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ELECTRODEPOSITION OF ANTIMONY

Walter P. Karash, Cleveland, Ohio, assignor to The Harshaw Chemical Company, Cleveland, Ohio, a corporation of Ohio

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13 Claims. (Cl. 29—196.6)

This invention relates to antimony plating and to electrodeposited coatings including a layer of antimony.

Many attempts have been made to produce satisfactory coatings of antimony but they all have left something to be desired. Poor adherence has perhaps presented the greatest difficulties and proposed solutions of that problem have been very unsatisfactory. Antimony seems to be inherently rather brittle but a deposit characterized by good adherence and fine texture does not scale and can be very useful since it easily buffs to full brightness, by the use of suitable addition agent can be plated bright or semi-bright, resists corrosion and, when coated with bright chromium, is bright and hard enough for most purposes.

The principal object of the present invention is to produce satisfactory electrodeposited coatings including highly adherent antimony of fine texture and solutions and methods for producing such coatings.

Other objects will be obvious from the following description.

It has now been discovered in accordance with the present invention that in high pH, acid, antimony plating fine-grained, readily buffable deposits which exhibit remarkable adherence to underlying electrodeposits of lead, tin and silver can be produced by electrolyzing between an anode and a cathode at a pH in the range from 2.5 to 6.0 a solution containing a soluble antimony compound and an addition agent of the class hereinafter defined. In producing deposits according to the invention on lead, tin and silver, the antimony very quickly, almost instantaneously, covers the cathode uniformly instead of initially covering only portions and later filling out bare areas. These deposits also exhibit excellent resistance to corrosion. For example, a laminar coating made up of 0.0002 inch of lead and 0.0008 inch of antimony from a solution according to the invention has been produced which exhibited corrosion resistance (salt spray) superior to that of 0.0010 inch of nickel both in the as produced state and after deformation of a sheet steel strip carrying the lead-antimony and the nickel coatings by bending on radii of less than one-eighth of an inch and then straightening out to approximate flatness again.

So far as applicant is aware, no antimony plating process or solution heretofore known will produce deposits in the pH range from 2.5 to 6.0 which will adhere strongly to lead, nor, so far as applicant is aware, will any heretofore known antimony plating process or solution produce deposits at a pH below 2.5 which exhibit the same fineness of grain and still attain the excellent adherence to lead which applicant attains in the pH range from 2.5 to 6.0. Bloom (U. S. Patent No. 2,389,131) indicates that good adherence to lead can be had below pH 6 if the lead is first roughened by acid etching or sand blasting. This roughening technique does improve adherence, but it has been found that antimony deposits from Bloom's bath on untreated (that is, unroughened) lead electrodeposits do not adhere strongly whereas from solutions according to the present invention, they do adhere very strongly to untreated electrodeposits of lead, tin, and silver and sufficiently well for some commercial purposes on untreated electrodeposits of copper. Adherence of antimony electrodeposits according to the present invention to lead electrodeposits which have been buffed to maximum brightness is equal to their adherence to untreated electrodeposits of lead. Deposits from Bloom's bath on buffed lead exhibit extremely poor adherence. The solutions of this invention exhibit an extremely low rate of immersion deposition on lead. The corrosion rate of lead in Bloom's solution is more than 50 times as fast as in solutions according to the present invention.

The invention then consists in the novel electroplating solutions hereinafter described, the processes which comprise electrolyzing such solutions and the novel laminar deposits including: antimony electrodeposited on lead, tin, or silver in turn electrodeposited on steel when the antimony deposit is more firmly adherent and of finer grain size due to the use of one of the novel solutions in its production and therefore has occluded therein a trace of the addition agent; and copper or "alkaline antimony" on zinc base die castings followed by acid antimony where the final coat of antimony contains a trace of the addition agent as a result of being produced in one of the novel solutions. By "alkaline" or "acid" antimony is meant an antimony deposit produced in an alkaline or acid antimony plating solution respectively.

Examples of antimony halide plating solutions in connection with which the invention may be realized in the pH range from 2.5 to 6.0 by the addition thereto of an addition agent or addition agents as herein indicated, when electrolyzed between an anode and a cathode which cathode has a surface of lead, tin, silver, or copper, are as follows, batch compositions being indicated in view of the uncertainty which exists as to the nature of the complexes formed in solution.

Example I

SbF_3	From 100 to 300, suitably 250 g./l.
NH_4F	From 100 to 300, suitably 200 g./l.
NH_4OH to give pH	From 3.5 to 5.5, suitably 4.5.
H_2O	Remainder.

Example II

SbF_3	From 100 to 300, suitably 200 g./l.
$(NH_4)_2SO_4$	From 100 to 200, suitably 148 g./l.
NH_4OH to give pH	From 3.5 to 5.5, suitably 4.0.
H_2O	Remainder.

Example III

Sb_2O_3	From 100 to 200, suitably 113 g./l.
NaFHF	From 125 to 250, suitably 142 g./l.
NH_4OH to give pH	From 3.0 to 5.5, suitably 4.5.
H_2O	Remainder.

Example IV

Sb_2O_3	From 100 to 200, suitably 163 g./l.
KF.2HF	From 110 to 250, suitably 164 g./l.
$(NH_4)_2SO_4$	From 0 to 200, suitably 100 g./l.
KOH or NH_4OH to give pH	From 3.0 to 5.5, suitably 3.5.
H_2O	Remainder.

Example V

Sb_2O_3	From 100 to 250, suitably 163 g./l.
NH_4FHF	From 100 to 220, suitably 191 g./l.
H_2SO_4	From 63 to 200, suitably 110 g./l
NH_4OH to give pH	From 3.5 to 5.5, suitably 5.0.
H_2O	Remainder.

Example VI

SbF_3	From 100 to 300, suitably 200 g./l.
HF	From 40 to 125, suitably 81 g./l.
Monoethanolamine to give pH	From 3.0 to 5.5 (ordinarily from 100 to 337 g./l.).
H_2O	Remainder.

Example VII

$SbCl_3$	From 100 to 300, suitably 200 g./l.
NH_4FHF	From 100 to 200, suitably 145 g./l.
NH_4OH to give pH	From 3.5 to 5.5, suitably 5.0.
H_2O	Remainder.

Example VIII

$SbCl_3$	From 100 to 350, suitably 285 g./l.
NH_4F	From 100 to 200, suitably 136 g./l.
Rochelle Salts	From 50 to 150, suitably 100 g./l.
pH	From 2.5 to 4.5, suitably 4.0.

Example IX

Sb_2O_3	From 80 to 250, suitably 180 g./l.
$NH_4F.HF$	From 70 to 220, suitably 105 g./l.
Glycolic acid	From 25 to 100, suitably 52 g./l.
NH_4OH to pH	From 2.5 to 4.0, suitably 3.0

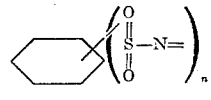
Example X

SbF_3	From 150 to 250, suitably 179 g./l.
$(NH_4)_2SO_4$	From 100 to 200, suitably 132 g./l.
Glycolic acid	From 25 to 100, suitably 57 g./l.

Examples III, IV, V, and IX should be regarded as basically antimony fluoride solutions since the Sb_2O_3 will react with fluoride to form SbF_3. Preferably the antimony halide solutions will contain a fluoride such as ammonium fluoride, ammonium bifluoride, hydrogen fluoride, sodium fluoride or potassium fluoride. The solution may also contain an agent such as the Rochelle salt or the glycolic acid for assisting in holding the antimony in solution. The antimony halide should be present in concentration molecularly equivalent to from 100 to 300 grams per liter of SbF_3 and a fluoride should be present in concentration molecularly equivalent to from 40 to 125 grams per liter of HF.

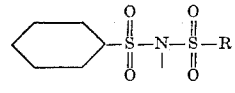
The addition agents of the present invention are aromatic sulfonamides which term includes substituted sulfonamides, sulfonimides, etc. free from double ring groups such as exist in e. g. naphthalene or saccharine, falling into two structurally similar groups having similar although somewhat different effects. These sulfonamides contain a nitrogen atom carrying from 1 to 2 aromatic radicals of the structural form RSO_2—, where R is a single ring aromatic radical containing six carbon atoms.

Group I compounds are of the structural form:



where *n* is an integer from 1 to 2, the aromatic nucleus has six carbons, the free valences of the aromatic nucleus are satisfied by hydrogen and from 0 to 3 radicals of the class consisting of Cl, Br, F, OH, OCH_3 CH_3, C_2H_5, CO_2H, and NH_2 and the free valences of the nitrogen atom are satisfied by from 0 to 2 atoms of hydrogen and from 0 to 2 aliphatic radicals of the class consisting of CH_2COOH and C_2H_2OH, the number of hydrogen atoms being equal to 2 minus the number of said aliphatic radicals.

Group II compounds are of the structural form:



where R is a radical of the class consisting of aromatic

radicals of six carbon atoms, benzyl and aliphatic radicals having from 2 to 4 carbon atoms, such aliphatic radicals being made up of carbon and atoms of the class consisting of hydrogen, oxygen, Cl, Br, and F, the free valences of each aromatic nucleus being satisfied by hydrogen and from 0 to 3 radicals of the class consisting of Cl, Br, F, CH_3, C_2H_5, CO_2H, OH, OCH_3 and NH_2 and the free valences of the nitrogen atom being satisfied by a radical of the class consisting of hydrogen and aliphatic radicals having from 1 to 4 carbon atoms, preferably alkyl radicals or alkyl radicals substituted by Cl, Br, F, CO_2H or NH_2.

When in the above identified addition agents the benzene nucleus is replaced by the naphthalene nucleus, the benefits of the invention are not obtained. Expanding group II formula to $BzSO_2NHSO_2BzSO_2NHSO_2Bz$ (Bz indicating the benzene nucleus) or to

$$BzSO_2NHSO_2BzBzSO_2NHSO_2Bz$$

destroys the improved effect. Substituting the thiophene or pyridine nucleus for the benzene nucleus renders the addition agent ineffective. Saccharine (o-benzoyl sulfimide) has practically no effect. Replacing a benzene nucleus by urea destroys the effect. Cresol, resorcinol, coumarin, naphthalene sulfonic acids, formaldehyde, sulfobenzaldehyde, hypo, clove oil, aloin, chloral, furfural, pyridine, thiourea, salicyclic acid, phenol, glue and many other common electroplating addition agents were found to be unsatisfactory.

The addition agents should be used in concentration from .2 to 5 grams per liter. Usually from 2 to 3 grams per liter is satisfactory.

Some specific examples of the compounds of group I are as follows:

	Preferred range of concentration, g./l.	Preferred concentration, g./l.
1. $PhSO_2NH_2$	.2–5 or saturation.	2½
2. $CH_3C_6H_4SO_2NH_2$	.2–5 or saturation.	2½
3. $PhSO_2NHCH_2CO_2H$	.2–4	2½
4. $PhSO_2N(OC_2H_5)_2$	.2–4	2½
5. $CH_3C_6H_4SO_2NHOC_2H_5$	.2–4	2½
6. $H_2NSO_2C_6H_4SO_2NH_2$	.2–4	2½
7. $H_2NC_6H_4SO_2NH_2$	.2–4	2½

Specifiic examples of the compounds of Group II are as follows:

	Preferred range of concentration, g./l.	Preferred concentration, g./l.
1. $C_6H_5NHSO_2C_6H_5$ (Dibenzene sulfonamide)	.2–5	3
2. $Cl_2C_6H_3SO_2NHSO_2C_6H_5$	.2–5	2
3. $CH_3CH_2CH_2CH_2SO_2NHSO_2C_6H_5$	.2–5	2½
4. $CH_3CH_2SO_2NHSO_2C_6H_5$	.2–5	2½
5. $C_2H_5C_6H_4SO_2NHSO_2C_6H_5$	.2–5	2½
6. $HO_2CC_6H_4SO_2NHSO_2C_6H_5$	.2–5	2½
7. $CH_3C_6H_4SO_2NHSO_2C_6H_4CH_3$	.2–5	2½
8. $CH{=}C(CH_3)CH_2{-}SO_2NHSO_2C_6H_5$	.2–5	2½

The addition agents of the above indicated classes are effective, without any auxiliary addition agent, to produce grain refinement and more adherent deposits on the indicated metals and somewhat on roughened steel. Compounds of group I tend to give more lustrous and somewhat more brittle deposits, while those of group II give superior ductility but less lustre although producing fine grained, very white deposits without auxiliary addition agents.

The novel class of compounds can be effectively used in combination with other addition agents with the result that there is produced bright or nearly bright deposits having good adherence to lead, copper, etc., and solutions containing such cooperating addition agents are capable

of being operated trouble-free for long periods of time. Examples of such cooperating addition agents are as follows:

	Preferred range of concentration, g./l.	Preferred Concentration
Copper salts, e. g. copper fluoride (CuF_2)	.05–.2	.1
Polymerized tetraethylene pentamine	.02–.2	.07

These auxiliary brighteners may be used in concentration ranges indicated above, the compounds of Tables I, II in conjunction with which they are used being employed in concentrations as indicated in said tables.

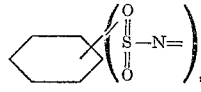
An example of an alkaline antimony solution suitable for plating a preparatory coating on zinc base die castings prior to application of acid antimony is as follows:

Tartaric emetic	g./l.	150
Rochelle salts	g./l.	128
NaOH to	pH	8–13

Having thus described the invention, what is claimed is:

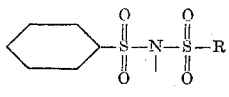
1. A process for production of strongly adherent deposits of antimony on metallic surfaces of the class consisting of lead, tin, copper and silver comprising electrolyzing between an anode and a cathode having a surface of a metal of the class consisting of lead, tin, copper and silver, a solution containing a soluble antimony halide and an aromatic sulfonamide containing a nitrogen atom carrying from 1 to 2 aromatic groups of the structural form RSO_2—, where R represents an aromatic radical containing six carbon atoms, said solution being maintained in the pH range from 2.5 to 6.0 and said aromatic sulfonamide being present in concentration from 0.2 to 5 grams per liter.

2. A process for production of strongly adherent deposits of antimony on metallic surfaces of the class consisting of lead, tin, copper, and silver comprising electrolyzing between an anode and a cathode having a surface of a metal of said class a solution containing a soluble antimony halide and an aromatic sulfonamide having the structural form:



where n is an integer from 1 to 2, the free valences of the aromatic nucleus are satisfied by hydrogen and from 0 to 3 radicals of the class consisting of Cl, Br, F, OH, OCH_3, CH_3, C_2H_5, CO_2H, NH_2, and the free valences of the nitrogen atom are satisfied by from 0 to 2 atoms of hydrogen and from 0 to 2 aliphatic radicals of the class consisting of CH_2COOH and C_2H_4OH, the number of hydrogen atoms being equal to 2 minus the number of said aliphatic radicals, said solution being maintained in the pH range from 2.5 to 6.0 and said aromatic sulfonamide being present in concentration from 0.2 to 5 grams per liter.

3. A process for production of strongly adherent deposits of antimony on metallic surfaces of the class consisting of lead, tin, copper, and silver, comprising electrolyzing between an anode and a cathode having a surface of a metal of said class, said solution containing a soluble antimony halide and an aromatic sulfonamide having the structural form:



where R is a radical of the class consisting of aromatic radicals containing six carbon atoms, benzyl, and aliphatic radicals having from 2 to 4 carbon atoms, such aliphatic radicals being made up of carbon and atoms of the class consisting of hydrogen, oxygen, Cl, Br and F, the free valences of each aromatic nucleus being satisfied by hydrogen and from 0 to 3 radicals of the class consisting of Cl, Br, F, CH_3, C_2H_5, CO_2H, OH, OCH_3 and NH_2 and the free valence of the nitrogen atom being satisfied by a radical of the class consisting of hydrogen and aliphatic radicals having from 1 to 4 atoms, said solution being maintained in the pH range from 2.5 to 6.0 and said aromatic sulfonamide being present in concentration from 0.2 to 5 grams per liter.

4. An antimony plating solution comprising a soluble antimony halide, and an addition agent, the pH of said solution being from 2.5 to 6.0 and said addition agent being an aromatic sulfonamide containing a nitrogen atom carrying from 1 to 2 aromatic groups of the structural form RSO_2—, where R represents a single ring aromatic radical containing six carbon atoms, said antimony halide being antimony trifluoride, being present in concentration from 100 to 300 grams per liter, said solution also containing an ammonium salt in concentration molecularly equivalent to from 100 to 300 grams per liter of NH_4F and said addition agent being present in concentration from 0.2 to 5.0 grams per liter.

5. An antimony plating solution as defined in claim 4 further characterized in that said antimony halide is from 100 to 300 grams per liter of SbF_3, said solution containing an ammonium fluoride in concentration molecularly equivalent to 100 to 300 grams per liter of NH_4F and glycolic acid in concentration from 25 to 100 grams per liter, and said addition agent being present in concentration from 0.2 to 5.0 grams per liter.

6. An antimony plating solution comprising antimony trifluoride in concentration from 100 to 300 grams per liter, dibenzene sulfonamide in concentration from 0.2 to 5 grams per liter, an acidic material of the class consisting of alkali metal and ammonium fluorides and sulfates, and an organic compound of the class consisting of glycolic acid and Rochelle salts, the pH of the solution being within the range from 2.5 to 6.0.

7. An antimony plating solution comprising antimony trifluoride in concentration from 100 to 300 grams per liter, toluene sulfonamide in concentration from 0.2 to 5 grams per liter, an acidic material of the class consisting of alkali metal and ammonium fluorides and sulfates, and an organic compound of the class consisting of glycolic acid and Rochelle salts, the pH of the solution being within the range from 2.5 to 6.0.

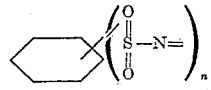
8. An antimony plating solution comprising antimony trifluoride in concentration from 100 to 300 grams per liter, chlorodibenzene sulfonamide in concentration from 0.2 to 5 grams per liter, an acidic material of the class consisting of alkali metal and ammonium fluorides and sulfates, and an organic compound of the class consisting of glycolic acid and Rochelle salts, the pH of the solution being within the range from 2.5 to 6.0.

9. An antimony plating solution comprising antimony trifluoride in concentration from 100 to 300 grams per liter, benzene sulfonamide in concentration from 0.2 to 5 grams per liter, an acidic material of the class consisting of alkali metal and ammonium fluorides and sulfates, and an organic compound of the class consisting of glycolic acid and Rochelle salts, the pH of the solution being within the range from 2.5 to 6.0.

10. An electroplating solution containing a soluble antimony halide and an aromatic sulfonamide containing a nitrogen atom carrying from 1 to 2 aromatic groups of the structural form RSO_2—, where R represents an aromatic radical containing six carbon atoms, said solution being maintained in the pH range from 2.5 to 6.0 and said aromatic sulfonamide being present in concentration from 0.2 to 5 grams per liter.

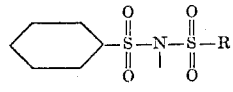
11. An electroplating solution containing a soluble anti-

mony halide and an aromatic sulfonamide having the structural form:



where n is an integer from 1 to 2, the free valences of the aromatic nucleus are satisfied by hydrogen and from 0 to 3 radicals of the class consisting of Cl, Br, F, OH, OCH_3, CH_3, C_2H_5, CO_2H, NH_2, and the free valences of the nitrogen atom are satisfied by from 0 to 2 atoms of hydrogen and from 0 to 2 aliphatic radicals of the class consisting of CH_2COOH and C_2H_4OH, the number of hydrogen atoms being equal to 2 minus the number of said aliphatic radicals, said solution being maintained in the pH range from 2.5 to 6.0 and said aromatic sulfonamide being present in concentration from 0.2 to 5 grams per liter.

12. An electroplating solution containing a soluble antimony halide and an aromatic sulfonamide having the structural form:



where R is a radical of the class consisting of aromatic radicals containing six carbon atoms, benzyl, and aliphatic radicals having from 2 to 4 carbon atoms, such aliphatic radicals being made up of carbon and atoms

of the class consisting of hydrogen, oxygen, Cl, Br and F, the free valences of each aromatic nucleus being satisfied by hydrogen and from 0 to 3 radicals of the class consisting of Cl, Br, F, CH_3, C_2H_5, CO_2H, OH, OCH_3 and NH_2 and the free valence of the nitrogen atom being satisfied by a radical of the class consisting of hydrogen and aliphatic radicals having from 1 to 4 atoms, said solution being maintained in the pH range from 2.5 to 6.0 and said aromatic sulfonamide being present in concentration from 0.2 to 5 grams per liter.

13. An article of manufacture comprising a ferrous metal body, an adherent coating of lead overlying said ferrous metal body and an adherent coating of antimony overlying said coating of lead, said coating of antimony having been applied upon an unroughened surface of said lead coating, and said antimony coating being fine grained and adherent and having occluded therein a trace of an aromatic sulfonamide containing a nitrogen atom carrying from 1 to 2 aromatic groups of the structural form RSO_2—, where R represents an aromatic radical containing 6 carbon atoms.

References Cited in the file of this patent

UNITED STATES PATENTS

1,780,944	Roscher	Nov. 11, 1930
2,191,813	Brown	Feb. 27, 1940
2,389,131	Bloom	Nov. 20, 1945
2,441,810	Glover et al.	May 18, 1948