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(54) PROTECTION OF LEAD-CONTAINING ANODES DURING CHROMIUM ELECTROPLATING

SCHUTZ VON BLEIENTHALTENDEN ANODEN WÄHREND DER ELEKTROBESCHICHTUNG MIT CHROM

PROTECTION DES ANODES CONTENANT DU PLOMB PENDANT L'ELECTRODEPOSITION DE CHROME

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- **DENNIS et al., Nickel and Chromium Plating, "Anodes" section at pp. 205-206**
- **(1973).**

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Description

This invention is in the field of protecting lead anodes from corrosion during metal-electroplating processes. More particularly, this invention provides a process and composition for electroplating chromium, using lead or lead-containing anodes under conditions which produce adherent, bright chromium deposits at high efficiencies, where cathodic low-current-density etching is substantially reduced in comparison with existing high-efficiency catalyst systems.

Several advantages of certain short-chain alkylsulfonic acids in chromium electroplating have been described for both decorative and functional systems. Our US-A- 3,745,097 discloses decorative electroplating baths containing alkylsulfonic or haloalkylsulfonic acids in combination with certain carboxylic acids to produce bright, iridescent chromium surfaces on the articles plated. In US-A- 4,588,481, we further disclose functional chromium electroplating processes which use baths containing alkylsulfonic acids having a ratio of sulfur to carbon of 1/3 or greater, but free of carboxylic acids; the processes result in hard, adherent chromium deposits produced at elevated temperatures and high efficiencies without cathodic low-current-density etching. However, the chromium-plating baths taught by US-A- 4,588,481, while yielding the high-efficiency plating described in that disclosure, also resulted in severe problems of scale buildup on, and etching and corrosion of the anode. The disclosure of U.S.-A- 4,588,481 specifies a variety of sulfonic acids, including methane-sulfonic acid (MSA), ethane-sulfonic acid (ESA), methanedisulfonic acid (MDSA) and 1,2-ethanedisulfonic acid (EDSA). Generally for economic reasons, MSA has become the agent of choice in a number of commercial embodiments for chromium plating which have appeared in the marketplace, even though severe scale buildup and anodic corrosion are encountered.

As noted hereinabove, when chromium-plating processes using MSA have been installed and utilized commercially, difficulty has arisen in functional plating using lead or conventional lead-alloy anodes; investigation into the matter of anode corrosion subsequent to the issuance of U.S.-A- 4,588,481 has revealed that MSA in the plating baths generally causes the excessive corrosion of those anodes after extended operation, relative to the corrosion observed in conventional plating processes.

"Conventional plating processes" or "conventional baths" are herein defined as those which are conducted with a plating bath consisting of chromic acid and sulfate ion as the essential ingredients, the sulfate ion generally being provided by sulfuric acid or sodium sulfate, although those are not limiting sources, the requirement being solely that a soluble sulfate be provided. It has been found that as a lead anode is used repeatedly in functional chromium electroplating with baths containing MSA, the anode disintegrates at a faster rate than in conventional baths, and it must therefore be replaced much sooner than the anode in an analogous conventional bath. In this specification, the term "lead anode" is intended to define plating-bath anodes formed of lead or lead alloys commonly containing varying percentages of tin or antimony, either alone or in combination with other metals. Such materials are well known to those skilled in the art, and as such form no part of this invention.

In US-A- 4,786,378, we disclosed introducing bismuth, arsenic or antimony ion into the bath with MSA in an attempt to reduce anode corrosion. Thereafter, in U.S.-A- 4,810,337, describing the use of sulfonic acids in electroplating processes, we disclosed another treatment of the anode-corrosion problem described here in connection with the use of MSA. In that patent, we noted that a heavy scale deposit occurs in plating processes using MSA, and applied a relatively high voltage across the electrodes prior to the plating process in order to reduce the observed scale buildup and concomitant corrosion.

Another attempted solution to the problem has been the investigation of materials which are resistant to attack by bath compositions containing MSA. For instance, in DE-A- 3 625 187 anodes made of lead containing up to about 9% by weight of antimony or about 1% by weight of palladium, with or without small amounts of tin, silver and/or selenium are reported to show "good results" when used in functional chromium electroplating processes carried out at 55°C, with a cathodic current density in the range of 30 to 32 amperes per square decimeter (as.d.) and an anodic current density of from 25 to 30 a.s.d.

I have also investigated the effect of the purity of MSA on anode corrosion, on the supposition that impurities accompanying MSA might be at least a part of the problem. As noted in connection with Table II hereinbelow, this has been found not to be the case.

The foregoing publications and experimental work indicate at least in part the magnitude of the effect of anode scale and corrosion on plating, and the variety of approaches to its solution. However, until the evaluations leading to the present invention, workers in the art of chromium plating did not recognize that alkylpolysulfonic acids used as plating catalysts could both improve plating efficiency *and* decrease anode corrosion.

MSA and ESA have been generically identified as useful additives in plating baths for functional chromium-plating processes. However, as discussed hereinabove, the relevant references have indicated the problem of severe anodic corrosion when chromium is functionally electroplated for an extended period of time with lead anodes in plating baths containing MSA, the industry standard. Significantly, those references fail to suggest or disclose any particular means for an economical solution to the problem without sacrificing cost or process efficiency, or the other advantages obtained using baths containing MSA.

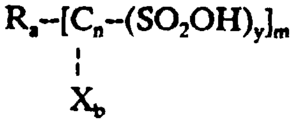
The present invention provides the use of an alkylpolysulphonic acid, halogenated alkylpolysulphonic acid, or salt thereof as a sulphonic additive, in order to keep down the extent of corrosion of a lead anode,

in a process in which a functional chromium deposit is electroplated onto a basis-metal cathode at a current density of at least 30 A/dm^2 and temperature of from 45°C to 70°C using the lead anode in a plating bath free of anode corrosion-inhibiting amounts of bismuth, arsenic or antimony ions and containing chromic acid and sulphate ion and said sulphonic additive, which is an alkylsulphonic acid, halogenated alkylsulphonic acid or salt thereof having from one to three carbon atoms and giving a cathode efficiency of at least 20%.

A composition for securing chromium electroplated from an etch-free, high-efficiency, plating bath onto a basis-metal cathode with a lead anode in the substantial absence of corrosion-causing amounts of monosulfonic acids, comprises chromic acid and sulfate ion in amounts sufficient to obtain the desired deposit of chromium, and at least one alkylpolysulfonic acid, halogenated alkylpolysulfonic acid, or salt thereof, which acid or salt contains from one to three carbon atoms. The process comprises contacting a basis-metal cathode and a lead anode with a plating bath consisting essentially of chromic acid and sulfate ion in amounts sufficient to obtain a useful deposit of chromium, and at least one alkylpolysulfonic acid, halogenated alkylpolysulfonic acid, or salt thereof, which acid or salt contains from one to three carbon atoms, and electrodepositing chromium at a cathode efficiency of at least 20%, at a current density of from about 11 to about 230 as.d., and at a plating temperature of about 45 to about 70°C for a time sufficient to obtain a bright, adherent chromium deposit.

In the course of attempting to reduce anode corrosion in chromium-plating processes, it has surprisingly been discovered that substantial replacement of MSA by certain alkylpolysulfonic acids in chromium electroplating baths for use with lead anodes dramatically reduces the amount of anode corrosion without sacrificing plating efficiency or chromium adherence. Specifically, the use of the alkylpolysulfonic acids or salts thereof enables the production of useful chromium-plated items; i.e., those whose characteristics are at least as good as those obtained in the course of high-efficiency baths of the prior art.

The benefits of the present invention may be realized by the use in the plating bath of at least one material selected from the group consisting of alkylpolysulfonic acids containing from one to about carbon atoms, halogenated alkylpolysulfonic acids, and salts of such acids and halogenated acids, which acids or salts contain from one to three carbon atoms. Halogenated acids are those containing fluorine, chlorine, bromine or iodine bound to a carbon atom; fluorine- and chlorine-substituted derivatives are preferred. Representative acids and salts include MDSA, mono- and dichloromethanedisulfonic acid, 1,1-ethanedisulfonic acid, and monochloro- or 1,2-dichloroethanedisulfonic acid and their salts, provided that there is no precipitation of chromium or sulfate moieties caused by the addition of the salt. Preferred cations are chosen from alkali metals. Particularly preferred are sodium and potassium salts. The alkylpolysulfonic acids or salts have the formula



$$R_a\text{--}[\underset{\substack{\vdots\\ X_b}}{C_n}\text{--}(SO_2OH)_y]_m$$

where **a** and **b** are independently from 0 to 2, **n** is from 1 to 3, **m** and **y** are independently from 1 to 3, provided that the total number of sulfonic groups in the molecule is not less than 2, **X** is halogen or oxygen, **R** is unsubstituted lower alkyl or substituted lower alkyl, where the substituents on **R** are halogen or oxygen, and where hydrogen occupies any positions otherwise unaccounted for, i.e., to satisfy unfilled valences of carbon or oxygen. Those skilled in the art will realize that the salts can be formed by the replacement of the labile hydrogen of the sulfonic group by a metal, such as, e.g., sodium, potassium, or the like.

As set forth in the formula above, the alkylpolysulfonic acids contain at least two sulfonic acid groups connected to carbon, and any one carbon atom can have up to three sulfonic acids groups attached thereto.

The polysulfonic acids or salts thereof are incorporated into a functional chromium-plating bath in substantially catalytic amounts. Depending upon plating conditions, that amount has been determined to be usually from about 0.25 to about 40 grams per liter (g/l), and preferably from about 1 to about 12 g/l, of the alkylpolysulfonic acid, halogenated alkylpoly-sulfonic acid or salt thereof. Particularly preferred amounts range from about 2 to about 8 g/l. In a preferred embodiment, the alkylpolysulfonic acid is MDSA.

As used in this specification, "excessive corrosion" is that amount of corrosion perceptibly in excess of the corrosion observed in conventional plating processes. "Extended" use is the amount of use of a lead anode in a conventional system which leads to detectable corrosion of that anode.

The present invention enables a functional chromium electroplating bath which is useful to produce bright, adherent chromium deposits at high efficiencies, but which substantially avoids the excessive anode corrosion which is characteristic of industrial baths containing MSA.

Useful chromic acid amounts range from about 100 to about 450 g/l, preferred ranges being from about 200 to about 300 g/l. Sulfate ion is incorporated in amounts ranging from about 1 to about 5 g/l, and preferably ranging from about 1.5 to about 3.5 g/l.

The electroplating baths may include other ingredients which do not substantially affect process efficiency, chromium adherence or brightness in a negative manner. Such additives may be incorporated to improve handling of the baths, such as, e.g., fume suppressants, brightening agents and the like.

In a preferred embodiment, current density is from about 50 to about 100 A/dm^2. Plating temperature is of from 45 to 70°C. Plating efficiencies of at least 20% are achieved, with values of from about 22 to about 28% being typical under the described most-preferred conditions.

The functional electroplating system includes a lead anode, a cathode generally comprising a work-piece for plating, and the chromium electroplating bath as described above. Typical cathode items include crankshafts, piston rings and the like. As previously noted, typical anode materials include substantially pure lead, but are more generally alloys containing lead in combination with tin, antimony, tellurium and a variety of other metals, either singly or in combination. In the nomenclature of the examples herein, a term such as "Pb-7%Sn" is a tin-lead composition being primarily lead, and having about 7% tin by weight as the alloying metal. In such compositions, there may further be minor amounts of other materials present.

The utility of this invention is shown by the following examples, which are illustrative rather than limiting:

Example 1

Accelerated anode-corrosion tests were conducted using previously weighed Pb-7%Sn anodes in several different chromium-plating baths as described here:

(a) a conventional chromium-plating bath (chromic-acid:sulfate-ion ratio of 100:1);
(b) an analogous bath containing chromic acid, sulfate ion and MSA; and
(c) a bath according to the present invention, containing MDSA as a representative disulfonic acid in place of MSA.

Extended bath usage was simulated by plating at 60°C at an anode current density of 0.5 A/dm^2 for 30 minutes, followed by 30 minutes of non-plating. This process was conducted for about eight hours and the power turned off overnight, during which time the bath was allowed to cool. These steps were repeated for a period of several weeks; the anodes were occasionally removed, dried, weighed and then re-inserted into the bath. The results are given in Table I.

TABLE I

Anode Weight Loss (g)		
Electroplating Bath	600 amp-hrs	1605 amp-hours
(a) Conventional (250 g/l chromic acid; 2.5 g/l sulfate ion)	13.32	37.33
(b) MSA (bath [a] with 3.0 g/l MSA)	16.29	41.77
(c) MDSA (bath [a] with 3.2 g/l MDSA/Na salt)	13.41	37.31

It is seen that in bath (c), containing MDSA as set forth herein for use in the process of this invention, anode corrosion remains substantially at the level of a conventional chromium-plating bath (a), whereas bath (b), with MSA as the plating-improvement medium, leads to corrosion at a substantially higher rate. In bath (b), there was evidence of serious interfacial attack on the anode, while in the conventional bath (a) and inventive bath (c), the appearance of the anode was substantially unaffected by the plating process. The quality of the deposit obtained with the invention was at least as good as, and possibly somewhat harder than, the plating achieved with either the conventional commercial plating bath or that containing MSA.

Example 2

In a second type of accelerated test, a measured direct current was applied to the Pb-7% Sn anode in bath solutions deliberately kept low in chromic acid and high in MSA or MDSA. The percentage of current which formed soluble products (i.e., the percentage of current leading to corrosion) was determined by measuring actual anode weight loss and dividing that value by the weight loss predicted by Faraday's Law; this calculation assumed that all weight loss resulted from the corrosion reaction Pb → Pb(II). The results are presented in Table II.

TABLE II

	Concentration, Moles/Liter	
	0.13	0.25
Material	Current, Percent	
Chromic Acid, 100 g/*l* (control)	0.61	0.61
70% assay MSA	1.64	3.40
99.9% assay MSA, sample 1	1.72	5.79
ESA	2.29	3.81
1-Propanesulfonic acid	3.18	5.76
1-Butanesulfonic acid	6.30	5.56
Methanedisulfonic acid disodium salt	0.72	0.79
1,2-Ethanedisulfonic acid sodium acid	0.55	0.35
2-Propanesulfonic acid sodium salt	1.90	3.67
2-Chlorosulfonic acid sodium salt monohydrate	1.55	3.19
2-Ketopropane-1,3-disulfonic acid dipotassium salt	0.51	--

It will be observed from a consideration of the foregoing table that the teaching of a sulfur-to-carbon ratio of 1/3 in U.S.-A- 4,588,481 was in fact overbroad for present purposes. Both the ethane- and propanesulfonic acids, while adequate plating catalysts falling squarely within the disclosed limits of Chessin et al., also promote unacceptable levels of corrosion in chromium-plating baths.

These results also demonstrate that corrosion of the anode in the presence of MDSA is substantially the same as the conventional bath, whereas the presence of MSA caused substantially increased anode corrosion.

Utility in accordance with this invention has been found in a replenishment composition for a chromium-plating bath having chromic acid and at least one alkylpolysulfonic acid, halogenated alkylpolysulfonic acid or salt thereof in amounts from about 1 to about 40 g per kilogram (kg) of CrO_3, and preferably from about 2 to about 25 g per kg, of replenishment composition. This composition can be either a solid mixture or a solution. Those skilled in the art will realize that the chromium can be present as the oxide, the acid or a salt, and that the amount of chromium is calculated and expressed for convenience as CrO_3, irrespective of the exact nature of the chromium-containing material present.

Modifications and improvements to the preferred forms of the invention disclosed and described herein may occur to those skilled in the art who come to understand the principles and precepts hereof.

Claims

1. Use of an alkylpolysulphonic acid, halogenated alkylpolysulphonic acid, or salt thereof as a sulphonic additive, in order to keep down the extent of corrosion of a lead anode,

in a process in which a functional chromium deposit is electroplated onto a basis-metal cathode at a current density of at least 30 A/dm^2 and temperature of from 45°C to 70°C using the lead anode in a plating bath free of anode corrosion-inhibiting amounts of bismuth, arsenic or antimony ions and containing chromic acid and sulphate ion and said sulphonic additive, which is an alkylsulphonic acid, halogenated alkylsulphonic acid or salt thereof having from one to three carbon atoms and giving a cathode efficiency of at least 20%.

2. Use according to claim 1 in which the sulphonic additive is selected from

methanedisulphonic acid,
monochlorethane 1,2-disulphonic acid,
dichloroethane 1,2-disulphonic acid,
1,1-ethanedisulphonic acid,
monochloromethanedisulphonic acid,
dichloromethanedisulphonic acid, and
salts thereof.

3. Use according to claim 2 in which the sulphonic additive is methanedisulphonic acid or salt thereof.

4. Use according to any one of the preceding claims in which the salt is alkali metal salt.

5. Use according to any one of the preceding claims in which the amount of sulphonic additive is from 0.5 to 20 g/l.

6. Use according to claim 5 in which the amount of sulphonic additive is from 1 to 12 g/l.

7. Use according to any one of the preceding claims in which the temperature is from 50°C to 60°C.

8. Use according to any one of the preceding claims in which the current density is from 30 to 100 A/dm^2.

9. Use according to claim 8 in which the current density is from 45 to 90 A/dm^2.

10. Use according to any one of the preceding claims in which the amount of chromic acid in the plating bath is from 100 to 450 g/l.

11. Use according to any one of the preceding claims in which the amount of sulphate in the plating bath is from 1 to 5 g/l.

Patentansprüche

1. Verwendung einer Alkylpolysulfonsäure, einer halogenierten Alkylpolysulfonsäure oder eines Salzes davon als Sulfonadditiv, um das Ausmaß der Korrosion einer Bleianode niedrig zu halten, bei einem Verfahren, bei dem eine funktionelle Chromabscheidung auf eine Grundmetallkathode bei einer Stromdichte von mindestens 30 A/dm^2 und einer Temperatur von 45°C bis 70°C unter Verwendung einer Bleianode in einem Plattierungsbad, das frei ist von Anodenkorrosions-inhibierenden Mengen an Wismut-, Arsen- oder Antimonionen und Chromsäure und Sulfationen und das Sulfonadditiv enthält, welches eine Alkylsulfonsäure, eine halogenierte Alkylsulfonsäure oder ein Salz davon mit 1 bis 3 Kohlenstoffatomen ist, elektroplattiert wird, und wobei eine Kathodenausbeute von mindestens 20% erhalten wird.

2. Verwendung nach Anspruch 1, dadurch **gekennzeichnet**, daß das Sulfonadditiv ausgewählt wird aus

Methandisulfonsäure,
Monochlorethan-1,2-disulfonsäure,
Dichlorethan-1,2-disulfonsäure,
1,1-Ethandisulfonsäure,
Monochlormethandisulfonsäure,
Dichlormethandisulfonsäure und
den Salzen davon.

3. Verwendung nach Anspruch 2, dadurch **gekennzeichnet**, daß das Sulfonadditiv Methandisulfonsäure oder ein Salz davon ist.

4. Verwendung nach einem der vorhergehenden Ansprüche, dadurch **gekennzeichnet**, daß das Salz ein Alkalimetallsalz ist.

5. Verwendung nach einem der vorhergehenden Ansprüche, dadurch **gekennzeichnet**, daß die Menge an Sulfonsäureadditiv von 0,5 bis 20 g/l beträgt.

6. Verwendung nach Anspruch 5, dadurch **gekennzeichnet**, daß die Menge an Sulfonsäureadditiv von 1 bis 12 g/l beträgt.

7. Verwendung nach einem der vorhergehenden Ansprüche, dadurch **gekennzeichnet**, daß die Temperatur von 50°C bis 60°C beträgt.

8. Verwendung nach einem der vorhergehenden Ansprüche, dadurch **gekennzeichnet**, daß die Stromdichte von 30 bis 100 A/dm^2 beträgt.

9. Verwendung nach Anspruch 8, dadurch **gekennzeichnet**, daß die Stromdichte 45 bis 90 A/dm^2 beträgt.

10. Verwendung nach einem der vorhergehenden Ansprüche, dadurch **gekennzeichnet**, daß die Menge an Chromsäure in dem Plattierungsbad von 100 bis 450 g/l beträgt.

11. Verwendung nach einem der vorhergehenden Ansprüche, dadurch **gekennzeichnet**, daß die Menge an Sulfat in dem Plattierungsbad von 1 bis 5 g/l beträgt.

Revendications

1. Utilisation d'un acide alkylpolysulfonique, d'un acide alkylpolysulfonique halogéné ou d'un de ses sels comme additif sulfonique, afin de maintenir à une valeur basse le degré de corrosion d'une anode contenant du plomb,

dans un procédé dans lequel un dépôt de chrome fonctionnel est formé par électrodéposition sur une cathode métallique de base à une densité de courant d'au moins 30 A/dm^2 et à une température de 45°C à 70°C en utilisant l'anode contenant du plomb dans un bain de placage dépourvu de quantités, ayant un effet d'inhibition de corrosion d'anode, d'ions bismuth, arsenic et antimoine et contenant de l'acide chromique, des ions sulfate et ledit additif sulfonique, qui est un acide alkylsulfonique, un acide alkylsulfonique halogéné ou un de ses sels ayant 1 à 3 atomes de carbone et engendrant un rendement cathodique d'au moins 20 %.

2. Utilisation suivant la revendication 1, dans laquelle l'additif sulfonique est choisi entre

l'acide méthanedisulfonique,
l'acide monochloréthane-1,2-disulfonique,
l'acide dichloréthane-1,2-disulfonique,
l'acide 1,1-ethanedisulfonique,
l'acide monochlorométhanedisulfonique,
l'acide dichlorométhanedisulfonique, et
leurs sels.

3. Utilisation suivant la revendication 2, dans laquelle l'additif sulfonique consiste en l'acide méthane-disulfonique ou un de ses sels.

4. Utilisation suivant l'une quelconque des revendications précédentes, dans laquelle le sel est un sel de métal alcalin.

5. Utilisation suivant l'une quelconque des revendications précédentes, dans laquelle la quantité d'additif sulfonique va de 0,5 à 20 g/l.

6. Utilisation suivant la revendication 5, dans laquelle la quantité d'additif sulfonique va de 1 à 12 g/l.

7. Utilisation suivant l'une quelconque des revendications précédentes, dans laquelle la température est comprise dans l'intervalle de 50°C à 60°C.

8. Utilisation suivant l'une quelconque des revendications précédentes, dans laquelle la densité de courant est comprise dans l'intervalle de 30 à 100 A/dm^2.

9. Utilisation suivant la revendication 8, dans laquelle la densité de courant est comprise dans l'intervalle de 45 à 90 A/dm^2.

10. Utilisation suivant l'une quelconque des revendications précédentes, dans laquelle la quantité d'acide chromique dans le bain de placage est comprise dans l'intervalle de 100 à 450 g/l.

11. Utilisation suivant l'une quelconque des revendications précédentes, dans laquelle la quantité de sulfate dans le bain de placage est comprise dans l'intervalle de 1 à 5 g/l.