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CHEMICAL GOLD PLATING

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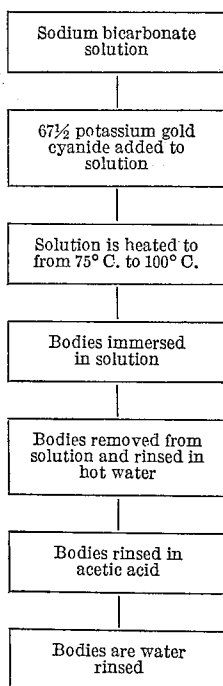
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11 Claims. (Cl. 117—130)

This invention relates to a method of metal plating and more particularly to a method of depositing a noble metal coating upon a metallic surface.

In various areas in different industries it is desirable to plate the surfaces of a metallic object with a noble metal in order to provide a corrosion resistant coating, to present a more decorative and pleasing appearance, and to provide a coating of high electrical conductivity to facilitate electrical connections.

A simple flow diagram of the process in accordance with the presently preferred embodiment of this invention is as follows:



In the prior art noble metal coatings usually were plated or deposited upon base metals by electroplating, a process in which metals are plated by electrolysis from solutions containing metallic ions. In the electroplating operation the base metal object is connected electrically to a cathode, and from an anode there is suspended a specimen of the metal being deposited. The cathode and anode are disposed in an electrolyte solution which contains dissolved salts of metal to be plated. In order to increase the conductivity of the electrolyte other highly ionizable chemicals are added. A direct current potential is applied between the cathode and anode which produces a migration of the metallic ions to the cathode which ions, upon losing their charge, deposit as a metal coating of the object to be plated. There are, however, several limitations and undesirable characteristics associated with prior art electroplating techniques. In accordance with

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the prior art methods, it is difficult to evenly electroplate an irregularly shaped object as interstices in the surfaces are usually not plated, and there is a build-up of plate thickness on points and edges of the object being plated.

In addition, the relatively thick coating produced by electroplating is subject to chipping and flaking, especially at points and edges. Also, the electroplating process requires an external source of electrical current and relatively frequent replenishment of the metal being plated thereby increasing costs and causing inconvenience.

To overcome the aforementioned limitations and undesirable characteristics associated with electroplating a chemiplating method has been used. Chemiplating is similar in operation to electroplating except that no external source of electrical current is used to effect ionic displacement. Chemiplating is possible because of the tendency for metals lower in the electromotive force series to displace from solution metals higher in the series; that is, if a metal low in the series is immersed in a solution of a salt of a metal high in the series, ions of the low metal go into solution while a coating of the high metal will be deposited on the surface of the low metal. For example, in accordance with one prior art method of gold chemiplating the metallic object to be plated is immersed in a heated, strongly basic solution of potassium hydroxide containing a gold salt such as 41% gold content potassium gold cyanide.

The chemiplating process hereinabove described produces a relatively thin coating not subject to chipping or flaking; interstices in the surfaces are plated and there is no build-up plate thickness on points and edges. No external source of electrical current is required and the process is less expensive and more convenient to operate than the electroplating process. Although overcoming the major objections to the electroplating process, the chemiplating process according to the above described prior art method, has certain undesirable characteristics of its own. In the strongly basic solution the hydroxide will attack most base metals, thereby preventing deposition of the desired coating. In practice it has been found that only copper can be satisfactorily plated with a noble metal by the prior art chemiplating process. In addition, the use of a strong hydroxide solution is objectionable if the object to be plated contains glass because the hot caustic solution etches the glass. Also, it is difficult to rinse the surfaces completely free of hydroxide. In general, the prior art chemiplating process, in addition to being restricted in its use as indicated hereinabove, usually produces a fairly dull porous coating. Further, the prior art chemiplating process is not very reliable due to difficulty in control caused by the necessity of maintaining a relatively constant bath composition. The result is that the plating bath cannot be continually reused until the plating metal is exhausted.

Accordingly, it is an object of the present invention to provide an improved method of chemiplating a noble metal coating upon a metallic surface.

It is another object of the present invention to provide a method for depositing a relatively thin nonporous noble metal coating of uniform thickness upon a metallic surface.

It is a further object of the present invention to provide a method for depositing a bright uniform noble metal coating upon a metallic surface.

Yet another object of the present invention is to provide a reliable inexpensive method for depositing a noble metal coating upon a metallic surface.

The novel features which are believed to be characteristic of the present invention, together with further objects and advantages thereof, will be better understood from the following description in which the invention is illustrated by way of example. It is to be

expressly understood, however, that this description is for the purpose of illustration only, and that the true spirit and scope of the invention is defined by the accompanying claims.

In general, the present invention provides a method for depositing a noble metal coating upon "metallic surfaces," as defined hereinafter, the coating being deposited in a mildly basic solution, instead of the usually employed strongly basic solution, and without the use of an external source of electrical current. The source of noble metal ions is a salt containing a sufficient percentage of the noble metal to insure that only an insignificant number of its salt ions remain unused in the electrolyte, thereby enabling reuse of the same plating solution until substantially all of the noble metal has been plated out. Hence, there is no need for maintenance of a constant bath composition. A soluble salt of a carbonate or bicarbonate of an alkali metal such as sodium carbonate, or sodium bicarbonate, forms one of the basic components of the electrolyte. The desired range of alkalinity in accordance with the method of the present invention has been found to be from pH 8 to pH 10, rather than the pH of 13 to 14 which is required by the prior art chemiplating techniques. The electrolyte may be heated in order to facilitate more rapid plating. To produce a gold plating by the method of the present invention a carbonate concentration of from 100 to 200 grams per liter provides the desired degree of electrolyte alkalinity. An electrolyte temperature of approximately 100° C. provides a rapid plating rate, the plating thickness increasing with immersion time until a maximum thickness of from 6×10^{-6} to 9×10^{-6} inch is reached after approximately three minutes. For the plating of other noble metals by the method of the present invention proportionate adjustments of these parameters will be obvious to one skilled in the art and will provide equally satisfactory results.

In the semiconductor art semiconductor devices are frequently packaged in a glass envelope with Kovar (Kovar is the trade name for an iron base alloy manufactured by the Stupokoff Ceramic and Manufacturing Company of Latrobe, Pa. It includes 29% nickel, 17% cobalt, 53.7% iron and 0.3% manganese.) metallic sleeves, one such envelope being described in United States Patent No. 2,815,474 by William Lewis and Henry Frazier, issued December 3, 1957. It is desirable to gold plate the Kovar sleeves in order to provide a corrosion resistant surface to which a soldered connection can easily be made. The method of the present invention is particularly valuable in this application since Kovar sleeves cannot be satisfactorily gold plated by the prior art chemiplating methods and since the caustic electrolyte used in such methods would etch the glass envelope. As an example of the practice of the method of the present invention in such an application the contact surfaces of the semiconductor are first cleaned in any suitable manner by means commonly used in the plating art. A gold dip bath is prepared by adding to each liter of distilled water 160 grams of sodium bicarbonate, U.S.P., and 8 grams of potassium gold cyanide of at least 67½% gold content. This designated gold content has been found by the inventors to be the minimum required in order to satisfactorily produce the results as called for by the present invention method. The solution is heated and its temperature maintained within the range from 75° C. to 105° C. The entire semiconductor envelope is immersed in the solution for at least three minutes, during which time a uniform gold coating is deposited upon the Kovar sleeve surfaces. The envelope is then withdrawn from the solution and rinsed in hot water of about 75° C. for at least 30 seconds, after which it is rinsed with a 1% acetic acid solution, or in a weak solution of any acid which destroys cyanides and bicarbonates. While 75° C. for the water rinse and 1% acetic acid for the acid rinse has been found to be the

optimum value, a water temperature in the range from 50° C. to 100° C. is quite satisfactory. The acid solution should preferably be no more than 1% by volume but other higher percentages are also permissible. Thereafter the envelope is subjected to a water rinse. Thus, the metallic areas of the semi-conductor envelope are plated with a thin non-porous gold coating of uniform thickness, thereby providing the desired increased resistance to corrosion, better electrical conductivity, and a more pleasing appearance. It is appreciated that if it desired to plate only a portion of a metallic surface, only that portion need be immersed in the electrolyte or alternatively a maskant may be placed over that portion of the surface which is not to be plated.

In general, the method of the present invention overcomes the disadvantages of prior art chemiplating methods while still retaining their desirable advantages over electroplating methods. The disadvantages resulting from the use of strongly basic electrolytes have been overcome by the elimination of hydroxides, while costs and necessary degree of control have been reduced by the elimination of excess noble metal salt from the solution thereby resulting in a more reliable and efficient process.

Thus there has been described an improved method of chemiplating a noble metal coating upon metallic surfaces or bodies resulting in a relatively thin, bright, uniform, non-porous coating, the present method being efficient, reliable and inexpensive, and capable of plating most any base metal. The inventors have actually successfully plated the following "base metals": copper, nickel, tin, nickel-silver, soft solder, steel, Kovar, cobalt and zinc in accordance with the present invention. Thus, the term "base metal" as used herein is intended to include the above listed metals. The method of the present invention may also be used to deposit a noble metal coating upon the surface of semiconductor materials such as silicon. Thus, the term "metallic surface" as used herein is intended to include base metals as defined hereinabove and semiconductor materials.

What is claimed is:

1. A method of gold plating the surface of a metallic body which comprises immersing the metallic body in a solution having a pH value in the range from 8 to 10, said solution containing potassium gold cyanide having a gold content of at least 67½% and a soluble alkali metal salt selected from the group consisting essentially of carbonates and bicarbonates.
2. A method of gold plating the surface of a metallic body which comprises immersing the metallic body in a solution having a pH value in the range from 8 to 10, said solution containing potassium gold cyanide of at least 67½% gold content and sodium bicarbonate.
3. A method of gold plating the surface of a metallic body which comprises immersing the metallic body in a solution having a pH value in the range from 8 to 10, said solution containing potassium gold cyanide of at least 67½% gold content and sodium carbonate.
4. A method of gold plating the surface of a metallic body which comprises immersing the metallic body in a solution having a pH value in the range from 8 to 10, and a temperature within the range from 75° C. to 105° C., said solution containing potassium gold cyanide of at least 67½% gold content and a soluble alkali metal salt selected from the group consisting essentially of carbonates and bicarbonates.
5. A method of gold plating the surface of a metallic body which comprises immersing the metallic body in a solution having a pH value in the range from 8 to 10 and a temperature within the range from 75° C. to 105° C., said solution containing potassium gold cyanide of at least 67½% gold content and sodium bicarbonate.
6. A method of gold plating the surface of a metallic

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body which comprises immersing the metallic body in a solution having a pH value in the range from 8 to 10 and a temperature within the range from 75° C. to 105° C., said solution containing potassium gold cyanide of at least 67½% gold content and sodium carbonate.

7. A method of gold plating the surface of a metallic body comprising the steps of: immersing the metallic body for at least three minutes in a solution having a pH value in the range from 8 to 10, said solution containing potassium gold cyanide of at least 67½% gold content and a soluble alkali metal salt selected from the group consisting essentially of carbonates and bicarbonates; rinsing the metallic body with water at a temperature within the range from 50° C. to 100° C.; rinsing the metallic body with an acid solution which neutralizes carbonates and gold salts; and rinsing the metallic body with water.

8. A method of gold plating the surface of a metallic body comprising the steps of: immersing the metallic body for at least three minutes in a solution having a pH value in the range from 8 to 10, said solution containing potassium gold cyanide of at least 67½% gold content and a sodium bicarbonate; rinsing the metallic body with water at a temperature within the range from 50° C. to 100° C.; rinsing the metallic body with an acid solution which neutralizes sodium bicarbonate and gold salts; and rinsing the metallic body with water.

9. A method of gold plating the surface of a metallic body comprising the steps of: immersing the metallic body for at least three minutes in a solution having a pH value in the range from 8 to 10, said solution containing

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potassium gold cyanide of at least 67½% gold content and a sodium carbonate; rinsing the metallic body with water at a temperature within the range from 50° C. to 100° C.; rinsing the metallic body with an acid solution which neutralizes sodium carbonate and gold salts; and rinsing the metallic body with water.

10. A gold plating composition comprising a solution having a pH value in the range from 8 to 10 and a temperature within the range from 75° C. to 105° C., said solution containing potassium gold cyanide of at least 67½% gold content and sodium carbonate.

11. A method of gold plating the surface of a metal body consisting essentially of 29% nickel, 29% cobalt, 53.7% iron and ⅓% manganese which comprises immersing said body in a solution having a pH value in the range from 8-10, said solution containing potassium gold cyanide having a gold content of at least 67½% and a soluble alkali metal salt selected from the group consisting essentially of carbonates and bicarbonates.

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