

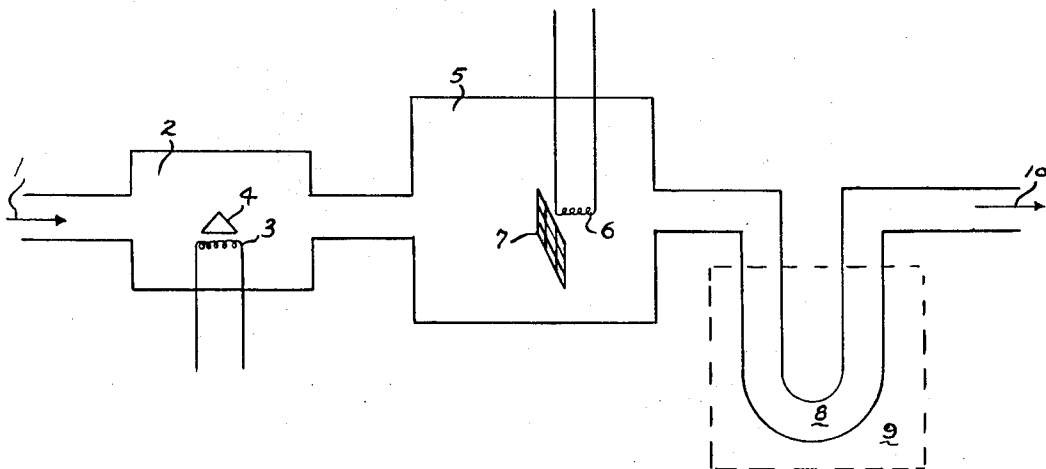
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VAPOR-PLATING METALS FROM FLUOROCARBON KETO METAL COMPOUNDS

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3,356,527

## VAPOR-PLATING METALS FROM FLUORO-CARBON KETO METAL COMPOUNDS

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### ABSTRACT OF THE DISCLOSURE

Process for depositing a metal or an alloy coating on a hot target substrate by the reduction of a metal chelate selected from the group of copper, nickel, cobalt and lead acetylacetonate, hydrates, halides, alkyl, aryl, hydroxyl and nitro-compounds at 250-500° C. and at one atmosphere of pressure.

The invention described herein may be manufactured and used by or for the United States Government for governmental purposes without payment to any of us of any royalty thereon.

This invention relates to the deposition of metals on substrates and more particularly to the deposition on heated targets of metal coatings by the reduction or the decomposition of halocarbon beta-diketonate metal chelates, such illustratively as chelates of the metals copper, nickel, cobalt, lead and the like.

A metal chelate of a beta-diketone of the formula  $R''''R''''R'C(:O)CHR''C(:O)CR''''R''''R^V$  wherein R' is halogen and R'', R''', R''', and R<sup>V</sup> is selected from the class consisting of hydrogen, halogen, alkyl, haloalkyl, perhaloalkyl, aryl, haloaryl, hydroxyl and nitro groups. Those members of the metal chelates of the formula cited above, which are volatile at the temperatures disclosed herein, come within the scope of the present invention.

The chelates in some instances may occur as solvates, as for example cobalt (II) hexafluoroacetylacetonate hydrate or copper (II) hexafluoroacetylacetonate hydrate.

It has been common practice heretofore to deposit metal coatings from the metal vapor phase by decomposing the halides, carbides, hydrides or the like, salts of the metals. The prior practices in general require high temperatures in the order of from 600° C. to 1500° C., which severely limits the substrates that can be plated.

The present invention, by comparison, discloses the plating of the representative metals copper, nickel, cobalt, lead and the like, from their 1,1,1-trifluoro-2,4-pentanedionato and 1,1,1,5,5,5-hexafluoro-2,4-pentanedionato chelates at temperatures about in the range of from 250 to 500° C. and about at atmospheric pressure. These low temperatures permit the plating of these metals on a broadened range of materials, such as rubber, plastic, paper etc. that will survive these modest temperatures, as well as high temperature ceramics, metals and the like.

The object of the present invention is the provision of means and methods for depositing metal coatings from the gaseous phases at relatively low working temperatures and about at atmospheric pressure.

Another object of this invention is to provide tightly adherent deposited coatings of high purity metals by reactions that yield the elemental metal as the only non-volatile component of the process.

A further object is to provide a plating system with easy control over the rate of plating and the thickness of the metal plate deposit.

A further object is the provision of control over the mix-

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tures of metals that form the plate, by a desired mixing of the vapors of a plurality of chelates used in the plating reaction to provide a desired allow of the metals involved.

Another object is to provide a means and a method for depositing metals selectively on desired portions of the object to be plated, on complicated, intricate and embedded patterns, printed electrical circuitry, and the like.

A generalized diagrammatical flow diagram of the metal plating apparatus used in practicing the present invention is illustrated in the single figure of the accompanying drawing.

In the drawing, hydrogen gas 1 at atmospheric pressure is passed into the subliming chamber 2, where a heat source 3 causes the chosen metal chelate 4 to sublime. The hydrogen gas serves functionally as both a carrier gas and as a reducing agent. The flow of the hydrogen gas causes the vaporized chelate to pass from the subliming chamber 2 into the plating chamber 5.

Within the plating chamber 5 a second heat source 6 supplies heat to a target assembly 7 at a controlled temperature for plating to occur on the hot exposed surfaces of the target. The physical conditions at the surface of the target 7 and the time of target exposure are controlled to provide the optimum desired plating results at a desired metal thickness.

The reaction products, such as hydrogen gas, unreacted chelate etc. are carried by the hydrogen carrier gas from the plating chamber 5 into a cold trap 8 where unreacted chelate, less volatile reaction products and the like, are collected and from which the more volatile components are treated further or are vented at 10 to the atmosphere. The unreacted hydrogen and regenerated chelating agent may be recycled advantageously. The cold trap 8 is immersed in a cold bath 9. The cold bath 9 illustratively may contain a Dry Ice-acetone coolant or another desired coolant.

The heating units 3, 6, etc. for the subliming chamber 2 and the plating chamber 5, respectively, are advantageously selected from available types that operate by induction, radiation, resistance etc.

The target 7 is of a chosen material that remains stable at the maximum temperature to which it is subjected, and that is of a design that allows a sufficient concentration of the chelate in the gaseous phase in the proximity of the target surface to allow a satisfactory rate of metal deposition.

An illustrative cold trap 8 may be a single collector of one or more non-volatile components in the vapors entering the cold trap, or it may be comprised of a desired plurality of fraction collecting compartments at graduated temperatures for collecting separately and selectively, the unreacted chelate in a first zone, the regenerated chelating agent in a second zone of a lower temperature, etc.

Suitable precautions are taken to maintain the inner walls of the plating chamber at a temperature that is above the recrystallization temperature of the metal chelate to avoid the deposition of the vaporized chelate on the surfaces and yet not at temperatures high enough to cause deposition of the metal at undesired places on the walls of the chamber. The chamber inner wall surfaces contacted by the vapor is preferably maintained slightly above the sublimation temperature of the particular chelate that is being caused to flow through the apparatus.

The deposition heating element 6 is positioned to avoid the deposition of metal thereon. In one form of the invention, the heating element 6 was positioned within the target 7. In another form of the invention the heating element was wound outside of a cylindrical deposition chamber 5.

The reducing and carrier gas may also be hydrazine, carbon monoxide or the like.

## Example 1

In the application of a surface coat of copper on glass, such as on the surface of a glass tubing, or the like, a 0.1 gram sample of copper hexafluoroacetylacetonate is weighed and placed in one end of a glass tube that has a 1 centimeter inner diameter and that is 15 inches in length. The glass tube that was plated experimentally was a borosilicate glass and its end that contained the sample was positioned as the metal chelate 4 in the subliming chamber 2 of the drawing and the remainder of the tube comprised the plating chamber 5 in the drawing.

The carrier and reducing gas hydrogen is flowed through the glass tube at an average velocity of about 1/2 inch per second.

During the deposition reaction, the portion of the tube containing the sample 4 is heated by the winding 3 at about 80 to 95° C. while the remainder of the tube, representing the plating chamber 5 is maintained at a temperature of about 300° C. Copper is deposited in this latter, hotter zone on the inner surface of the glass tube at a rate of thickness growth of about 800 A. per minute, in a band that is about 2 inches in width. At the termination of the deposition run the copper plate was about 25,000 A. thick. The thickness of the plate may be increased by the use of a higher concentration of the metal chelate in the gas phase or by the use of longer plating times. The copper plate so deposited on glass is of a high degree of purity, is electrically highly conductive, shiny, ductile and adheres well to the glass. The excess chelate and less volatile reaction products including the regenerated chelating agent, from the reaction is trapped in the cold trap 8 by immersion in the Dry Ice-acetone bath 9. The excess hydrogen and more volatile reaction products escape from the vent 10 to the atmosphere.

## Example 2

Cobalt is plated on a chosen metal, such as a ribbon of stainless steel, placed as the target 7 in the plating chamber 5. A small sample of cobalt II hexafluoroacetylacetonate dihydrate, is placed at 4 in the subliming chamber 2. The subliming chamber 2 is maintained at about between 110 and 130° C. by means of the heat source 3. Hydrogen gas is caused to flow through the apparatus at the rate of about 1/2 inch per second.

The vapor mixture so produced is passed from the subliming chamber 2 into the plating chamber 5, where the ribbon of stainless steel 7 is maintained at about 350° C. by means of the heat source 6. The residual vapor is then, as before, passed through the cold trap 8 to the atmosphere.

Coatings of metals plated on supports in the making of printed electrical circuits and the like, are readily accomplished by the techniques disclosed herein.

The disclosed metals copper, nickel, cobalt, and lead are in the lower part of the electromotive series. Metals that appear to have plating potentialities similar to those of copper, nickel, cobalt, and lead appear to be those below thallium in the series and include, molybdenum, tin, mercury, silver, rhodium, palladium, platinum and gold.

The technique that is disclosed herein has the further utility of minimizing the erosion of a metal surface or replacing worn metal surfaces, such for example as within a nozzle. The maximum wear on a nozzle expelling hot gas occurs at the point of highest temperature and greatest gas flow rate. The injection in the gas stream of a chelate of the nozzle lining metal and its decomposition yields the free metal deposited as a coating that slows, stops, or that reverses the erosion of the nozzle lining metal.

The metal plating potentialities of the present invention include cobalt memory cores for computers, metallized decorative plastics, metal plating on any surface that will withstand the modest deposition temperature require-

ments disclosed herein, including the application of abrasion resistance surfaces and linings on paper, rubber, plastics and the like. Metal films of micro-thinness are of use in radiation detection and counting, particle bombardment studies etc. in the production of films of precisely controlled thickness, purity and compositions.

It is to be understood that the compounds, reactants, reagents, temperatures, pressures and reactions that are disclosed herein are submitted as operatively successful reductions to practice of at least a third of the group of metals that are contemplated hereby, and that modifications may be made in the present invention without departing from the spirit and the scope thereof.

The cobalt plate so deposited on the surface of the stainless steel ribbon has a high degree of purity, has a high electrical conductivity, is shiny, ductile and adheres well to the metal substrate.

## Example 3

Odd and intricate shapes are successfully plated in desired patterns by following the present process. Illustratively a glass tube was plated with a spiral strip of copper plate on its inner surface by winding a resistance wire spirally on the outside of the glass tube and maintaining the spiral winding at 350° C. as the vaporized copper chelate of Example 1 is passed through the tube. The copper plate is deposited on the glass along the resistance wire spiral, using copper hexafluoroacetylacetonate at 4 as the metal chelate. The copper plate may be applied in lines, points or other desired patterns, and appears as a brilliant, closely adherent film.

The temperatures at which experimental chelates sublime and at which the targets are maintained are shown in the chart:

	Chelate	Sublimed at—	Target	Atmos.
		° C.	° C.	
40	Copper (II) hexafluoroacetylacetonate.....	80-95	250-500	H <sub>2</sub>
	Copper (II) trifluoroacetylacetonate.....	135-160	250-500	H <sub>2</sub>
	Nickel hexafluoroacetylacetonate.....	140-190	250-450	H <sub>2</sub>
	Nickel trifluoroacetylacetonate.....	150-190	250-450	H <sub>2</sub>
	Cobalt (II) hexafluoroacetylacetonate.....	110-130	250-500	H <sub>2</sub>
	Cobalt (II) trifluoroacetylacetonate.....	120-150	250-500	H <sub>2</sub>
45	Lead hexafluoroacetylacetonate.....	150	375-500	H <sub>2</sub>

Both copper hexafluoroacetylacetonate and copper trifluoroacetylacetonate in a nitrogen or other inert gas atmosphere, deposits the copper on a target maintained at 350 to 500° C. It is noted therefore that for some chelates such illustratively as copper trifluoroacetylacetonate and copper hexafluoroacetylacetonate, deposition of the metal can be made to occur at the heated surface without the presence of a reducing gas, such as the hydrogen cited here.

We claim:

1. The process of applying a metal coating to the surface of a substrate target by heating a metal chelate selected from the group that consists of fluorocarbon keto metal compounds that consists of the hexafluoroacetylacetonates and the trifluoroacetylacetonates of the metals copper, nickel, cobalt II and lead to its sublimation temperature, passing a reducing agent in vapor form over the metal chelate as a carrier gas, and decomposing the metal chelate in its vapor state and depositing at least a part of the metal content of the chelate on the surface of a substrate target maintained at the deposition temperature of the metal content of the chelate.

2. The process of applying a copper coating on the surface of a substrate by passing a vapor selected from the group that consists of copper hexafluoroacetylacetonate and copper trifluoroacetylacetonate together with a reducing agent thereof over the substrate at 250-500° C. temperature and at about one atmosphere

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of pressure in decomposing the vapor and applying a metal coating on the substrate.

3. The process of simultaneously depositing a plurality of metals as a mixed metal coating forming a layer on a substrate by heating to their vapor states a desired plurality of metal chelates selected from the hexafluoroacetylacetonates and the trifluoroacetylacetonates of the group of metals that consists of copper, nickel, cobalt II and lead, heating the substrate to the metal deposition temperature, combining the vaporous metal chelates with a reducing carrier gas, and conducting the combined vaporous metal chelates and reduced carrier gas to the heated substrate for causing the deposition on the substrate of a mixed metal coating.

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