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E. R. BREINING ET AL
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PHASE PLATING METHOD
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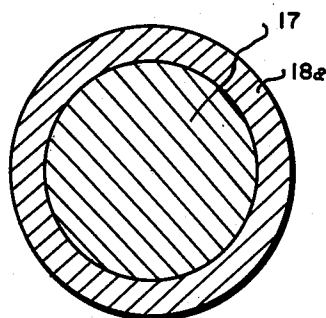
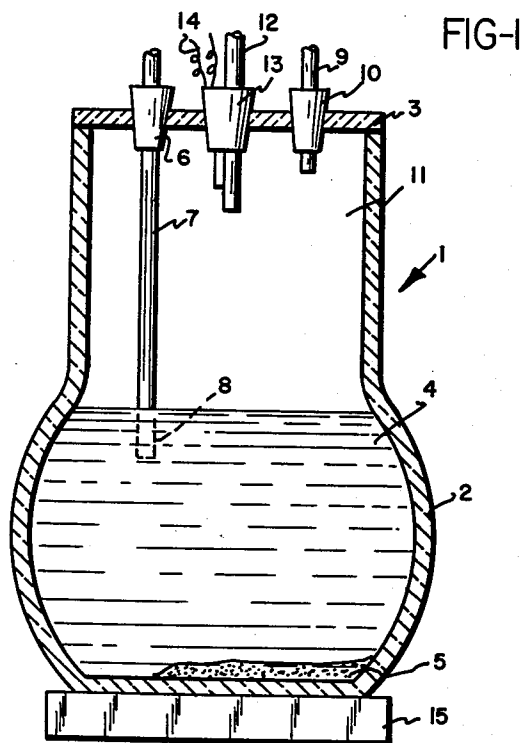
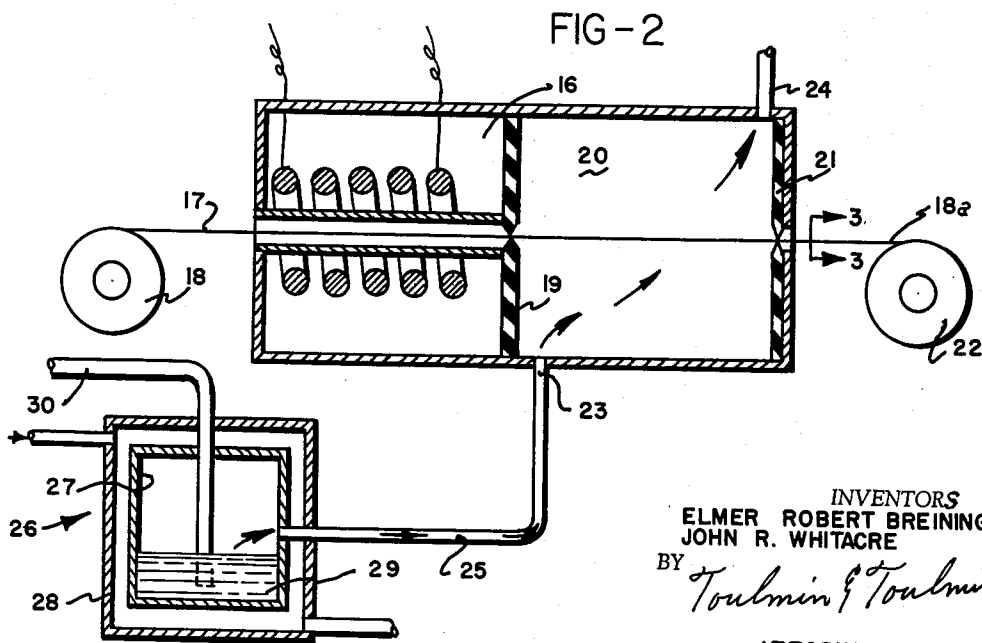


FIG-3



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DEPOSITION OF COMPOSITE COATINGS BY VAPOR PHASE PLATING METHOD

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1 Claim. (Cl. 117-107)

This invention relates to the coating of substrates with metallic composites deposited from thermally decomposable compounds, which compounds normally exhibit a low vapor pressure and which are difficultly soluble without undergoing decomposition.

More specifically the invention relates to the deposition of a composite coating by the thermal decomposition of heat decomposable compounds in the vapor state and in the presence of vapors of a common solvent for the compounds.

It has been found that cyclic ethers of at least five and not more than six membered rings dissolve the carbonyls or hexacarbonyls of molybdenum, chromium and tungsten and that coatings may be effected utilizing a solution containing the aforementioned constituents.

Normally plating with mixtures of the carbonyls of chromium, tungsten and molybdenum is relatively slow in the vapor state as the vapor pressure of the constituents is low, about 0.1 mm. at normal temperatures. Further these compounds are solids exhibiting usually a decomposition temperature of about 150° C.

It is a purpose of this invention to provide a method of plating mixtures of the carbonyls of tungsten, chromium and molybdenum at a relatively rapid rate and to deposit coatings on substrates such as iron, steel and other materials which may be heated to at least 150° C. and preferably to a temperature of 200-250° C. The higher temperatures of the substrate provide for more rapid deposition and substrate temperatures up to 315° C. (600° F.) are practical.

Cyclic ether suitable for the practice of the invention includes tetrahydrofuran.

The cyclic ethers are stable at the decomposition temperatures of the carbonyls as practiced in the invention, and do not interfere with the deposition process. The ethers employed however should be maintained free of water and oxidizing constituents as such tend to decompose the carbonyls.

The coating procedure is accomplished by passing the substrate to be coated, while heated to at least the decomposition temperature of the carbonyl, into vapors of the carbonyl. The temperature of the solution should be such that it is at or closely approaching the boiling point. At such temperatures vapors emanating from the solution have a large carbonyl percentage and the vapors are voluminous.

With tetrahydrofuran the temperature employed is at or near the boiling point of the tetrahydrofuran itself; however, when saturated solutions are employed the boiling point is raised considerably above that of tetrahydrofuran.

When plating from the vapors a carrier gas which is inert under the conditions involved is preferably employed to facilitate the escape of the carbonyls from the solution. Such gases include nitrogen, carbon dioxide, argon and similar gases.

Solution of the carbonyls may be made by mixing the powders and dissolving the mixture in the cyclic ether. Alternatively each powder may be separately dissolved and the solutions mixed. In either event in the plating solution an excess of each constituent is preferably pro-

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vided in order to maintain a saturated solution throughout the plating operation.

Accordingly it is a principal object of this invention to provide a novel method for the deposition of composite coatings from heat decomposable compounds.

It is an important object of this invention to provide a novel method for the deposition of continuous non-porous adherent composite coatings of metals on substrates, the metals including alloys.

A particular object of the present invention is the provision of substrates coated with composites and in which the coating is deposited thermally by decomposition in the vapor phase of a mixture of carbonyls, such as molybdenum, chromium and tungsten carbonyls.

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

FIGURE 1 schematically illustrates an apparatus arrangement for the practice of the invention by a static method;

FIGURE 2 schematically illustrates an apparatus arrangement for the practice of the method of invention as applied to wire, tape and similar configured materials; and

FIGURE 3 is a cross-sectional view of a wire metalized with a composite in accordance with the invention. Referring to the drawings, the numeral 1 in FIGURE 1 designates generally apparatus useful in the practice of a static method for the substrate to be plated.

In FIGURE 1 a glass vessel 2 is provided with an enclosure 3 of glass. Within the vessel and substantially half filling the same is a solution 4. This solution in the present instance comprises the hexacarbonyls of molybdenum, tungsten and chromium. The carbonyl of molybdenum is present in the mixture of carbonyls to the extent of about 74 percent by weight, while the tungsten is present to the extent of about 19 percent by weight, and the chromium carbonyl constituting substantially the balance.

A mixture of the solid carbonyls in contact with the solution is indicated at 5, the mixture being the same as indicated above as to proportions.

Through the closure 3 there is provided a stopper 6 of polytetrafluoroethylene which receives a conduit 7 for the passage of the entraining gas to the solution as indicated at 8. The conduit 7 dips well into the solution. The numeral 9 designates an exhaust conduit passing through the stopper 10. Extending into the space 11 above the solution 4 is a substrate 12, such as a rod of stainless steel; this stainless steel rod is supported in a stopper 13 which also supports a thermocouple, the leads of which are indicated generally at 14. The rod is heated to about 277° C. (527° F.).

If desired the substrate 12 may be heated electrically, for example, during the course of the plating operation. The solution 4 is itself heated by an electric element, such as a hot plate, designated at 15 in FIGURE 1. Preferably the temperature of the solution is maintained at very nearly the boiling point of the solution in order that the quantity of carbonyl in the vapor phase will be as high as practicable. However, the solution may be as low as 90° C. and still provide adequate plating within a reasonable time.

Also the flow of the entraining gas is in the present instance such that a voluminous bubbling of the gas through the solvent is apparent. 0.25 cubic foot per minute is sufficient when about 50 grams of the solvent are employed in a beaker.

Referring now to FIGURE 2, the numeral 16 indicates a resistance heater of substantially cylindrical contour, through the center of which there passes a copper wire 17, unrolled in any conventional manner from a reel

indicated at 18. The wire 17 in its traverse passes through a gas seal 19, chamber 20 and an outlet gas seal 21 to a winding device 22. The chamber 20 is provided with an inlet port 23 and an exhaust port 24. The inlet port 23 is connected by a conduit 25 with a vaporizer 26, which itself consists of a tank 27 surrounded by a steam jacket 28. The jacket 28 maintains the temperature of the solution of tetrahydrofuran and carbonyls indicated at 29 to within the range of about 90–100° C. or below.

The entraining gas, which as previously indicated may be an inert gas, such as CO₂ or nitrogen, is passed through a conduit 30 into the solution 29 and the vapors exit through the conduit 25 to the chamber 20. In the chamber 20 the vapors contact the wire 17, which has been heated to a temperature of 250–275° C., and the product of decomposition passes through exhaust 24 to any suitable exhaust arrangement.

Referring now to FIGURE 3, the numeral 17 designates a section of copper wire and the numeral 18a indicates a hard coating of the metallic constituents of the carbonyls completely surrounding the wire.

The following example describes the process:

Solutions of chromium carbonyl, molybdenum carbonyl and tungsten carbonyl in tetrahydrofuran were made up employing 10 grams of the carbonyl and 20 cc. of the tetrahydrofuran; in each instance the solvent was heated to effect the solution, and while hot the three solutions were poured together. The temperature of the solutions was maintained at about 55° C. in order to provide the carbonyls in solution.

A steel substrate was heated to a temperature of about 550° F. (288° C.), while the solution was heated to the boiling point, and carbon dioxide passed therethrough at approximately 0.25 to 0.28 cubic foot per minute. The substrate when exposed to the vapors of the thus described solution for a period of about three minutes received a heavy coat; when analyzed by spectrograph the composite deposit was found to contain molybdenum, tungsten and chromium, and was highly resistant electrically. The coating itself was somewhat brittle, but completely covered the exposed area of the substrate.

It may be noted in connection with the procedures described that somewhat better appearing coats are obtained when the solutions are dissolved separately and then mixed together, even though ultimately solid carbonyl is provided in contact with the solutions to provide saturated solutions as the method proceeds.

It also appears that while tungsten carbonyl tends to enter solution slightly more easily than the chromium or molybdenum carbonyls, it also tends to come out of solution somewhat more easily. In the case of tetrahydrofuran the tungsten carbonyl precipitates first if the temperature is allowed to drop below about 55° C.

While the invention has been specifically described in connection with tetrahydrofuran as the solvent for the carbonyls, it has been contemplated that it may be possible to employ other equivalent ethers, or mixtures of ethers. In general 5 and 6 membered cyclic ether rings, which exhibit stability at the temperatures of decomposition of the carbonyls and which dissolve the carbonyls, are useful in the practice of the invention.

It is important to note that the pressure within the plating chamber may be substantially atmospheric and that the exhaust at 9 (FIGURE 1) and at 24 (FIGURE 2) may lead to the atmosphere.

Generally, since such gases contain in addition to the carbon dioxide and vaporized solvent some small amount of undecomposed carbonyl and some carbon monoxides, it is well to provide for the combustion of the exhaust or for the recovery thereof.

Also, it is to be noted that cooling the coated material, to prevent oxidation in the atmosphere while the coated material is highly heated, is frequently a desirable precaution against reaction of the atmosphere.

Also, the coating itself may be presented on the substrate to the vapors to build up thicknesses where such is desired. Normally an exposure of three minutes to the vapors of a saturated solution is sufficient to produce a coating thickness of 0.2 to 0.3 mm.

Where mixtures of carbonyls having materially different thermal decomposition points are employed it is necessary to heat the substrate to the decomposition temperature of the metal bearing constituent having the highest decomposition temperature.

Deposition by presentation of the substrate to the vapors of the carbonyls results in less rapid cooling of the substrate. Accordingly the substrate presented to the carbonyls at a given temperature may normally be maintained in effective plating contact somewhat longer than with solutions.

Dipping the substrate or drawing the substrate through the solution offers the advantage of intimate contact of the substrate with the thermally decomposable components. Dipping, however, should be accomplished relatively rapidly for the solution is normally considerably cooler than the substrate and tends to cool the substrate below decomposition temperature. Higher temperatures of the substrate are accordingly desired in dip or similar operations.

This application is related to the co-pending application of Elmer Robert Breining and John R. Whitacre, entitled "Vapor Phase Deposition of Coatings and Apparatus Therefor," Serial No. 706,843, filed January 2, 1958, now U.S. Patent 3,023,491.

It will be understood that this invention is susceptible to modification in order to adapt 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 claim.

What is claimed is:

The process of gas plating metal composite on metal substrates, comprising the steps of heating the substrate to the decomposition temperature of a mixture of the metal carbonyls consisting of molybdenum, tungsten and chromium carbonyls, dissolving a mixture of said metal carbonyls in tetrahydrofuran by heating said hydrofuran in contact with the metal carbonyls to a temperature of about 55° C., passing an inert gas through the resultant heated metal carbonyl solution to entrain the mixture of carbonyl vapors and maintain a saturated solution of the metal carbonyl mixture, contacting the heated substrate with said entrained metal carbonyl vapors while concurrently passing the inert gas through the saturated solution of the metal carbonyl mixture to facilitate contact of the vapors of the metal carbonyl compounds with the substrate whereby said vapors are thermally decomposed and the metal constituents deposited on the substrate at a relatively high rate of deposition.

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