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ELECTRODEPOSITION OF ANTIMONY

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This invention relates to electrodeposition of antimony and more especially to electrodeposition of adherent and lustrous deposits of antimony.

It is an object of the invention to deposit on cathode surfaces adherent deposits of high quality and having sufficient lustre to eliminate or greatly reduce buffing necessary to achieve full brightness. Other and more specific objects of the invention will become apparent as the description proceeds.

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 a plating solution of aqueous, acid antimony type, from which deposits on lead, tin, or silver (or their alloys as indicated) are to be taken, of co-operating addition agents. Lustrous and usefully adherent deposits directly on roughened steel (e. g., sand blasted or etched) can also be produced from solutions according to the present invention.

The fundamental plating bath should be an aqueous, acid solution of an antimony compound, suitable antimony trifluoride, which should also contain means for adjusting the pH of the solution and means for holding the antimony in solution, that is, means for preventing precipitation of antimony up to a concentration of at least about 0.7 mol and preferably up to 1.5 mols of SbF_3 per liter. The pH may be adjusted by means of ammonium ion or less desirably by sodium or potassium ion. An amine such as triethanolamine may be used for adjusting pH. Precipitation of antimony fluoride may be prevented by the use of an alpha-hydroxy carboxylic acid such as tartaric, citric, gluconic, glycolic, or lactic acid or by the ammonium, sodium, or potassium or amine salt thereof or an excess of fluoride ion in a fluoride solution. In case the salt is used, it can be also, at least in part, the means for adjusting the pH of the solution. For example, antimony trifluoride, ammonium glycolate, and water make a fundamental bath in which addition agents according to the invention may be used. Antimony chloride may be substituted in part for antimony fluoride in the fluoride bath, for example up to 40% by weight of the antimony content. The pH should be from 3.5 to 5.0.

For solutions containing antimony fluoride, the

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quantity of alpha-hydroxy carboxylic acid, if used, may be within the range of ⅛ to 2 hydroxy equivalent weights of the acid per atomic weight of antimony, the preferred concentration being about 1 alpha hydroxy equivalent weight of acid per atomic weight of antimony. (By alpha hydroxy equivalent weight is meant the molecular weight of the alpha hydroxy acid divided by the number of its alpha hydroxy groups.)

Sulfate ion is desirable as a means for insuring against immersion deposition and, when used should preferably be present in concentration from 50 to 150 mol per cent of the alpha hydroxy acid. Sulfate ion is not absolutely essential but is highly desirable for the purpose indicated.

In making up the solutions, the adjustment of the pH may be accomplished or partly so by the choice of compounds. Thus, for example, by using Sb_2O_3 and NH_4FHF, SbF_3 is produced in situ in the bath or in the tank used for manufacture of concentrate and ammonia is left over for reaction with alpha hydroxy or other acid and thus raises the pH. 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 or a concentrate which requires little if any addition of ammonia to the plater's tank. Also, it is cheaper to make use of antimony oxide and an ammonium fluoride instead of using antimony trifluoride as such in making up baths or concentrates. As shown by Examples 13 and 14, Table III, it is feasible to operate without further adjustment of pH after making up the solutions there indicated.

Preferred solutions consist of Sb_2O_3, NH_4FHF and glycolic acid in proportions to yield SbF_3 and ammonium glycolate, each from 0.5 to 2 and NH_4OH to yield a pH from 2.5 to 5.0.

Addition agents used in the above described solutions are of two classes, the first comprising benzene sulfonamides such as those listed in Table I which should be present to the extent of from 0.5 to 6 grams per liter and the second comprising aryl guanidines such as those listed in Table II, which should be present in concentration from 0.005 to 0.07 gram per liter.

Table I

Benzene sulfonamide, $C_6H_5SO_2NH_2$

Toluene sulfonamide, $CH_3C_6H_4SO_2NH_2$

Di-benzene sulfonamide, $C_6H_5SO_2NHSO_2C_6H_5$

Bi-di-benzene sulfonamide, $C_6H_5SO_2NHSO_2C_6H_4SO_2NHSO_2C_6H_5$

Di-benzene sulfonamide ether, $C_6H_5SO_2NHSO_2C_6H_4OC_6H_4SO_2NHSO_2C_6H_5$

Table II

Diphenyl guanidine, $(C_6H_5NH)_2C=NH$
Triphenyl guanidine, $(_6H_5NH)_2S=NC_6H$

Specific examples of batch formulations for plating solutions according to the invention employing representative examples of these addition agents are shown in Table III. All the examples shown in said table yield deposits which are firmly adherent to lead, tin and silver and fairly adherent to roughened steel and exhibit improved lustre resulting from the presence of the cooperating addition agents.

Table III

Example	Preferred Range
1. $SbCl_3$, .87 mol/l	.5–1.5 mols/l.
NaF, 2.61 mols/l	1.5–4.5 mols/l.
Tartaric acid, 0.8 mol/l	.25–1.5 mols/l.
NaOH to pH, 3.0	2.7–3.5.
Dibenzene sulfonamide, 2 g./l	1–4 g./l.
Diphenyl guanidine, .02 g./l	.01–.05 g./l.
2. $SbCl_3$, 1.25 mols/l	.5–1.5 mols/l.
$NH_4F.HF$, 1.875 mols/l	.7–2.5 mols/l.
Ammonium citrate, .31 mol/l	.1–.6 mol/l.
NH_4OH to pH, 4.0	2.5–5.
Dibenzene sulfonamide, 3.0 g./l	1–5 g./l.
Diphenyl guanidine, .02 g./l	.01–.05 g./l.
3. SbF_3, 1.25 mols/l	.5–1.5 mols/l.
$(NH_4)_2SO_4$, 1.25 mols/l	.25–1.5 mols/l.
Glycolic Acid, 0.75 mol/l	.25–1.5 mols/l.
NH_4OH to pH 4.0	2.5–4.5.
Dibenzene sulfonamide, 1.0 g./l	0.5–6.0 g./l.
Diphenyl guanidine, 0.01 g./l	0.005–0.07 g./l.
4. Sb_2O_3, 0.62 mol/l	.25–.75 mol/l.
H_2SO_4, 1.25 mols/l	.50–1.50 mols/l.
KF.HF, 1.87 mols/l	.75–2.25 mols./l.
Gluconic Acid, .75 mol/l	.25–1.50 mols/l.
KOH to pH 4.5	2.5–5.0.
Dibenzene sulfonamide, 1.0 g./l	0.5–6.0 g./l.
Diphenyl guanidine, 0.01 g./l	0.005–0.07 g./l.
5. Sb_2O_3, 0.7 mol/l	.3–1.0 mol/l.
HF, 4.2 mols/l	.6–2.0 mols/l.
Tartaric acid, .35 mol/l	.25–1.5 mols/l.
Triethanolamine to pH 4.0	2.5–5.0.
Dibenzene sulfonamide, 2 g./l	1–5 g./l.
Diphenyl guanidine, .02 g./l	.01–.05 g./l.
6. Sb_2O_3, 0.62 mol/l	.3–1.0 mol/l.
$NH_4F.HF$, 1.85 mols/l	1.0–3.0 mols/l.
Glycolic acid, 1.23 mols/l	0.6–2.0 mols/l.
NH_4OH to pH 4.0	2.5–5.
Dibenzene sulfonamide, 0.5 g./l	.5–2 g./l.
Bi-dibenzene sulfonamide, 2.0 g./l	.5–2 g./l.
Diphenyl guanidine, 0.04 g./l	.01–.05 g./l.
7. Sb_2O_3, 0.62 mol/l	.3–1.0 mol/l.
$NH_4F.HF$, 1.85 mols/l	1–3 mols/l.
Glycolic acid, 1.23 mols/l	.6–2 mols/l.
$(NH_4)_2SO_4$, 50 to 150 mol percent of the glycolic acid.	
NH_4OH to pH 4.0	2.5–4.0.
Dibenzene sulfonamide, 3 g./l	1–6 g./l.
Triphenyl guanidine, .03 g./l	.01–.1 g./l.
8. Sb_2O_3, 0.62 mol/l	.3–1.0 mol/l.
$NH_4F.HF$, 1.85 mols/l	1.0–3.0 mols/l.
Glycolic acid, 1.23 mols/l	.6–2.0 mols/l.
$(NH_4)_2SO_4$, 50 to 150 mol percent of the glycolic acid.	
NH_4OH to pH 4.0	2.5–5.
Dibenzene sulfonamide ether, 2.0 g./l	.5–4 g./l.
Diphenyl guanidine, .02 g./l	.01–0.1 g./l.
9. Sb_2O_3, 0.62 mol/l	.3–1.0 mol/l.
$NH_4F.HF$, 1.85 mols/l	1.0–3.0 mols/l.
Glycolic acid, 1.23 mols/l	.6–2.0 mols/l.
$(NH_4)_2SO_4$, 50 to 150 mol percent of the glycolic acid.	
NH_4OH to pH 4.0	2.5–5.0.
Toluene sulfonamide, 2.5 g./l	2.0–3.0 g./l.
Diphenyl guanidine, .01 g./l	.005–.03 g./l.
10. Sb_2O_3, .615 mol/l	.25–.75 mol/l.
$NH_4F.HF$, 1.23 mols/l	.5–1.50 mols/l.
HF, 1.23 mols/l	.5–1.50 mols/l.
Glycolic acid, 1.23 mols/l	.5–1.50 mols/l.
$(NH_4)_2SO_4$, 1.23 mols/l	.5–1.50 mols/l.
NH_4OH to pH 4.0	2.5–4.5.
Dibenzene sulfonamide, 2.0 g/l	0.5–6.0 g/l.
Diphenyl guanidine, 0.02 g/l	0.005–0.07 g/l.
11. SbF_3, 1.4 mols/l	.8–1.5 mols/l.
NH_4F, 5.4 mols/l	4.0–6.0 mols/l.
NH_4OH to pH 3.5	3.0–4.7.
Dibenzene sulfonamide, 2.5 g/l	2.0–6.0 g/l.
Triphenyl guanidine, .02 g/l	.01–.04 g/l.
12. SbF_3, 1.4 mols/l	.8–1.5 mols/l.
NH_4F, 5.4 mols/l	4.0–6.0 mols/l.
NH_4OH to pH 3.5	3.0–4.7.
Benzene sulfonamide, 2.0 g/l	1–2.5 g/l.
Diphenyl guanidine, .01 g/l	.005–.03 g/l.
13. SbF_3, 1.23 mols /l	0.8–1.5 mols/l.
Ammonium glycolate, 1.23 mols/l	0.6–2.0 mols/l.
Dibenzene sulfonamide, 2.0 g/l	0.5–6.0 g/l.
Diphenyl guanidine, 0.02 g/l	0.005–0.07 g/l.

Table III—Continued

Example	Preferred Range
14. SbF_3, 1.23 mols/l	0.8–1.5 mols/l.
Ammonium glycolate, 1.23 mols/l	0.6–2.0 mols/l.
Ammonium sulfate, 1.23 mols/l	0.6–1.8 mols/l.
Dibenzene sulfonamide, 2.0 g/l	0.5–6 g/l.
Diphenyl guanidine, 0.02 g/l	0.005–0.07 g/l.
15. Sb_2O_2, .172 mol/l	.15–.20 mol/l.
Citric acid, .96 mol/l	.5–1.0 mol/l.
Potassium citrate, .445 mol/l	.4–.6 mol/l.
KOH to pH 4.2	3.0–4.5.
Dibenzene sulfonamide, 2 g/l	1–5 g/l.
Diphenyl guanidine, .02 g/l	.01–.03 g/l.
16. $SbCl_3$, .153 mol/l	.13–.18 mol/l.
Oxalic acid, .119 mol/l	.10–.20 mol/l.
Ammonium oxalate, .8 mol/l	.70–1.0 mol/l.
NH_4OH to pH 4.0	3.0–4.5.
Dibenzene sulfonamide, 2 g/l	1–5 g/l.
Diphenyl guanidine, .02 g/l	.01–.03 g/l.
17. Tartar emetic, .15 mol/l	.10–.30 mol/l.
Ammonium citrate, .206 mol/l	.2–.5 mol/l.
pH 4.0	3–4.5 mols/l.
Dibenzene sulfonamide, 1 g/l	0.5–2.0 g/l.
Diphenyl guanidine, .02 g/l	.01–.03 g/l.

Temperature is not sharply critical but may be suitably in the range from 100 to 160° F.

Cathode current density is, likewise, not sharply critical but preferably is in the range from 10 to 200 amperes per square foot.

Having thus described the invention, what is claimed is:

1. A process for electrodeposition of an adherent, lustrous coating of antimony on lead comprising electrolyzing between an antimony anode and a lead cathode an aqueous, acid solution affording a source of antimony ions and containing cooperating adherence promoting and brightening addition agents one thereof being of the class consisting of benzene sulfonamide, dibenzene sulfonamide, bi-di-benzene sulfonamide, di-benzene sulfonamide ether, and toluene sulfonamide and being present in solution in concentration from 0.5 to 6 grams per liter, and the other thereof being of the class consisting of diphenyl guanidine and triphenyl guanidine and being present in concentration from 0.005 to 0.07 gram per liter.

2. A process for electrodeposition of an adherent, lustrous coating of antimony on lead comprising electrolyzing between an antimony anode and a lead cathode an aqueous, acid solution of antimony tri-fluoride, the pH of said solution being from 2.5 to 5.0, and said solution containing cooperating adherence promoting and brightening addition agents one thereof being of the class consisting of benzene sulfonamide, di-benzene sulfonamide, bi-di-benzene sulfonamide, di-benzene sulfonamide ether, and toluene sulfonamide and being present in solution in concentration from 0.5 to 6 grams per liter, and the other thereof being of the class consisting of diphenyl guanidine and triphenyl guanidine and being present in concentration from 0.005 to 0.07 gram per liter.

3. A process for electrodeposition of an adherent, lustrous coating of antimony on surfaces of the class consisting of lead, tin, silver, alloys of a plurality thereof and rough steel, comprising electrolyzing between an anode and a cathode of said class an aqueous, acid solution containing an antimony compound affording a source of antimony ions and means for adjusting the pH of said solution to form 2.5 to 5.0, said solution also containing cooperating adherence promoting and brightening addition agents one thereof being of the class consisting of benzene sulfonamide, di-benzene sulfonamide, bi-di-benzene sulfonamide, di-benzene sulfonamide ether, and toluene sulfonamide and being present in solu-

tion in concentration from 0.5 to 6 grams per liter, and the other thereof being of the class consisting of diphenyl guanidine and triphenyl guanidine and being present in concentration from 0.005 to 0.07 gram per liter.

4. A process for electrodeposition of an adherent, lustrous coating of antimony on surfaces of the class consisting of lead, tin, silver, alloys of a plurality thereof and rough steel, comprising electrolyzing between an antimony anode and a cathode of said class, an aqueous, acid solution containing an antimony compound affording a source of antimony ions, means for holding said antimony compound in solution to a concentration in the range from 0.7 to 1.5 mols of said antimony compound per liter of solution and means for adjusting the pH of said solution to from 2.5 to 5.0, said solution also containing cooperating adherence promoting and brightening addition agents one thereof being of the class consisting of benzene sulfonamide, di-benzene sulfonamide, bi-di-benzene sulfonamide, di-benzene sulfonamide ether, and toluene sulfonamide and being present in solution in concentration from 0.5 to 6 grams per liter, and the other thereof being of the class consisting of diphenyl guanidine and triphenyl guanidine and being present in concentration from 0.005 to 0.07 gram per liter.

5. A process for electrodeposition of an adherent, lustrous coating of antimony on a metal base comprising electrolyzing between an antimony anode and a cathode of the class consisting of lead, tin, silver, alloys of a plurality thereof and rough steel, an aqueous, acid solution containing antimony trifluoride, means for holding said antimony trifluoride in solution up to a concentration in the range from 0.7 to 1.5 mols per liter and comprising an alpha-hydroxy carboxylic acid in concentration from ⅛ to 2 hydroxy equivalents per atomic weight of antimony, said solution also containing sulfate ion and cooperating adherence promoting and brightening addition agents one thereof being of the class consisting of benzene sulfonamide, di-benzene sulfonamide, bi-di-benzene sulfonamide, di-benzene sulfonamide ether, and toluene sulfonamide and being present in solution in concentration from 0.5 to 6 grams per liter, and the other thereof being of the class consisting of diphenyl guanidine and triphenyl guanidine and being present in solution in concentration from 0.005 to 0.07 gram per liter.

6. A process for electrodeposition of an adherent, lustrous coating of antimony on lead comprising electrolyzing between an antimony anode and a lead cathode an aqueous, acid solution containing an antimony compound affording a source of antimony ions, an alpha-hydroxy carboxylic acid in concentration from ⅛ to 2 hydroxy equivalents per atomic weight of antimony and cooperating adherence promoting and brightening addition agents one thereof being of the class consisting of benzene sulfonamide, di-benzene sulfonamide, bi-di-benzene sulfonamide, di-benzene sulfonamide ether, and toluene sulfonamide and being present in solution in concentration from 0.5 to 6 grams per liter, and the other thereof being of the class consisting of diphenyl guanidine and triphenyl guanidine and being present in solution in concentration from 0.005 to 0.07 gram per liter.

7. A process for electrodeposition of an adherent, lustrous coating of antimony on lead comprising electrolyzing between an antimony anode and a lead cathode an aqueous, acid solution affording a source of antimony ions and containing from 0.7 to 1.5 mols per liter of antimony trifluoride, a radical of the class consisting of glycolate, tartrate, citrate, gluconate, and lactate in concentration from ⅛ to 2 hydroxy equivalents per atomic weight of antimony, said solution also containing sulfate ion and means for adjusting the pH to from 2.5 to 5.0 and cooperating adherence promoting and brightening addition agents one thereof being of the class consisting of benzene sulfonamide, di-benzene sulfonamide, bi-di-benzene sulfonamide, dibenzene sulfonamide ether, and toluene sulfonamide and being present in solution in concentration from 0.5 to 6 grams per liter, and the other thereof being of the class consisting of diphenyl guanidine and triphenyl guanidine and being present in concentration from 0.005 to 0.07 gram per liter.

8. An aqueous, acid electroplating solution for electrodeposition of antimony, the same containing:

Antimony trifluoride	0.5 to 2 mols per liter.
Ammonium glycolate	0.5 to 2 mols per liter.
Sulfate ion	50 to 150 mol percent of the ammonium glycolate.
Dibenzene sulfonamide	0.5 to 6 grams per liter.
Diphenyl guanidine	0.005 to 0.07 gram per liter.
Ammonium hydroxide to pH	2.5 to 5.0.

9. A process for electrodeposition of an adherent, lustrous coating of antimony on lead comprising electrolyzing between an antimony anode and a lead cathode an aqueous, acid solution affording a source of antimony ions and containing antimony trifluoride in concentration in the range from 0.7 to 1.5 mols per liter, means for holding said antimony trifluoride in solution in said concentration and comprising an alpha-hydroxy carboxylic acid present in concentration from ⅛ to 2 hydroxy equivalents per atomic weight of antimony, said solution also containing sulfate ion to the extent of from 50 to 150 mol per cent of said alpha hydroxy carboxylic acid and cooperating adherence promoting and brightening addition agents one thereof being of the class consisting of benzene sulfonamide, dibenzene sulfonamide, bi-di-benzene sulfonamide, di-benzene sulfonamide ether, and toluene sulfonamide and being present in solution in concentration from 0.5 to 6 grams per liter, and the other thereof being of the class consisting of diphenyl guanidine and triphenyl guanidine and being present in solution in concentration from 0.005 to 0.07 gram per liter.

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