

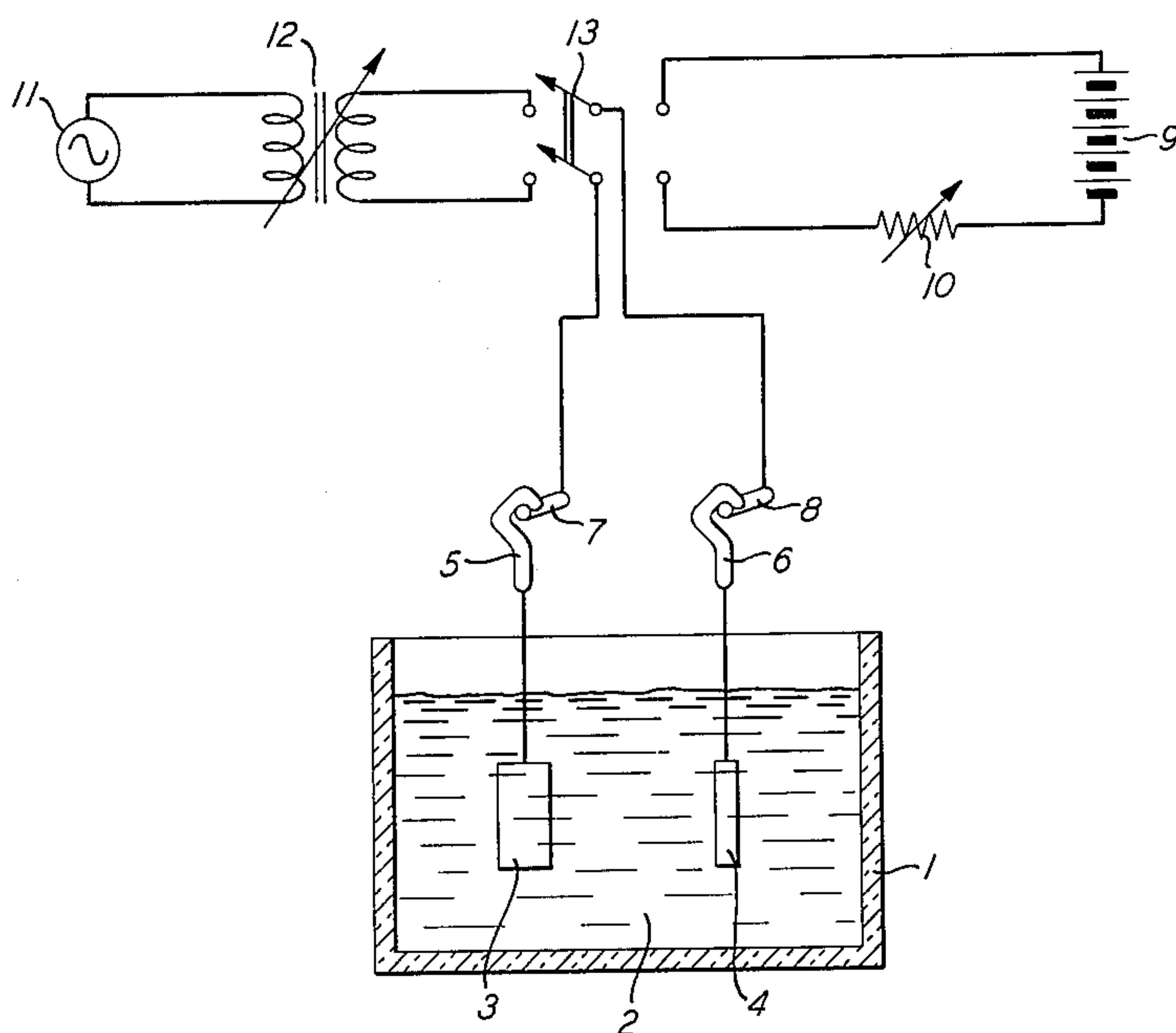
March 8, 1966

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3,239,439

ELECTRODEPOSITION OF METALS

Filed July 9, 1962



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3,239,439
ELECTRODEPOSITION OF METALS
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Filed July 9, 1962, Ser. No. 208,538
6 Claims. (Cl. 204-52)

This invention relates to the electrodeposition of copper, gold or silver onto molybdenum or tungsten. More particularly, the technique utilizes a sequential combination of alternating current and direct current to initiate an adherent deposit onto the base metal. This expedient in combination with a specific plating solution has been found to give extremely useful and unexpected results.

The electrodeposition of copper, gold or silver directly onto molybdenum or tungsten is useful for the manufacture of many electrical devices, notably electron tubes. Because of difficulty in obtaining a truly clean surface on which to initiate the electrodeposition, a lack of adherence to the base metal often occurs, and in many cases the deposit is blistered. In some procedures this difficulty is overcome by sintering the piecepart in a hydrogen atmosphere furnace at a temperature somewhat below the melting point of the deposited metal.

This invention is directed to a newly developed plating technique by which copper can be electrodeposited onto molybdenum directly with good adherence, and one which eliminates the need for the sintering operation. By formulating the electrolyte with either a gold or a silver salt it is possible to deposit these metals onto molybdenum in the same way as copper. Further, by using the same operating conditions adherent electrodeposits can be made directly on tungsten.

These and other aspects of the invention may be more fully understood from a consideration of the drawing in which:

The figure is a schematic representation of an apparatus useful in conducting the plating operation of this invention.

The figure shows a plating tank 1 containing electrolyte 2. Suspended within the electrolyte is a workpiece 3 and an anode 4. The anode is preferably an insoluble metal such as platinum. Supporting the workpiece 3 and electrode 4 are conductive holders 5 and 6 which engage electrical bus bars 7 and 8. The circuit for providing the desired current is connected as shown. The circuit consists of a D.C. power supply 9 adjustable by variable resistor 10 and an A.C. source 11 varied by autotransformer 12. These current supplies may be alternatively selected by double pole, double through switch 13. The D.C. power supply was rated at 0 to 15 v., 0 to 25 amps. The A.C. source provided 0 to 24 v. current, 0 to 30 amps.

Specific exemplary procedures of this invention are presented in the following detailed description.

A typical plating solution formulation for copper deposition is shown in Example 1. This technique relies in part on the cleaning and striking (or flash plating) of the base metal in a single solution, and the reduction of copper ions at the cathode at an extremely low cathode efficiency and high hydrogen evolution voltage.

Example 1

Sodium hydroxide	grams/liter	53
Cuprous cyanide	do	1.5
Sodium cyanide	do	6.7
Workpiece current density (A.C.)	amperes/square inch	7
Cathode current density (D.C.)	do	2.3

The solution (Example 1) contains a relatively high concentration of hydroxide, 5%, and a relatively low con-

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centration of copper cyanide, 0.15%. The pretreatment phase of the plating operation is carried out through the use of the A.C. power supply. A conventional D.C. supply is used for the flash plating phase. The two supplies are connected to the electrodes through the double pole, double throw switch. The power supplied to the bath thus can be readily changed from one power source to another. The pretreating operation owes much of its effectiveness to the scrubbing action of hydrogen evolved when the part is alternately made anodic and cathodic. Copper does not deposit at either electrode during this operation because of the changing polarity. This alternating current treatment is carried out for 1/5 to 20 seconds, following which the double pole, double throw switch is used to connect the direct current power supply to the plating electrodes.

With direct current applied across the electrolyte, the part to be plated is held steadily at a negative (cathodic) potential. Copper and hydrogen ions reduce at the cathode but because of the formulation of the electrolyte, this deposition takes places with a high hydrogen deposition potential and a low cathode efficiency for copper. This efficiency has been measured at less than 2%. The low efficiency of this strike contributes to the good adherence which parts plated in this bath exhibit.

The A.C. pretreatment, D.C. flash plating process is used to deposit amounts of the order of 1 milligram per square inch or less of copper. This deposit can then be effectively built up to the desired thickness by conventional copper plating techniques. Such procedures are well established in the art. For instance, see Modern Electroplating, edited by A. G. Gray, pages 98 to 114 and 194 to 225 (1953).

Example 2

Sodium hydroxide	grams/liter	40
Silver cyanide	do	2
Sodium cyanide	do	6
Workpiece current density (A.C.)	amperes/inch ²	10
Cathode current density (D.C.)	do	3

Example 3

Sodium hydroxide	grams/liter	15
Potassium gold cyanide	do	2
Sodium cyanide	do	2
Workpiece current density (A.C.)	ampere/inch ²	1
Cathode current density (D.C.)	do	4

Example 2 has been used to deposit silver directly onto molybdenum or tungsten and Example 3 to deposit gold directly onto molybdenum or tungsten by the same procedure presented in Example 1.

The foregoing embodiments are given by way of example. Limited deviations from the specific current density values and plating conditions can be tolerated while still providing the unexpected results to which this invention is directed. For instance, potassium salts may be substituted for the sodium salts to achieve similar results. Other deviations and permissible operating ranges are set forth below.

Prior art cyanide plating solutions typically use hydroxide-to-metal salt ratios of the order of a fraction to one. As previously indicated, this invention relies in part on a significantly higher hydroxide-to-metal salt ratio. For the purposes of this invention this ratio should lie in the range of 10:1 to approximately 160:1. This, in terms of percentage composition of the aqueous electrolyte, is expressed as 3 to 8% hydroxide: 0.05 to 0.3% metal salt. The remaining ingredient, a soluble cyanide salt, such as an alkali metal cyanide, is included to facilitate and maintain the dissolution of the metal salt. This component is used in any amount appropriate for this purpose, generally 1 to 30%.

The cathode current density useful for the A.C. pre-plating operation generally falls within the range of 1 to 15 amperes/inch². The cathode current density for the D.C. plating operation is preferably 1 to 5 amperes/inch². These current densities, as compared with prior art procedures, are quite high, which contributes in part to the success of the present invention.

Various other modifications and extensions of this invention will become apparent to those skilled in the art. All such variations and deviations which basically rely on the teachings through which this invention has advanced the art are properly considered within the spirit and scope of this invention.

What is claimed is:

1. A process for electro-depositing a metal selected from the group consisting of copper, gold and silver onto a substrate selected from the group consisting of molybdenum and tungsten which comprises the steps of: placing the substrate in an electrolyte comprising the following aqueous solution:

	Percent
AOH -----	3 to 8
MCN -----	0.05 to 0.3

where A is selected from the group consisting of K and Na and MCN is a solubilized cyanide salt selected from the group consisting of copper cyanide, silver cyanide and gold cyanide, passing an alternating current through

said substrate as an electrode in said electrolyte for a period of 3 to 60 seconds, and passing a D.C. current through said substrate as cathode in said electrolyte to electrodeposit said metal on the substrate.

2. The process of claim 1 wherein the MCN is CuCN and the metal electroplated is copper.

3. The process of claim 1 wherein the MCN is AuCN and the metal electroplated is gold.

4. The process of claim 1 wherein the MCN is AgCN and the metal electroplated is silver.

5. The process of claim 1 wherein the current density at the substrate during the A.C. pretreatment is maintained within the range 1 to 15 amperes/inch² and the cathode current density during the D.C. electrodeposit is maintained within the range 1 to 5 amperes/inch².

6. The process of claim 1 wherein the electrolyte contains a soluble cyanide salt in an amount sufficient to facilitate dissolution of the MCN.

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