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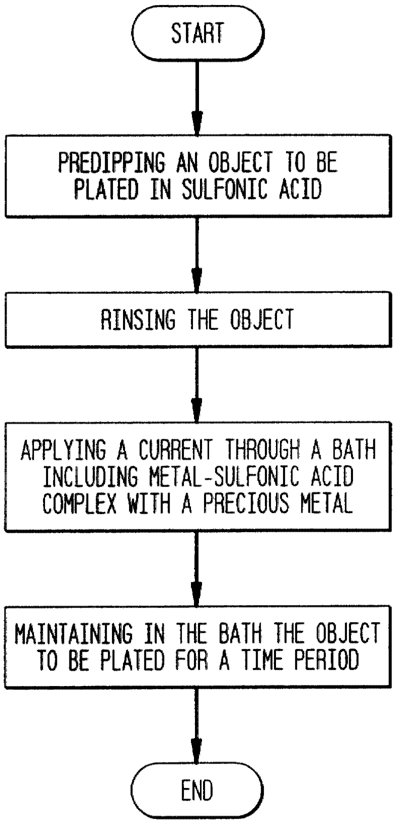
(54) Palladium electroplating bath and process for electroplating

(57) An electroplating bath includes a metal-sulfonic acid complex wherein the metal is a precious metal, and free sulfonic acid. The precious metals include Pd, Au, Hard Au (with Ni or Co as hardening agents), Pt, Rh, Ru, Ag and alloys thereof.

FIG. 2



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Description

BACKGROUND OF THE INVENTION

1. Technical Field

[0001] The present invention is related to electroplating and, more particularly, to an electroplating salt, bath and process.

2. Art Background

[0002] Precious metals are used in a.variety of industrial applications including electrical circuits as electrical contact surfaces, conducting paths and heat sinks. Various properties of precious metals make their use in such applications highly advantageous. These properties include physical and chemical stability, high electrical conductivity, low porosity, and high thermal conductivity. Precious metals are often used in high-density circuits such as integrated circuits because of one or more of the properties set forth above.

[0003] One problem with precious metal electroplating processes involves the selection of a suitable compound to supply the plating metal initially to the bath. The compound should be stable, easily made in reasonably pure form and readily soluble in the electroplating bath. The problem is particularly difficult where rapid, high quantity palladium electroplating is being carried out. In this case, relatively large amounts of palladium metal are being plated out and therefore large amounts of palladium must be added to the bath. Under these circumstances, high solubility and high rate of solubility is extremely important.

[0004] In addition, compatibility of the components of the palladium compound (complexing species, anion, etc.) as well as the complexity of the bath are also of much practical importance since these factors may limit the lifetime of the electroplating bath, alter the electroplating characteristics of the bath as well as add contaminants to the main plating tank.

SUMMARY OF THE INVENTION

[0005] In accordance with one embodiment, an electroplating bath includes a metal-sulfonic acid complex wherein the metal is a precious metal, and free sulfonic acid. As used herein, the term "precious metals" include Pd, Au, Hard Au (with Ni or Co as hardening agents), Pt, Rh, Ru, Ag and alloys thereof.

[0006] The sulfonic acid may be an acid having the following structure:

$$R[SO_3]\text{-}X$$

wherein R = alkyl or aryl group and X = cationic species.

The sulfonic acid may for example be methane sulfonic acid (MSA). The resulting bath may have a pH less than 2.5, particularly less than 1.0.

[0007] The electroplating bath may include only a single additive, such as a brightener or brightening agent.

[0008] When a precious metal alloy is to be plated, the electroplating bath may also include an alloying metal-sulfonic acid complex. For example, the bath for plating an Pd-Ni alloy may include a Pd-sulfonic acid complex and a Ni-sulfonic acid complex. The concentration of the two metal complexes is largely dictated by the desired percentage composition of the alloy.

[0009] In accordance with a further embodiment, a process of electroplating a metal on an object (e.g., a substrate), involves maintaining an object to be plated in a solution including a metal-sulfonic acid complex having a precious metal, and free sulfonic acid while providing current through the bath. The object may be pre-dipped in sulfonic acid.

[0010] In one example, the precious metal may be Pd which is immersion deposited on a substrate, such as Cu or an alloy thereof

[0011] In accordance with another embodiment, a metal salt for use in an electroplating bath to electroplate Pd or Pd alloys is provided. The chemical formula for the Pd salt may be expressed as follows:

$$Pd(NH_3)_xMSA_2$$

wherein x is in the range of 0 to 4.

[0012] In accordance with a further embodiment, a process of synthesizing a metal salt for use in supplying a plating metal to an electroplating bath is provided. The process may involve mixing sulfonic acid with a source of metal ions to form a slurry, the metal being a precious metal; filtering the slurry to collect the precious metal-sulfonic acid salt; washing the collected salt with alcohol; and drying the washed salt. The mixing may occur at approximately room temperature.

[0013] Other and further aspects of the present invention will become apparent during the course of the following description and by reference to the attached drawings.

BRIEF DESCRIPTION OF THE DRAWINGS

[0014]

Fig. 1 illustrates a flow chart of a general process for synthesizing a metal-sulfonic acid complex or salt or electrolyte for use in supplying a plating metal to a bath or solution to electroplate precious metals (including their alloys);

Fig. 2 illustrates a flow chart of a general process for employing a bath or solution including a metal-sulfonic acid complex to electroplate precious metals; and

Figs. 3A-3D illustrate images obtained with a scanning electron microscope of a Pd layer deposited on a substrate or object using the processes of Figs. 1 and 2 at various thicknesses.

DETAILED DESCRIPTION OF THE SEVERAL EMBODIMENTS

[0015] The present invention is directed to a metal composition, particularly a metal complex of methane sulfonic acid (MSA), for supplying a plating metal to an electroplating bath and a process of synthesizing the metal-MSA complex.

[0016] The present invention is further directed to an electroplating bath including a metal complex of sulfonic acid and a process of employing such a bath to electroplate precious metals on an object (e.g., a substrate). The term "precious metals" as used herein include Pd, Au, Hard Au (with Ni or Co as hardening agents), Pt, Rh, Ru, Ag and alloys thereof.

[0017] It has been discovered that metal complexes of a sulfonic acid may generally be employed to supply a plating metal to an electroplating bath to electroplate precious metals onto a surface of an object. A process to form the metal-sulfonic acid complex is provided herein which results in high yields of the metal salt with little or minimal waste of the underlying metal.

[0018] Through the use of such metal-sulfonic acid complexes, it is possible to obtain a very acidic bath for electroplating precious metals which is particularly suitable in plating a strike or underlayer onto an object. Additionally, the metal-sulfonic acid complex provides an electrolytic bath or solution which requires less chemicals and additives, reduces contamination or the likelihood of contamination of the main plating tank, produces quality-grade plated products, and may reduce the overall costs in maintaining the main plating tanks.

[0019] In accordance with one embodiment, an electrolytic bath or solution is provided for plating precious metals onto a surface of an object. The bath or solution comprises a metal-sulfonic acid complex or salt wherein the metal is a precious metal, and free sulfonic acid. The bath may also include an alloying metal-sulfonic acid complex or salt for plating precious metal alloys. Such an arrangement provides for an acidic bath with a pH level less than 2.5, preferably less than 1.0.

[0020] In one example, the bath or solution may be limited only to a single additive, such as a brightening agent or brighteners or other well known plating additives. For example, additive systems for Pd plating can typically be grouped in to two classes.

[0021] Class I - (brighteners) are generally unsaturated sulfonic compunds where unsaturation is in the alpha- or beta -position with respect to the sulfonic group. Such compounds have the formula $A - SO_3 - B$ where A is an aryl or alkylene group, substituted or unsubstituted, and B may be OH, OR, OM, NH2, etc.

[0022] Class II organic brighteners are generally unsaturated or carbonyl organic compounds. Examples are coumpounds containing >C=O, >C=C<, >C=N-, (-N=N-), etc.

[0023] Accordingly, the reduction or minimization of chemicals in the bath or solution reduces contamination or the potential for contamination of the main plating tank.

[0024] In accordance with another embodiment, a process of plating precious metals is provided herein. The plating process generally involves maintaining an object (e.g., a substrate) to be plated in a bath or solution containing metal-sulfonic acid complex wherein the metal is a precious metal, while providing a current through the bath. For plating precious metal alloys, the bath may further include an alloying metal-sulfonic acid complex.

[0025] The process may be employed to deposit a strike or underlayer of a precious metal.

[0026] In accordance with a further embodiment, an electrolyte or salt and a process of manufacturing thereof are provided for use in plating precious metals, such as Pd. The Pd electrolyte or salt may comprise a palladium-amine methane sulfonic acid complex:

$$Pd(NH_3)_xMSA_2$$

where

x is in the range of 0 to 4,
MSA is methane sulfonic acid.

The Pd complex of sulfonic acid may generally be formed by mixing free sulfonic acid, in this example MSA, with a solution containing an ion source of Pd, such as a Pd salt.

[0027] The use of a metal-sulfonic acid salt provides various benefits and advantages over current approaches. For example, the use of Pd-MSA salt provides a very acidic bath with a pH below at least 2.5, preferably below 1.0, which is particularly useful to plate a strike (e.g., a layer having an approximate thickness of 3-4 μ-inches) as well as to plate other-types of metal layers having an approximate thickness of 10-20 μ-inches. The high acidity of the bath scrubs off the surface layer (e.g., an oxide layer) on the substrate to be plated without requiring additional chemicals or additives which typically increase the complexity and cost of the bath. The bath may be limited to a single additive.

[0028] By requiring less chemicals and additives, this in effect reduces contamination or the likelihood of contamination of the main plating tank due to substrate corrosion and/or metal salts which are dragged into the tank from a previous plating operation. The reduction in contaminants in the main plating tank ensures the production of quality-grade plated products, and reduces the overall costs in maintaining the main plating tanks.

[0029] Furthermore, the Pd-MSA salt provides a plating bath which is particularly suitable for depositing a strike. This results in additional benefits including improved adhesion on easily passivated surfaces such as Ni, reduction of porosity of subsequent deposits and further protects the main plating bath from contamination caused by substrate corrosion and metal salts dragged-in from previous plating operations.

[0030] Additionally, the Pd-MSA salt provides a plating bath that is compatible with other plating operations, such as non-halide and halide based chemistries, which may be performed by the main plating tank.

[0031] An example of a reaction scheme involving the preparation of a Pd-MSA salt, in this example $Pd(NH_3)_x[MSA]_2$, is shown below in equation (3).

$$[Pd(NH_3)_x]A + \text{excess MSA} \rightarrow [Pd(NH_3)_x][MSA]_2 + MSA + HA \qquad (3)$$

where :

x preferably ranges from 0 to 4,
A is an anion.

In this example, the sulfonic acid is methane sulfonic acid and the metal ion source for Pd is $Pd(NH_3)A$ salt, where the anion A may be, for example, a sulfate, halide (e.g., fluorine, chlorine, bromide and iodide), nitrate, nitrite, acetate, phosphate or sulfamate. With regard to equation (3), NH_3 may be eliminated to provide a pure metal-sulfonic acid complex or replaced with other organic amines to provide complexed species of Pd-MSA salt.

[0032] While the above describes a reaction scheme involving one example of an Pd-MSA salt, the same or similar anion exchange reaction may be applied generally to obtain other precious metal-sulfonic salts as well as to obtain alloying metal-sulfonic salts.

[0033] For example, a reaction scheme of an alloying metal-MSA salt may generally be expressed as follows:

$$[M][A]+MSA\ (\text{excess}) \rightarrow [M][MSA]+MSA+HA \qquad (4)$$

where:

M is an alloying metal, such as Ni, Co, Ag, Sn, etc.,
MSA is methane sulfonic acid.

As with equation (3), the anion A may be a sulfate, halide (e.g., fluorine, chlorine, bromide and iodide), nitrate, nitrite, acetate, phosphate or sulfamate. M may be any desired alloying metal, such as Ni, Co Ag or Sn, which may be selected according to the desired application. The alloying metal M may be initially in the form of an alloying metal ion source, such as a metal salt including the alloying metal. The concentration of the alloying metal depends upon the alloy composition to be deposited (10% to 95% Pd by weight).

[0034] In plating alloys, the bath or solution may be prepared by mixing a solution of the alloying metal-MSA complex together with a Pd-MSA complex and free MSA.

[0035] For facilitating the plating of alloys, a mixed ligand system may also be employed as desired. An appropriate ligand may be selected depending on the metals in the desired alloy. For example, the ligand for Pd is ammonia.

[0036] While the above has been described with reference to methane sulfonic acid, other sulfonic acids in the group having the structure $R[SO_3]$-X where R = alkyl or aryl group and X = cationic species, e.g. H^+ or Na^+, etc. may be employed to provide a metal-sulfonic acid complex and bath thereof for electroplating precious metals.

[0037] With reference to Fig. 1, the general process for synthesizing a precious metal complex of sulfonic acid for use in supplying a precious metal plating metal to a bath, may involve:

(a) adding sulfonic acid to a solution with a source of precious metal ions (e.g., precious metal salt) to form a slurry,
(b) stirring the slurry with precipitates for an appropriate amount of time,
(c) filtering the slurry and collecting the metal-sulfonic salt,
(d) washing the salt with an alcohol such as isopropanol, and
(e) air drying the washed metal-sulfonic salt.

[0038] The remaining filtrates and alcohol may be collected and recycled accordingly.

[0039] The above provides an efficient process for manufacturing metal-sulfonic salts, particularly, Pd-MSA salts, at significantly high yields with minimal waste of the metal. This is particularly important when dealing with precious metals which are costly.

EXAMPLE #1

[0040] An example of a process of synthesizing Pd-MSA salt is provided herein. In this example, an amount of 250 ml of methane sulfonic acid (70% v/v solution) was added slowly to 1 liter of $[Pd(NH_3)_4][SO_4]$ which contained 70 g/L of Pd (as metal), with stirring at room temperature. The resulting pale yellow suspension was continuously stirred after the complete addition of MSA for an additional 30 minutes. The contents of the reaction vessel were then emptied into a large Büchner funnel. The slightly off-white, finely crystalline product was washed three times with 40 mL portions of isopropanol (IPA) and allowed to air dry. This resulted in a yield of 220 g of Pd-MSA salt (91% based on a 70 g/L Pd from a $[Pd(NH_3)_4][SO_4]$ solution).

[0041] The remaining filtrates were collected and sent to recycle for Pd recovery. If desired, the alcohol used to wash the product may also be recycled by evaporation and condensation using standard equipment.

[0042] With reference to Fig. 2, the general process by which a precious metal may be electroplated onto an object (e.g., a substrate) through the use of a bath including metal-sulfonic salt for supplying the precious metal preferably involves:

(a) pre-dipping an object whose exposed surface portions are to be plated with a precious metal or alloys thereof, such as palladium or palladium alloy, in a sulfonic acid compatible with the plating metal-sulfonic salt(s);
(b) rinsing the object;
(c) applying through the bath a current density greater than 5 mA/cm^2 dependent on the type of process (e.g. rack or continuous), and
(d) maintaining in the bath the object to be plated for a time sufficient to develop upon the exposed surface portions a precious metal layer of desired thickness.

[0043] The above electroplating process may be employed to immersion deposit Pd on a substrate, such as Cu or an alloy thereof.

[0044] Examples of the plating bath or solution for Pd and Pd alloys are provided below. The bath may be employed with various plating processes, such as low speed plating which is typical for rack mounted articles or high speed plating which is typical of reel-to-reel type continuous feeding for electronic components (e.g., connectors, printed circuit boards, printed wiring boards, etc.).

EXAMPLE #2

[0045] In this example, a composition of a bath or solution for electroplating Pd is provided. The single additive may be a class I or II brightening agent (brightener), as discussed above. Pd may be deposited at a pH below 1.

$[Pd(NH_3)_4]MSA_2$;	0.5-20 g/L of Pd
a single additive	0.5-10mL/L
Free MSA	50-300 mL/L
pH	less than (<) 1
Temperature	**Room Temperature**
Current density	5-50 ASF
Rotation	100-500 rpm

EXAMPLE #3

[0046] In this example, a composition of a bath or solution for electroplating Pd-Ni alloy is provided. The single additive may be a class I or II brightening agent (brightener), as discussed above. Pd-Ni alloy may be deposited at a pH below 1.

$[Pd(NH_3)_4]MSA_2$;	0.5-20 g/L of Pd
Ni[MSA]	0.5-20 g/l of Ni
a single additive	0.5-10mL/L
Free MSA	50-300 mL/L
pH	less than (<) 1
Temperature	**Room Temperature**
Current density	5-50 ASF
Rotation	100-500 rpm

[0047] Various tests were performed to investigate the use of Pd-MSA to electroplate Pd on an object or substrate, such as one formed of Cu, and are described below.

[0048] Figs. 3A-3D illustrate images obtained with a scanning electron microscope at different thickness levels at 2200x of Pd layer deposited on a substrate or object using the processes of Figs. 1 and 2. As shown, the deposited layer did not evidence any micro-cracking.

[0049] On copper substrates, immersion deposition with the use of the Pd-MSA bath resulted in a bright, white Pd layer. This phenomenon may find particular use in the electronics industry. More specifically, in printed wire board (PWB), printed circuit board (PCB) manufacture and plating on plastics.

[0050] To test metallic contamination of the main plating tank, Ni and Cu were both added up to 50 ppm with no negative impact on deposit quality. Regarding drag-in concerns from other plating operations, up to 20 ml/l was deliberately added to both halide and non-halide systems with no resulting problems.

Claims

1. An electroplating bath comprising:

   a metal-sulfonic acid complex wherein the metal is a precious metal; and
   free sulfonic acid.

2. The electroplating bath according to claim 1, further including only a single additive.

3. The electroplating bath according to claim 1, further comprising an alloying metal-sulfonic acid complex.

4. The electroplating bath according to claim 2, wherein the precious metal is Pd and the alloying metal is selected from the group consisting of Ni, Co, Ag and Sn.

5. The electroplating bath according to claim 1, wherein the pH is less than 2.5.

6. The electroplating bath according to claim 5, wherein the pH is less than 1.0.

7. The electroplating bath according to claim 1, wherein the sulfonic acid is an acid having the following structure:

$$R[SO_3]\text{-}X$$

wherein R = alkyl or aryl group and X = cationic species.

8. The electroplating bath according to claim 1, wherein the single additive is one of a group I or II brightening agents.

9. The electroplating bath according to claim 1, wherein the sulfonic acid comprises methane sulfonic acid, and the metal-sulfonic acid complex comprises a metal-methane sulfonic complex.

10. A process of electroplating a metal on an object, comprising maintaining an object to be plated in a solution including a metal-sulfonic acid complex having a precious metal, and free sulfonic acid while providing current through the bath.

11. The process according in claim 10, further comprising pre-dipping the object in sulfonic acid.

12. The electroplating bath according to claim 10, wherein the bath only includes a single additive.

13. The electroplating bath according to claim 10, wherein the bath further comprises an alloying metal-sulfonic acid salt.

14. The electroplating. bath according to claim 13, wherein the precious metal is Pd and the alloying metal is selected from the group consisting of Ni, Co, Ag and Sn.

15. The electroplating bath according to claim 10, wherein the pH is less than 2.5.

16. The electroplating bath according to claim 15, wherein the pH is less than 1.0.

17. The electroplating bath according to claim 10, wherein the sulfonic acid is an acid in the following structure:

$$R[SO_3]\text{-}X$$

wherein R = alkyl or aryl group and X = cationic species.

18. The electroplating bath according to claim 10, wherein the sulfonic acid comprises methane sulfonic acid and the metal-sulfonic acid complex comprises a metal methane sulfonic complex.

19. The electroplating bath according to claim 10, wherein the precious metal is Pd which is immersion deposited on the substrate.

20. The electroplating bath according to claim 19, wherein the object comprises at least one of Cu or Cu alloy.

21. A metal salt for use in an electroplating bath to electroplate Pd or Pd alloys, comprising:

$$Pd(NH_3)_xMSA_2$$

wherein x is in the range of 0 to 4.

22. A process of synthesizing a metal salt for use in supplying a plating metal to an electroplating bath, comprising:

mixing sulfonic acid with a source of metal ions to form a slurry, the metal being a precious metal; and filtering the slurry to collect the precious metal-sulfonic acid salt.

23. The process according to claim 22, further comprising:

washing the collected salt with alcohol; and
drying the washed salt.

24. The process according to claim 22, wherein the mixing occurs at approximately room temperature.

25. The process according to claim 22, wherein the precious metal is Pd and the sulfonic acid is methane sulfonic acid.

FIG. 1

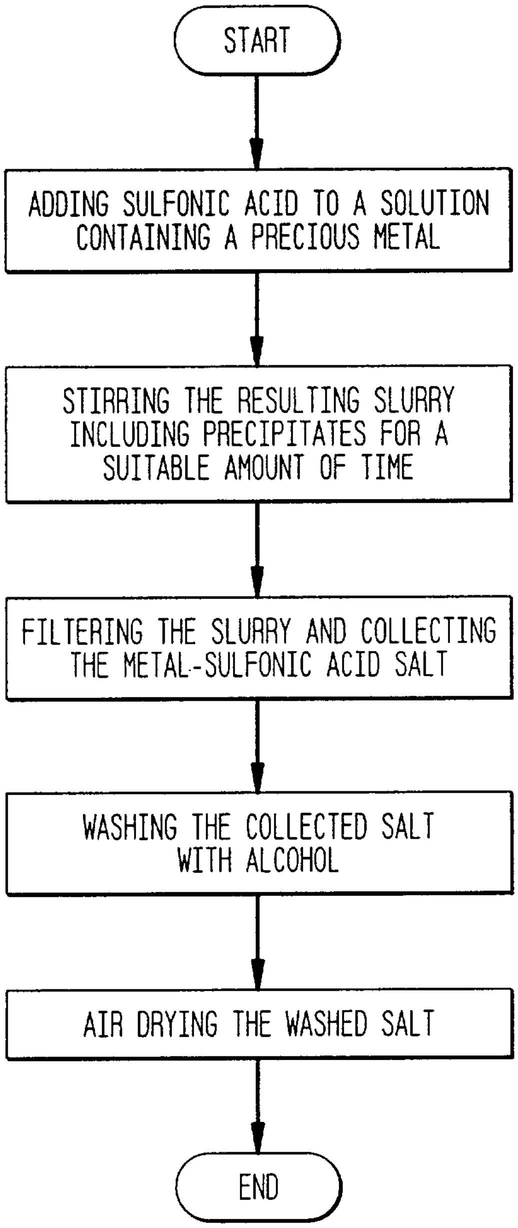

START
ADDING SULFONIC ACID TO A SOLUTION CONTAINING A PRECIOUS METAL
STIRRING THE RESULTING SLURRY INCLUDING PRECIPITATES FOR A SUITABLE AMOUNT OF TIME
FILTERING THE SLURRY AND COLLECTING THE METAL-SULFONIC ACID SALT
WASHING THE COLLECTED SALT WITH ALCOHOL
AIR DRYING THE WASHED SALT
END

FIG. 2

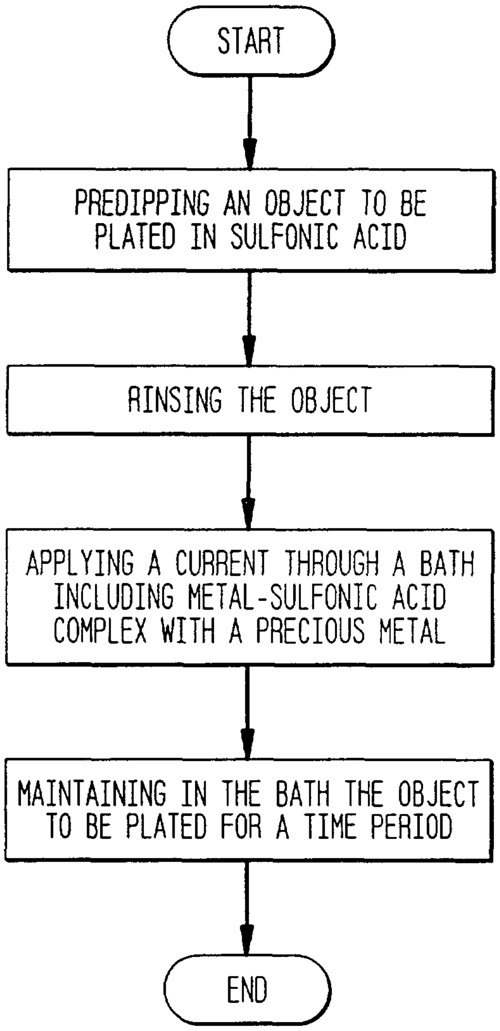

START
PREDIPPING AN OBJECT TO BE PLATED IN SULFONIC ACID
RINSING THE OBJECT
APPLYING A CURRENT THROUGH A BATH INCLUDING METAL-SULFONIC ACID COMPLEX WITH A PRECIOUS METAL
MAINTAINING IN THE BATH THE OBJECT TO BE PLATED FOR A TIME PERIOD
END

FIG. 3A

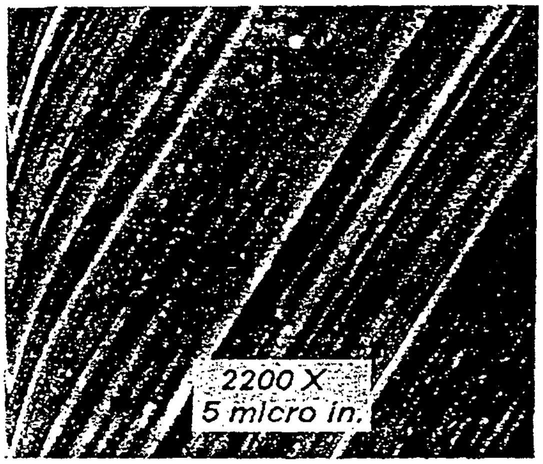


FIG. 3B

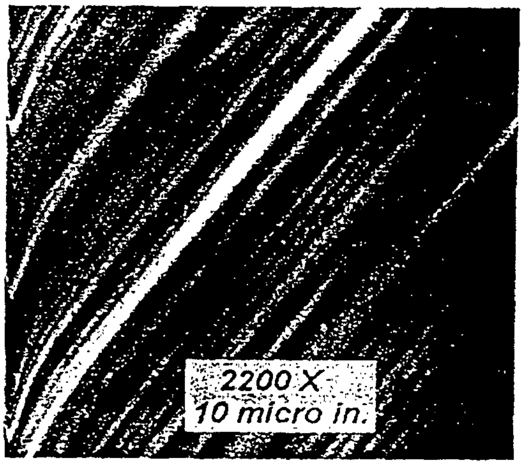


FIG. 3C

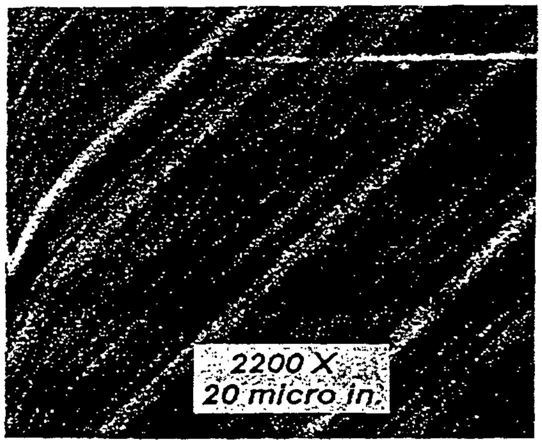
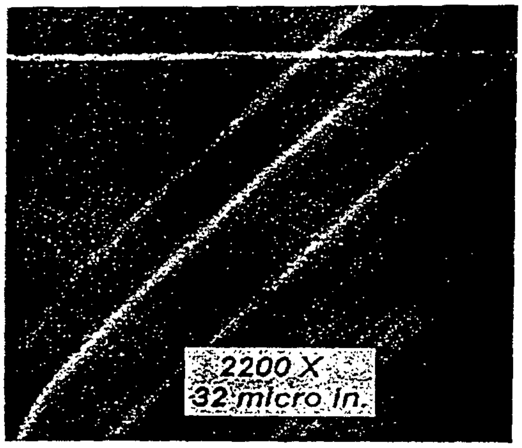


FIG. 3D



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EUROPEAN SEARCH REPORT

Application Number
EP 01 30 4721

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.7)
X	PATENT ABSTRACTS OF JAPAN vol. 1998, no. 13, 30 November 1998 (1998-11-30) & JP 10 204676 A (C UYEMURA &CO LTD), 4 August 1998 (1998-08-04) * abstract * -& US 6 099 713 A (ISAMU YANADAAND MASANOBU TSUJIMOTO) 8 August 2000 (2000-08-08) *comparative example 1* * examples 5,6 * ---	1-3, 5-10,12, 13,15-18	C25D3/50 C25D3/56
X	PATENT ABSTRACTS OF JAPAN vol. 1996, no. 06, 28 June 1996 (1996-06-28) & JP 08 041676 A (EBARA YUUJIRAITO KK), 13 February 1996 (1996-02-13) * abstract * ---	1-3,7,9, 10,12, 13,17,18	
X	US 4 244 739 A (CAGNASSI ROBERTO) 13 January 1981 (1981-01-13) * column 2, line 56 - column 3, line 24 * * column 6, line 56 - column 7, line 4 * * column 5, line 4-35 * * examples 1,4 * ---	1,3,4,7, 9-11,13, 14,17-21	**TECHNICAL FIELDS SEARCHED (Int.Cl.7)** C25D
X	US 4 465 563 A (NOBEL FRED I) 14 August 1984 (1984-08-14) * column 1, line 45-57 * * column 2, line 14-16 * * examples 1,5 * * claims 1,6-8,12,13 * --- -/--	1,3,4,7, 9,10,13, 14,17,19	

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	7 August 2001	Zech, N

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
O : non-written disclosure
P : intermediate document

T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
D : document cited in the application
L : document cited for other reasons
& : member of the same patent family, corresponding document

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DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.7)
P,X	WO 00 56952 A (TECHNIC ;SPECIALTY CHEMICAL SYSTEMS INC (US)) 28 September 2000 (2000-09-28) * page 15 * * page 16 * * page 18 * ---	1,3,7,9,10,13,17,18	
P,X	US 6 165 342 A (KUHN WERNER ET AL) 26 December 2000 (2000-12-26) * column 3, line 34 - column 4, line 20 * * column 1, line 66 - column 2, line 63 * ---	1,3,10,13	
X	US 4 673 472 A (MORRISSEY RONALD J ET AL) 16 June 1987 (1987-06-16)	1,5,7-10,15,17,18,21	
A	* claims 1,6,7 * * column 2, line 25 - column 3, line 7 * * column 3, line 48-56 * * example 7 * ---	3,4,13,14	
			TECHNICAL FIELDS SEARCHED (Int.Cl.7)
E	US 6 251 249 B1 (CHEVALIER JEAN W ET AL) 26 June 2001 (2001-06-26) * column 7, line 8-20,47-55 * * examples 2,4,7,8 * --- -/--	1,5,7,9-11,15,17,18,20	

The present search report has been drawn up for all claims

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O : non-written disclosure
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T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
D : document cited in the application
L : document cited for other reasons
& : member of the same patent family, corresponding document

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DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.7)
X	MASAKI S: "Mirror-Bright Silver Plating from a Cyanide-Free Bath" METAL FINISHING, ELSEVIER SCIENCE PUBLISHING, NEW YORK, NY, US, vol. 96, no. 1, 1998, pages 16,18-20, XP004113126 ISSN: 0026-0576 * page 1, column 2, paragraph 2 - column 3, paragraph 1 * * table 1 * * page 2, column 2, paragraph 3 * ---	1,7,9, 10,17, 18,20	
P,X	DE 199 28 047 A (HOFFACKER GERHARD) 21 December 2000 (2000-12-21) * claims 16-18 * * example 2 * * column 4, line 6-31 * * column 3, line 6-10 * ---	1,7,9, 10,17	
X	TETSUYA KONDO ET AL: "SILVER PLATING FROM SILVER METHANESULFONATE-POTASSIUM IODIDE BATH" METAL FINISHING, ELSEVIER SCIENCE PUBLISHING, NEW YORK, NY, US, vol. 89, no. 10, 1 October 1991 (1991-10-01), pages 32-36, XP000261679 ISSN: 0026-0576 * page 1 * ---	1,8-10, 17,18,22	TECHNICAL FIELDS SEARCHED (Int.Cl.7)
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The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	7 August 2001	Zech, N

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
O : non-written disclosure
P : intermediate document

T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
D : document cited in the application
L : document cited for other reasons

& : member of the same patent family, corresponding document

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