United States Patent

Skomoroski

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[54] IRIDIUM PLATING

[72] Inventor: **Robert M. Skomoroski**, Paterson, N.J.

[73] Assignee: **The International Nickel Company, Inc.**, New York, N.Y.

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[58] **Field of Search** ..... 204/47, 109; 106/1; 117/130 E

[56] **References Cited**

OTHER PUBLICATIONS

Gordon A. Conn, Plating, pp. 1258– 1261, Dec. 1965.

Primary Examiner—G. L. Kaplan

Attorney—Maurice L. Pinel

[57] **ABSTRACT**

An iridium electroplating bath is prepared by digesting an aqueous solution of iridium trichloride and sulfamic acid in a molar ratio of sulfamic acid to iridium of at least 7 at 100° C. for an extended period of time then adjusting the iridium content of the bath to about 3 to 20 grams per liter, adding about 3 to 20 grams per liter of ammonium sulfamate and electrodepositing iridium from the bath upon a conductive substrate with a bath pH of about 1 to 7 (adjusted by ammonia additions) and at a temperature of about 50° to 75° C. with insoluble anodes and a cathode current density of about 0.1 to 8 amperes per square decimeter to produce adherent crack-free iridium deposits.

4 Claims, No Drawings

IRIDIUM PLATING

The present invention is directed to the electrodeposition of iridium. Iridium is a platinum group metal which is hard and dense and has a high melting point, together with excellent resistance to high temperature oxidation. It has been found that iridium provides a desirable catalytic effect of particular interest in "antismog" devices for use in conjunction with internal combustion engine exhaust gases. Insofar as the electrodeposition of iridium is concerned, the art indicates that little prior work has been done. Aqueous electroplating baths are available for the electrodeposition of iridium but the available baths are still subject to difficulty. Thus, existing baths are subject to instability at some operating conditions and in many cases it has been found not possible to produce adherent iridium deposits on substrates such as stainless steel using such baths.

It is an object of the present invention to provide an iridium electroplating bath which is stable and which yields iridium deposits which adhere firmly to metal substrates of various types, including stainless steel.

In accordance with the invention, an iridium electroplating bath is prepared by digesting an aqueous solution of iridium trichloride with sulfamic acid in a molar ratio of sulfamic acid to iridium of about 7 to about 44 for at least about 15 hours at a temperature of about 100° C. The solution containing the digestion product of iridium trichloride and sulfamic acid is then adjusted to provide an iridium content of about 3 to about 20 grams per liter. Ammonium sulfamate in the amount of about 3 to about 20 grams per liter is then incorporated into the solution and the pH of the solution is adjusted to the range of about 1 to about 7 by means of ammonia. Iridium can be deposited using the insoluble anode plating process upon a properly prepared metal substrate immersed in the bath using a cathode current density of about 0.1 to about 8 amperes per square decimeter with a bath temperature in the range of about 50° to about 75° C. Anodes such as platinum or platinized titanium may be employed. Iridium deposits having a thickness up to about 10 microinches, e.g., about 2 to about 10 microinches, can be produced from the bath which are adherent to the substrate and which are substantially free from cracks. The bath prepared in the aforedescribed way is stable and can be stored for periods of months without encountering deleterious effects. Substrates which may be electroplated with iridium in accordance with the invention include stainless steel, nickel base alloys, mild steel, copper, brass, gold, iron-nickel-cobalt alloys, etc. In plating a substrate such as stainless steel, the steel surface should be carefully cleaned and provided with a thin coating of nickel, for example, from an acid nickel chloride plating bath containing about 240 grams per liter of nickel chloride hexahydrate and about 36 grams per liter of HCl. The work treated in the bath is first made anodic for about 1½ to 2 minutes and is then made cathodic for about 6 minutes to coat the surface of the work with a thin nickel electrodeposit. A current density of about 25 to about 30 a.s.f. is employed.

In order to give those skilled in the art a better understanding of the invention the following example was given:

Iridium trichloride containing about 54.13 percent by weight of iridium was dissolved in 2700 cc. of distilled water in the amount of 74.1 grams of iridium trichloride. 296.3 grams of sulfamic acid were then introduced. The solution was refluxed at about 100° C. for about 30 hours. The solution was then cooled to room temperature and 33.44 grams of ammonium sulfamate were added. The pH of the solution was adjusted to pH 6 using 223 cc. of concentrated ammonium hydroxide. The solution volume was then adjusted to 9 liters. A 40-mesh stainless steel screen cathode having an area of about 18.9 square centimeters was prepared for plating by degreasing in acetone, cathodic alloy cleaning in an alkaline bath, followed by an anodic cleaning in an alkaline bath. The cleaned screen was then immersed in an acid nickel strike bath containing about 240 grams per liter of nickel chloride hexahydrate and about 36 grams per liter of hydrochloric acid and was made anodic in the bath at an anodic current density of 25 amperes per square foot for 1.5 minutes. Without removing the stainless steel screen from the acid nickel strike bath it was then made cathodic in the bath for 6 minutes at a cathode density of about 25 amperes per square foot. A thin nickel coat was thus produced on the stainless steel screen. The nickel-coated stainless steel screen was then electroplated with about 1 micron of ruthernium in a bath containing 12 grams per liter of ruthenium, 10 grams per liter of ammonium sulfamate, having a pH of about 1.5, a temperature of 70° C. and using a cathode current density of 10 milliamperes per square centimeter. The ruthenium coated screen was then immersed in a portion of the aforementioned iridium bath and was plated for 20 minutes at a current density of 3 milliamperes per square centimeter at a bath temperature of 70° C. The resulting iridium deposit was about 1.5 microinches in thickness. The deposit was essentially crack-free, was strongly adherent to the substrate and was metallic in appearance. The plated stainless steel screen exhibited good catalytic activity in an experimental antipollution device designed to reduce nitrogen oxides in automobile exhaust gases.

In preparing the iridium solution by refluxing iridium trichloride with sulfamic acid, the solution should contain at least about 9 grams per liter and up to about 55 grams per liter of iridium and sulfamic acid should be present in the solution in a molar ratio of sulfamic acid to iridium of about 7 to about 44. Refluxing should be conducted at substantially the boiling point of the solution for at least about 15 hours and up to about 60 hours. Thirty hours has been found to be adequate. Preferably the iridium content of the solution is about 13 grams per liter, and the molar ratio of sulfamic acid to iridium is about 15. The foregoing conditions must be adhered to as otherwise iridium deposits of only poor adherence are obtained from the resulting bath.

A preferred bath in accordance with the invention contains about 12 grams per liter of iridium, about 10 grams per liter of ammonium sulfamate, is operated at a temperature of about 70° C. over a pH range of about 2.5 to about 6 at a cathode current density of about 0.3 amperes per square decimeter. Normally, no agitation is employed although moderate agitation may be used without harmful effects.

It is to be understood that when a ratio is expressed herein, for example, as being about 7 to about 44, ratios of about 7:1 to about 44:1 are expressed.

Although the present invention has been described in conjunction with preferred embodiments, it is to be understood that modifications and variations may be resorted to without departing from the spirit and scope of the invention, as those skilled in the art will readily understand. Such modifications and variations are considered to be within the purview and scope of the invention and appended claims.

I claim:

1. The method for preparing an iridium electroplating bath which comprises digesting an aqueous solution of iridium trichloride containing about 9 to about 55 grams per liter of iridium with sulfamic acid in a molar ratio of sulfamic acid to iridium of about 7 to about 44 for at least about 15 hours at a temperature of about 100° C., cooling the resulting solution to about room temperature, adjusting the iridium content of the solution to about 3 to about 20 grams per liter, introducing about 3 to about 20 grams of ammonium sulfamate into the solution and adjusting the solution pH to about 1 to about 7 by means of ammonia.

2. The method according to claim 1 wherein the final bath contains about 12 grams per liter iridium, about 10 grams per liter ammonium sulfamate and has a pH of about 2.5 to about 6.

3. The method for electroplating iridium which comprises immersing at least one insoluble anode and a cathode to be plated in a bath prepared by digesting an aqueous solution of iridium trichloride containing about 9 to about 55 grams per liter of iridium with sulfamic acid in a molar ratio of sulfamic acid to iridium of about 7 to about 44 for at least about 15 hours at a temperature of about 100° C., cooling the resulting

solution to about room temperature, adjusting the iridium content of the solution to about 3 to about 20 grams per liter, introducing about 3 to about 20 grams per liter of ammonium sulfamate into the resulting solution, adjusting the solution pH to about 1 to about 7 by means of ammonia to form an iridium electroplating bath, adjusting the bath temperature to the range of about 50° C. to about 75° C., and passing current from said anode to said cathode at a cathode current density

of about 0.1 to about 8 amperes per square decimeter to electrodeposit iridium at said cathode.

4. The method according to claim 3 wherein the bath contains about 12 grams per liter of iridium, about 10 grams per liter of ammonium sulfamate, has a pH of about 2.5 to 6 and a temperature of about 70° C. and current is passed at a cathode current density of about 0.3 amperes per square decimeter.

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