forming in the chamber, for mixes of oxygen, carbon monoxide and carbon dioxide may be rendered slightly explosive in the presence of such constituents. Normally if the oxygen is introduced as dry air the presence of the nitrogen of the air will serve as a sufficiently effective diluent to prevent any deleterious reactions.

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

Figure 1 is a schematic representation of the apparatus for the carrying out of one embodiment of the invention;

Figure 2 illustrates a carrier for the objects to be plated; and

Figure 3 illustrates schematically apparatus for the carrying out of another embodiment of the invention.

In Figure 1 the major components of the apparatus utilized to carry out the invention are indicated at **1**, **2**, **3** and **4**. Numeral **1** indicates a source of carrier gas; the numeral **2** a constant temperature bath containing a carburetor and the compounds to be vaporized; the numeral **3** indicates the plating chamber; while the numeral **4** designates generally a recovery system.

The tank **5** of inert carrier gas (carbon dioxide) is provided with a valve **6** and flow meter **34** having connected thereto a length of copper tubing **7**, which passes to the constant temperature unit **2**. The tubing **7** is wound as at **8** into a coil which surrounds the carburetor **9** and the tubing is itself connected into the lower end of the carburetor. The carburetor **9** and coil **8** are each immersed in oil **10** contained in tank **11** and maintained at a constant temperature by means of heater **12** and the thermostat unit indicated generally at **13**. Since such thermostats in themselves are well known no detailed description thereof will be given herein.

The bath is also provided with a stirrer **14** actuated through belt **15** by motor **16**. The carburetor contains solid layers of copper acetylacetonate **17** and a length of insulated tubing extends from the top of the carburetor and passes to the gas plating chamber **19** of plating chamber unit **3**.

The connection between tubing **18** and chamber **19** may be made through stopper **20** although any suitable means of connection may be employed, the only requirement being that the seal be gas tight.

Gas chamber **19** is provided externally thereof with a resistance heating element **21** provided with electrical energy from a source not shown. Mounted in chamber **19** is an object carrier **22**, more clearly shown in Figure 2.

The carrier **22** consists of a rack of insulating material extending the length of chamber **19** and having supports thereon for the carrying of ceramic discs **23** of substantially ½ inch diameter. Chamber **19** is provided at the remote end thereof with an outlet in which tubing **25** is secured, the tubing **25** passing directly to the recovery system **4** where it is secured in the bulb of trap **26**. Trap **26** is surrounded by cooling water **27** contained in tank **28** having inlet **29** and outlet **30** for the passage of the cooling water. The remote end of the trap is provided with tube **31** for the emission of exhaust gases to the temperature.

Positioned between the constant temperature bath **2** and the plating unit **3** in the line **18** is a pump **32** for the maintenance of a steady flow of gases to the chamber **19**.

In the operation of the apparatus of invention, to attain a resistive coating having a resistance value of approximately 300 ohms per centimeter, a ceramic disc or discs **23** are inserted on the carrier **22** in the plating chamber **19**. The resistance heater **21** is adjusted to supply a temperature of about 600° F. within the chamber **19** at a point approximately ¼ of an inch above the positioned ceramic disc. The temperature of the oil **10** is adjusted to about 375° F.

Under these conditions the valve **6** on tank **5** is open to permit a flow of carbon dioxide of about one liter per minute through line **7** and coil **8** wherein it is heated to approximately 375° F. The gas then passes into the carburetor where it contacts the copper acetylacetonate. The copper acetylacetonate having already been subjected to a temperature of 375° F. by means of the oil bath will have built up a considerable vapor pressure and the entering CO_2 will sweep these vapors out through tubing **18**.

As the packing of the copper compound in the carburetor **9** may tend to restrict to some extent the gas flow, pump **32** is actuated to insure of the steady flow of gas to the plating chamber **19**. The gases passing into chamber **19** at the flow rate specified will contact the object or workpiece **23** and will tend to maintain the same cool, that is below the temperature of the surrounding atmosphere and below the temperature at the thermocouple **24**. The gases under this condition will decompose and deposit on the workpiece, forming a film consisting substantially only of cuprous and cupric oxide. The waste gases together with any undecomposed copper compound will then pass through tubing **25** to the trap **26** where the cooling effect of water **27** will cause the copper acetylacetonate to deposit out from the decomposition vapors, the decomposition vapors themselves then flow on to the atmosphere.

The time of plating of the above noted process is approximately 30 minutes in order to secure a deposit having a resistance of 300 ohms.

In Figure 3 there is shown an embodiment in which there is provided an oxygen inlet to the system. Since the system is otherwise the same as shown in Figure 1 the same reference numerals will be employed. In line **18** there is shown an inlet **33** for dry air.

In the operation of the system shown in Figure 3 oxygen to the extent of .05% by volume of the plating gases is bled into the system in a dry condition. When the gases passing from the carburetor **9** through line **18** containing the dry air from inlet **33** enter the chamber **19** the presence of oxygen tends to prohibit the formation of any copper metal.

The system of plating of Figure 1 is preferred to that of Figure 3. However in some instances it may be necessary to use a high temperature in the plating chamber thus raising the temperature of the ceramic to such an extent that metallic copper may tend to deposit. In this circumstance the air bleed of Figure 3 provides in the chamber sufficient air to convert the copper to copper oxide. Where temperature conditions in the chamber are lower and more favorable the system of Figure 1 offers close control of the deposition and is preferred.

By way of illustration raising the temperature of the object to 650° F. and the temperature of the flowing gas to 400° F. results in a substantially electrically non-conductive layer after 30 minutes' exposure of the insulated object in the system of Figure 1. Thus by adjusting the flow temperature and/or the chamber atmosphere temperature, it is possible with relatively small temperature steps to attain layer resistance between 300 ohms and infinity.

A temperature rise in the chamber to 700° F. should be avoided with the system of Figure 1 however for metallic copper may then deposit.

The inert gases useful in the system of invention include, as well as carbon dioxide, argon, helium, nitrogen, etc.

Substantially all materials of heat insulating nature are suitable for the practice of the invention. Metallic objects however do not in general maintain a sufficiently low surface temperature to permit the attainment of controlled resistive coatings in the flow ranges presently explored. Flow rates of between about 1 to 10 liters of carrier gas per minute are however effective with heat insulating materials and a particular flow condition may be readily chosen in conjunction with a specific carburetor temperature to attain a desired result.

This application is related to copending applications, Serial Nos. 250,301; 250,302; 250,304; 250,305; 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. In a process of depositing copper oxide on heat insulating material the step of passing vapors of copper acetylacetonate together with an inert carrier gas heated to a temperature of less than about 450° F. over the insulating material maintained at a lower temperature than that at which said vapors decompose to metallic copper but above that of the vapors.

2. In a process of depositing copper oxide on heat insulating material the step of passing mixed vapors of copper acetylacetonate and carbon dioxide at a temperature of less than about 450° F. over insulating material maintained at a lower temperature than that at which said vapors decompose to metallic copper but above that of the vapors.

3. In a process of depositing copper oxide on heat insulating material the steps of heating an atmosphere to a temperature of less than about 700° F. in a chamber, exposing the insulating material to the heat of said atmosphere, and passing vapors of a plating gas containing copper acetylacetonate and inert gas vapors at a temperature of less than about 450° F. over the heat insulating material at high flow rates of such a nature that temperature of the atmosphere and copper oxides are deposited by said atmosphere on said material.

4. A process for the formation of controlled amounts of the oxides of copper on heat insulating material comprising the steps of flowing a given quantity of heated carbon dioxide gas through layers of copper acetylacetonate maintained at a temperature of about 375° F. to form a given gaseous mixture having definite amounts of each gas at a temperature of about 375° F., and pressuring the gaseous mixture formed thereby through a heated chamber containing a ceramic material in an atmosphere having a temperature greater than that of said material and also greater than that of said flowing gaseous mixture, said gaseous mixture having a flow rate such that said insulating material does not attain the temperature of the said atmosphere and whereby said copper acetylacetonate decomposes depositing oxides of copper on said material in amounts proportioned to the flow rate of said given gaseous mixture.

5. A process for the formation of controlled amounts of the oxides of copper on heat insulating materials comprising the steps of flowing a given quantity of heated carbon dioxide gas through layers of copper acetylacetonate maintained at a temperature of about 375° F. to form a given gaseous mixture having definite amounts of each gas therein at a temperature of about 375° F., and pressuring the gaseous mixture past a supply of dry air to draw a portion thereof into said mixture, and passing the pressured gases through a heated chamber containing a ceramic material having a temperature slightly above that necessary for the initiation of the decomposition of the copper acetylacetonate and below that at which the copper acetylacetonate decomposes to metallic copper at a flow rate of the gases such that said copper containing compound is decomposed and copper oxides are deposited on said material.

6. A process for the formation of an electrical resistance layer having a value of approximately 300 ohms comprising the steps of establishing an atmosphere at a temperature of about 600° F. at a distance of about ¼ of an inch from a ceramic disc in the same atmosphere, and contacting the said disc with a flow of plating gas for about thirty minutes, said gas containing copper acetylacetonate and carbon dioxide and having a temperature of about 375° F. at substantially atmospheric pressure.

7. A process for the formation of an electrical resistance layer having a value of approximately infinite resistance comprising the steps of establishing an atmosphere at a temperature of about 650° F. at a distance of about

¼ of an inch from a ceramic disc in the same atmosphere, and contacting the said disc with a flow of plating gas for about thirty minutes, said gas containing copper acetylacetonate and carbon dioxide and having a temperature of about 400° F. at substantially atmospheric pressure.

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