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HETEROCYCLIC NITROGEN COMPOUND CONTAINING ANTIMONY PLATING SOLUTIONS AND PROCESS

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This invention relates to the electrodeposition of antimony, most particularly from solutions wherein the antimony is present as a soluble fluoride. Specifically, the invention relates to the use of heterocyclic amines in antimony fluoride containing plating solution for the purpose of increasing the brightness of the deposit obtained therefrom.

It is an object of the invention to provide a process and plating solution for the electrodeposition of antimony from antimony fluoride solutions containing one or more compounds which add to the luster of the deposit obtained therefrom. It is a further object to provide for new and novel antimony plating processes and solutions containing compounds which enhance the brightness of the deposits obtained therefrom. It is a further object to provide for a new and novel process of electroplating from antimony fluoride containing solutions characterized by the incorporation therein of one or more compounds which enhance the brightness of the plate obtained therefrom. It is still another object to provide for cooperating addition agents for antimony fluoride containing plating solutions, which addition agents decrease the amount of misplating and promote greater uniformity of color in the plates obtained therefrom. Other and further objects will be apparent from the following description and disclosure.

The invention is specifically directed to the use of antimony plating solutions wherein the antimony is primarily present therein as a soluble fluoride. Specific examples of plating solutions to which reference herein is had will be found in the Bloom U. S. Patent No. 2,389,131, and in my co-pending application U. S. Serial No. 303,160, filed August 7, 1952, and entitled "Electrodeposition of Antimony." The fundamental plating bath should be an aqueous acid solution of an antimony compound, such as antimony trifluoride. Such baths may also utilize one or more compounds for adjusting the pH of the solution as well as chemical means for holding the antimony in solution. The pH may be adjusted by the use of ammonium hydroxide or carbonate or, less desirable, by the use of sodium or potassium hydroxide or carbonate. An amine, such as triethanolamine, may also suitably be used for adjusting the pH. Precipitation of the antimony fluoride should be prevented so that suitably about 0.7 mol and, preferably, up to about 1.5 mols of antimony trifluoride per liter are present therein under most of the preferred operating conditions. The precipitation of the antimony fluoride may be prevented by utilizing such alpha-hydroxy carboxylic acids as tartaric, citric, gluconic, glycolic or lactic, or by the ammonium, sodium or potassium or amine salts thereof. An excess of the halogen ion is also suitable for this purpose. In the event that salts of the alpha-hydroxy carboxylic acids are employed, the salts can be utilized simultaneously as a means or partial means for adjusting the pH of the solution. For example, antimony trifluoride, ammonium glycolate and water make a fundamental bath in which the addition agents according to the invention may be used.

Although it is preferred that the antimony be present in the form of its fluoride, antimony trichloride may be substituted in part for the antimony fluoride in the bath. For example, up to about 40% by weight of the antimony content may be present as the chloride. In this event, however, it will still be recognized that the antimony is present in the bath primarily as the soluble fluoride.

When alpha-hydroxy carboxylic acids are employed for preventing the precipitation of antimony fluoride, the quantity thereof may be within the range of about ⅛ to 2 hydroxy equivalent weights of the acid per atomic weight of antimony, the preferred concentration being about one alpha-hydroxy equivalent weight of acid per atomic weight of antimony. (By alpha-hydroxy equivalent weight, it is meant the molecular weight of the alpha-hydroxy acid divided by the number of its alpha-hydroxy groups.)

As a measure for insuring against immersion deposition of the antimony upon the cathodes, it is highly desirable that sulfate ion be present in the solution. When used, the concentration of the sulfate ion should be from about 50 to 150 mol percent of the alpha hydroxy acid. Obviously the sulfate ion is not an essential ingredient in the bath but is merely highly desirable for the purpose of preventing immersion deposition of the antimony on the cathodes.

In making up the fundamental plating bath, the adjustments of the pH may be accomplished or partly so by the choice of compounds. Thus, for example, by using antimony trioxide (Sb_2O_3) and an acid ammonium fluoride (NH_4HF_2), antimony trifluoride (SbF_3) is produced in situ in the bath or in the tank used for manufacture of concentrates thereof. Additional alkaline material may or may not be needed to secure the desired pH. As a practical matter, it is very desirable to form a bath of a concentration which requires little or very little addition of ammonia to the plating tank. It is also proper to make use of antimony oxide and ammonium bifluoride instead of using antimony trifluoride as such in making baths or concentrates. Preferably, the solutions consist of antimony oxide, acid ammonium fluoride and glycolic acid in proportions to yield antimony trifluoride and ammonium glycolate at pH's from .5 to 2.0 with additional ammonium hydroxide to yield a pH 2.5 to 5.0.

According to the invention, it has been discovered that heterocyclic amines when employed with cooperating aromatic sulfonamides and derivatives thereof such as the sulfonimides, which are considered herein as encompassed in the term sulfonamides, are especially suitable for improving the luster of deposits obtained from antimony plating solutions wherein the antimony is present primarily as the soluble fluoride. Alone, the heterocyclic amines do not appear to enhance the lustrous nature of antimony deposits. However, when utilized with what may be termed as cooperating brightening agents, it appears that they materially increase the brightness of the deposit obtained. In general, the use of the heterocyclic amines with one or more cooperating agents, such as those of the aromatic sulfonamide types are productive of bright deposits, although occasionally only semi-bright finishes are obtainable. In every instance of the compounds tried, however, it has been found that the heterocyclic amines enhanced the lustrous nature of the deposit obtained from the aforementioned fluoride containing baths above and beyond the nature of the deposits usually obtained without the employment of the novel additives. In addition to the novel combinations of aromatic sulfonamides and heterocyclic amines within the scope of

the invention, it has been found that copper, coumarin and zinc additions impart further advantages in the form of still increased brightness, and/or leveling and/or deposit uniformity.

It has been found that these compounds of the aromatic sulfonamide type are especially suitable for use with the heterocyclic amines of the herein described invention. Especially beneficial results have been obtained when the aromatic sulfonamides utilized according to the herein described invention are selected from the following class of sulfonamides:

Benzene sulfonamide $C_6H_5SO_2NH_2$
Toluene sulfonamide $CH_3C_6H_5SO_2NH_2$
Di-benzene sulfonamide $C_6H_5SO_2NHSO_2C_6H_5$
Di-benzene sulfonamide ether

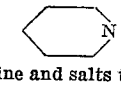
$$C_6H_5SO_2NHSO_2C_6H_4OC_6H_4SO_2NHSO_2C_6H_5$$

Bi-(di-benzene sulfonamide)

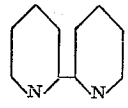
$$C_6H_5SO_2NHSO_2C_6H_4C_6H_4SO_2NHSO_2C_6H_5$$

Although the aforementioned sulfonamide derivatives of benzene are preferably employed as cooperating brightening agents according to the invention, it will be apparent that other sulfonamides of the aromatic classification may be employed with beneficial results, for example, sulfonamide derivatives of naphthalene. Aromatic sulfonates and sulfinates have been found to have a cooperating action with the heterocyclic amines. In many instances, however, results obtained therefrom have been considerably less satisfactory than the results obtained with the sulfonamides in that misplating and other common plating difficulties occur. For example, saccharin has been employed as a cooperating brightening agent with the aromatic amines but with considerably less success than that found with the benzene sulfonamide type compounds.

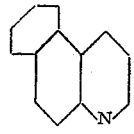
Examples of the heterocyclic amines which have been found especially beneficial in their cooperating brightening action with the benzene type sulfonamides are



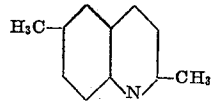
pyridine and salts thereof,



di-pyridyl and salts thereof,

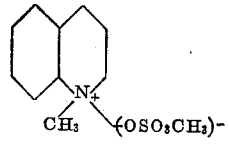


β-naphthoquinoline and salts thereof,

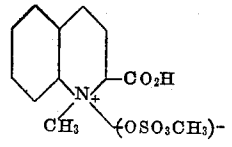


di-methyl quinoline and salts thereof,

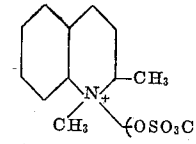
as well as such specific heterocyclic amines as



N-methyl quinolium methosulfate



N-methyl-2-carboxy quinolinium methyl sulfate



N-methyl quinaldine methosulfate

Other heterocyclic amines may be employed with cooperating brightening results and accordingly, the invention is not be be construed as limited to the specific heterocyclic amines set forth heretofore, except as provided by the claims. It will be noted that the heterocyclic amines described have at least one 6-membered ring and may be described generically as "heterocyclic nitrogen containing compounds having at least one 6-membered ring."

Preferably the cooperating aromatic sulfonamides are employed in amounts ranging from 0.25 to about 6 grams per liter. In certain circumstances, however, it may be desirable to employ the aromatic sulfonamides in amounts in excess of 6 grams per liter for the most beneficial result, although it has generally been determined that quantities thereof falling within the range heretofore given will produce the greatest brightness when utilized with the heterocyclic amines in their preferred quantities.

When employed with the aromatic sulfonamides in the preferred amounts, the heterocyclic amines have been found to produce the greatest brightness and most lustrous deposits in amounts ranging generally from about .01 to about 3.5 grams per liter thereof. In certain circumstances it may be found desirable to operate outside of this range, that is, for example, to employ greater amounts of the heterocyclic amines to obtain the most beneficial over-all results from the plating solution and, accordingly, the invention is not to be construed as limited to the specific ranges except as specifically set forth in the claims appended hereto.

The following are specific examples showing the cooperating brightening action attributed to the combination of aromatic sulfonamides and heterocyclic amines falling within the scope of the invention. In each case the aromatic sulfonamides and heterocyclic amines were added to an aqueous antimony plating solution which consisted of the following ingredients:

	Grams per liter
Sb_2O_3	180
NH_4FHF	105
Glycolic acid	133
NH_4SO_4	162

The solutions were neutralized to a pH of 4 prior to the electroplating of the panels and plating was carried out on a lead surface utilizing a current density of about 40 amperes per square foot, at temperatures of about 145° F.

Example No. 1

	Grams per liter
Toluene sulfonamide	2
Di-pyridyl	.05

The panel obtained showed a bright antimony deposit.

Example No. 2

	Grams per liter
Di-benzene sulfonamide	1
Pyridine	.5

The panel plated had a bright finish and when the pyridine concentration was raised to one gram per liter, the panel obtained was also bright.

Example No. 3

	Grams per liter
Bi-di-benzene sulfonamide	2
Di-pyridyl	.02
Pyridine	.2

The panel obtained had a bright finish. A similar result

was obtained when the pyridine concentration was .4 gram per liter and the di-pyridyl concentration was .0025 gram per liter. Similar results were again obtained when the pyridine concentraton was .8 gram per liter and the di-pyridyl concentration was .005 gram per liter.

Example No. 4

	Grams per liter
Di-benzene sulfonamide	1
N-methyl quinolinium methosulfate	.025

A bright finish was obtained on the plate and similar results were obtained when the concentration of the heterocyclic amine was increased to about .130 gram per liter.

Example No. 5

	Grams per liter
Di-benzene sulfonamide	2
β-Naphthoquinoline	.09

In this case the plate obtained was bright and the brightness was still produced when the concentration of the β-naphthoquinoline was doubled. A reduction in the amount of the β-naphthoquinoline to .05 gram per liter decreased the brightness to the point where it was comparable with usual commercial semi-bright finishes.

Example No. 6

	Grams per liter
Di-benzene sulfonamide	1
2,6-dimethyl quinoline	.05

The plate obtained in this case was bright and similar results were obtained when the concentration of the di-benzene sulfonamide was but .5 gram per liter. A good bright deposit was also obtained when the di-benzene sulfonamide concentration ranged from .5 gram per liter to 1 gram per liter and the 2,6-dimethyl quinoline concentration ranged from .05 gram to .1 gram per liter.

Example No. 7

	Grams per liter
Di-benzene sulfonamide	1
N-methyl-2-carboxy quinolinium methyl sulfate	.05

The plate in this specific case was semi-bright, yet more lustrous than plates obtained from the antimony bath without the cooperating addition agents.

Example No. 8

	Grams per liter
Di-benzene sulfonamide	1
N-methyl quinaldine methosulfate	.05

The plate obtained in this case was bright and similar results were obtained when the heterocyclic amine concentration was raised to .125 gram per liter.

Of the aromatic sulfonamides set forth heretofore, it has been found that di-benzene sulfonamide is the preferred cooperating brightening agent utilizable with the heterocyclic amines. The best results with this sulfonamide (dibenzene sulfonamide) appear to be obtained when the concentration thereof falls from about .25 to 3 grams per liter.

Of the heterocyclic amines heretofore referred to, pyridine, 2,6-dimethyl quinoline and N-methyl quinaldine methosulfate and di-pyridyl have been found to be especially effective when employed with the preferred amounts of di-benzene sulfonamide. In this regard, concentrations of the four aforementioned heterocyclic amines should be within the range of about .01 to 1.0 gram per liter.

As a separate and distinct phase of the herein described invention, it has been found that small additions of a soluble copper salt such as the chloride, fluoride or sulfate to the plating solution produces an exceptional luster in the plate obtained from solutions incorporating the aromatic sulfonamides and heterocyclic amines of the present invention. Although the copper imparts superior brightness when utilized with the combinations heretofore set forth, exceptionally bright plates are obtained when the copper

is employed with di-benzene sulfonamide within the range of about .75 to 1.5 grams per liter as used in combination with N-methyl-quinolinium methosulfate and/or N-methyl quinaldine methosulfate in amounts ranging from about .01 to .20 gram per liter. In these specific combinations it has been found that the most beneficial results are obtained when the copper is employed in amounts ranging from about .003 to .1 gram thereof per liter as the metal. In general, and with reference to applications utilizing the copper in combination with other aromatic sulfonamides and other heterocyclic amines, the amount of copper may fall without the aforementioned range set forth for the preferred combinations but it will be found that optimum results are usually obtained when the copper concentration is less than about 2 grams per liter.

Specific examples of the preferred aromatic sulfonamides, heterocyclic amines and copper combinations are set forth in Examples No. 9 and No. 10 which follow. In Examples No. 9 and No. 10, the antimony fluoride bath and operating conditions were essentially the same as the bath set forth heretofore.

Example No. 9

	Grams per liter
Di-benzene sulfonamide	1
N-methyl quinolinium methosulfate	.025
Copper	.025

In this case plates obtained from the solution were very bright and indicated that the copper material contributed to the filling of recesses as well as imparted excellent bright throwing powers to the plating solution. Similar results were obtained when the copper concentration was increased to about .075 gram per liter.

Example No. 10

	Grams per liter
Di-benzene sulfonamide	1
N-methyl quinaldine methosulfate	.05
Copper	.0125

The plates obtained in this particular case were again very bright, showing substantially the same benefits as set forth in Example No. 9. It should be noted that the brightness of the plate was considerably reduced when an identical bath was run without the addition of the heterocyclic amine set forth in the example.

Although combinations of the heterocyclic amines and aromatic sulfonamides generally within the ranges heretofore set forth produce bright plates, it has been found occasionally that only semi-bright plates are produced which although being of an increased lustrous nature are less desirable than the bright plates. It is obvious that the ultimate goal in most plating situations is the production of a very bright plate so as to eliminate any buffing otherwise necessary for the attainment of this result. In this regard, it has been found that small additions of coumarin have materially affected the brightness of the plate obtained, such that the semi-bright plating solutions utilizing the combinations of aromatic sulfonamides and heterocyclic amines according to the herein described inventions may be converted into bright plating solutions. Although additions of coumarin and derivatives thereof appear to be generally beneficial when employed with combinations of di-benzene type sulfonamides and generally heterocyclic amines, when utilizing di-benzene sulfonamide, pyridine and/or N-methyl-2-carboxy quinolinium methyl sulfate, and coumarin, it is preferable to employ these addition agents in amounts ranging from about .75 to about 2.5 grams per liter for the sulfonamide, about .01 to 1.5 grams per liter for the amine and about .03 to .35 gram per liter for coumarin.

Specific examples showing the beneficial results derived from coumarin additions in these situations are shown in Examples 11 and 13. The antimony plating solution and conditions of operation were substantially the same as those described heretofore.

Example No. 11

	Grams per liter
Di-benzene sulfonamide	2
Pyridine	1.5

In this specific case the deposit was semi-bright and it was found that by the addition of .2 gram per liter of coumarin a bright, uniform plate was obtained.

Example No. 12

	Grams per liter
Di-benzene sulfonamide	2
N,N'-(oxydiethylene)-bis isoquinolinium	.01

In this case the deposit obtained was semi-bright and it was found the addition of 0.1 gram per liter of coumarin materially increased the brightness of the plate.

Example No. 13

	Grams per liter
Di-benzene sulfonamide	1
N-methyl-2-carboxy quinolinium methyl sulfate	.15

The plate here was again semi-bright and it was found that by the addition of .1 gram per liter of coumarin, a bright uniform plate was obtained.

Occasionally it has been found in attempting to obtain a bright plate by the cooperating action of the aromatic sulfonamides and heterocyclic amines that misplating occurs. In such situations, it has been found that the addition of a soluble zinc salt, such as zinc fluoride, chloride, or sulfate substantially overcomes this problem and that furthermore, the zinc contributes appreciably to the covering power of the solution and the leveling power thereof. In this regard it has been found that additions of zinc, generally within the range of about .03 to 3.5 (as the metal) grams per liter, are especially effective in obtaining the desired result. Occasionally a zinc ion concentration in excess of this amount may be desirable and accordingly, the invention is not to be construed as specifically limited to the range of zinc heretofore set forth. A particularly desirable concentration of ingredients is one wherein the aromatic sulfonamide is di-benzene sulfonamide utilized in amounts ranging from 0.25 to 6 grams per liter, the heterocyclic amine being employed in amounts ranging from .01 to 2 grams per liter. Specific examples of this combination are set forth hereinafter. The antimony plating solution and conditions were substantially the same as those heretofore referred to.

Example No. 14

	Grams per liter
Di-benzene sulfonamide	3
Di-pyridyl	.05
Zn (as metal)	1.9

The plate obtained in this case was a bright plate and exhibited a uniform color. Additions of di-pyridyl to .11 gram per liter increased the brightness of the plate, whereas without the di-pyridyl in the plating bath a gray deposit was obtained.

Example No. 15

	Grams per liter
Di-benzene sulfonamide ether	2
Di-pyridyl	.025
ZnF_2	.63

The plate obtained from this particular solution was a bright plate which showed a uniform color and deposit thereon.

From the foregoing disclosure, it is apparent that heterocyclic amines are especially beneficial when employed with cooperating brightening agents for the obtainment of increased brilliance in antimony plating operations. Such plates are especially desirable for subsequent chrome plating operations wherein lustrous antimony deposits are essential for the obtainment of acceptable chrome finishes.

Furthermore, it is apparent that various combinations of the heterocyclic amines and of the various aromatic sulfonamides may be employed for producing the desired results. Thus a plurality of the sulfonamides may be utilized in a bath with one or more heterocyclic amines and vice versa.

In general, the current density of the plating operation does not appear critical to the obtainment of the desired results, satisfactory deposits being obtained from as low a current density as 10 amps. per square foot and from as high as 200 amps. per square foot. Similarly the temperature of the solution during plating is not sharply critical, good results being generally obtained in the range of from about 100 to 165° F. Preferred pH ranges are between about 2.5 and 5 pH.

No completely satisfactory method of causing an antimony electrodeposit to adhere to steel directly is known, so far as I am aware. However lead, tin, and silver adhere well to steel and in accordance with the present invention, antimony can be made to adhere well to lead, tin or silver or alloys of two or more thereof and exhibit semi-brightness or full brightness by the inclusion in the plating solution of the aqueous, acid fluoride type from which deposits on lead, tin or silver are to be taken, of the novel addition agents described herein. Lustrous useful deposits directly on roughened steel (e. g. etched or sand blasted) can also be produced according to the present invention.

Having thus described the invention, what is claimed is:

1. In a process for the electrodeposition of antimony from a plating solution containing the antimony primarily as the soluble fluoride, the step of electrolyzing said solution between an anode and a cathode wherein said solution contains an aromatic sulfonamide and a heterocyclic nitrogen containing compound having at least one 6-membered ring, said aromatic sulfonamide and heterocyclic nitrogen containing compound being contained in said solution in amounts sufficient to produce an antimony deposit of enhanced brightness.

2. A process according to claim 1 wherein said aromatic sulfonamide is selected from the class consisting of benzene sulfonamide, toluene sulfonamide, dibenzene sulfonamide, dibenzene sulfonamide ether and Bi-(di-benzene sulfonamide).

3. A process according to claim 1 wherein said heterocyclic nitrogen containing compound is selected from the class consisting of pyridine, di-pyridyl, N-methyl quinolinium methosulfate, 2,6-dimethyl quinoline, N-methyl quinaldine methosulfate, N-methyl-2-carboxy quinolinium methyl sulfate and β-naphthoquinoline.

4. A process according to claim 1 wherein said aromatic sulfonamide is selected from the class consisting of benzene sulfonamide, toluene sulfonamide, di-benzene sulfonamide, di-benzene sulfonamide ether and Bi-(di-benzene sulfonamide) and wherein said heterocyclic nitrogen containing compound is selected from the class consisting of pyridine, di-pyridyl, N-methyl quinolinium methosulfate, 2,6-dimethyl quinoline, N-methyl quinaldine methosulfate, N-methyl-2-carboxy quinolinium methyl sulfate and β-naphthoquinoline.

5. In a process for the electrodeposition of antimony from a plating solution containing the antimony primarily as a soluble fluoride the step of electrolyzing said solution between an anode and a cathode wherein said solution contains an aromatic sulfonamide, a heterocyclic nitrogen containing compound having at least one 6-membered ring, and a soluble copper salt, said aromatic sulfonamide, heterocyclic nitrogen containing compound, and soluble copper salt being contained in said solution in amounts sufficient to produce an antimony deposit of enhanced brightness.

6. A process according to claim 5 wherein said aromatic sulfonamide is selected from the class consisting of benzene sulfonamide, toluene sulfonamide, di-benzene sulfonamide, di-benzene sulfonamide ether and Bi-(di-benzene sulfonamide).

7. A process according to claim 5, wherein said heterocyclic nitrogen containing compound is selected from the class consisting of pyridine, di-pyridyl, N-methyl quinolinium methosulfate, 2,6-dimethyl quinoline, N-methyl quinaldine methosulfate, N-methyl-2-carboxy quinolinium methyl sulfate and β-naphthoquinoline.

8. A process according to claim 5 wherein said aromatic sulfonamide is selected from the class consisting of benzene sulfonamide, toluene sulfonamide, di-benzene sulfonamide, di-benzene sulfonamide ether and Bi-(di-benzene sulfonamide) and wherein said heterocyclic nitrogen containing compound is selected from the class consisting of pyridine, di-pyridyl, N-methyl quinolinium methosulfate, 2,6 - dimethyl quinoline, N - methyl quinaldine methosulfate, N-methyl - 2 - carboxy quinolinium methyl sulfate and β-naphthoquinoline.

9. A process according to claim 8 wherein the soluble copper salt is selected from the class consisting of copper fluoride, copper chloride and copper sulfate.

10. In a process for the electrodeposition of antimony from a plating solution containing the antimony primarily as the soluble fluoride, the step of electrolyzing said solution between an anode and a cathode wherein said solution contains an aromatic sulfonamide, a heterocyclic nitrogen containing compound having at least one 6-membered ring, and coumarin, said aromatic sulfonamide, heterocyclic nitrogen containing compound and coumarin being contained in said solution in amounts sufficient to produce an antimony deposit of enhanced brightness.

11. A process according to claim 10 wherein said aromatic sulfonamide is selected from the class consisting of benzene sulfonamide, toluene sulfonamide, di-benzene sulfonamide, di-benzene sulfonamide ether and Bi-(di-benzene sulfonamide).

12. A process according to claim 10 wherein said heterocyclic nitrogen containing compound is selected from the class consisting of pyridine, di-pyridyl, N-methyl quinolinium methosulfate, 2,6-dimethyl quinoline, N-methyl quinaldine methosulfate, N-methyl-2-carboxy quinolinium methyl sulfate and β-naphthoquinoline.

13. A process according to claim 10 wherein said aromatic sulfonamide is selected from the class consisting of benzene sulfonamide, toluene sulfonamide, di-benzene sulfonamide, di-benzene sulfonamide ether and Bi-(di-benzene sulfonamide) and wherein said heterocyclic nitrogen containing compound is selected from the class consisting of pyridine, di-pyridyl, N-methyl quinolinium methosulfate, 2,6-dimethyl quinoline, N-methyl quinaldine methosulfate, N-methyl - 2 - carboxy quinolinium methyl sulfate and β-naphthoquinoline.

14. In a process for the electrodeposition of antimony from a plating solution containing the antimony primarily as a soluble fluoride, the step of electrolyzing said solution between an anode and a cathode wherein said solution contains an aromatic sulfonamide, a heterocyclic nitrogen containing compound having at least one 6-membered ring, and a soluble zinc salt, said aromatic sulfonamide, heterocyclic nitrogen containing compound, and soluble zinc salt being contained in said solution in amounts sufficient to produce an antimony deposit of enhanced brightness.

15. A process according to claim 14 wherein said aromatic sulfonamide is selected from the class consisting of benzene sulfonamide, toluene sulfonamide, di-benzene sulfonamide, di-benzene sulfonamide ether and Bi-(di-benzene sulfonamide).

16. A process according to claim 14 wherein said heterocyclic nitrogen containing compound is selected from the group consisting of pyridine, di-pyridyl, N-methyl quinolinium methosulfate, 2,6-dimethyl quinoline, N-methyl quinaldine methosulfate, N-methyl - 2 - carboxy - quinolinium methyl sulfate and β-naphthoquinoline.

17. A process according to claim 14 wherein said aromatic sulfonamide is selected from the group consisting of benzene sulfonamide, toluene sulfonamide, di-benzene sulfonamide, di-benzene sulfonamide ether and Bi-(di-benzene sulfonamide) and wherein said heterocyclic nitrogen containing compound is selected from the class consisting of pyridine, di-pyridyl, N-methyl quinolinium methosulfate, 2,6-dimethyl quinoline, N-methyl quinaldine methosulfate, N - methyl - 2 - carboxy quinolinium methyl sulfate and β-naphthoquinoline.

18. A process according to claim 17 wherein said soluble zinc salt is selected from the class consisting of zinc chloride, zinc sulfate and zinc fluoride.

19. In a process for the electrodeposition of antimony from a plating solution containing the antimony primarily as a soluble fluoride, the step of electrolyzing said solution between an anode and a cathode wherein said solution conatins a heterocyclic nitrogen containing compound having at least one 6-membered ring, and another co-operating brightening agent selected from the group consisting of aromatic sulfonamides, sulfonates, and sulfinates, said heterocyclic nitrogen containing compound and co-operating brightening agent being contained in said solution in amounts sufficient to produce an antimony deposit of enhanced brightness.

20. A process according to claim 19 wherein said heterocyclic nitrogen containing compound is selected from the class consisting of pyridine, di-pyridyl, N-methyl quinolinium methosulfate, 2,6-dimethyl quinoline, N-methyl quinaldine methosulfate, N-methyl-2-carboxy quinolinium methyl sulfate and β-naphthoquinoline.

21. An antimony plating solution comprising antimony primarily as the soluble fluoride, di-benzene sulfonamide in amounts ranging from about .25 to about 3 grams per liter, and a heterocyclic nitrogen containing compound having at least one 6-membered ring selected from the class consisting of pyridine, di-pyridyl, 2,6-di-methyl quinoline, and N-methyl quinaldine methosulfate in amounts ranging from about .01 to 1 gram per liter.

22. An antimony plating solution comprising antimony primarily as the soluble fluoride, di-benzene sulfonamide in amounts ranging from about .75 to 1.5 grams per liter, a heterocyclic nitrogen containing compound having at least one 6-membered ring selected from the group consisting of N-methyl quinolinium methosulfate, N-methyl quinaldine methosulfate, ranging in amounts from about .01 to .2 gram per liter and copper in amounts ranging from about .003 to .1 gram per liter.

23. An antimony plating solution comprising antimony primarily as the soluble fluoride, di-benzene sulfonamide in amounts ranging from about .75 to 2.5 grams per liter, a heterocyclic nitrogen containing compound having at least one 6-membered ring selected from the class consisting of pyridine and N-methyl-2-carboxy quinolinium methyl sulfate in amounts ranging from about .01 to about 1.5 grams per liter and coumarin in amounts ranging from about .03 to .35 gram per liter.

24. An antimony plating solution comprising antimony primarily as a soluble fluoride, an aromatic sulfonamide, a heterocyclic nitrogen containing compound having at least one 6-membered ring, and a soluble zinc compound, said aromatic sulfonamide, heterocyclic nitrogen containing compound, and zinc compound being contained in such solution in amounts sufficient to produce an antimony deposit of enhanced brightness during electrodeposition of antimony therefrom.

25. An antimony plating solution comprising antimony primarily as the soluble fluoride, di-benzene sulfonamide in amounts ranging from about .25 to 6 grams per liter, a heterocyclic nitrogen containing compound having at least one 6-membered ring in amounts ranging from about .01 to 2 grams per liter and a soluble zinc compound in amounts equivalent to the zinc of about .03 to 3.5 grams per liter.

26. An antimony plating solution comprising antimony primarily as a soluble fluoride, a heterocyclic nitrogen containing compound having at least one 6-membered ring, and a co-operating brightening agent selected from

the group consisting of aromatic sulfonamides, sulfonates, and sulfinates, said heterocyclic nitrogen containing compound and co-operating brightening agent being contained in said solution in amounts sufficient to produce an antimony deposit of enhanced brightness during electrodeposition of antimony therefrom.

27. A solution according to claim 26 wherein said heterocyclic nitrogen containing compound is selected from the class consisting of pyridine, di-pyridyl, N-methyl quinolinium methosulfate, 2,6-dimethyl quinoline, N-methyl quinaldine methosulfate, N-methyl-2-carboxy quinolinium methyl sulfate and β-naphthoquinoline.

28. A solution according to claim 27 wherein said heterocyclic nitrogen containing compound is present in amounts ranging from about .01 to 3.5 grams per liter.

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