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METHOD OF ELECTROPLATING AND ELECTROFORMING GOLD IN AN ULTRASONIC FIELD

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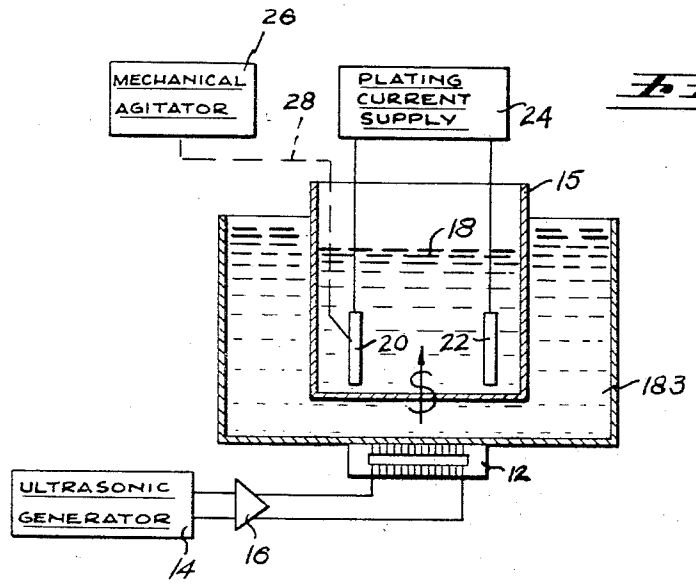
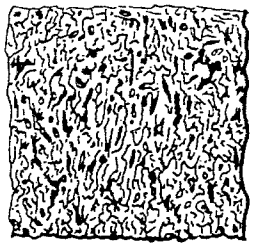


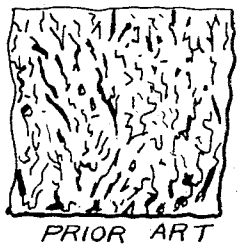
Fig. 1

Fig. 3



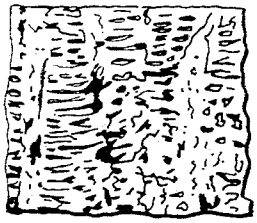
DENSE COLUMNAR GOLD

Fig. 2



PRIOR ART ACID GOLD

Fig. 4



LAMINAR GOLD

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METHOD OF ELECTROPLATING AND ELECTROFORMING GOLD IN AN ULTRASONIC FIELD

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ABSTRACT OF THE DISCLOSURE

A method of electrodepositing gold as a coating or to electroform articles. The method ultrasonically agitates an aqueous solution comprising at least 5 troy ounces of gold as alkali metal gold cyanide per gallon of solution. The combination of high gold content of the solution and ultrasonic agitation during deposition permits pure gold deposits which are also very hard.

This invention pertains to a method for electroplating substantially pure gold onto a basis metal, to a novel electrolytic bath used in that plating, and to a method for electroplating said gold in the presence of an ultrasonic field. The gold which is plated is exceptionally pure, uniform, and dense. The method may also be used for electroforming.

Gold plate may be electro deposited, in accordance with this invention, with a purity of a Type I plate and a hardness equal to or better than a Type II plate as those types are defined in Military Specification MIL–G–45204, dated Mar. 7, 1960, and set forth in the "Metal Finishing Directory Guidebook for 1965," published by Metals & Plastics Publications, Inc., of 99 Kinderkamack Road, Westwood, N.J.

The general state of the art of gold plating is set forth under the heading "Gold Plating" between pages 239 and 257 of the "Metal Finishing Directory Guidebook for 1965."

In accordance with this invention, a novel gold plating bath is placed in an ultrasonic field which prevents polarization at the electrodes, allows exceptionally high current densities to be used, and substantially increases the throwing power of the plating solution to cause the electroplated gold to be uniformly distributed over the basis metal, to cause the plated gold to be exceedingly pure, to cause the plated gold to be exceptionally dense, and to cause the gold to deposit at an exceptionally rapid rate. In one run under high plating current densities, the metallurgical structure of the plated gold assumed a novel configuration, hereinafter designated as laminar gold plate.

Some ultrasonic plating processes are known. For example, one apparatus and process for ultrasonic plating is described on page 47 of MPM magazine dated March 1962. A discussion of "The Effects of Ultrasonic Waves on Electrolytes and Electrode Processes," by S. Barnardt is found in volume 7, pages 84 to 101, of the Quarterly Review (London, 1953).

The process of this invention uses an ultrasonic generator and transducer in combination with a plating solution. The plating solution is composed of alkali gold double cyanide salt in water which is heated, for example, to 150° F. to keep the required amount of alkali gold double cyanide in solution.

A typical alkaline gold double cyanide plating bath of the prior art has a gold concentration of 1 to 2 troy ounces of gold per gallon of plating bath. However, the plating bath of this invention uses over 5 troy ounces of gold (in the form of an alkali gold double cyanide) per

gallon of plating solution, with a preferred range of 7 to 9 troy ounces of gold at 150° F. The upper limit of the amount of gold which is useful is determined by the saturation constant of the alkali gold double cyanide in the plating solution at the elevated temperature in the presence of an ultrasonic field.

Although some prior known acid-type gold plating baths or solution operate in the range of 140 to 160° F., prior known alkaline gold plating baths or solutions normally are used below 130° F. because in the use of the prior art alkaline baths the gold plate becomes softer when plated at higher temperatures. In the process and using the plating solution of this invention, the plating solution temperature may be increased to boiling. Because the purpose of increasing the temperature is to allow a greater concentration of gold to be placed into solution, 150° F. is typical for this invention. At higher temperatures additional gold may be placed into solution.

When the gold is used in the form of potassium gold double cyanide, additional potassium cyanide and/or sodium cyanide may be added to increase the conductivity and throwing power of the solution. When sodium cyanide is used, brightness is increased directly as a function of the amount of free sodium ion which is added. Hardness and throwing power are also increased.

The usual current density range for plating gold, in accordance with the prior art, is between 2 and 10 amperes per square foot. Any increase beyond that range causes a polarization at the electrodes with resultant deterioration in the plate quality. In the presence of an ultrasonic field, in accordance with this invention, the plating current may be increased indefinitely. Typically, plating current densities between 30 and 50 amperes per square foot are used. It is possible, however, to use plating currents, for example, of the order of 1000 amperes per square foot.

Because of the use of ultrasonics, the plating bath of this invention does not require a continuous filtration to remove the contaminants in order to produce substantially pure deposits of gold.

It has been observed in the process of this invention that the pH of the plating solution does not vary, but remains substantially constant whereby the quality and characteristics of the plated gold is substantially constant from plated piece to plated piece.

Further, the gold plate in accordance with this invention is substantially 24 karat or 100% pure gold produced from a plating solution which contains only the alkali earth metals and gold as the metallic ion. Gold purity exceeding 99.999% has been observed.

Although typical high cyanide, high gold content electroplating solutions produce rough or granular deposits, the gold plating bath of this invention, together with the ultrasonics in accordance with this invention produces a gold plate which neither needs to be burnished nor polished, nor scratched to yield a bright finish. The plating solution of this invention, when used in accordance with the process of this invention, may yield bright electroplated gold even when the plate is a very heavy deposit, for example in excess of 0.0100 inch.

In addition to the fact that bright gold is deposited, the gold is further brightened by the ultrasonic agitation of the plating solution itself.

The gold deposit produced in accordance with this invention is dimensionally uniform and accurately reflects the machining tolerances of the basis metal. For example, reflection of the machining tolerances of the basis metal have been observed to an accuracy of 500 millionths of an inch.

Because the bath or plating solution of this invention does not use organic materials, it does not require aging before use.

The plating rate of the gold bath or solution of this invention in the process of ultrasonics varies over wide ranges. For example, it has been observed that the plating rate may vary between 0.0002 inch per hour to a preferred rate of substantially 0.0001 inch per minute to a higher rate of 0.001 inch per minute. The rate of deposition is a function of the plating current density.

For any particular plating bath, the hardness of the plate is also a function of the plating current density (corresponding to rate of deposition) varying from a Knoop hardness of 125 to 220 with a corresponding current density range between approximately 30 and 1000 amperes per square foot.

Knoop hardness is a microhardness determined from the resistance of metal to indentation by a pyramidal diamond indenter, having edge angles of 172° 30′ and 130°, making a rhombohedral impression with one long and one short diagonal.

The formula for Knoop hardness in kilograms per square millimeter is:

$$\text{Knoop hardness} = \frac{(14230)\ (\text{load in grams})}{(\text{length of the longer diagonal, in microns})^2}$$

Further, because of the high rate of deposition available, electroforming of gold is practical with the process of this invention.

A direct result of the high density gold plate produced by the process of this invention is that a re-solderable condition is obtained, i.e. if one solders to the plate produced by said process with any of the well-known solder materials and then wishes to remove what has been soldered and later re-solder the same area, sufficient gold remains for solderability because with the dense gold deposit of this invention only half as much gold goes into solution the first time with the solder.

Because of the greater density of the gold plate produced by the process of this invention, the required thickness for corrosion resistance of the basis metal can be greatly reduced.

With the ultrasonic gold plating process of this invention, a leveling effect is caused, i.e. because of the throwing power of the bath in the presence of ultrasonics no bridging of holes occurs. Further, because of the throwing power, plating can be produced in blind areas such as threaded holes and areas—for example—of less than 0.0005 inch in diameter or width. When an article to be plated is immersed into the plating solution and into the ultrasonic field, it acts as a secondary transducer, causing gas entrapped in blind areas to be degassed from the solution. The gas is then immediately replaced by the solution carrying the gold ions.

Because of the presence of cyanide, the solution must be maintained basic, i.e. the pH of the solution is preferably in the alkaline range between 8.0 and 14.0 with an optimum range between 10.5 and 11.5 for brightness and smoothness.

A typical plating bath of this invention uses 7 to 9 troy ounces of gold (in the form of potassium gold double cyanide) per gallon of plating solution. If free potassium cyanide is added, between 3.6 ounces and 6 ounces of cyanide ion per gallon of solution is a typical concentration. If instead of potassium cyanide, free sodium cyanide is added, up to 2 ounces per gallon may be used. Either potassium cyanide or sodium cyanide increases the conductivity of the bath, adjusts the pH of the bath, and increases the leveling of the plate. The sodium cyanide also increases the throwing power and the hardness of the plate.

Although not needed, carbonates and Rochelle salts may be added if desired.

It is frequently desirable to use a wetting agent such as pentadecafluoro-octanoic acid up to 0.1% by weight. Alternatively, sodium laural sulfonate may be used as a wetting agent but these wetting agents are not necessary.

The minimum plating current density that can be used is that current density at which plating occurs without being pulled off by the ultrasonic cavitation. With an ultrasonic field intensity between 7 and 10 watts per square inch, the minimum plating current density which can be used is of the order of 15 amperes per square foot. With an ultrasonic field intensity of between 2.5 and 5 watts per square inch, the minimum plating current density is about 10 amperes per square foot. To characterize it differently, the cavitation created by the ultrasonic field prevents the metal ions from reaching the cathode unless the plating current density exceeds a predetermined minimum value.

In general, the plating bath efficiency increases as the frequency of the applied ultrasonics decreases until some critical frequency in the audio range is reached, after which the efficiency decreases rapidly. However, because of the audio power which is used, it is usually desirable that the frequency which is used be above the audible range of operators of the equipment. Accordingly, a frequency of the order of 20 kilocycles for the ultrasonics is typical.

Using an ultrasonic generator to produce an ultrasonic field in the plating solution, and using the plating solution of this invention, the metallographic section of the plate has closely substantially uniformly spaced cells as shown in FIGS. 3 and 4. In one example (FIG. 4), where the plating current density was approximately 50 amperes per square foot, a laminar gold plate was found, i.e. the cells were flattened to cause the cell boundaries to be substantially parallel to the basis metal in a laminar pattern.

The plated pure gold has a Knoop hardness of over 125 which means that it is a Type I gold in a Type II hardness range.

According to the prior art, to increase the throwing power of the gold solution, the amount of gold in solution should be decreased. However, according to this invention, the amount of gold is increased and the throwing power of the gold is also increased.

It is, therefore, a first object of this invention to electroplate gold.

It is a second object of this invention to electroplate gold at an extremely rapid rate.

It is a third object of this invention to electroplate gold with heretofore unobtainable adhesion properties.

It is a further object of this invention to electroplate gold with a controllable surface finish.

It is likewise an object of this invention to electroplate gold which has a Type I purity and a Type II hardness.

It is yet another object of this invention to achieve the above enumerated objects by ultrasonically agitating a plating bath.

It is a specific object of this invention to provide a new process for gold electroplating and a new gold plating bath, solution, or electrolyte for use with that process.

It is also an object of this invention to electroform gold.

Other objects will become apparent from the following description, taken in connection with the accompanying drawings in which:

FIGURE 1 is a partly schematic and partly structural view of a typical plating tank containing the plating bath of this invention and using an ultrasonic generator to generate an ultrasonic field to practice the process of this invention;

FIGURE 2 is a sketch of a metallographic view, magnified 1500×, of a section of gold plated in an acid bath in accordance with the prior art;

FIGURE 3 is a sketch of a metallographic section, magnified 1500×, of gold plated in accordance with this invention at 30 amperes per square foot, and showing a columnar grain structure; and

FIGURE 4 is a sketch of a metallographic section, magnified 1500×, of gold plated, in accordance with this invention, at 50 amperes per square foot, and showing a laminar gold plate structure.

Referring to FIGURE 1, an ultrasonic transducer **12**, which is preferably symmetrically placed with respect to the electrodes **20** and **22**, is driven by an ultrasonic generator **14** and power amplifier **16**. The plating solution **18** of this invention is then agitated by the ultrasonic waves produced by transducer **12**. In general, the efficiency of the plating increases as the frequency of the ultrasonic generator is reduced until, as some very low frequency, the efficiency suddenly drops off. However, as the frequency of the ultrasonic generator reaches the audible range, it becomes annoying to the operator. Hence, a lowest inaudible frequency is desired. Typically, ultrasonic generators which are used in ultrasonic cleaning, and the like, have a frequency of approximately 20 kilocycles. A 20 kilocycle ultrasonic generator operates satisfactorily in the process of this invention.

A cathode **20** and an anode **22** are submerged, during plating, in the plating solution **18** with the item being plated at the cathode. Plating current is supplied by a plating current supply **24**, preferably at a rate above ten amperes per square foot. In another embodiment, (not shown) the anode is annular about the cathode.

It may be desirable to move the cathode **20** slightly during plating to eliminate any pattern formed by the ultrasonic waves. To that end, a mechanical agitator **26** is mechanically connected to the cathode **20** by a linkage **28**.

In a preferred embodiment, the transducer **12** excites another liquid **183**, such as water. The plating tank **15** is immersed into the water to excite the plating solution **18**.

In operation, the ultrasonic generator is started before the cathode is submerged into the plating solution **18**. Plating current supply **24** applies a voltage between the anode **22** and cathode **20**, preferably before the cathode **20** is submerged into the plating solution **18**. As the cathode **20** is submerged into the plating solution **18**, the plating current starts to flow. It is desirable that the voltage from the plating current supply **24** and the ultrasonics be applied prior to the submersion of the cathode **20** into the plating bath **18** in order to avoid passivation of the cathode **20**.

By using a loose holder (not shown) to hold the item to be plated, no marks appear on the finished plate due to the holder. The holder is agitated by the ultrasonics and ion-carrying electrolyte gets under the holder.

Prior to the submersion of the cathode **20**, to be plated, into the plating bath **18**, conventional preparation of the specimen **20** by cleaning, zincating, flashing and the like is performed. Thus, the gold may immediately be plated onto the cathode **20**. It is to be stressed that the chosen steps depend upon the basis metal as set forth in descriptions of the prior art.

As the gold is plated onto the cathode **20**, the alkaline gold double cyanide releases gold ions and changes to an alkaline cyanide. The resulting alkaline cyanide residue, such as potassium cyanide, remains in the plating solution **18** while the ultrasonics is on and falls to the bottom of the tank only after removal of the ultrasonics and cooling of the solution.

It is to be stressed that although potassium gold cyanide has been mentioned as a typical carrier of the gold, that other gold salts, such as other alkaline gold cyanides, which are compatible with the remaining components in the plating solution **18** may be used as the gold ion carrier.

In excess of 5 troy ounces of gold (in the form of an alkali gold double cyanide) per gallon of plating solution, with a preferred range of 7 to 9 troy ounces of gold at 150° F. is used. The upper limit of the amount of gold which may be used is determined by the saturation of the alkali gold double cyanide in the plating bath in the presence of an ultrasonic field.

Examples in accordance with the invention of specific plating baths which may be used in the process of the invention are:

EXAMPLE I

In a first example, between 7 and 9 troy ounces of gold (in the form of potassium gold double cyanide) per gallon of plating solution at a solution temperature of 150° F. is used with between 7 and 10 ounces per gallon of potassium cyanide, 4 to 6 ounces per gallon of potassium carbonate, 0.5 to 5.0 ounces per gallon of Rochelle salts, and up to 0.1% by weight of pentadecafluoro-octanoic acid.

EXAMPLE II

In a second example, the potassium gold double cyanide and the potassium cyanide of Example I are used alone in an aqueous solution.

EXAMPLE III

In a third example, between 7 and 9 troy ounces of gold (in the form of potassium gold double cyanide) per gallon of plating solution is used with from 3.6 ounces to 6 ounces of free cyanide per gallon of plating solution in the form of potassium cyanide and up to 2 ounces of sodium cyanide per gallon of plating solution. The plating solution may also contain carbonates and Rochelle salts if desired. A wetting agent such as up to 0.1% by weight of pentadecafluoro-octanoic acid or sodium laural sulfonate may be used.

In the above plating solution the pH of the bath is maintained between 8 and 14 with a preferred range between 10.5 and 11.5 for brightness and smoothness.

Referring now to FIGURE 2, a sketch of a metallographic section, magnified 1500 times, of a typical gold plate which is plated with a conventional acid bath, and no ultrasonic field, is shown. It is to be noted that it is completely non-crystalline in structure.

Referring to FIGURE 3, a sketch of a metallographic section, magnified 1500 times, of a gold plate which was plated in accordance with this invention at a current density of 30 amperes per square foot is shown. Note the columnar grains substantially perpendicular to the basis metal and the dense packing of the associated grain boundaries.

At between 45 and 50 amperes per square foot of plating current density, the character of the crystalline structure of the gold changed in one run to a laminar structure which is shown in FIGURE 4. Note the gold laminates which contribute to increasing the density and hardness of the plate. The laminates are shown in stacks with their boundaries substantially parallel to the basis metal.

Further, because the gold is more densely packed, its electrical and thermal conductivity is increased. Because the produced hard surface is pure gold, it is joined more easily to other metals, by soldering and welding, than a gold alloy.

Because of the high deposition rate of gold in the process of this invention, electroforming of gold is practical. Electroforming of gold may be achieved by any of the known processes in conjunction with the novel plating process and electrolyte of this invention. Examples of electroformed gold:

Example A

Plate gold onto clean unactivated copper or aluminum, then physically withdraw the aluminum or copper.

Example B

Deposit copper over plaster of appropriate shape, plate gold onto the copper, dissolve out the plaster with water and the copper with acid.

Example C

Plate gold onto a basis metal, then machine off the gold where it is not desired.

Copper, nickel, silver, and other conventional strike coatings may be used as a basis metal for the gold plate of this invention. For example, zincated aluminum may be covered with a copper strike before the gold is plated.

Although the invention has been described above in detail, it is not to be limited by that description, but only in accordance with the spirit and scope of the appended claims.

We claim:

1. In the method of electroplating gold onto a basis metal in an aqueous electrolyte bath by application of a plating potential, the improvement in said method wherein said electrolyte contains at least 5 troy ounces of gold in the form of alkali metal gold cyanide per gallon of electrolyte, said electrolyte is ultrasonically agitated, and said potential is sufficient to plate with plating current densities in excess of that required to overcome the cavitation action of the ultrasonic agitation.

2. A method as recited in claim 1 in which said gold is in the form of potassium gold double cyanide and said plating bath further contains potassium cyanide in sufficient quantity to adjust the pH of said bath to between 10.5 and 11.5.

3. A method as recited in claim 2 in which said plating bath further has up to 2 ounces per gallon of sodium cyanide.

4. A method as recited in claim 3 and further comprising the step of moving said item to be plated relative to said ultrasonic field during the plating process.

5. A method as recited in claim 4 in which said item to be plated is loosely held.

6. A method as recited in claim 3 wherein the coated basis metal is subsequently machined to remove excess gold.

7. A method as recited in claim 1 in which said gold is plated over a clean unactivated basis metal, then removing said basis metal to produce an electroformed gold article.

8. A method as recited in claim 7 in which said basis metal is attached to other dissolvable material, then dissolving said other material to create an electroformed gold article.

9. The method of claim 1 wherein the plating potential is sufficient to provide a plating current density exceeding 10 amperes per square foot.

10. The method of claim 9 wherein the current density is at least 30 amperes per square foot.

11. The method of claim 1 wherein said aqueous plating solution is alkaline.

12. The method of claim 1 wherein said plating solution contains between 7 and 9 troy ounces of gold per gallon of solution.

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