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PLATING SOLUTIONS FOR RHODIUM AND RHODIUM ALLOY PLATINGS HAVING LOW INTERNAL STRESS

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ABSTRACT OF THE DISCLOSURE

An electrolyte for electroplating low stress rhodium and rhodium alloy deposits. The electrolyte comprises a rhodium salt, optionally a salt of another metal capable of alloying with rhodium, and at least one member of the group consisting of hexametaphosphoric acid and alkali metal and ammonium hexametaphosphates.

The present invention relates to novel and improved plating solutions for plating rhodium and rhodium alloy platings.

For the formation of rhodium plating industrially, plating solutions of sulfuric acid type (rhodium sulfate+sulfuric acid) and phosphoric acid type (rhodium phosphate+orthophosphoric acid) have heretofore been used. Rhodium alloy plating is not widely employed at the present time. Recently, there has been a desired for an improved rhodium plating in various industries in the light of the fact that the rhodium platings obtained with the conventional plating solutions for said platings had the drawback of the internal stress of the electrodeposition obtained being high. Additionally, with the conventional plating solutions, the surface of the resultant platings are apt to be clouded or current efficiency is poor, that it to say that the industrial control of the plating operation is not easy.

Furthermore, in recent years, the rhodium platings are required not only to have a low internal stress, but also to have specifically improved physical properties, such as high hardness and improved wear-resistance of the surface of the platings. In order to meet such requirements, an attempt is being made, as a solution, to develop a method of electrodepositioning rhodium in the form of an alloy but such a method has not yet been practised widely industrially. In electrodepositioning rhodium in the form of an alloy between it and another metal, it is difficult to obtain a rhodium alloy plating having a uniform composition or to vary the alloy composition as desired, even by the use of a plating solution consisting of the conventional rhodium plating solution as a base and a solution having a different metal dissolved therein.

According to the present invention, there are provided novel and improved plating solutions for rhodium and rhodium alloy platings, with which the above-mentioned drawbacks can be alleviated. Namely, according to this invention, the drawbacks possessed by the conventional plating solutions can be effectively avoided by adding to a plating solution a polyphosphoric acid or a salt thereof or a mixture of said polyphosphoric acid and said salt.

The object of the invention, therefore, is to provide novel and improved plating solutions of the composition described above for rhodium and rhodium alloy platings. The rhodium platings and rhodium alloy platings produced with the conventionally known plating solutions had the tendency of being separated from the core metal or cracked due to an extremely high electro-

deposition internal stress. In order to eliminate such undesirable phenomena, there has been proposed (1) to raise the concentration of a plating solution to be used, (2) to raise the concentration of an acid to be used, (3) to elevate the temperature of the plating solution, (4) to minimize impurities present in the plating solutions, and (5) to subject a core metal to be plated to etching. However, these methods only, though effective to some extent, are not sufficiently satisfactory. There has also been proposed a plating solution bath in which the conventional plating solution is added with magnesium sulfamate or selenic acid but again such a bath has proved only insufficiently satisfactory. The use of these plating solutions has frequently resulted in low current efficiency and clouded surface of the platings formed, and it is very difficult to remove impurities in the plating solutions during plating operation.

It is also very difficult to obtain a rhodium alloy plating having a hard and wear-resistant surface, with the use of the conventional rhodium plating solution which has a salt of different metal dissolved therein. The plating obtainable with such a plating solution is uneven and has an insufficient hardness and wear-resistance. In addition, with such a plating solution, it is impossible to form an alloy of consistent composition or to vary the composition of the alloy as desired. For these reasons, the plating solution of the type described is rarely used for industrial purposes.

The present invention contemplates to provide novel plating solutions for rhodium and rhodium alloy platings, with which the aforementioned drawbacks of the conventional plating solutions can be markedly alleviated.

The term "alloy" as used herein includes alloys between rhodium and other metals, e.g. platinum, gold, silver, ruthenium, indium, palladium, iridium, nickel, cobalt, copper, tin, lead, antimony, zinc, cadmium, tungsten, molybdenum, which are normally used for electroplating, and said alloys may be of binary or of even more elements, such as of tertiary and quaternary.

According to an aspect of the present invention, a plating solution for rhodium plating is obtained by adding to a salt of rhodium at least either one of a polyphosphoric acid and an alkali salt thereof.

According to another aspect of the invention, a plating solution for rhodium alloy plating is obtained which consists of a salt of rhodium, a salt of a metal specified above and at least either one of a polyphosphoric acid and a salt thereof.

A plating solution according to this invenion may be acidic, neutral or basic.

The invention plating solutions are novel in respect of containing therein a phosphoric acid or a salt thereof, and have the advantage that they can be formed of any noble metal indiscriminately and yet they are capable of forming an excellent layer of plating. This advantage is brought about presumably because the polyphosphoric acid and the salt thereof form a complex salt with the metal, with the result that the concentration of metal ions is lowered and also because of the fact that the polyphosphoric acid and the salt thereof basically act somewhat like a surface active agent.

The plating solutions for rhodium platings according to the invention consists of a rhodium salt and a polyphosphoric acid or an alkali salt thereof. Rhodium salts usable in the present invention include inorganic and organic salts, such, for example, as sulfates, chlorides, nitrates, phosphates, polyphosphates, gluconates, sorbitol salts and other water-soluble salts. Polyphosphoric acids to be employed in the invention include polyphosphoric acids having a chain bond, such, for example, as pyrophosphoric acid, tripolyphosphoric acid, tetrapolyphos-

phoric acid, hexapolyphosphoric acid, and polymetaphosphoric acids having a cyclic bond, such, for example, as metaphosphoric acid, trimetaphosphoric acid, tetrametaphosphoric acid and hexametaphosphoric acid. Polyphosphates to be used in the invention include alkali salt of the polyphosphoric acids depicted above, i.e. sodium polyphosphates and potassium polyphosphates having a chain bond, such, for example, as sodium pyrophosphate, potassium pyrophosphate, sodium tripolyphosphate, potassium tripolyphosphate, sodium tetrapolyphosphate, potassium tetrapolyphosphate, sodium hexapolyphosphate, potassium hexapolyphosphate, and polymetaphosphates having a cyclic bond, such, for example, as sodium metaphosphate, potassium metaphosphate, sodium trimetaphosphate, potassium trimetaphosphate, sodium tetrametaphosphate, potassium tetrametaphosphate, sodium hexametaphosphate and potassium hexametaphosphate.

The alkali salts of the invention also include ammonium salts because ammonium salts act in the same manner as alkali salts.

In practising the present invention, a solution of the above-mentioned rhodium salts is mixed with a solution of a polyphosphoric acid or an alkali salt thereof to give a desired plating solution. Alternatively, the desired plating solution may be obtained by dissolving a solid of one component in a solution of another component. Preferably, the concentrations of the component compounds are generally in the ranges specified below.

	G./liter
Rhodium	0.3–100
Polyphosphate	5–400
Polyphosphoric acid	2–400

Where it is necessary to perform plating at the optimum concentration of the plating solution for the reasons of the concentration of rhodium and other industrial plating conditions, it is recommendable to verify the plating solution by the Hull cell method prior to the plating. At any rate, the above-specified concentration ranges should be suitably selected in consideration of (1) economy, (2) lowering of electric conductivity for the determination of a lower limit and (3) lowering of the effect of the resultant plating due to increase in viscosity of the plating solution for the determination of an upper limit.

The present invention, therefore, includes the use of a mixture of a polyphosphoric acid and an alkali salt thereof for the purpose of bringing the pH of the resultant plating solution in the pH range specified above. The inventive plating solution is used for plating according to conventional methods, whereby a desired plating is obtained.

The plating solutions according to this invention have the advantages listed below:

(1) It is possible to obtain a rhodium plating which has an improved uniformity and gloss as compared with that obtainable with conventional plating solution baths, e.g. rhodium sulfate bath.

(2) It is possible to form a rhodium plating of as thick as about 5μ without losing the inherent gloss, in contrast to conventional rhodium platings.

(3) Current efficiency with the inventive plating solutions is higher than that with conventional plating solutions for rhodium platings. The difference therebetween is particularly remarkable where the concentration of rhodium is low.

(4) Internal stress in electrodeposits is extremely low as compared with that of conventional rhodium platings.

Now, a description will be given in detail with regard to plating solutions for rhodium alloy platings. The inventive plating solutions for rhodium alloy platings consist of a salt of rhodium, a salt of ther metal and a polyphosphoric acid or a salt thereof.

Salts of rhodium and other metals to be employed in the invention include inorganic and organic salts, e.g. sulfates, chlorides, nitrates, phosphates, polyphosphates, gluconates, sorbitol salts and mannitol salts. A polyphosphoric acid and polyphosphate to be used may be selected from the group mentioned previously.

As stated hereinbefore, ammonium salts may be included in the alkali salts to be used in the invention, since they act in the same manner as alkali salts.

In practising the present invention, a desired plating solution for rhodium alloy plating may be obtained by mixing solutions of the afore-mentioned rhodium salt and salt of other metal and a solution of a polyphosphoric acid or an alkali salt thereof. The plating solution may alternatively be formed by dissolving solid of two or one component in solutions of one or two components. Preferably, the concentrations of the components are generally in the ranges specified below:

	G./liter
Rhodium	0.3–100
Salt of other metal	0.05–100
Polyphosphate	10.0–400

With the plating solution formed of the components of the concentrations specified above, a satisfactory electrodeposition can be obtained, presumably because a part or whole of the metals forms of a polyphosphate, with the result that the concentration of the metal ions is extremely lowered. Thus, the present invention include the use of a mixture of a polyphosphoric acid and an alkali salt thereof.

The plating solution defined above has the following advantageous features.

(1) The solution produces a highly uniform electrodeposition.

(2) The gloss of a plating obtained does not vary with the thickness increasing.

(3) The composition of an alloy used can be varied in a wide range according to the electroplating conditions.

(4) The plating obtained has an excellent hardness and wear-resistance.

(5) The plating obtained has a uniform alloy composition.

Examples of the inventive plating solutions for rhodium and rhodium alloy platings will now be provided hereinafter.

EXAMPLE 1.—RHODIUM PLATING

A solution of rhodium sulfate of a concentration of 4 g./liter as rhodium was added with a solution having dissolved therein 100 g./liter of potassium hexametaphosphate to prepare a plating solution. With this plating solution, electroplating was conducted at a pH of 5.0, a temperature of 30° C., and a current density of 8 A./dm.^{2}, using platinum as an anode and a copper plate as a cathode. A glossy, uniform rhodium plating was obtained.

EXAMPLE 2.—RHODIUM PLATING

A solution of rhodium sulfate of a concentration of 2 g./liter as rhodium was added with a solution having dissolved therein 80 g./liter of hexametaphosphoric acid and 50 cc./liter of sulfuric acid to prepare a plating solution. With this plating solution, electroplating was conducted at a pH of 1.0, a temperature of 45° C., and a current density of 2 A./dm.^{2}, using platinum as an anode and a brass plate as a cathode. A glossy, uniform rhodium plating was obtained.

EXAMPLE 3.—RHODIUM PLATING

A solution of rhodium phosphate of a concentration of 4 g./liter as rhodium was added with a solution having dissolved therein 70 g./liter of trimetaphosphoric acid and 50 cc./liter of phosphoric acid to prepare a plating solution. With this plating solution, electroplating was conducted at a pH of 0.01, a temperature of 45° C., and a current density of 2 A./dm.^{2}, using platinum as an anode and a copper plate as a cathode. A glossy rhodium plating of an excellent uniformity was obtained.

EXAMPLE 4.—RHODIUM PLATING

A solution of rhodium sulfate of a concentration of

5 g./liter as rhodium was added with a solution having dissolved therein 200 g./liter of potassium tripolyphosphate and 25 cc./liter of sulfuric acid to prepare a plating solution. With this plating solution, electroplating was conducted at a temperature of 45° C. and a current density of 7 A./dm.^{2}, using platinum as an anode and a nickel-plated copper plate base as a cathode. A glossy rhodium plating having an excellent uniformity was obtained.

EXAMPLE 5.—RHODIUM-TIN ALLOY PLATING

A solution having dissolved therein 10 g./liter of rhodium sulfate as rhodium and 50 cc./liter of sulfuric acid was added with a solution having dissolved therein 100 g./liter of hexaphosphoric acid and 15 g./liter of sodium stannate to prepare a plating solution. With this plating solution, electroplating was conducted at a temperature of 45° C. and a current density of 2 A./dm.^{2}, using platinum as an anode and a nickel-plated copper plate as a cathode. A glossy rhodium-tin alloy plating having an excellent uniformity was obtained.

EXAMPLE 6.—RHODIUM-NICKEL ALLOY PLATING

A solution having dissolved therein 100 g./liter of rhodium sulfate as rhodium and 25 cc./liter of sulfuric acid was added with a solution having dissolved therein 80 g./liter of trimetaphosphoric acid and 25 g./liter of nickel sulfate to prepare a plating solution. With this plating solution, electroplating was conducted at a temperature of 30° C. and a current density of 5 A./dm.^{2}, using a platinum as an anode and grass as a cathode. A glossy rhodium-nickel alloy plating having an excellent uniformity was obtained.

EXAMPLE 7.—RHODIUM-GOLD ALLOY PLATING

A solution of rhodium sulfate of a concentration of 0.5 g./liter as rhodium was added with a solution having dissolved therein 100 g./liter of sodium hexametaphosphate and 10 g./liter of potassium gold cyanide to prepare a plating solution. With this plating solution, electroplating was conducted at a temperature of 50° C. and a current density of 2 A./dm.^{2}, using platinum as an anode and a brass plate as a cathode. A glossy rhodium-gold alloy plating having an excellent uniformity was obtained.

EXAMPLE 8.—RHODIUM-GOLD-NICKEL ALLOY PLATING

A solution having dissolved therein 4 g./liter of rhodium phosphate and 5 g./liter of nickel sulfate was added with a solution having dissolved therein 100 g./liter of potassium tripolyphosphate and 5 g./liter of potassium gold cyanide to prepare a plating solution. With this plating solution, electroplating was conducted at a temperature of 45° C. and a current density of 4 A./dm.^{2}, using platinum as an anode and a nickel-plated copper plate base as a cathode. A glossy rhodium-gold-nickel alloy plating having an excellent uniformity was obtained.

EXAMPLE 9.—RHODIUM-NICKEL-GOLD ALLOY PLATING

A solution of rhodium sulfate of a concentration of 8 g./liter was added with a solution having dissolved therein 40 g./liter of sodium tetrapolyphosphate, 3 g./liter of nickel gluconate and 4 g./liter of potassium gold cyanide to prepare a plating solution. With this plating solution, electroplating was conducted at a pH of 6.7, a temperature of 30° C. and a current density of 8.0 A./dm.^{2}, using a stainless steel plate as an anode and a brass plate as a cathode. A glossy rhodium-nickel-gold alloy was obtained which had a whitish yellow color and a hardness of H_v 270.

The internal stresses of the platings obtained with the plating solutions of the compositions described in the foregoing examples were measured by a simple method described below.

Internal stress measuring method

A 0.08 mm. thick Phosphor bronze of a size of 130 x 5 mm. was annealed for 1 hour in an atmosphere of carbon dioxide at a temperature of 600° C. and used as a specimen for electrodeposition. The specimen was placed on a 1 mm. thick vinyl chloride sheet of a size of 110 x 30 mm. which had been thinly coated with vaseline. Then, the specimen was superposed by packing of 0.5 mm. in thickness and 110 x 30 mm. in size, made of synthetic rubber and having the central portion cut out in a size of 70 x 5 mm., which was further superposed by a packing of 1 mm. in thickness made of a vinyl sheet and having the central portion cut out in the same size as that of the cutout formed in the synthetic rubber packing. The entire assembly was tightly bounded together with rubber bands and used as a cathode for having rhodium electrodeposited thereon. Upon completion of the electrodeposition, the specimen was taken out and the layer of vaseline on the back side thereof was washed away with a solvent. The sample plating thus obtained was subjected to reflection test.

The plating was conducted in the conditions mentioned below:

(1) Plating solution
Rhodium—2 g./liter
Hexaphosphoric acid—80 g./liter
Sulfuric acid—50 cc./liter
(2) Current density—2A./dm.^{2}
(3) Temperature of bath—45° C.
(4) Plating time—2 to 15 minutes (the thickness of the resultant platings ranged from about 0.2μ to about 4μ.)

The result of the deflection test was as follows:

Plating bath	Plating time		
	2 minutes	8 minutes	15 minutes
Conventional rhodium sulfate bath.	0.9 mm. deflection.	3.0 mm. deflection.	4.1 mm. deflection.
Inventive rhodium plating bath.	No deflection.....	0.7 mm. deflection.	1.0 mm. deflection.

What is claimed is:

1. A plating solution for rhodium electroplating, consisting essentially of an aqueous solution of a rhodium salt and at least one member selected from the group consisting of hexametaphosphoric acid and alkali metal and ammonium hexametaphosphates, in which the concentration of said rhodium is from 0.3 to 100 g./liter, the concentration of said hexametaphosphate is from 5 to 400 g./liter and the concentration of said hexametaphosphoric acid is from 2–400 g./liter.

2. A plating solution as described in claim 1, in which said rhodium salt is selected from the group consisting of sulfates, chlorides, phosphates, polyphosphates, gluconates, sorbitol salts, and nitrates.

3. A plating solution as described in claim 1, in which said solution contains hexametaphosphoric acid and said hexametaphosphate.

4. A plating solution for electroplating alloys of rhodium and another metal, consisting essentially of a rhodium salt, a salt of another metal capable of alloying with

rhodium, and at least one member selected from the group consisting of hexametaphosphoric acid and alkali metal and ammonium hexametaphosphates, in which the concentration of said rhodium salt is from 0.3 to 100 g./liter, the concentration of said salt of said alloying metal is from 0.05 to 100 g./liter and the concentration of said member is from 10.0 to 400 g./liter.

5. A plating solution as described in claim 4, in which said rhodium salt and said salt of other metal are selected from the group consisting of sulfates, chlorides, nitrates, phosphates, polyphosphates, gluconates and sorbitol salts.

6. A plating solution as described in claim 4, in which said solution contains hexametaphosphoric acid and said hexametaphosphate.

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