United States Patent Office 3,528,895
Patented Sept. 15, 1970

3,528,895

PLATING LOW STRESS BRIGHT RHODIUM

Atkin Yervant Simonian, Fort Lee, N.J., assignor to Sel-Rex Corporation, Nutley, N.J., a corporation of New Jersey

No Drawing. Filed July 10, 1967, Ser. No. 651,998
Int. Cl. C23b 5/24, 5/32
U.S. Cl. 204—44 3 Claims

ABSTRACT OF THE DISCLOSURE

An aqueous acid electrolyte for the deposition of bright low stress rhodium containing rhodium and copper ions in synergistic combination with sulfamic acid.

The present invention relates to the electrodeposition of rhodium. More particularly this invention relates to the deposition of a bright rhodium deposit which is under low stress.

The properties of rhodium which make it useful to the jewelry trade, manufacturers of scientific instruments, and the electronic industry include, among others, excellent hardness, exceptional corrosion-resistance to chemicals, a high and stable reflectivity in the visible range and low electrical conductivity combined with stability of contact resistance. To the jewelry industry, rhodium is preferable to platinum because it has a whiter color and wears much longer. To the electronics industry, rhodium can be preferable to platinum for certain purposes because of its hardness, reflectivity and somewhat higher melting point.

Regrettably, deposits in the range of 0.00001–0.002 inch (0.25–50μ) have a pronounced tendency to crack, peel or distort. That tendency which is especially noticeable in bright deposits is the result of internal stresses which will increase in proportion to the thickness of the electroplate deposited.

There are presently three (3) commercially used rhodium electroplating baths commonly identified as rhodium phosphate, rhodium sulfate and proprietary low stressed rhodium plating baths. Each of these has found acceptance in a select industry for specific end results and are not used interchangeably.

For example, a rhodium phosphate electrolyte is almost exclusively used for flash jewelry plating to provide a white, bright, tarnish preventive coating, usually 1 or 2 millionths of an inch thick. This deposit is very highly stressed and cannot be utilized successfully in thicker deposits without cracking, peeling or distortion.

A rhodium sulfate bath is generally used in the electronic industry on various electrical contacts, since rhodium is very hard and an excellent corrosion protector. The consumer in this industry usually deposits between 20 to 100 millionths of an inch. Deposits obtained from this electrolyte are milky white to hazy in appearance and are highly stressed so that in use, cracking or failure of the components may occur.

Efforts to achieve a low stress rhodium plating are described by Karl Schumpelt in his U.S. Pats. 2,895,889 and 2,895,890 and by Frank Herbert Reid in his U.S. Pats. 2,866,740 and 2,992,099. To varying extents, Messrs. Schumpelt and Reid have achieved a measure of success. Unfortunately, the electrodeposits obtained from the electrolytes described by Messrs. Schumpelt and Reid are generally dull in appearance. Because of the dull surface finish, the parts plated are also subject to severe staining when handled. The stains, which theoretically may be attributed to organic polymerization products, are very tenacious and cannot be removed except by subsequent electro-chemical or mechanical treatment. Such treatment

does not always completely remove the stains. This, in turn, may interfere in the end use of the plated device by impairing the electrical qualities of the rhodium deposits and/or its appearance.

Accordingly, it is an object of my invention to provide an electroplating composition capable of plating a bright rhodium metal under low stress.

Another object of my invention is to provide a process for the deposition of bright rhodium under low internal stress. And further, to provide a bright alloy of rhodium which is under low internal stress.

I have discovered that electrodeposits of commercially practiced thicknesses of bright rhodium under low internal stress with no tendency to crack, peel or distort, can be obtained from an electrolyte containing rhodium, sulfamic acid and a small amount of a soluble copper ion.

Sulfamic acid is a preferred source of sulfamate anion and enhances the brightness of the deposit when small amounts of copper ions are present. The combination of sulfamic acid and a copper salt are synergistic and the effect of one without the other will not yield the desired end result, namely simultaneous brightness and low internal stress.

The electroplating bath, according to this invention, has the following approximate composition:

	Grams/liter
Rhodium metal (added as rhodium sulfate)	0.5–20
Sulfamic acid	5–100
Copper ions (added as a soluble salt)	.10–.50

Water to 1 liter volume.

The range of operating the bath may be varied from about room temperature to about 180° F., from about 5–60 a.s.f., with mechanical solution agitation being the preferred method of replenishing the cathode film.

It will be recognized that there are any number of ingredients that can be added to the foregoing electrolyte without significant affect on the properties of the deposit obtained from the electrolyte. For example, the commercially available rhodium sulfate frequently contains some excess sulfuric acid. It is feasible to increase the free sulfuric acid content in the electrolyte by adding even more sulfuric acid. In the latter instance there would be no appreciable affect on the properties of the deposit obtained from the bath with up to five percent (5%) by volume of free sulfuric acid present in the electrolyte. Similarly, other relatively inert ingredients can be added to the electrolyte.

The rhodium and copper can be added as soluble salts, e.g. rhodium sulfamate, rhodium sulfate copper sulfamate, copper sulfate, copper nitrate, etc.

The copper present in the electrodeposit is generally a minute amount but can vary up to as much as five percent (5%) of the rhodium metal present in the deposit.

The following examples are intended to illustrate but not limit the formulations and parameters used to practice this invention.

EXAMPLE 1

A polished brass sheet 1" x 3½" was made the cathode in an electroplating bath comprising of 2 g./l. rhodium metal (as the sulfate), 0.30 g./l. copper metal (as the sulfate), 20 g./l. sulfamic acid, at a temperature of 100° F., a cathode current density of 10 amperes per square ft. and the panel was plated for 15 minutes. The plating rate was 11 mg. per ampere minute. The deposit weighed .085 gram equivalent to .000060 inch in thickness.

The deposit was bright and low stressed as shown when placed in a desiccator with HNO_3 fumes for 2 hours, no cracks or chemical attack on the brass substrate were evident, indicating a crack-free deposit.

EXAMPLE 2

A second bath was prepared with a final concentration containing 5 g./l. rhodium metal (as the sulfate), 20 g./l. sulfamic acid, 0.060 gram copper metal (as the sulfate) at 120° F., 20 a.s.f., a brass panel, similar to Example 1, was plated for 8 minutes, the plating was 15 mg./ampere minute, the deposit weighed 0.119 gram, equivalent to 0.000084 inch in thickness. The deposit was bright and low stressed as shown when the edges of the panel were filed off with No. 284A grit size silicon carbide paper to expose the brass and the panel was then immersed in a 50% by volume nitric acid to dissolve the basis metal and recover the thin rhodium foil completely intact.

EXAMPLE 3

Another polished brass panel was used in a bath containing 5 g./l. rhodium metal (as the sulfate) 50 g./l. sulfamic acid, .060 g./l. copper metal (as the sulfate). Temperature was maintained at 110° F. and at 30 a.s.f. plated for 10 minutes. The plated rate was 7 mg./amp. minute, the deposit weighed .104 gram, equivalent to 0.000074 inch. The deposit was bright and low stressed as in the previous examples.

The present invention may be practiced on any basis metal which will not be attacked by the acid electrolyte or any metal which can be plated with a thin layer of a metal not attacked in the electrolyte.

The features and principles underlying the invention described above in connection with specific examples will suggest to those skilled in the art many modifications thereof. It is accordingly desired that the appended claims shall not be limited to any specific feature or details thereof.

I claim:

1. An electrolyte for the deposition of a uniform bright rhodium deposit under low internal stress consisting essentially of: rhodium sulfate in the amount of about 0.5 to about 20 grams per liter of rhodium metal; free sulfamic acid in the amount of about 5 to about 100 grams per liter; a soluble salt of copper in the amount of about .01 to about .05 gram of copper metal per liter; and sufficient water to reach the liter volume.

2. A method of electrodepositing a bright rhodium under low internal stress upon substrate materials which compromises electrolyzing an aqueous acid bath consisting essentially of: rhodium sulfate in the amount of about 0.5 to about 20 grams per liter of rhodium metal; free sulfamic acid in the amount of about 5 to about 100 grams per liter; a soluble salt of copper in the amount of about .01 to about .50 gram of copper metal per liter; and sufficient water to reach the liter volume.

3. The process of claim 2 wherein the bath is electrolyzed at a temperature of from about room temperature to about 180° F. at a cathodic current density of from about 5 to about 60 amperes for square foot.

References Cited

Parker, Edward A.: Plating, vol. 42, pp. 882–892 (1955).

Reid, F. H.: Bulletin of the Institute of Metal Finishing, vol. VI, No. 2, pp. 126–129 (1956).

Von G. Hansel, Metalloberflaeche 20 (2), pp. 67–70 (1996).

GERALD L. KAPLAN, Primary Examiner

U.S. Cl. X.R.

204—47

UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

Patent No. 3,528,895 Dated September 15, 1970

Inventor(s) Atkin Yervant Simonian

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Claim 1, line 7, ".05" should read -- .50 --.

Signed and sealed this 26th day of November 1974.

(SEAL)
Attest:

McCOY M. GIBSON JR.
Attesting Officer

C. MARSHALL DANN
Commissioner of Patents

FORM PO-1050 (10-69)

USCOMM-DC 60376-P69
U.S. GOVERNMENT PRINTING OFFICE : 869-930