1

ABSTRACT OF THE DISCLOSURE

An aqueous acid bath for producing bright rhodium
electrodeposits having low internal stress contains rhodium
ion, aluminum ion sulfate radical and a polycarboxylic
organic acid. Preferably, it also contains a small amount
of the phosphate radical.

BACKGROUND OF THE INVENTION

Electrodeposits of rhodium are beneficially used in
decorative applications for jewelry and for tarnish resist-
ant silver surfaces, in the electronics industry for printed
circuitry and the like, and in general to improve the
wear and/or corrosion resistance of various base metals.
Commercial baths for rhodium plating, which usually
comprise relatively strong acid phosphate, sulfate, or com-
bination phosphate/sulfate solutions are generally quite
satisfactory for many applications. However it is well
known that high internal stresses, typically of an order
of magnitude of 150,000 pounds per square inch, are
frequently encountered in rhodium electrodeposits pro-
duced with such baths. Stress in the deposits tends to
cause peeling, cracking, and distortion of the deposited
metal, and in some instances adversely affects the sub-
strate metal.

Attempts have been made to relieve the internal stress
in rhodium plate by the addition of chloride ion or mag-
nesium sulfate to the plating baths. Although these
additives may tend to lower the internal stress of the
deposit, they generally also reduce the brightness of the
plate to a degree that is objectionable for many applica-
tions. As far as is known, no practical rhodium plating
bath is presently available which is capable of producing
a low-stress deposit that is clear, bright and substantially
free of pin holes and other surface imperfections.

Accordingly, it is an object of the present invention to
provide a novel rhodium electroplating bath which is
capable of producing a rhodium deposit exhibiting a rela-
tively low level of internal stress.

It is also an object to provide such a bath which is
capable of producing a bright rhodium deposit that is
substantially free from cloudiness, pin holes and other
surface imperfections.

A further object is to provide a novel composition for
producing such a bath.

Still another object of the invention is to provide a
novel method for depositing rhodium from an acid bath
to produce a bright electroplate that is relatively free
from internal stress.

SUMMARY OF THE INVENTION

It has now been found that the foregoing and related
objects of the present invention can be readily attained
in an aqueous acid rhodium plating bath. The bath com-
prises about 1.0 to 30.0 grams per liter of rhodium ion,
about 0.05 to 5.0 grams per liter of aluminum ion, and
about 50.0 to 400.0 grams per liter of sulfate radical, and
it has a pH of about 0.1 to 2.0.

The bath also contains about 1.0 to 25.0 grams per
liter of polycarboxylic organic acid which may be selected
from the group consisting of azelaic acid, pimelic acid,

2

oxalic acid, malonic acid, adipic acid, glutaric acid,
tartaric acid, succinic acid, citric acid, maleic acid, fumaric
acid, and mixtures thereof. Most desirably, plating baths
embodying the present invention will contain 2.0 to 10.0
grams per liter of rhodium ion, 0.2 to 4.0 grams per liter
of aluminum ion, 3.0 to 10.0 grams per liter of the poly-
basic organic acid, and 100.0 to 250.0 grams per liter
of sulfate radical; such a bath will preferably have a pH
of at least 1.2.

Certain objects of the invention are attained by the
provision, in accordance herewith, of a rhodium electro-
plating composition comprised of rhodium sulfate, a sol-
uble aluminum salt, and a polybasic organic acid that
is at least slightly soluble in water under plating con-
ditions. The amounts of the various components of the
composition will be selected so as to provide, upon dis-
solution in water, the respective amounts of the various
components set forth hereinbefore.

Other objects of the invention are attained by the
method of the invention, wherein a rhodium electroplat-
ing bath is employed containing the components and
amounts thereof previously defined. The bath is prepared
and maintained at a temperature of about 20.0 to 65.0°
centigrade, and a workpiece having a metallic surface and
an anode member are immersed therein. A voltage which
is controlled to provide a current density of about 0.5
to 20.0 amperes per square foot at the surface of the
workpiece is applied across the workpiece and anode
member to deposit rhodium from the bath upon the metal-
lic surface. In the preferred embodiments of the method,
the bath has a pH of at least 1.2 and is maintained at a
temperature of about 40.0° to 55.0° centigrade, and the
current density at the workpiece surface is about 5.0 to
15.0 amperes per square foot. Most desirably, the method
utilizes a preferred bath having a composition as previ-
ously set forth.

DETAILED DESCRIPTION OF THE PREFERRED
EMBODIMENTS

The essential components of the novel plating bath of
the present invention are rhodium ion, aluminum ion,
polycarboxylic organic acid and sulfate radical, and it
has been found that acid plating baths containing only
these active components produce bright rhodium deposits
which exhibit relatively low levels of internal stress. So
long as the presence of interfering ions and contaminat-
ing metals is substantially avoided, the foregoing essential
components may be provided by any suitable soluble salt
or other compound. However, baths free of extraneous
ions and radicals may be readily be produced by dis-
solving in water appropriate quantities of rhodium sulfate
and aluminum sulfate, with increases in acidity being
effected by the addition of sulfuric acid thereto.

However, because relatively pure industrial grades of
aluminum sulfate, i.e., those that are substantially free
of contaminating metals, are not generally available, the
aluminum constituent has conveniently been provided
as the phosphate salt (i.e., aluminum orthophosphate).
In fact, about 10.0 to 70.0 grams per liter of the phos-
phate radical, the content of which may be provided or
augmented by phosphoric acid, appears to have a levelling
effect in relatively thick deposits and to reduce the sen-
sitivity of the bath to contamination; on the other hand,
the optimum levels of brightness and stress relief may
be achieved with the all-sulfate type of bath, and too
much phosphate has been found to be detrimental. There-
fore, in mixed sulfate/phosphate baths, the weight ratio
of sulfate radical to phosphate radical should be at least
2.0:1.0, with the concentration of phosphate radical not
exceeding 120.0 grams per liter and preferably being in
the range set forth hereinabove. Most desirably, the bath
and compositions used for the production thereof will

3

be substantially free of phosphate. To avoid any question, perhaps it should be pointed out that, as used herein, the term "phosphate radical" refers to the trivalent group having the formula "PO_4," such as may be provided by aluminum orthophsphate and orthophosphoric acid.

The rhodium salt must be added in an amount sufficient to provide to the bath at least about 1.0 gram per liter of rhodium ion, since smaller amounts will tend to produce dull or otherwise unacceptable deposits. Conversely, the amount of the rhodium salt should not exceed that which will furnish rhodium ion to the bath in a concentration of more than 30.0 grams per liter, because greater amounts tend to be unduly expensive and wasteful, largely as a result of high drag-out losses, without affording concomitant advantages. The best results are achieved when the amount of rhodium ion in the bath is between 2.0 and 10.0 grams per liter, and no need for amounts in excess of about 10.0 grams has been encountered.

For satisfactory deposits, it has been found that the aluminum ion should be included in the bath in an amount ranging between 0.05 and 5.0 grams per liter, and preferably the amount thereof will be from 0.2 to 4.0 grams per liter. Smaller quantities of the ion are quite ineffective, and more than about 5.0 grams per liter is uneconomical and tends to adversely affect quality. Generally, the concentration of the aluminum ion will not exceed that of the rhodium ion, and in most instances it will be considerably lower.

In addition to the essential components set forth hereinbefore, the presence of at least about 1.0, and preferably 3.0 to 10.0 grams per liter of a polycarboxylic organic acid has been found to be very beneficial. Although the organic acid may be present in an amount up to the limit of its solubility, about 25.0 grams per liter will generally be a practical maximum concentration. Exemplary of the various polycarboxylic organic acids that may be used are azelaic acid, pimelic acid, oxalic acid, malonic acid, adipic acid, glutaric acid, tartaric acid, succinic acid, citric acid, maleic acid, fumaric acid, and mixtures thereof. Although the dicarboxylic acids are especially preferred, it appears that virtually any polycarboxylic organic acid that is at least slightly soluble in the aqueous bath under plating conditions may be employed with some degree of benefit to the deposits produced thereby. The polycarboxylic acid appears to further reduce internal stress in the deposit, as well as to counteract the adverse effects of contaminating substances, such as the small amounts of silver and zinc that may be introduced with the rhodium salt and the elemental sulfur that may be produced by sulfate oxidation.

A typical plating formulation embodying the present invention is as follows:

	Ounces per gallon
Rhodium sulfate	2.0
Sulfuric acid	7.0 to 10.0
Aluminum orthophosphate	0.3
Dicarboxylic organic acid	1.0
Water to one gallon.	

Azelaic acid and pimelic acid have been used with equivalent efficacy as the dicarboxylic organic acid in the foregoing formulation.

The pH of the bath should be maintained at a level within the range of about 0.1 to 2.0, with most satisfactory results usually being attained at pH values of at least 1.2. Lowering of the pH will generally be effected with sulfuric acid; in the event that the bath is more acidic than desired, the pH may be altered without introducing foreign ions or radicals simply by dilution with water and adding such amounts of active ingredients as

4

are necessary to provide the required concentrations of ions and radicals.

The best operating temperature for the bath is in the range of 20.0° to 65.0° centigrade and preferably the bath is maintained at 40.0° to 55.0° centigrade. As is commonly known, plating at unduly low temperatures tends to be inefficient, whereas temperatures that are to high tend to cause excessive consumption of bath components and also to render operation rather inconvenient and difficult. The current density range of bright deposits will generally be from about 0.5 to 20.0 amperes per square foot, and usually the most satisfactory deposits will be produced at current densities within the range of 5.0 to 15.0 amperes per square foot. Normally, the applied voltage will be about 2 to 6 volts and will be regulated to provide an average current density at the workpiece of about 5 to 15 amperes per square foot. Whereas the actual current will depend upon the dimensions and configuration of the workpiece, values of 1 to 100 amperes are typical.

The baths of the invention may be employed for rack and also for barrel plating, and in both cases moderate to vigorous agitation is beneficial. In accordance with conventional practice, insoluble anodes will normally be used, and they may appropriately be of platinum or platinum-surfaced construction; with such insoluble anodes, the bubbling of generated gas may be relied upon to provide the desired level of agitation in the bath. The configuration of the anode will vary depending upon the plating method and the associated equipment used; however expanded composite anodes of platinum clad tantalum or platinized titanium of the type commercially available from the American Chemical & Refining Company, Inc. of Waterbury, Conn., may be used to particular advantage.

With the present bath, rhodium deposits can be produced upon substantially any of the various metallic surfaces that previously have been so plated, including silver, nickel, gold, etc. The quality of the deposits that are produced upon copper and copper alloy surfaces is so exceptional, using the formulations defined herein that plating upon such metals represents a surprising advance in the art. The surfaces of the workpiece should be adequately cleaned in accordance with accepted practice to ensure that a high quality, adherent deposit is produced, and when the metal of the surface to be plated is soluble in the bath, a strike of insoluble metal may be applied as a precaution against contamination.

With further regard to contamination, continuous carbon treatment and filtration of the bath is recommended to remove impurities, and surfaces coming into contact with the bath should be fabricated of an inert material, such as glass, polyethylene, unplasticized polyvinyl chloride, acrylic polymers and the like. The components of the bath may be replenished on a predetermined schedule or as needed based upon bath analyses. It will, of course, be appreciated that additions of the rhodium salt will have to be made to replenish the rhodium ion, due to the use of an insoluble anode.

Although numerous techniques may be employed for the determination of internal stress in the metal deposit as is discussed by R. Weil at pages 1231–1237 of volume 12 (1970) of Plating Magazine, the plated strip method described in the examples which follow is relatively simple and affords a high level of accuracy if carefully done. The Soderberg and Graham formula for quantitively correlating the curvative of the plated strip to internal stress, which is employed in the examples, is also presented and explained in the cited publication. It may be desirable to use a second technique to check the accuracy of original values obtained, and a device such as the Brenner/Senderoff contractometer may be employed for that purpose.

5

Exemplary of the efficacy of the present invention are the following specific examples:

EXAMPLE 1

Part A

An aqueous acid rhodium plating bath is prepared by admixing with water 15.0 grams per liter (as rhodium) of rhodium sulfate, 0.225 gram per liter (as aluminum) of aluminum phosphate, and 60.0 milliliters per liter of 97% sulfuric acid; the resulting solution has a pH of 0.5. Using the bath in a 267 cubic centimeter Hull cell with a platinum anode, a gold plated brass panel is electroplated at a bath temperature of about 48° centigrade and at a current of 2 amperes for 5 minutes with about 6 volts applied, thereby producing upon the panel a rhodium deposit approximately 0.1 mil thick.

Upon inspection of the plated panel, the deposit is found to be ductile and adherent, and to be clear and fully bright over a current density range of about 0.5 to 20.0 amperes per square foot. Parenthetically, it should be noted that prior art commercial rhodium baths generally develop deposits that are undesirably dark at current densities below about 10.0 amperes per square foot.

Part B

A plating bath having the composition described in Part A hereof is employed in a circular plating cell for use in an internal stress determination. A rectangular strip of copper foil 1.0 mil in thickness and measuring 0.5 inch by 5.0 inches is coated on one surface, with an acid-resistant cellulosic masking composition, and is immersed on an appropriate support backing to a depth of three inches in the bath solution. Using an inert platinum anode, a voltage is applied to produce a cathode current density at the copper foil strip of 10.0 amperes per square foot. Plating of rhodium from the solution, which is maintained at about 48° centigrade, is continued with agitation for about 15 minutes to produce a 0.13 mil deposit. The strip is removed from the beaker, carefully washed, rinsed and dried; it is then placed upon graph paper onto which its curvature is transcribed and from which the parameters necessary for using Soderberg/Graham equation are obtained. The deposit is thereby calculated to have an internal stress of about 60,000 to 61,000 pounds per square inch, compared to the typical value of about 150,000 pounds per square inch for commercial industrial rhodium plating formulations. The deposit on the strip is also found to be ductile and adherent and to have the desirable brightness and surface characteristics referred to in Part A.

EXAMPLE 2

A phosphate-free bath comparable to that prepared in accordance with Example 1 is prepared by substituting 0.4 gram per liter (as aluminum) of aluminum sulfate for the aluminum phosphate employed therein and by decreasing the sulfuric acid concentration to 50 milliliters per liter. The other components of the bath, and the plating procedures of both Parts A and B of the preceding example are employed without substantial deviation. Upon inspection of the Hull cell panel, it is found to have a rhodium deposit that is somewhat brighter than that produced with the phosphate-containing bath of Example 1. The deposit is found to be comparably ductile and adherent, and the deposit on the copper foil strip is calculated to have an internal stress of about 50,000 to 53,000 pounds per square inch.

EXAMPLE 3

For comparison with the results obtained with the baths of the two foregoing examples, a third bath is prepared wherein about 0.4 gram per liter of magnesium sulfate is employed in place of the aluminum salts employed therein, all other components in the bath and the plating procedures being substantially identical thereto. Although a

6

relatively bright rhodium deposit is produced, it is less bright than are the deposits produced in Examples 1 and 2, and whereas the internal stress is comparable to that in the deposit produced from the phosphate-containing bath, it is found to be significantly higher than that of the deposit from the all-sulfate formulation.

EXAMPLE 4

The procedure of Example 1 is substantially repeated utilizing a formulation containing 12.0 grams per liter (as rhodium) of rhodium sulfate, 40 milliliters per liter of sulfuric acid, 0.4 gram per liter (as aluminum) of aluminum sulfate, and about 2.0 grams per liter of glutaric acid. Evaluation of the panel indicates that the presence of the dicarboxylic organic acid reduces the internal stress and improves the quality of the deposit. Substitution of oxalic, malonic, succinic, and adipic acids for the glutaric acid is found to produce comparable improvements. The substitution of azelaic or pimelic acids is also found to produce improved results, even though they are only slightly soluble in water, and maleic and fumaric acids are also found to be beneficial from the standpoint of reducing stress and producing desirable surface characteristics.

EXAMPLE 5

A bath comparable to that of Example 1 is prepared, using however sufficient aluminum phosphate and rhodium sulfate to provide only 1.4 grams per liter each of rhodium ion and aluminum ion. Although plating efficiency and stress relief are reduced, as compared with the results obtained in that previous example, a good quality deposit is obtained in which the level of internal stress is reduced from that obtained with industrial rhodium baths.

Thus, it can be seen that the present invention provides a novel rhodium electroplating bath which is capable of producing a rhodium deposit wherein the level of internal stress is relatively low. The bath also produces a bright rhodium plate that is substantially free of cloudiness, pin holes, and other surface imperfections. It generally operates with a current efficiency in excess of about 85 to 90 percent, and has excellent covering and throwing power compared to presently used industrial formulations. Also provided are a novel composition for producing such a bath and a novel method for producing a rhodium electrodeposit having the foregoing advantages and features.

Having thus described the invention, we claim:

1. An aqueous acid bath for the electrodeposition of rhodium comprising: about 1.0 to 30.0 grams per liter of rhodium ion, about 0.05 to 5.0 grams per liter of aluminum ion, about 50.0 to 400.0 grams per liter of sulfate radical and about 1.0 to 25.0 grams per liter of a polycarboxylic organic acid, said bath having a pH of about 0.1 to 2.0.

2. The bath of claim 1 wherein the amount, in grams per liter, of rhodium ion is 2.0 to 10.0, of aluminum ion is 0.2 to 4.0, of polycarboxylic organic acid is 3.0 to 10.0, and of sulfate radical is 100.0 to 250.0, said bath having a pH of 1.2 to 2.0.

3. The bath of claim 1 wherein said polybasic organic acid is selected from the group consisting of azelaic acid, pimelic acid, oxalic acid, malonic acid, adipic acid, glutaric acid, tartaric acid, succinic acid, citric acid, maleic acid, fumaric acid, and mixtures thereof.

4. The bath of claim 1 additionally containing about 10.0 to 70.0 grams per liter of phosphate radical, wherein the weight ratio of sulfate radical to phosphate radical is at least 2.0:1.0.

5. In a method for electrodepositing rhodium, the steps comprising:

(a) preparing an aqueous acid bath comprising about 1.0 to 30.0 grams per liter of rhodium ion, about 0.05 to 5.0 grams per liter of aluminum ion, about 1.0 to 25.0 grams per liter of a polycarboxylic organic

3,729,396

7

acid and about 50.0 to 400.0 grams per liter of sulfate radical, said bath having a pH of about 0.1 to 2.0;

(b) maintaining said bath at a temperature of about 20.0° to 65.0° centigrade;

(c) immersing in said bath a workpiece having a metallic surface and an anode member; and

(d) applying a voltage across said anode member and said workpiece to deposit rhodium from said bath upon said metallic surface, said voltage providing a current density of about 0.5 to 20.0 amperes per square foot at the surface of said workpiece.

6. The method of claim 5 wherein said bath contains 2.0 to 10.0 grams per liter of rhodium ion, 0.2 to 4.0 grams per liter of aluminum ion, 3.0 to 10.0 grams per liter of polycarboxylic organic acid, and 100.0 to 250.0 grams per liter of sulfate radical, and wherein said organic acid is selected from the group consisting of azelaic acid, pimelic acid, oxalic acid, malonic acid, adipic acid, glutaric acid, tartaric acid, succinic acid, citric acid, maleic acid, fumaric acid, and mixtures thereof.

7. The method of claim 6 wherein said bath has a pH

8

of 1.2 to 2.0 and is maintained at a temperature of about 40.0° to 55.0° centigrade, and wherein said current density at said workpiece is about 5.0 to 15.0 amperes per square foot.

References Cited

UNITED STATES PATENTS

1,949,131	2/1934	Shields	204—47
2,067,534	1/1937	Keitel	204—47
2,866,740	12/1958	Reid	204—47
2,097,630	11/1937	Lutz	204—50 Y
2,895,889	7/1959	Schumpelt	204—47
2,895,890	7/1959	Schumpelt	204—47
3,515,651	6/1970	Ohkubo	204—47 X
3,528,895	9/1970	Simonian	204—47 X

OTHER REFERENCES

F. H. Reid, Metalloberfläche, vol. 15, pp. 33–37 (1961).

GERALD L. KAPLAN, Primary Examiner