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(21) International Application Number: PCT/US00/07362 (22) International Filing Date: 17 March 2000 (17.03.00) (30) Priority Data: 09/272,800 19 March 1999 (19.03.99) US 09/272,551 19 March 1999 (19.03.99) US 09/273,119 19 March 1999 (19.03.99) US 09/272,550 19 March 1999 (19.03.99) US (71) Applicants: TECHNIC, INCORPORATED [US/US]; 1 Spectacle Street, Cranston, RI 02910 (US). SPECIALTY CHEMICAL SYSTEMS, INC. [US/US]; 40 First Avenue, Royersford, PA 19468 (US). (72) Inventors: GILLMAN, Hyman, D.; 400 First Avenue, Royersford, PA 19468 (US). FERNANDES, Brenda; 1 Spectacle Street, Cranston, RI 02910 (US). WIKIEL, Kazimierz; 1 Spectacle Street, Cranston, RI 02910 (US). (74) Agents: LINEK, Ernest, V. et al.; Banner & Witcoff, Ltd., 28th floor, 28 State Street, Boston, MA 02109 (US).		(81) Designated States: AU, CA, JP, KR, MX, SG, European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published <i>With international search report.</i>
(54) Title: ELECTROPLATING BATHS (57) Abstract The use of alkali metal, alkaline earth metal, ammonium and substituted ammonium salts of alkyl and alkanol sulfonic acids as additives in various types of electroplating baths (e.g., sulfate, sulfonic acid, fluoroborate, and halide baths) has a number of unexpected benefits including wider useful current density range, improved appearance and in the case of tin improved oxidative stability.		

ELECTROPLATING BATHS

BACKGROUND OF THE INVENTION

[0001] Electroplating solutions are usually aqueous. Every plating solution contains ingredients to perform at least the first, and usually several, of the following functions: (1) provide a source of ions of the metal(s) to be deposited; (2) form complexes with ions of the depositing metal; (3) provide conductivity; (4) stabilize the solution against hydrolysis or other forms of decomposition; (5) buffer the pH of the solution; (6) regulate the physical form of the deposit; (7) aid in anode corrosion; and (8) modify other properties peculiar to the solution involved.

[0002] The present invention improves the plating performance of the solution, particularly by increasing the useful current density over previously accepted norms. The current density is the average current in amperes divided by the area through which that current passes; the area is usually nominal area, since the true area for any but extremely smooth electrodes is seldom known. Units used in this regard are amperes per square meter (A/m^2).

[0003] It is also in the best interest of efficiency to run these plating baths at as high a current density as possible. The higher the current density the faster the coating plates on the surface. The current is carried by the ions in these baths and each type of ion has its own specific conductance. In plating bath, however, ionic conductance is only one variable that must be considered in

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choosing an electrolyte. The final criterion is the quality of the coating at the desired current density.

SULFATE BATHS

[0004] A variety of metals and metal alloys are commercially plated from solutions with sulfate as the primary anion. See for example U.S. Patent Nos. 4,347,107; 4,331,518 and 3,616,306. Certain sulfate electroplating baths have limitations that can sometimes be alleviated with the addition of additives including other anions. For example the steel industry has been tin plating steel for many years from sulfuric acid/tin sulfate baths where phenol sulfonic acid is used as a special electrolyte additive which improves both the oxidative stability of the tin as well as increasing its current density range. This is known as the ferrostan process but because of environmental problems with phenol derivatives the steel industry is looking to replace this bath with one which is less harmful to the environment.

[0005] Similarly nickel sulfate is used for nickel plating but nickel chloride must also be present to provide enough conductivity and improve anode dissolution. This bath is known as the Watts bath but although economical, suffers from a number of disadvantages including a nickel plate that is highly stressed.

[0006] It is therefore worthwhile to identify other additives that can improve the performance of metal sulfate electroplating baths. There are many examples in the prior art where surfactants and other organic additives are used to provide a more desirable finish. In the case of tin the prior art also describes additives which can improve the oxidative stability of the tin and therefore provide a bath with less sludge formation. It is less common to find examples of additives which improve the plating range especially at the high current density end.

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Increasing the current density is a very desirable feature but it has been difficult to identify additives which can do this without creating other problems in the bath.

[0007] Many plating baths are also very sensitive to the presence of impurities and often as impurities build up in the bath they affect the quality of the deposit. Therefore either these impurities must be removed or the baths must be replaced. For example in tin plating steel, iron builds up in the bath and eventually affects the quality of the deposit and must be removed. It is very desirable to find additives that will make the bath less sensitive to these impurities.

SULFONIC ACID BATHS

[0008] In the last decade the commercial use of sulfonic acid metal plating baths has increased considerably because of a number of performance advantages. See for example U.S. Patent Nos. 5,750,017; 4,849,059; 4,764,262 and 4,207,150. This growth has slowed dramatically in the last few years because of large increases in the cost of the alkyl sulfonic acid. The preferred sulfonic acid used has been methane sulfonic acid (MSA) although the prior art includes examples of other alkyl and alkanol sulfonic acids. These other alkyl or alkanol sulfonic acids are more expensive than methane sulfonic acid and are therefore not competitive with methane sulfonic acid.

[0009] Several manufacturers produce salts of 2-hydroxy ethyl sulfonic acid (isethionic acid) commercially on a large scale but it is not commonly available in the free acid form. These salts are considerably less expensive than methane sulfonic acid but in the present plating technology only the acid form of the alkyl or alkanol sulfonic acid is used in the bath.

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[0010] The performance advantages of alkyl sulfonic acid baths include low corrosivity, high solubility of salts, good conductivity, good oxidative stability of tin salts and complete biodegradability. The predominant metals plated in these sulfonic acid baths are tin, lead and copper as well as alloys of these metals with each other.

FLUOROBORATE BATHS

[0011] Fluoroborate plating baths are widely used for coating a variety of metals on all types of metal substitutes including both copper and iron. See for example, U.S. Patent Nos. 5,431,805; 4,029,556 and 3,770,599. These baths are preferred where plating speed is important and the fluoroborate salts are very soluble. A variety of additives have been developed to improve the performance of these baths. These additives either improve the quality of the deposit, the efficiency of the bath or they reduce environmental effects. See for example, U.S. Patent No. 4,923,576.

HALIDE BATHS

[0012] Plating baths with the main electrolyte being a halide ion (Br^- , Cl^- , F^- , I^-) have been used for many decades. See for example, U.S. Patent Nos. 4,013,523; 4,053,374; 4,270,990; 4,560,446 and 4,612,091. The main halide ions in these baths have been chloride and fluoride. The metals plated from these baths typically include tin, nickel, copper, zinc, cadmium and alloys of these metals. As with all other types of baths it has been found that improvements on the performance of the bath can be made by incorporating additives into the bath. For example, U.S. Patent Nos. 5,628,893 and 5,538,617 describe additives which can be used in a halogen tin plating bath for the purpose of reducing sludge formation by stabilizing the tin against oxidation.

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[0013] There are many other properties of a bath that can be improved by additives. All of these properties are basically concerned with either the efficiency of the bath itself, the quality of the deposit or the reduction of environmental effects. For example the additives for the tin bath described in U.S. Patent Nos. 5,628,893 and 5,538,617 improve the efficiency of the bath and by decreasing the amount of waste also reduce the environmental effects.

SUMMARY OF THE INVENTION

[0014] One embodiment of the present invention relates to the use of alkali metal, alkaline earth metal, ammonium and substituted ammonium salts of alkyl and alkanol sulfonic acid which have been found to improve the performance of sulfate electroplating baths. When used in these electroplating baths these salt additives were found to generally increase the plating range so that these baths can be used at much higher current densities. Thus these baths can be run at greater speeds than those without these additives. Further improvements are seen in the quality of the deposits. In the case of stannous sulfate plating solutions, some improvements in the oxidative stability of the tin was also observed.

[0015] Thus, one preferred embodiment of the present invention is directed to a method of improving the plating performance of an aqueous sulfate based electroplating bath comprising the step of adding an effective performance enhancing amount of a salt of an alkyl and/or alkanol sulfonic acid to said bath.

[0016] The salts used to improve the bath plating performance characteristics are particularly selected from the group consisting of alkali metal, alkaline earth metal, ammonium and substituted ammonium salts. Especially preferred are salts of 2-hydroxy ethyl sulfonic acid, especially the sodium salt (sodium isethionate).

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[0017] The baths that can be improved by this embodiment include tin and tin alloys, nickel and nickel alloys, copper and copper alloys, chromium and chromium alloys, cadmium and cadmium alloys, iron and iron alloys, rhodium and rhodium alloys, ruthenium and ruthenium alloys, and especially the iron/zinc and tin/zinc alloy plating baths.

[0018] Preferably, tin and tin alloy baths are improved by this embodiment of the invention. Examples include tin-antimony, tin-cadmium, tin-copper, tin-lead, tin-nickel, tin-niobium, tin-titanium, tin-zirconium, and tin-antimony-copper alloy baths. Alloy compositions comprising these metals are well known to those having ordinary skill in this art, and are the subjects of numerous patents.

[0019] Another preferred embodiment of the present invention relates to the use of salts of alkyl and alkanol sulfonic acid which were found to improve the performance of sulfonic acid, especially alkyl sulfonic acid electroplating baths. Advantageously the salts are selected from the group consisting of alkali metal, alkaline earth metal, ammonium and substituted ammonium salts of 2-hydroxyethyl sulfonic acid (isethionic acid).

[0020] When used in electroplating baths such as MSA, these salt additives were found to generally increase the plating range so that the baths can be used at much higher current densities. Thus these baths can achieve greater speeds than baths without these additives can. Further improvements are seen in the quality of the deposits. In the case of stannous alkyl sulfonate plating solutions some improvement in the oxidative stability of the tin was also observed.

[0021] As an added benefit, these salts are not harmful to the environment, they are completely biodegradable and the products of the biodegradation are common ions and molecules found in the environment. In

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addition they have a number of other advantages including high solderability, low corrosivity to equipment, good stability at high temperatures, and compatibility with many other metal salts.

[0022] Generally these baths will also contain the corresponding metal salt or metal salts if an alloy plate is required, and various additives to control the quality and appearance of the plated surface and the stability of the bath solution. Typical additives include a surfactant such as an ethoxylated fatty alcohol, a brightening agent if required and an antioxidant such as hydroquinone or catechol, if tin is one of the metals being plated.

[0023] The tin in these baths is in the stannous or reduced form. If oxidation occurs the tin will be converted to the stannic or oxidized form which then commonly precipitates to form sludge. This process adds to the inefficiency of these baths and also creates a requirement for constant filtering. Prior art patents, for example U.S. Patent Nos. 4,717,460, 5,538,617 and 5,562,814, describe products that can decrease the amount of tin being oxidized.

[0024] Another advantage of using the salts of alkyl or alkanol sulfonates is that they are much less expensive than their corresponding acid. Currently the only bulk commercial alkyl/alkanol sulfonic acid suitable for electroplating is methane sulfonic acid and the only bulk commercial alkali/alkaline earth/ammonium alkyl/alkanol sulfonate salt suitable for electroplating is sodium isethionate. When comparing the price of these two large commercial products the sodium isethionate is less than half the price of the methane sulfonic acid either on a mole basis or on a weight basis.

[0025] Another embodiment of the present invention relates to the use of alkali metal, alkaline earth metal, ammonium and substituted ammonium salts of alkyl and alkanol sulfonic acid which were found to improve the performance of

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fluoroborate electroplating baths. When used in these electroplating baths these salt additives were found to generally increase the plating range so that these baths can be used at much higher current densities. thus these baths can be run at greater speeds than those without these additives. Further improvements are seen in the quality of the deposits.

[0026] Thus, this embodiment of the present invention is directed to a method of improving the plating performance of a fluoroborate ion based electroplating bath comprising the step of adding an effective performance enhancing amount of a salt of an alkyl and/or alkanol sulfonic acid to said bath.

[0027] The salts used to improve the bath plating performance characteristics are particularly selected from the group consisting of alkali metal, alkaline earth metal, ammonium and substituted ammonium salts. Especially preferred are salts of 2-hydroxy ethyl sulfonic acid, especially the sodium salt (sodium isethionate).

[0028] The baths that can be improved by this embodiment include tin and tin alloy plating baths; nickel and nickel alloy plating baths; copper and copper alloy plating baths; zinc or zinc alloy plating baths; as well as cadmium and cadmium alloy plating baths.

[0029] Yet another embodiment of the present invention relates to the use of alkali metal, alkaline earth metal, ammonium and substituted ammonium salts of alkyl and alkanol sulfonic acid which have been found to improve the performance of halide electroplating baths. When used in these electroplating baths these salt additives were found to generally increase the plating range so that these baths can be used at much higher current densities than previously. Thus these baths can be run at greater speeds than those without these additives. Further improvements are seen in the quality of the deposits.

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[0030] Thus, this embodiment of the present invention is directed to a method of improving the plating performance of an aqueous halide ion based electroplating bath comprising the step of adding an effective performance enhancing amount of a salt of an alkyl and/or alkanol sulfonic acid to said bath. In preferred embodiments, the halide ion of the bath is usually either chloride or fluoride.

[0031] The salts used to improve the bath plating performance characteristics are particularly selected from the group consisting of alkali metal, alkaline earth metal, ammonium and substituted ammonium salts. Especially preferred are salts of 2-hydroxy ethyl sulfonic acid, especially the sodium salt (sodium isethionate).

[0032] The baths that can be improved by this embodiment include tin and tin alloy plating baths; nickel and nickel alloy plating baths; copper and copper alloy plating baths; zinc or zinc alloy plating baths; as well as cadmium and cadmium alloy plating baths.

DETAILED DESCRIPTION

[0033] The use of alkali metal, alkaline earth metal, ammonium and substituted ammonium salts of alkyl and alkanol sulfonic acids as additives in pure metal and metal alloy sulfate electroplating baths has a number of unexpected benefits including wider useful current density range, improved appearance and in the case of tin improved oxidative stability. These baths can be run at greater speeds than those without these additives. Further improvements are seen in the quality of the deposits and greater tolerance to impurities such as iron. In the case of stannous sulfate plating solutions some improvements in the oxidative stability of the tin was also observed.

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[0034] Unlike phenol sulfonic acid these salts are not harmful to the environment. They are completely biodegradable and the products of the biodegradation are common ions and molecules found in the environment. In addition they have a number of other advantages including high solubility, low corrosivity to equipment, good stability at high temperatures, and compatibility with many other metal salts.

[0035] These baths also contain the corresponding metal salt or metal salts if any alloy plate is required, and various additives to control the quality and appearance of the plated surface and the stability of the bath solution. Typical additives include a surfactant such as an ethoxylated fatty alcohol, a brightening agent if required and an antioxidant such as hydroquinone or catechol, if tin is one of the metals being plated.

[0036] The tin in these baths is in the stannous or reduced form. If oxidation occurs the tin will be converted to the stannic or oxidized form which then commonly precipitates to form a sludge. The process adds to the inefficiency of these baths and also creates a requirement for constant filtering. Several patents, for example U.S. Patent Nos. 4,717,460, 5,538,617 and 5,562,814, describe additives and/or processes that can decrease the amount of tin being oxidized.

[0037] The present invention will be further illustrated with reference to the following examples which will aid in the understanding of the present invention, but which is not to be construed as a limitation thereof. All percentages reported herein, unless otherwise specified, are percent by weight. All temperatures are expressed in degrees Celsius.

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Sulfate Baths**Example 1**

[0038] Laboratory plating baths were evaluated on the Hydrodynamically controlled Hull Cell with a 1 minute plate time at up to 30 Amps. Plating strips were made of steel and were pretreated by soaking for 15 seconds in an alkaline bath, rinsing then immersing for 15 seconds in 10% sulfuric acid and rinsing again. The following bath was evaluated to which various levels of sodium isethionate were added.

Bath Composition:

5% Sulfuric Acid
20.0 g/l Sn (as stannous sulfate)
3 g/l JWL 5000 surfactant
0.1 g/l salicylic acid
5 ppm 2.9 - Dimethyl - phenanthroline

Run #	Additive and Level	Results of Plating Tests
1	No additive	Dark burn on high current density edge at 5 Amps. Burn is 12 mm wide at high current density edge at 10 Amps.
2	10 g/l Sodium isethionate (calculated as isethionic acid)	Even light gray satin deposit at 10 Amps - no burn.
3	20 g/l Sodium isethionate (calculated as isethionic acid)	Even light gray satin deposit at 30 Amps - no burn.
4	1 g/l Sodium Sulfate	Burn is 12 mm wide at high current density edge at 10 Amps.

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Run #	Additive and Level	Results of Plating Tests
5	30 g/l Sodium Sulfate	Burn is 4 mm wide at high current density edge at 10 Amps.

[0039] These results show that by adding sodium isethionate to this sulfate bath the current density range is increased significantly. A 15 Amp panel is indicative of current densities at 600 Amp/ft² and a 30 Amp range is equivalent to 1200 Amp/ft². They also show that sodium ions can have a positive effect on increasing the current density range but the sodium alkanol sulfonate has a much greater effect.

Example 2

[0040] The same bath and procedure as in Example 1 was utilized but in this case the additive was sodium methyl sulfonate and current used was up to 10 Amps.

Run #	Additive and Level	Results of Plating Tests
1	No additive	Dark burn on high current density edge at 5 Amps.
2	10 g/l Sodium Methane Sulfonate (Calculated as Methane Sulfonic Acid)	At 10 Amps, even light gray, slightly reflective, satin deposit No burn.
3	20 g/l Sodium Methane Sulfonate (Calculated as Methane Sulfonic Acid)	At 10 Amps, light gray satin deposit to the high current density end which was reflective. No burn.

[0041] These results show that by adding sodium methane sulfonate to this sulfate bath the current density range is increased significantly.

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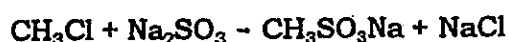
Example 3

[0042] The following experiments illustrate the inhibiting effect of the hydroxyl alkyl sulfonic acid salt in stannous sulfate/sulfuric acid solutions. The effect of iron to stabilize these stannous ion against oxidation is also illustrated when comparing Run # 3 with others. Oxygen was bubbled through 150 ml of the following solutions for 64 hours at 120°F.

RUN #	SnSO ₄ Sn ⁺² g/liter	FeSO ₄ Fe ⁺² g/liter	H ₂ SO ₄ g/liter	NaO ₃ SCH ₂ CH ₂ OH g/l	Decrease in Sn ²⁺ Conc g/l
1	23	10	10	0	10.3
2	23	10	10	30	8.6
3	23	0	60	30	23
4	23	10	60	30	4.0
5	23	10	80	0	3.2
6	23	10	80	30	0.2

Sulfonic Acid Baths

[0043] There has been little previous use of alkali/alkaline earth/ammonium alkyl/alkanol sulfonate salts in electroplating, and when used, the salts were first converted to acids. The present invention thus is directed to the direct use of these salts in electroplating. The use of such salts will enable the viability of inexpensive production technology such as the Steckler process to produce these salts. For example:



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In this reaction, the sodium chloride can be crystallized out and the resulting sodium methane sulfonate can then be used in an electroplating bath.

**Lowering Levels of Free Acid and
Making Additions of Sodium Isethionate:**

[0044] Plating tests have proven that additions of sodium isethionate to a known MSA Tin/Lead system allow the decrease of the amount of methane sulfonic acid required in the plating bath. The decrease in MSA, with the addition of sodium isethionate allows for optimum bath performance with a decrease in cost and an overall lightening of the tin or tin/lead deposit. Plating tests were performed with a decrease of the acid to 1/3 typical level and no negative effects were noted. Some plating tests showed a significant improvement of the overall deposit with additions of sodium isethionate. A decrease in the burn and band(s) opened up the upper CD range. A commercially available plating system (Technic MSA 90/10, Technic, Inc.) had an increase in CD range from 120 ASF to greater than 240 ASF.

[0045] It has been found that the overall benefits of the addition of sodium isethionate vary from plating system to plating system, but decreasing the total free acid (MSA) up to 2/3 (66%) by the addition of sodium isethionate was acceptable in the examples that follow.

[0046] A typical commercial MSA plating system contains approximately 15% v/v MSA. The results that follow reflect plating tests performed with two plating baths made with two different levels of MSA. The first bath, Examples 4 and 5 were made with 15% v/v MSA and Examples 6 and 7 were made with 5% v/v MSA.

[0047] Plating performance tests were conducted using the HCHC (Hydrodynamically Controlled Hull Cell). Due to the increase in agitation versus a

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typical Hull Cell setup, the overall benefits at the upper current densities (CD's) can be noted with the additions of sodium isethionate. The results show the width of the burn and band in mm, if applicable. Both the burn and band, at the HCD to MCD region, influence the overall operable CD Range of the plating bath. The CD Range noted in the final column of the result tables, indicates the CD range for the optimal deposit. The addition of Sodium Isethionate to the plating baths, decreased or eliminated the burn and band, widening the optimum CD Range.

[0048] The plating tests performed at 5% v/v MSA, had no banding at the HCD region. However, the maximum amperage obtainable with 5% v/v MSA was 10 amps. The addition of 15 g/l sodium isethionate to a system containing only 5% v/v MSA allowed the application of up to 20 amps. See the result tables that follow.

Bath Solution:

15% v/v MSA
55 g/l Sn (as stannous methane sulfonate)
12 g/l Pb (as lead methane sulfonate)
2 g/l TECHNI Tin/Lead Salt #2 (Technic Inc.)
5% v/v TECHNI 800 HS MakeUp (Technic Inc.)
1% v/v TECHNI 800 HS Secondary "A" (Technic Inc.)

[0049] Plate Conditions: 10 A, 1 min, 1500 rpm, 110°F. An increase in amperage was attempted for this plating system under these plate conditions.

[0050] Example 4 shows the results of the plating bath listed above with no sodium isethionate additions.

[0051] Example 5 shows the results of the plating bath listed above, under

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the same plating conditions with a 15 g/l sodium isethionate addition.

Example 4

Amperage:	Additions:	Burn/mm:	Band at HCD/ mm:	CD Range:
10A, 1 min	NONE	3 mm	10 mm	400 - 1 ASF
15A, 1 min	NONE	15 mm	15 mm	400 - 1 ASF
20A, 1 min	NONE	60 mm	5 mm	200 - 1 ASF

Example 5

Amperage:	Additions:	Burn/mm:	Band at HCD's/ mm:	CD Range:
10A, 1 min	15 g/l Sodium Isethionate	2 mm	NONE	+400 - 1 ASF
15A, 1 min	15 g/l Sodium Isethionate	7 mm	NONE	+600 ASF - LCD edge
20A, 1 min	15 g/l Sodium Isethionate	7 mm	NONE	+800 ASF - LCD edge

Bath Solution:

5% v/v MSA

55 g/l Sn (as stannous methane sulfonate)

12 g/l Pb (as lead methane sulfonate)

2 g/l TECHNI Tin/Lead Salt #2 (Technic Inc.)

5% v/v TECHNI NF 800 HS MakeUp (Technic Inc.)

1% v/v TECHNI NF 800 HS Secondary "A" (Technic Inc.)

[0052]

Plate Conditions: 10 a, 1 min, 1500 rpm, 110°F. An increase in

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amperage was attempted for this plating system under these plate conditions.

[0053] Example 6 shows the results of the plating bath listed above, with no sodium isethionate additions.

[0054] Example 7 shows the results of the plating bath listed above, under the same plating conditions with a 15 g/l sodium isethionate addition.

[0055] Using the Hull Cell Ruler, the CD ranges of both 10 amp panels look similar. However, the initial panel without the presence of sodium isethionate, has treeing along the panel edge. There is no treeing visible on the panel with the sodium isethionate addition. In application, the presence of the treeing would actually narrow the operating range of the plating bath.

Example 6

Amperage:	Additions:	Burn/mm:	Band at HCD/ mm:	CD Range:
10A, 1 min	NONE	3 mm, with treeing along the HCD edge	NONE	+400 - 60 ASF
15A, 1 min	NONE	Unable to achieve 15 amps, 10 amps max.		
20A, 1 min	NONE	Unable to achieve 20 amps, 10 amps max.		

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Example 7

Amperage:	Additions:	Burn/mm:	Band at HCD/ mm:	CD Range:
10A, 1 min	15 g/l sodium isethionate	2 mm, no treeing	NONE	+400 - 60 ASF
15A, 1 min	15 g/l sodium isethionate	2 mm, no treeing	NONE	+600 - LCD
20A, 1 min	15 g/l sodium isethionate	10 mm, no treeing	NONE	+800 - LCD

[0056] Different sodium sources were added to a pure Tin MSA and banding was significantly decreased or eliminated completely. The change in the banding widened the current density range significantly, opening the operating window of the system.

Bath Composition:

10% v/v MSA

20 g/l Sn (as stannous methane sulfonate)

0.1 g/l salicylic acid

3 g/l Jeffox WL 5000 (Huntsman)

5 ppm 2,9 - Dimethyl - 1,10-phenanthroline

[0057] Plating Conditions: using the HCHC, 10A, 1 min, 1500 rpm, 100°F.

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Example 8

Additions:	Burn/mm:	Band in LCD's /mm:	CD Range:
NONE	5 mm	25 mm	400 - 200 ASF
1 g/l sodium methane sulfonate	5 mm	25 mm	400 - 200 ASF
10 g/l sodium methane sulfonate	5 mm	20 mm	400 - 200 ASF
20 g/l sodium methane sulfonate	5 mm	NONE	400 - 60 ASF

[0058] The same MSA Tin plating bath was prepared as above, and additions of sodium isethionate were made. Plating Conditions; using the HCHC, 10A, 1min, 1500 rpm, 100°F.

Example 9

Additions:	Burn/mm:	Band at the LCD's/mm:	CD Range:
NONE	5 mm	25 mm	400 - 200 ASF
5 g/l sodium isethionate	2.5 mm	20 mm	400 - 200 ASF
20 g/l sodium isethionate	2.5 mm	NONE	400 - 20 ASF

[0059] Looking at the CD ranges, both sodium methane sulfonate and sodium isethionate additions look to have similar benefits. The additions of sodium isethionate are preferred however, since the sodium isethionate minimizes the burn as compared to the sodium methane sulfonate. In practice

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there would be a wider operating window. In addition, the sodium isethionate lightens the overall deposit evenly across the entire CD range.

Example 10

[0060] This example illustrates the ability of the alkanol sulfonate salt to inhibit the oxidation of the stannous ion in methane sulfonate based tin plating bath solutions.

[0061] Air was bubbled through 100 ml of the following solutions at a rate of 100 ml/minute, at room temperature for 288 hours.

RUN#	$\text{Sn}(\text{O}_3\text{SCH}_3)_2$ Sn ⁺² g/liter	FeSO_4 Fe ⁺² g/liter	$\text{NaO}_3\text{S}(\text{CH}_2)_2\text{OH}$ g/liter	HO_3SCH_3 g/liter	Decrease in Sn ⁺² Concentration g/liter
1	23	10	0	0	5.7
2	23	10	30	0	4.2
3	23	10	0	15	4.5
4	23	10	30	15	3.6

[0062] The use of alkali metal, alkaline earth metal, ammonium and substituted ammonium salts of alkyl and alkanol sulfonic acids as additives in pure metal and metal alloy fluoroborate electroplating baths has a number of

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unexpected benefits including wider useful current density range and improved appearance. The metals and metal alloys include but are not limited to tin, lead, copper, cadmium, indium, iron, tin/lead and tin/lead copper.

Fluoroborate Baths**Example 11**

[0063] Standard Hull Cell tests using a 267 mm Hull Cell were run at 2 Amps for 5 minutes using cathode rod agitation. Copper panels were plated after acid cleaning and rinsing.

Bath Composition:

35% v/v HBF_4 (as a 50% solution)
15 g/liter Tin (as Tin Fluoroborate)
12 g/liter Lead (as Lead Fluoroborate)
2 g/liter Hydroquinone
26 g/liter Boric Acid
2% v/v HBF_4 Makeup

Run #	Additive	Results
1	None	Gray matte deposit with a 5 mm wide burn at the high current density edge.
2	20 g/l Sodium Methane Sulfonate	Lightening of deposit and burn narrows to 4 mm wide burn.
3	20 g/l Sodium Isethionate	Lightening of deposit and burn narrows to 3.5 mm wide.

[0064] This Example shows that upon addition of sodium methane sulfonate or sodium isethionate, this bath can be used at a higher current

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density and the appearance of the coating expands.

Halide Baths

[0065] The use of alkali metal, alkaline earth metal, ammonium and substituted ammonium salts of alkyl and alkanol sulfonic acids as additives in pure metal and metal alloy halide electroplating baths has a number of unexpected benefits including wider useful current density range and improved appearance. The metals and metal alloys include, but are not limited to tin, lead, copper, nickel, zinc, cadmium, tin/zinc, zinc/nickel and tin/nickel.

Example 12

[0066] A halogen based plating bath was evaluated on the HCHC or Hydrodynamically Controlled Hull Cell. Plating strips were made of steel and were pretreated by soaking for 15 seconds in an alkali, rinsing then immersing for 15 seconds in 10% sulfuric acid and rinsing again.

[0067] The following bath was evaluated to which various levels of sodium isethionate was added.

Bath Composition (room temp.):

19.6 g/l NaHF_2

26.5 g/l NaF

12.68 g/l NaCl

33.0 g/l SnF_2

4 g/l Miranol ASC (an Amphoteric Surfactant)

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Run #	Current/Time	Additive	Results
1	2 Amps/2 minutes	None	Dendrite growth 2 mm wide at high current density edge, remainder white matte/satin color
2	3 Amps/2 minutes	None	Heavy burn at high current density edge 6 mm wide. Same color as Run No. 1.
3	3 Amps/2 minutes	4 g/l Sodium Isethionate	Burn not as pronounced and has narrowed to about 3 mm. Nice even smooth matte finish
4	3 Amps/2 minutes	6 g/l Sodium Isethionate	Burn diminished only to high current density edge. Same nice even smooth matte finish as Run No. 3.

[0068] This Example clearly shows that adding even small amounts of sodium isethionate to a halide bath can increase the workable current density range by a factor of 50%.

THEORY SECTION

[0069] While not wishing to be bound by theory, the results of the present invention are believed to be based upon the following:

[0070] The mixture of different ionic species forms a unique combination that can produce metallic coatings with required properties. It is well known that the overall ionic conductivity of the solution depends on the character of individual ionic species and their concentrations. The specific interactions

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between different ionic species and/or solvent molecules determine the overall conductivity and may affect electrodeposition processes. However, ionic conductivity is only one variable, which must be considered in formulating plating baths.

[0071] It is also well known that the structure of the electrical double layer can affect the rates of electrodeposition. It was proven experimentally, see for example, Lasia et al., *Journal of Electroanalytical Chemistry*, 266, 68-81 (1989); Fawcett et al., *Journal of Electroanalytical Chemistry*, 279, 243-256 (1990); Lasia et al., *Journal of Electroanalytical Chemistry*, 288, 153-165 (1990) and Balch et al., *Journal of Electroanalytical Chemistry*, 427, 137-146 (1997), that the rate constant of electroreduction of certain metal ions (like Cu^+ , Cd^{2+} or Zn^{2+}) depends on the solvating ability of the solvent and the size of the cation of the electrolyte. The effect was attributed to the electrostatic interactions in the inner layer of the electrical double layer.

[0072] According to the Frumkin model, the rate constant for the reduction process:



is given by:

$$\ln k_f = \ln (k_0 \gamma_M) + \alpha_a n F \phi^d / R T - \alpha_a n F (E - E_a) / R T$$

where the symbols are:

- k_f apparent rate constant
- k_0 potential independent portion of the rate constant
- γ_M activity coefficient of the species Met^{n+} in the bulk solution

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α_a	apparent transfer coefficient for reduction
n	number of electrons involved in electroreduction
F	Faraday constant
ϕ^d	potential drop across the diffuse layer
R	gas constant
T	temperature in K
E	potential
E_s	standard potential of the electroreduction reaction

[0073] It is also known that the size of the counter ion of supporting electrolyte affects the ϕ^d potential, and as a consequence, the rate constant of overall electroreduction process (Lasia et al., Fawcett et al., and Lasia et al., *supra*).

[0074] It is clear that the addition of one or more salts as taught herein modifies the double layer of metal/solution interface. The modification is caused by the alkali metal cation and/or alkanol-sulfonic acid anion and/or combination of both of them (maybe alkyl-, also). Therefore, the added salt of an alkyl and/or alkanol sulfonic acid should be considered as a plating additive, rather than as a simple modification of the supporting electrolyte.

[0075] In the present invention, the cation and/or anion are not added only to preserve ionic conductivity of the electrolyte and/or solubility of deposited ion(s); instead they directly affect the electrodeposition process, by affecting the double layer structure and in consequence the mechanism of the electroreduction process.

[0076] The present invention has been described in detail, including the preferred embodiments thereof. However, it will be appreciated that those skilled in the art, upon consideration of the present disclosure, may make modifications

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and/or improvements on this invention and still be within the scope and spirit of this invention as set forth in the following claims.

WHAT IS CLAIMED IS:

1. A method of improving the plating performance of an aqueous electroplating bath selected from the group consisting of sulfate, sulfonic acid, fluoroborate, and halide electroplating baths, said method comprising the step of adding an effective performance enhancing amount of a salt of an alkyl and/or alkanol sulfonic acid to said bath, wherein the added salt is selected from the group consisting of alkali metal, alkaline earth metal, and ammonium or substituted ammonium salts.
2. The method of Claim 1, wherein the salt is a salt of 2-hydroxy ethyl sulfonic acid.
3. The method of Claim 2, wherein the salt is sodium isethionate.
4. The method of Claim 1, 2, or 3, wherein the electroplating bath is a sulfate electroplating bath.
5. The method of Claim 1, 2, or 3 wherein the electroplating bath is a sulfonic acid electroplating bath.
6. The method of Claim 1, 2 or 3, wherein the electroplating bath is a fluoroborate electroplating bath.
7. The method of Claim 1, 2, or 3, wherein the electroplating bath is a halide electroplating bath.
8. The method of Claims 1-7, wherein the electroplating bath is a tin or tin alloy plating bath.
9. The method of Claims 1-7, wherein the electroplating bath is a nickel or nickel alloy plating bath.

10. The method of Claims 1-7, wherein the electroplating bath is a copper or copper alloy plating bath.
11. The method of Claims 1-7, wherein the electroplating bath is a chromium or chromium alloy plating bath.
12. The method of Claims 1-7, wherein the electroplating bath is a cadmium or cadmium alloy plating bath.
13. The method of Claims 1-7, wherein the electroplating bath is an iron or iron alloy plating bath.
14. The method of Claims 1-7, wherein the electroplating bath is a rhodium or rhodium alloy plating bath.
15. The method of Claims 1-7, wherein the electroplating bath is a ruthenium or ruthenium alloy plating bath.
16. The method of Claims 1-7, wherein the electroplating bath is a iron/zinc plating bath.
17. The method of Claims 1-7, wherein the electroplating bath is a tin/zinc plating bath.
18. The method of Claims 1-7, wherein the improvement in the plating performance comprises at least an increase in the useful upper current density range of the plating bath.
19. An aqueous sulfate electroplating bath comprising:
 - (a) an electrolyte comprising a source of sulfate anions;
 - (b) one or more soluble platable metal salts, wherein the platable metal is selected from the group consisting of tin, nickel, copper, chromium, cadmium, iron, rhodium, ruthenium, zinc and mixtures thereof; and

- (c) a salt of an alkyl sulfonic acid and alkanol sulfonic acid in an amount to improve the plating performance of the aqueous sulfate electroplating bath, wherein the salt is selected from the group consisting of alkali metal, alkaline earth metal, and ammonium or substituted ammonium salts.
20. The electroplating bath of Claim 19, wherein the sulfonic acid salt is a salt of 2-hydroxy ethyl sulfonic acid.
21. The electroplating bath of Claim 20, wherein the salt is sodium isethionate.
22. A method of improving the plating performance of sulfonic acid based electroplating baths, comprising the step of replacing at least a portion of the alkyl sulfonic acid electrolyte with a salt of an alkyl sulfonic acid and alkanol sulfonic acid in an amount to improve the plating performance of the aqueous sulfate electroplating bath, wherein the salt is selected from the group consisting of alkali metal, alkaline earth metal, and ammonium or substituted ammonium salts.
23. The method of Claim 22, wherein the sulfonic acid is an alkyl sulfonic acid.
24. The method of Claim 23, wherein the alkyl sulfonic acid is methane sulfonic acid.
25. The method of Claim 22, wherein the salt is a salt of 2-hydroxy ethyl sulfonic acid.
26. The method of Claim 22, wherein the electroplating bath is a tin plating bath.
27. The method of Claim 22, wherein the electroplating bath is a lead plating bath.
28. The method of Claim 22, wherein the electroplating bath is a tin/lead plating bath.
29. A method of increasing the useful upper current density range of a tin methane sulfonate plating bath and thereby allowing tin plating at higher speeds, said method comprising the

step of adding an effective amount of sodium or potassium methane sulfonate to the bath.

30. A method of increasing the useful upper current density range of a tin/lead methane sulfonate plating bath and thereby allowing plating at higher speeds, said method comprising the step of replacing at least a portion of the methane sulfonic acid with sodium isethionate.
31. The method of Claim 30, wherein up to 50% of the methane sulfonic acid is replaced by sodium isethionate.
32. The method of Claim 30, wherein up to 75% of the methane sulfonic acid is replaced by sodium isethionate.
33. The method of Claim 30, wherein up to 90% of the methane sulfonic acid is replaced by sodium isethionate.
34. A method of inhibiting the oxidation of stannous ions in a tin plating bath containing methane sulfonic acid, comprising the step of adding an effective amount of a salt of an alkyl and/or alkanol sulfonic acid.
35. The method of claim 34, wherein the salts are selected from the group consisting of alkali metal, alkaline earth metal, and ammonium or substituted ammonium salts.
36. An aqueous sulfonic acid electroplating bath comprising:
 - (a) an alkyl or alkanol sulfonic acid;
 - (b) one or more soluble platable metal salts, wherein the platable metal is selected from the group consisting of tin, lead, copper, cadmium, indium, iron and mixtures thereof; and
 - (c) a salt of an alkyl sulfonic acid and alkanol sulfonic acid in an amount to improve the plating performance of the aqueous sulfate electroplating bath, wherein the salt is selected from the group consisting of alkali metal, alkaline earth metal, and

ammonium or substituted ammonium salts.

37. The electroplating bath of Claim 36, wherein the sulfonic acid salt is a salt of 2-hydroxy ethyl sulfonic acid.
38. The electroplating bath of Claim 37, wherein the sulfonic acid salt is sodium isethionate.
39. A method of improving the plating performance of an aqueous fluoroborate based electroplating bath comprising the step of adding an effective performance enhancing amount of a salt of an alkyl sulfonic acid and alkanol sulfonic acid to said bath, wherein the salt is selected from the group consisting of alkali metal, alkaline earth metal and ammonium or substituted ammonium salts.
40. The method of Claim 39, wherein the salt is a salt of 2-hydroxy ethyl sulfonic acid.
41. The method of Claim 40, wherein the salt is sodium isethionate.
42. The method of any of claims 39-41, wherein the electroplating bath is a tin or tin alloy plating bath.
43. The method of any of claims 39-41, wherein the electroplating bath is a lead or lead alloy plating bath.
44. The method of any of claims 39-41, wherein the electroplating bath is a copper or copper alloy plating bath.
45. The method of any of claims 39-41, wherein the electroplating bath is an indium or indium alloy plating bath.

46. The method of any of claims 39-41, wherein the electroplating bath is a iron or iron alloy plating bath.
47. The method of any of claims 39-41, wherein the electroplating bath is a cadmium or cadmium alloy plating bath.
48. The method of any of claims 39-41, wherein the electroplating bath is a tin/lead plating bath.
49. The method of any of claims 39-41, wherein the electroplating bath is a tin/lead/copper plating bath.
50. The method of Claim 39, wherein the improvement in the plating performance comprises at least an increase in the useful upper current density range of the plating bath.
51. An aqueous fluoroborate electroplating bath comprising:
- (a) a source of fluoroborate anions;
 - (b) one or more soluble platable metal salts, wherein the platable metal is selected from the group consisting of tin, lead, copper, cadmium, indium, iron and mixtures thereof; and
 - (c) a salt of an alkyl sulfonic acid and alkanol sulfonic acid in an amount to improve the plating performance of the aqueous sulfate electroplating bath, wherein the salt is selected from the group consisting of alkali metal, alkaline earth metal, and ammonium or substituted ammonium salts.
52. The electroplating bath of claim 51, wherein the sulfonic acid salt is a salt of 2-hydroxy ethyl sulfonic acid.
53. The electroplating bath of claim 52, wherein the sulfonic acid salt is sodium isethionate.

54. A method of improving the plating performance of an aqueous halide ion based electroplating bath comprising the step of adding an effective performance enhancing amount of a salt of an alkyl and/or alkanol sulfonic acid to said bath.
55. The method of claim 54, wherein the halide ion is selected from chloride and fluoride.
56. The method of claim 54, wherein the salts are selected from the group consisting of alkali metal, alkaline earth metal, and ammonium or substituted ammonium salts.
57. The method of claim 56, wherein the salt is a salt of 2-hydroxy ethyl sulfonic acid.
58. The method of Claim 57, wherein the salt is sodium isethionate.
59. The method of any of claims 55 to 58, wherein the electroplating bath is a tin or tin alloy plating bath.
60. The method of any of claims 55 to 58, wherein the electroplating bath is a nickel or nickel alloy plating bath.
61. The method of any of claims 55 to 59, wherein the electroplating bath is a copper or copper alloy plating bath.
62. The method of any of claims 55 to 59, wherein the electroplating bath is a zinc or zinc alloy plating bath.
63. The method of any of claims 55 to 59, wherein the electroplating bath is a cadmium or cadmium alloy plating bath.

64. The method of Claim 54, wherein the improvement in the plating performance comprises at least an increase in the useful upper current density range of the plating bath.
65. An aqueous metal alloy halide electroplating bath comprising:
- (a) an electrolyte comprising a source of halide ions;
 - (b) one or more soluble platable metal salts, wherein the platable metal is selected from the group consisting of tin, nickel, copper, zinc, cadmium and mixtures thereof; and
 - (d) a salt of an alkyl sulfonic acid and alkanol sulfonic acid in an amount to improve the plating performance of the aqueous sulfate electroplating bath, wherein the salt is selected from the group consisting of alkali metal, alkaline earth metal, and ammonium or substituted ammonium salts.
66. The electroplating bath of Claim 65, wherein the sulfonic acid salt is a salt of 2-hydroxy ethyl sulfonic acid.
67. The electroplating bath of Claim 66, wherein the salt is sodium isethionate.