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LOW STRESS ELECTRODEPOSITED RHODIUM

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No Drawing. Application June 5, 1957

Serial No. 663,595

7 Claims. (Cl. 204—47)

This invention relates to a process for obtaining electrodeposited rhodium layers which have a low stress and to the bath for obtaining such low stress deposits.

Internal stress in metallic deposits causes the deposit to crack, peel or distort. Shrinkage in a highly stressed deposit may cause premature fatigue failure of the basis metal. Where it is known that a metal deposit is likely to be plated under stress a severe etching of the basis metal before plating is usually essential in order to obtain a satisfactory product. It is desirable, therefore, to be able to plate a metal such as rhodium under low stress but little is known as to the exact cause of internal stress in electrodeposited metals.

Among the objects of this invention is to provide an electroplating composition capable of plating rhodium metal under low stress.

Among other objects of the invention is to provide a body having a rhodium deposit under low internal stress.

Among other objects of the invention is to provide a process of plating rhodium under low stress.

A fairly comprehensive study of rhodium plating was made by Wiesner and reported in 39th Annual Proceedings and Technical Sessions, American Electroplater's Society (published in 1952), pp. 79-99. According to this article the addition of a minute amount of chloride ion to a rhodium electroplating bath (which may be the rhodium sulfate or the complex rhodium phosphate bath) reduces the stress of the deposit. The amount of chloride ion that can be present in the bath, however, is very limited as the chloride ion also causes a reduction in brightness. As little as 0.1 g./l. causes greying of the deposit and if the chloride ion exceeds a certain minimum amount of about 0.3 g./l. the deposit obtained is rough. Wiesner also found that operating the baths at higher temperatures (38-54° C., for example) reduced the stress in the deposit. Common organic addition agents such as saccharine employed for reducing stress of deposits from nickel baths were found to reduce the cathode efficiency of rhodium baths a prohibitive amount.

This application is a continuation-in-part of my application Serial No. 633,381, filed January 10, 1957. That application disclosed that rhodium deposits with reduced tensile stress could be obtained by adding 10 to 100 g./l. of magnesium sulfate to the bath. Although this addition to the bath reduces the tensile stress of the deposits obtained, it has been found that it is not always possible to obtain uniformly reproducible results from different batches of such baths.

This invention is based on the discovery that improved rhodium deposits which are free of tensile stress can be obtained if a portion or all of the magnesium sulfate of the bath of my prior application is replaced by magnesium

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sulfamate. The baths according to the invention have the following composition per liter of water:

	Range	Preferred
Rhodium sulfate (calculated as Rh).....g.	2-10	5
Sulfuric acid.....ml.	5-50	10
Magnesium sulfamate.....g.	10-100	30
Magnesium sulfate.....g.	0-50	10

The optimum amount of rhodium is around 5 g./liter. At 5 g. the efficiency of the bath is about 85% or more. Higher amounts of rhodium increase the efficiency slightly but not enough to compensate for the increased first cost of the bath and the increase in losses due to drag-out, etc. Below about 5g./liter of rhodium the efficiency decreases but the bath is still operable down to about 2 g. of rhodium.

The amount of sulfuric acid required in the improved bath may be reduced below the normal recommendations of about 20 cc. per liter. For example, as little as 5 cc. per liter of sulfuric acid may be employed.

The essential ingredient of the bath is the magnesium sulfamate. It is found, for example, that the addition of magnesium sulfamate to any conventional or any commercial rhodium sulfate bath results in deposits of reduced tensile stress over those obtained without the addition. The upper limit of sulfamate permitted is limited by the solubility of the latter in the particular bath which in turn depends on the proportion of other constituents particularly the sulfuric acid.

The magnesium sulfate is an optional constituent although very satisfactory results are obtained with about 10 g./liter of this ingredient which cooperates with the magnesium sulfamate to decrease the tensile stress in the deposit.

The bath may be operated from room temperature (approximately 20° C.) to about 50° C. and at current densities of from 4 to 20 amperes per square foot of cathode. The higher current densities produce slightly more stress. Plating at about 10 amperes per square foot and 50° C. with mild agitation yields a good deposit at about 85% cathode efficiency.

A convenient qualitative test to determine stress in the deposit is to dissolve away the basis metal from a rhodium deposited body with nitric acid, for example. If the basis metal is dissolved from an article having a rhodium film deposited from the common complex rhodium phosphate bath the rhodium disintegrates into small flakes. This indicates that the deposit has high internal stress and is rather porous.

The following examples further illustrate the principles and operation of the invention.

Example 1

A sheet of metal, for example, brass, is made the cathode in an electroplating bath comprising 5 g./l. of rhodium (as rhodium sulfate), 10 ml./l. of sulfuric acid, 30 g./l. of magnesium sulfamate, and 10 g./l. of magnesium sulfate. The bath is maintained at 50° C. and operated at a current density of approximately 10 amperes per square foot until a thickness of about 0.0003" is obtained. The deposit has a slight grey appearance with a semi-luster. The efficiency of the bath is 85%. Spectrographic examination of the plated article did not indicate the presence of any magnesium. The basis metal could be dissolved away from this product to leave a thin film of rhodium,

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The rhodium film is continuous, denser than usual rhodium deposits, and can be flexed without breaking. All of these properties show that the rhodium is under no substantial stress.

Example 2

When a layer of rhodium of .001 is deposited with the bath of Example 1 the product is matte grey in appearance but has all the other low stress features of the product of Example 1.

Example 3

When a layer of rhodium of about .0002" thickness is deposited on the unstopped (or unprinted) portions of a copper film which in turn is held on a plastic base material such as employed in the manufacture of printed circuits, there is no tendency for the rhodium to separate and curl away from the copper layer even after the previously stopped portions of the copper are dissolved away.

Example 4

A fine tungsten or molybdenum wire which is plated with rhodium by the bath of Example 1 can be wound as a grid wire around the grid supports of an electronic tube without cracking the rhodium layer. Heretofore, other precious metals (gold or possibly silver) have been employed as grid wire coatings to suppress the secondary emission of electrons from the grid. The rhodium coating on the grid wire because of its higher melting point has been recognized as superior to gold or silver as a grid coating but, heretofore, it has been impossible to make a grid wire with a rhodium coating which would not crack on winding.

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

I claim:

1. The process which comprises electrodepositing rho-

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dium upon a basis metal from an aqueous bath containing rhodium sulfate and 10-100 g. per liter of magnesium sulfamate dissolved therein.

2. A process of electroplating rhodium metal under low internal stress comprising electrolyzing an aqueous bath consisting essentially of 10-50 cc. per liter of free sulfuric acid, 2 to about 10 g. per liter of rhodium present as rhodium sulfate, 10-100 g. per liter of magnesium sulfamate and 0 to 50 g. per liter of magnesium sulfate, the remainder being water, electrodepositing rhodium from said bath at a current density of from 4 to 20 amperes per square foot and at a temperature of about 20° C. to about 50° C.

3. The process as set forth in claim 2 wherein said bath contains 50 cc. per liter of sulfuric acid and 30 grams per liter of magnesium sulfamate.

4. An aqueous rhodium sulfate electroplating bath containing 10-100 g. per liter of magnesium sulfamate dissolved therein.

5. An electroplating bath for depositing rhodium therefrom comprising an aqueous bath consisting essentially of 10-50 ml. per liter of free sulfuric acid, 2 to 10 g. per liter of rhodium as rhodium sulfate, 10-100 g. per liter of magnesium sulfamate, and 0-50 g. per liter of magnesium sulfate, the remainder being water.

6. The bath as claimed in claim 5 containing 10 cc. per liter of sulfuric acid and 30 g. per liter of magnesium sulfamate.

7. An electroplated article comprising a basis metal and a substantially stress free electrodeposited layer of rhodium thereon, said article having been prepared by the process of claim 1.

References Cited in the file of this patent

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