

[54] **ELECTRODEPOSITION OF RUTHENIUM**
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3,576,724 4/1971 Reddy et al..... 204/47
 3,625,840 12/1971 Mason et al..... 204/47
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OTHER PUBLICATIONS

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Primary Examiner—G. L. Kaplan

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 [58] Field of Search.. 204/47, 43 N, 44, 109; 106/1; 117/130 E

[57] **ABSTRACT**

An electroplating bath and process for electroplating ruthenium. The bath is prepared by dissolving Ru₂N-(OH)₅nH₂O in sulfuric or sulfamic acid and adjusting the pH to 4 or less.

[56] **References Cited**
UNITED STATES PATENTS
 2,057,638 10/1936 Zimmermann et al. 204/47

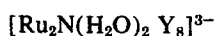
19 Claims, No Drawings

ELECTRODEPOSITION OF RUTHENIUM

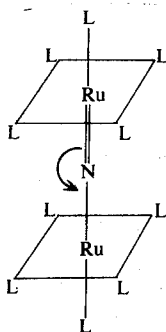
The present invention relates to the electroplating of bright, crack-free, relatively thick deposits of low-stress ruthenium from specially prepared ruthenium electro-

Electrodeposits of ruthenium are valuable as coatings for electrical contacts, e.g., those in reed switches, and for other surfaces requiring good resistance to wear. They have also been found useful for decorative coat-

One such ruthenium electroplating bath is described in U.S. Pat. No. 3,576,724. The electroplating bath is prepared from ruthenium compounds containing complex anions of the formula:



wherein Y is chlorine or bromine. Recent disclosures have indicated that in addition to chlorine and bromine being employed as Y, other groups such as nitrite, hydroxyl, nitrate, azido and thiocyanate may also be used. It is further disclosed in the above-identified patent that the anions are preferably introduced as their ammonium salts and that the method of electrodepositing ruthenium is from an aqueous acidic bath having a pH not exceeding 4. The complex anions are believed to be nitrogen-bridged compounds of ruthenium, the anion of which has the following structure:



in which L represents the aquo, chloro or bromo ligands. The deposits however, are bright only up to a thickness of about 2 to 3 millimicrons (μm). At greater thicknesses, surface-cracking becomes apparent and the deposits are matte and gray.

I have now discovered a new ruthenium electroplating bath and a process for plating therefrom bright, crack-free coatings of ruthenium up to thicknesses of about $5\mu\text{m}$ and above.

It is an object of the invention to provide a method for preparing a ruthenium electroplating bath capable of producing bright, crack-free electrodeposits of ruthenium up to thicknesses of $5\mu\text{m}$ and above.

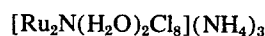
Another object of the invention is to provide a novel ruthenium electroplating bath composition.

It is a further object of the invention to provide a method for electroplating bright, crack-free deposits of ruthenium up to about $5\mu\text{m}$ and above, from specially prepared plating baths.

Other objects and advantages will become apparent from the following description:

Generally speaking, novel ruthenium electroplating baths of this invention are prepared by dissolving the compound $\text{Ru}_2\text{N}(\text{OH})_5\cdot n\text{H}_2\text{O}$ in either aqueous sulfuric or sulfamic acid and refluxing, for example, at about 100°C . or higher, for between about one and 80 hours. Generally, the sulfate ion concentration must exceed about 15 grams per liter (gpl) in order to obtain crack-free deposits, but does not normally exceed about 100 gpl as no further benefit is obtained and current efficiency is reduced. Normally, the resulting solution obtained after refluxing may be used directly as the plating bath; however, if the sulfate ion concentration is not sufficiently high, it may be increased by adding a sulfate salt, for example, ammonium, sodium or potassium sulfate. When employed, in this specification and claims, the term "sulfate ion" includes both sulfate and bisulfate ion and any mixture thereof. Any concentration of sulfate ion mentioned herein is to be deemed to be the result of complete ionization of any sulfate salts or acid added to the baths of the present invention. It is also essential that the pH of the bath solution does not exceed about 4.

In carrying the invention into practice, it is preferred that the plating bath be prepared by dissolving a quantity of the compound



in water and adding sufficient alkali, for example, potassium hydroxide, to precipitate the compound $\text{Ru}_2\text{N}(\text{OH})_5\cdot n\text{H}_2\text{O}$. This compound is then filtered off and thoroughly washed to remove chloride and other impurities. Alternatively, an aqueous solution of $\text{K}_2[\text{Ru}(\text{NO})\text{Cl}_5]$ is basified with alkali, e.g., potassium hydroxide, and then treated with a reducing agent such as formaldehyde. A precipitate of $\text{Ru}_2\text{N}(\text{OH})_5\cdot n\text{H}_2\text{O}$ is formed on warming the solution, for example, on a steam bath, which is then filtered off and thoroughly washed with water. The compound $\text{Ru}_2\text{N}(\text{OH})_5\cdot n\text{H}_2\text{O}$ is then used to prepare the plating bath in accordance with the procedures described hereinabove.

The pH of the bath solution should not exceed about 4. In practice, the pH should be from about 0.5 to about 4 and is preferably from about 1 to 3. If the pH of the bath solution is too low, the deposition of ruthenium takes place at a low cathode current efficiency. If the pH is too high, the resulting ruthenium deposit is black. Increasing the pH still further leads to the formation of a brownish deposit on the cathode that is not metallic ruthenium. The pH may be modified by the addition of suitable pH modifying agents such as potassium, sodium or ammonium hydroxides and sulfuric or sulfamic acids. If necessary, the pH of the bath can be similarly adjusted during operation so as to maintain the pH within the proper operating ranges.

The ruthenium concentration in the plating bath is advantageously from about one to about 20 gpl. Higher concentrations of ruthenium may be used although there is no practical advantage in doing so. Moreover, losses of ruthenium from the bath by drag-out are increased and the capital cost of the bath becomes unnecessarily high. Agitation of the bath is desirable at ruthenium contents exceeding about 20 gpl.

To avoid blackened deposits, the plating bath should be stabilized by the presence of sulfamate ions at a level of at least about 2 gpl and, preferably, about 20 gpl. This level should be maintained throughout the plating operation and additions to the bath may be made by

using such sulfamate salts as ammonium, potassium or sodium. Loss of sulfamate ions occurs through anodic oxidation and it is therefore necessary to periodically check the concentration during the plating operation and to add further sulfamate ions if required.

Although the temperature of the bath is not critical,

it is advantageous that the operating temperature of the bath be maintained between about 50°C. and 70°C. since plating proceeds more slowly at lower temperatures, while at higher temperatures excessive losses, due to evaporation, may occur. Moreover, at temperatures below about 50°C. the bath can only be operated within a limited range of current densities, since the cathode efficiency is found to rapidly decrease as the cathode current density is increased to about 1 ampere per square decimeter (A/dm²). In the temperature range of 50°C. to 70°C., it is preferred to use an essentially unidirectional electric current at a cathode current density of from about 1 to 4 A/dm² and, more advantageously, from about 1 to 2 A/dm² for optimum current efficiency.

As those skilled in the art will appreciate, satisfactory, crack-free deposits of ruthenium are dependent, in part, on the internal stress developed in the deposit. In the examples shown hereinbelow, this stress has been measured during plating by rigidly anchoring one end of the cathode being plated and exerting a constant force on the other end through a spring attached to a measuring device. The change in the applied force due to the stress of the electrodeposited ruthenium was noted and a calibration graph constructed of "change in force", i.e., "stress" against plating time. For comparison purposes the stress (in kilograms force per square millimeter (kg./mm²)) has been determined at the plating time when a standard plating thickness of 1 μm has been deposited.

For the purpose of giving those skilled in the art a better understanding of the invention, and/or a better appreciation of the invention, the following examples are given:

EXAMPLE I

Ten grams of [Ru₂N(H₂O)₂Cl₈](NH₄)₃ was dissolved in 400 cubic centimeters (cm³) of distilled water and the solution heated to 90°C. A concentrated potassium hydroxide solution was added dropwise until the pH of the solution was 9.5. The precipitate of Ru₂N(OH)₅·nH₂O which was formed was filtered off and thoroughly washed with water to remove chloride. A standard silver nitrate test confirmed the absence of chloride. No ruthenium could be detected in the filtrate or washings. The precipitate was added to an aqueous solution containing 20 grams of sulfamic acid and the total volume increased to 300 cm³. The solution was refluxed for 65 hours during which time a dark red clear solution was

formed. The solution was cooled and its pH found to be 1. The pH was increased to 1.5 by the addition of potassium hydroxide and this solution was then employed as the electrolyte from which ruthenium electrodeposits A and B were obtained on gold-flashed copper discs (cathodes) under the following conditions:

		A	B
Sulfate conc. (approx.)	(gpl)	60	60
Sulfamate conc. (approx.)	(gpl)	3	3
Ruthenium conc. (approx.)	(gpl)	11	11
Temperature of electrolyte	(°C.)	70	70
pH of electrolyte		1.5	1.5
Cathode current density	(A/dm ²)	2	4
Anode current density	(A/dm ²)	0.2	0.4
Time	(minutes)	140	140
Thickness of deposit	(μm)	9.3	11.2
Current efficiency	(%)	26	18
Internal stress after 1 μm deposited	(kg./mm ²)	17	17

The deposits were bright and crack-free.

EXAMPLE II

35.2 grams of [Ru₂N(H₂O)₂Cl₈](NH₄)₃ was dissolved in 500 cm³ of distilled water and the solution heated to 90°C. A concentrated potassium hydroxide solution was added dropwise until the pH of the solution was 9.5. The precipitate of Ru₂N(OH)₅·nH₂O was filtered off and thoroughly washed with water to remove chloride. A standard silver nitrate test confirmed the absence of chloride. No ruthenium could be detected in the filtrate or the washings. The precipitate was added to a solution of 10 cm³ concentrated sulfuric acid which had been diluted to a volume of 500 cm³ with water and the solution was refluxed for two hours. After cooling the resulting solution was diluted with water to reduce the ruthenium concentration to 6 gpl. Additions of 20 gpl of ammonium sulfate and 20 gpl ammonium sulfamate were then made and the pH of the solution was raised to 1.5 with aqueous ammonia. The final solution was employed as the plating electrolyte from which a ruthenium electrodeposit was obtained on a gold-flashed copper disc (cathode) under the following conditions:

Temperature of electrolyte	(°C.)	70
pH		1.5
Cathode current density	(A/dm ²)	1
Anode current density	(A/dm ²)	0.1
Time	(minutes)	120
Thickness of deposit	(μm)	5
Current efficiency	(%)	33
Internal stress after 1 μm deposited	(kg./mm ²)	20

The deposit was bright and crack-free.

Baths of this invention compare quite favorably with baths of known composition such as U.S. Pat. No. 3,576,724, noted hereinabove. These baths containing [Ru₂N(H₂O)₂Cl₈]³⁻, when measured under similar testing conditions, have internal stresses on the order of 40 to 60 kg./mm², which is significantly higher than the internal stress of baths of this invention, as shown hereinabove.

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 consid-

ered to be within the purview and scope of the invention and appended claims.

I claim:

1. A process for producing a ruthenium electroplating bath having a pH of about 4 or less which comprises:

a. dissolving a compound having the formula



in an aqueous acid selected from the group consisting of sulfuric acid and sulfamic acid;

b. refluxing the resulting solution to provide a bath; and

c. if necessary, adjusting the pH of said bath to a pH of about 4 or less.

2. A process in accordance with claim 1 further comprising adjusting the sulfate ion concentration of said bath to a level of at least about 15 gpl by the addition of sulfate salt.

3. A process in accordance with claim 2 wherein the sulfate salt is selected from the group consisting of ammonium sulfate, sodium sulfate and potassium sulfate.

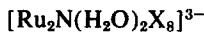
4. A process in accordance with claim 1 further comprising adjusting the sulfamate ion concentration to a level of at least about 2 gpl by the addition of a sulfamate salt.

5. A process in accordance with claim 4 wherein the sulfamate salt is selected from the group consisting of ammonium sulfamate, sodium sulfamate and potassium sulfamate.

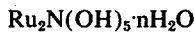
6. A process in accordance with claim 1 wherein said



is produced by providing an aqueous solution of a compound having, in the ionic state, a complex anion of the general formula

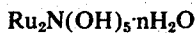


wherein X is at least one member selected from the group consisting of chlorine and bromine and adjusting the pH of said solution to precipitate



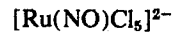
7. A process in accordance with claim 6 wherein said complex anion is a part of the ammonium salt.

8. A process in accordance with claim 1 wherein said



is produced by

a. providing an aqueous solution of a compound having, in the ionic state, a complex anion of the formula



b. adjusting the pH of said solution to an alkaline pH;

c. treating said solution with formaldehyde; and

d. heating said solution to form a precipitate of



9. A process in accordance with claim 8 wherein said complex anion is a part of the potassium salt.

10. A ruthenium electroplating bath producible by a process in accordance with claim 1.

11. A process for the electrodeposition of ruthenium from a bath prepared by a process in accordance with claim 1 which comprises cathodically depositing ruthenium by passing an essentially unidirectional electric current at a cathode current density of about 1 to about 4 A/dm² through said bath.

12. A process in accordance with claim 11 wherein a sulfate ion concentration of at least about 15 gpl is maintained in said bath.

13. A process in accordance with claim 12 wherein said temperature is maintained in the range of about 50°C. to about 70°C., and the cathode current density from about 1 to about 4 A/dm².

14. A process in accordance with claim 13 wherein the cathode current density is maintained at about 1 to about 2 A/dm².

15. A process in accordance with claim 14 wherein said pH is maintained in the range of from about 0.5 to about 4.

16. A process in accordance with claim 15 wherein the pH is maintained in the range of from about 1 to about 3.

17. A process in accordance with claim 12 further comprising maintaining a concentration of sulfamate ions in the bath of at least about 2 gpl.

18. A process in accordance with claim 11 wherein the ruthenium concentration is maintained in the range of from about 1 to about 20 gpl.

19. A process in accordance with claim 11 wherein the bath is agitated when the ruthenium content exceeds about 20 gpl.

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