ABSTRACT: Solutions containing stannous sulfate and aluminum sulfate, as well as free sulfuric acid, and preferably a chelating agent, are useful in forming a dense, adherent tin plate on conductive surfaces. They are particularly useful in plating tin metal on aluminum or aluminum alloys. Conventional additives such as brightening and conditioning agents, e.g., polyalkylene glycols, may be included.
ALUMINATED STANNOUS SULFATE SOLUTIONS THEIR PREPARATION AND THEIR USE IN PLATING ON CONDUCTIVE SURFACES, PARTICULARLY ON ALUMINUM

BACKGROUND OF INVENTION

There has been a long felt want for an effective process for plating tin on various conductive substrates, and particularly for plating directly on aluminum and its alloys. To provide a dense, smooth and strongly adherent coating, it has heretofore been necessary to preplate a reactive base metal such as aluminum with an intermediate layer of a metal such as copper before depositing a tin plate thereon, and even when this was done adhesion of the plate has often been unsatisfactory.

There are many reasons for wanting to plate a base metal such as aluminum with tin or a tin alloy. For example, aluminum bus bars are coated with tin to prevent interruption in the flow of electricity that a build up of nonconductive aluminum oxide on their surface would bring about. Aluminum automotive bearings must be plated with a harder metal because aluminum itself fails badly under the mechanical stresses involved. However, electroplating processes heretofore available for this purpose have been either relatively complex and expensive or relatively ineffective in producing strongly adherent, high quality tin plate. Moreover, the fact that different aluminum alloys behave differently toward the heretofore available tin electrolyte solutions has made tin plating a very difficult process to control and has made it virtually impossible to plate different alloys or combinations of metals in a single bath.

Immersion plating of tin on base metals such as aluminum has been plagued by similar difficulties. For instance, as described in U.S. Pat. No. 2,947,639, when a sodium stannate solution is used to plate aluminum, sodium hydroxide forms in the process which tends to react with the aluminum substrate, liberating hydrogen gas in the process and thereby forming blisters. As suggested in this patent, this tendency to form blisters can be counteracted by including an alkali metal polyphosphate in the solution. However, even this expedient has not been found completely satisfactory as occasional, localized blistering still is likely to occur and plate adhesion as well as plate density have not been as high as desired. More particularly, tin coatings produced in accordance with teachings of the prior art, when tested for their resistance to corrosion showed that the resistivity of the tin plate coupled with the residues of electrolyte, additives, impurities and reaction products on the aluminum surface contributed to the latent activity of the aluminum and led to the formation of blisters due to gas formed by electrolytic reactions, with progressive destruction of the bond between the plate and the substrate.

In the art of electroplating other metals such as antimony or bismuth it has been heretofore suggested that certain improvements in plating quality could be obtained by including in the electrolyte solution various chelating agents such as tartaric acid or gluconic acid or phytic acid or alkali metal salts of ethylene diamine-tetraacetic acid, generally using an alkali metal hydroxide or an alkylolamine base to adjust the pH of the solution to at least 8.5 and preferably between 9 and 11. U.S. Pat. Nos. 2,801,959 and 3,256,160 are representative of these prior teachings. The deposition of tin on stainless steel from a solution comprising tin chloride, sodium phytate and sodium hydroxide at a pH of about 12 has also been disclosed in U.S. Pat. No. 2,973,308. However, attempts to use a similar electrolyte solution in plating tin on aluminum have failed to give good results, either because of an unwanted reaction between the alkali metal hydroxide and the aluminum substrate, or because of the inability of the chelating agent to hold the tin properly in solution, or because of a combination of these and other factors.

Attempts to use a tin plating bath comprising stannous sulfate have also heretofore been generally unsuccessful unless such a bath also contained a chelating agent in an amount substantially approaching or exceeding stoichiometric proportions and was made substantially neutral, as taught in my recently filed copending patent application. In the absence of sufficient free sulfuric acid in the solution, the stannous sulfate quickly hydrolyzes and oxidizes to form a heavy sludge of tin hydroxysulfates and hydrated oxyxulfates. On the other hand, when acidity was raised the resulting solution caused a metal substrate such as aluminum to become excessively active, leading to blistering of the resulting tin plate with loss of adhesion.

OBJECTS AND SUMMARY OF INVENTION

It is an object of this invention to provide a stable tin plating solution capable of producing smooth, continuous, dense and strongly adherent tin deposits on conductive surfaces. A more particular object is to provide such a solution which is capable of use under acid conditions and of producing under such conditions a continuous, corrosion resistant, strongly adherent tin coating on aluminum and aluminum alloys. A still more particular object is to provide such a solution which uses stannous sulfate as the source of tin.

A further object is to provide an improved process for plating tin on conductive surfaces and especially on aluminum or aluminum alloys. Another object is to provide a process wherein tin can be plated on a substrate such as aluminum using stannous sulfate in an acid, nonsludging solution as the source of tin.

As described hereinafter, it has now been discovered that the foregoing and other objects can be effectively and unexpectedly attained by formulating tin plating solutions using a double sulfate, i.e., stannous sulfate and aluminum sulfate and including in the solution some free sulfuric acid and preferably also some chelating sugar acid, in addition to conventional additives such as conditioning and brightening agents.

DESCRIPTION OF INVENTION

According to this invention a clear, stable tin electrolyte solution suitable for plating aluminum as well as other less active substrates can be prepared from stannous sulfate by converting it into a double salt by the addition of aluminum sulfate and free sulfuric acid, and preferably also a chelating agent, especially a chelating sugar acid.

Satisfactory electrolyte solutions of this kind can be prepared containing from about 15 to about 80 grams per liter, preferably from 30 to 70 g.p.l. of dissolved stannous tin and about 0.5 to 2 moles or more, preferably about 0.8 to 1.1 mole, of aluminum sulfate per mole of stannous sulfate, and from about 30 to about 90 g.p.l. free H₂SO₄. The stability of such a solution for electroplating is preferably further increased by adding a small amount of a chelating agent, e.g., a chelating sugar acid, and most preferably gluconic acid. The inclusion of, for instance, 20 to 60 or even 150 grams or more of a chelating agent such as gluconic acid per liter of solution permits raising the H₂SO₄ concentration well above 30 grams per liter and up to 100 grams per liter or more while keeping the activity of aluminum metal to such a solution still low. In contrast, aluminum starts to become active in such solutions at room temperature at H₂SO₄ concentrations above 30 g.p.l. when an effective chelating agent is not present. And such activity increases as the operating temperature is raised. However, the inclusion of a chelating agent is not required if the plating solution contains 30 g.p.l. H₂SO₄ or less. When a chelating agent is used, the chelating sugar acids are preferred and gluconic acid has been found especially effective. However, other chelating agents of the hydroxycarbonylic acid type, such as tarteric aluminum acid, may be used.

The solutions of this invention characteristically are acid, usually possessing a pH of less than 4 or 3 and preferably less than 1.

The solutions prepared in accordance with this invention show increasing improvement in the quality and adhesion of the electrolatines obtained therefrom on aluminum, as well
as increased solution stability, as the mole ratio of aluminum sulfate to stannous sulfate approaches 1. Increasing the ratio above 1 is permissible within the limits of solubility though under most circumstances this does not produce any additional advantage. In addition to increasing the stability of the electrolyte solution, the aluminum sulfate has been found to inhibit the activity of an aluminum substrate exposed to an acid solution of this type.

If small concentrations, on the order of 1 to 6 g.p.l., of sulfates of other metals such as magnesium or zinc can also be practiced and may result in improving the fineness of the tin deposit.

As mentioned above, the stability of the stannous sulfate solution in the form of its double salt with aluminum sulfate, while not perfect, is satisfactory for many purposes when free sulfuric acid is also present. According to the preferred embodiment of the invention, however, practically complete stability of such a solution of aluminized stannous sulfate can be achieved by including in it a small amount of a chelating agent, preferably a chelating sugar acid. Particularly preferred are the hexonic acids, \( CH_2OH(CHOH)_2COOH \), among which are included gluconic, mannoonic, galactonic, talonic, altronic, allonic, and iconic acids. GLuconic acid has been found particularly useful, such chelating agents may be included in the concentration which may range from about 5 to 100 g.p.l., preferably 25 to 60 g.p.l., i.e., in a proportion which equals well under \( \frac{1}{2} \) mole equivalent relative to the tin which is present in solution. Inclusion of such a chelating agent in the solution permits increasing the free \( \text{H}_2\text{SO}_4 \) concentration and consequently the electrochemical efficiency without harm to the quality or adhesion of the tin plate produced from such a solution.

The solutions are somewhat sensitive to temperature and work best in the range between about 15° and about 30° C. in giving electrotiplates of good quality. The presence of the sugar acid affects somewhat this temperature sensitivity and as the concentration of the sugar acid is increased good tin plate quality at normal cathode current densities may be obtained at higher temperatures.

Boric acid, \( \text{H}_3\text{BO}_3 \), may be added to the present electrolyte solutions in concentrations up to 10 g.p.l. or even higher, e.g., 0.5 to 5 g.p.l. and may serve to further improve the fineness and adhesion of the resulting tin plate.

The best order of addition in making up such solution is as follows:

1. Add 30 to 100 parts sulfuric acid (calculated as \( \text{H}_2\text{SO}_4 \)) to enough distilled or demineralized water, e.g., 200 to 600 parts, for sufficient dilution of the strong acid to prevent any degrading reactions with organic additives such as gluconic acid and permit subsequent solution of the required salts.

2. Chelating agent, e.g., 20 to 150 parts gluconic acid.

3. 30 to 100 parts stannous sulfate.

4. Alumina sulfate (0.5 to 2 moles, preferably 0.5 to 1.1 mole, per mole \( \text{SnSO}_4 \)).

5. Conventional conditioning and brightening additives in small amounts.

6. Balance of water to make the solution up to volume, reducing the \( \text{H}_2\text{SO}_4 \) concentration to between about 30 and 100 grams per liter.

If another metal such as nickel in the form of its sulfate is added to the stannous electrolyte solution in the proper proportion, codeposition of a tin alloy (e.g., 72 percent Sn–28 percent Ni) may be obtained with the use of the proper composition anode. For optimum results, an additional amount of the chelating sugar acid and possibly an additional amount of aluminum sulfate as well may be added in such a case in view of the added presence of nickel or other metal ions used to form the desired tin alloy.

The electrolyte of the present invention can be used to form good quality electrotiplates on other conductive surfaces besides aluminum. For instance, the substrate may be a metal casting and assembly or other metal articles fabricated from aluminum, aluminum alloys, iron, nickel, stainless steel, zinc, copper, etc., or from a combination of two or more of any such metals. An exception is magnesium and alloys having a very high magnesium content. Magnesium is too active and displaces tin with evolution of hydrogen fom the electrolyte solutions. The articles being plated may be in various forms, simple or complex shapes, flat sheets of limited area, discs, wires and so on. The tin plates produced are bright, dense, soft, ductile, and generally have good adhesion to the base metal.

To obtain a good quality electrotiplate and to maintain good adhesion of the plate without blunting, it is essential to attain a chemically clean substrate surface with no oxide, hydroxide or any impurity present just before plating. Satisfactory cleaning of aluminum may be obtained, for instance, by immersion of the aluminum in a hot solution of an alkali detergent compound, such as a silicate-free sodium alkybenzene sulfonate, followed by etching at ambient temperature in a caustic alkali solution (e.g., 10 percent concentration), and finally etching in a nonoxidizing acid solution, such as dilute hydrochloric acid solution, preferably one containing 1 to 2 percent of a chelating agent such as citric or gluconic acid. Conventional nonionic wetting agents, such as ethoxy- lated alkyl phenols, may be included in such cleaning solutions. Washing with distilled water after each step is helpful.

The use of ounce from acid or etchants may vary with each size of degreasing power, such as nitric acid, should be avoided to preclude formation of any oxidation residue on the aluminum surface that tends to promote local action and consequently blistering of the tin plate.

Following the electrotiplating, the plated article is desirably washed with distilled or otherwise demineralized water. Böiling distilled water may be used. Drying the plated article in a hot air oven at 100° C. is useful in bringing about complete dehydration and at the same time testing the stability of the tin plate. However, when the tin plate is to be hot flowed, only limited air drying, e.g., at 50° to 60° C., suffices. The formation of aluminum oxide at high temperature may spoil the adhesion of the tin plate.

The tin coatings tend to be slightly crystalline and consequently produce surfaces that are not normally highly brilliant. This type of tin plate is particularly useful where resistance to corrosion and abrasion, or an improvement of surface lubrication properties are desired. The tin plate may be polished or burnedish so as to reduce residual porosity to a minimum. Burning the tin plate with soft tin metal can be used to produce a mirror finish. Flow brightening of the tin and base on aluminum may be achieved if the surface temperature is maintained close to the melting point of the tin and the time of exposure to heat is kept at a minimum. Excessively long exposure of the tin plate to high temperature may cause the formation of a brittle grey tin-aluminum alloy and the breaking away of excess tin in the form of beads. In contrast to the successful flow brightening of tin plate formulated in accordance with the present invention, such flow brightening is impossible when the tin plate is formed from an electrolyte solution containing any amount of an alkali metal such as sodium or potassium, as surface residues of such an alkali metal between the aluminum and the tin cause the melted tin plate literally to explode away from the aluminum.

To obtain tin plate of good quality, it is desirable to keep the cathode current density in the range of from 10 to 40 amperes per square foot, preferably between 15 and 25 amperes per square foot. At higher current densities the tin plate may become excessively crystalline or spongy unless special measures are taken to prevent this, such as causing the cathode surface to move rapidly relative to the electrolyte solution. Under special conditions involving rapid motion of the cathode surface relative to the solution or a short exposure time for thin plates the cathode current density may be increased to 60 amperes per square foot or even higher. In the case of aluminum wires (e.g., 14–17 gauge) or other shapes having a comparably high surface/volume ratio a cathode current density of 40 amperes/square foot and higher is permissible.
ble. Particularly when such wires move through the electrolyte solution at high speed, current densities of 100 amperes/square foot or even more can be used with satisfactory results.

A suitable current density is best determined for each specific situation by preliminary routine screening tests. Cathode current efficiencies in the order of 90 percent and up may be readily achieved. When the electrolyte solution is agitated while the plating operation is in progress, it is advisable to conduct the agitation in a manner such that air bubbles are not substantially entrained in the solution. Air in contact with the cathode tends to spoil the quality of the tin plate, particularly its homogeneity and adhesion.

For best results, the ratio of the area of the tin anode to the area of the cathode being plated should be at least 2:1. A ratio of about 3:1 is preferred in typical operations, but higher ratios may be used.

The fineness and brightness of the tin plate from the complex electrolyte solutions of this invention can be further improved in the usual manner by the addition of various brightening and conditioning agents. It is important, however, not to add such agents in the form of their alkali metal salts. Beta-naphthol at about between 0.5 and 2.0 grams per liter is very effective. Water soluble polyalkylene glycols such as the soluble polyethylene glycols (e.g., "Carbowax 1500," M.W. about 1500) or polypropylene glycols at a concentration of from between 0.5 to 1.0 grams per liter or higher are suitable. These polyglycols typically have a molecular weight from about 900 to about 6000 but polyglycols of higher or lower molecular weight may be used. Formamide and dimethyl formamide are useful in concentrations in the range from 0.5 to 20 grams per liter of solution.

Low concentrations of approximately 0.1 to 0.5 g.p.l. or more of glue, gelatin, peptone, or other components of these substances such as glycine, hydroxypropylene, lysine, arginine, etc. are effective. Small concentrations of alkyl or aryl amines, e.g., triethylenamine, diethyl amine and the like, also can be used to enhance tin plate quality. Conventional additives that tend to coat the cathode, e.g., wood tar extracts, aldehyde-amine complexes or any other substance that tends to form tar or a semisublebe polymeric suspensoid, should be avoided. Such coating of the cathode is undesirable in that it promotes local galvanic action with consequent gas formation, blistering and loss of adhesion of the tin plate.

ILLUSTRATIVE EMBODIMENTS

In order to exemplify the invention more particularly, described below in table I is the composition of the ammated stannous sulfate electrolyte solutions formulated in accordance with this invention which give particularly good performance in electroplating tin on aluminum or its alloys. Unless otherwise indicated, all proportions and percentages are expressed on a weight basis throughout this specifications.

### TABLE I

<table>
<thead>
<tr>
<th>Component</th>
<th>Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Representative Range</td>
</tr>
<tr>
<td></td>
<td>Typical</td>
</tr>
<tr>
<td>Stannous Sulfate</td>
<td>30-100 g/l.</td>
</tr>
<tr>
<td>( \text{Sn}^{2+} )</td>
<td>0.5 to 1.0 mole per mole ( \text{SnSO}_4 )</td>
</tr>
<tr>
<td>Free H(_2)SO(_4)</td>
<td>30-100 g/l.</td>
</tr>
<tr>
<td>Sugar Acid</td>
<td>20-60 g/l.</td>
</tr>
<tr>
<td>Conditioner</td>
<td>0.5-2.0 g/l.</td>
</tr>
</tbody>
</table>

### TABLE II

<table>
<thead>
<tr>
<th>Run No.</th>
<th>1</th>
<th>2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solution pH</td>
<td>less than 1</td>
<td>less than 1</td>
</tr>
<tr>
<td>Cathode</td>
<td>Sheet aluminum rectangle</td>
<td>Sheet aluminum rectangle</td>
</tr>
<tr>
<td>Cathode area, cm.(^2)</td>
<td>25</td>
<td>25</td>
</tr>
<tr>
<td>Solution temperature, C</td>
<td>31.6</td>
<td>32.0</td>
</tr>
<tr>
<td>Time, min.</td>
<td>12</td>
<td>18</td>
</tr>
<tr>
<td>Cell potential, volts</td>
<td>0.25</td>
<td>0.27</td>
</tr>
<tr>
<td>Cathode current density, amp./ft.</td>
<td>26.8</td>
<td>26.8</td>
</tr>
<tr>
<td>Nominal tinplate thickness, mil.</td>
<td>0.66</td>
<td>0.99</td>
</tr>
<tr>
<td>Tinplate quality</td>
<td>Smooth, bright white with excellent adhesion</td>
<td>Smooth, bright white with excellent adhesion</td>
</tr>
</tbody>
</table>

The two runs were conducted under very similar conditions except that the duration of the second run was 18 minutes whereas the duration of the first run was only 12 minutes. In both cases excellent plating quality was obtained. The plate thickness in Run No. 2 was about 50 percent greater than in Run No. 1, substantially in proportion to the duration of the run.

In electroplating tin on aluminum from electrolyte solutions of the kind described herein a cell potential ranging from about 0.2 to 1.5 volts has been found suitable. The optimum value may, of course, vary considerably from case to case depending on electrochemical characteristics such as the specific resistance of the particular solution, the operating temperature as well as the physical arrangement of the particular apparatus used. Consequently, an actual working potential above or below the range cited may give satisfactory results when working under different conditions or with a different apparatus than that used herein. The optimum value is readily established for each specific case by routine preliminary tests. At any rate, under proper conditions tin plate of good bright quality and good adhesion may thus be electroplated on a substrate such as aluminum in a thickness which typically may range from about 0.4 to about 1 mil.

Brightening and conditioning agents which may be used in the novel solutions disclosed herein include the following:

- Hydroquinone, to improve brightness, fineness and adhesion.
- Ethylene glycol, to improve solubility of low solubility additives such as beta-naphthol, and enhance brightness, fineness and adhesion.
- 2-naphthol-6-sulfonic acid, a wetting agent which increases covering power, brightness, fineness and adhesion.
- Formamide, greatly improves the brightness, fineness and especially adhesion of the tin plate with outstanding improvement in the quality and adhesion of flame floved tin plates.
- Dimethyl formamide, similar to formamide but even more effective.
- Polyalkylene glycols, improve fineness and brightness.

As indicated above, formamide and especially dimethyl formamide have displayed remarkable effects on the electrolyte
solutions and the electrotinplates on aluminum. Their solvent and electrolyte properties increased the solubility of other additives such as beta-naphthol and their effects on tin plate quality and greatly improved the adhesion of the tin plate. Other homologs of the formamide series may be used similarly.

Among the wetting agents, 2-naphthol-6-sulfonic acid is particularly preferred because of its high effectiveness in increasing covering power, brightness, fineness and adhesion. However, other wetting agents known in the metal plating art may be used similarly, e.g., cresol sulfonic acid, beta-naphthol sulfonic acid, etc. The only kind of wetting agent which has been found to be undesirable for use in connection with the present invention are alkali metal containing compounds.

When a tin plate of particularly high quality in terms of adhesion and absence of porosity is desired, various auxiliary expedients can be resorted to. For instance, greatly improved adhesion of the electrotinplate can be obtained by firstimmersing the clean etched aluminum in the tin electrolyte solution for at least 1 minute, e.g., for 1 to 10 minutes, before turning on the plating current. An almost imperceptible layer of tin deposited in the galvanic preplating step by a nonpassing immersions plating reaction is surprisingly effective in improving the quality of the electrotinplate deposits on tin.

Preplating with copper is beneficial when maximum adhesion is wanted. Of course, when the copper plated aluminum piece is immersed in the acid stannous solution, the current should be on and the piece should stay in a cathodic condition as otherwise the copper plate would tend to dissolve. Copper preplating improves the ease with which the tin plate can be flown brightened and increases corrosion resistance of the brightened tin. Preplating with copper also permits the resulting product to be readily and effectively soldered.

Tin plate quality can also be improved by rubbing a tin cathode at its point contact over the thoroughly air dried electrotinplate while conducting direct current of 1 to 15 amperes, e.g., 8 amperes, to the tin plate as an anode and thus releasing a considerable amount of heat. This semiwelding treatment improves the bond of the tin plate to the aluminum. The direction of the direct current can be reversed making the tin plate the cathode, but the bonding is usually less effective with this arrangement. As still another alternative, alternating current can be used in such semiwelding treatment.

A very significant reduction of tin plate porosity can also be obtained by naturally reducing natural gas flame to the tinplate after it has been air dried or by using infrared or especially induction microwave or radio frequency heating or any other existing electronic heating method which causes the tin plate to flow and become strongly bonded to the aluminum substrate. Heating the tinplate to a temperature above the melting point of the plated tin or tin alloy, e.g., to a temperature between about 232° and 280° C. is satisfactory. To obtain a substantially even, homogeneous tin coating it is desirable to control the melting time as short as possible. The optimum treating is readily determined for each type of tin plate by routine preliminary tests.

Heating in an atmosphere of nitrogen or other inert gas such as argon is beneficial, or the heating may be conducted under substantially reduced pressure so as to minimize any deleterious effect of oxygen.

Two or more of the treating methods described above may be combined for producing the desired final improvement in tin plate quality. In fact, the semiweld treatment described above may be modified so that the welding current simultaneously accomplishes the desired flowing of the tin plate. Electric resistance heating may also be used to fuse and flow the deposited tin plate on the copper substrate. Plasmas, flame torches, ultrasonic welding and explosive bonding may also be used.

The corrosion resistance of the electrotinplate may also be very greatly increased without appreciable loss of electric conductivity by applying a solution of any convenient insulating resin or polymer to the tin coating and then baking the tin plate. For instance, electrotinplates formed on aluminum in a thickness of between about 0.4 and 1.0 mils, after being air dried, may be dipped once or several times, with intermediate air drying, in solutions or dispersions containing 10 to 40 grams/liter of acrylic or polyvinyl-acrylic resin (such as polyvinylmethacrylate or a vinylidene chloride-acrylonitrile copolymer), in a suitable solvent such as methyl ethyl ketone or methyl isobutyl ketone. After such dipping the tinplate may be baked in a furnace at a temperature in the range from about 100° to 150° C. As long as the area density of the resin is minimized the electric conductivity on the tin plate remains substantially unimpaired.

In comparison with untreated electrotinplates on aluminum, the resin coated tin plates show exceptionally high resistance to corrosion even when exposed to an aerated agitated 20 percent NaCl solution and the specimen being tested is coupled by wire to a generator. Other resins such as polyethylene in ketone solution as well as other insulating resins such as phenol-formaldehydencondensates, polyurethanes, epoxy resins, polyvinyl chloride, poly styrene, silicone resins and so forth may be used similarly. However, chlorinated hydrocarbon solvents such as methylene chloride or trichloroethylene should be avoided as the solvents for resin being applied, as such chlorinated solvents are too active to the metals and cause degradation of the tin plate with loss of resistance to corrosion. Use of oxygen-containing solvents such as the lower ketones, alcohols such as methanol, isopropyl alcohol or amyl alcohol, as well as the glycol ethers is preferred. Of course, an appropriate solvent must be selected for each resin so as to make certain that the resin used will readily dissolve therein.

Although the electrotinplate solutions disclosed herein have been developed principally for electrolytic or galvanic plating of tin directly on aluminum, they are also useful for plating in multiple applications where intermediate layers of metals such as copper are plated on the aluminum to lower the activity of the base metal. The low activity of the nearly neutral solutions of the present invention may be valuable for limiting latent activity in tin plate on intermediate plates, thus promoting a more stable tin coating. These properties of the electrotinplate solutions are also beneficial in plating tin on conditioned plastics where very corrosive or active solutions are not desirable.

It should be understood that the foregoing description and examples have been presented principally for purposes of illustration and not for purposes of limitation. The invention for which protection is desired is particularly pointed out in the appended claims.

1. A neuous solution for the electropainting or galvanic plating of tin on a conductive substrate, which solution comprises (a) about 30 to about 100 grams SnSO₄ per liter, (b) about 0.5 to about 2 moles A₄(SO₄)₆ per mole of SnSO₄, (c) about 30 to about 100 grams free H₂SO₄ per liter, and (d) about 20 to 150 grams of a chelating sugar acid per liter.

2. A neuous solution according to claim 1 which comprises (a) about 40 to about 80 grams SnSO₄ per liter, (b) about 0.5 to 1.1 mole A₄(SO₄)₆ per mole of SnSO₄, (c) about 30 to about 100 grams H₂SO₄ per liter, and (d) about 20 to 150 grams of a chelating sugar acid per liter, said solution having a pH of less than 4.

3. A neuous solution according to claim 2 wherein the sugar acid is a hexonic acid and which also comprises about 0.2 to 2 grams per liter of polyethylene glycol of molecular weight between about 900 and 3000.

4. An aqueous solution according to claim 2 which contains 0.5 to 60 grams per liter of gluconic acid as said sugar acid.

5. An aqueous solution according to claim 1 which further comprises 0.5 to 20 grams per liter of formamide or dimethylformamide.

6. A process for making an aqueous solution of a stannous salt suitable for tin electropainting, which process comprises making up an aqueous sulfuric acid solution containing 30 to
100 parts by weight of $\text{H}_2\text{SO}_4$ and water in the range between about 200 and 600 parts by weight, the acid solution being sufficiently dilute to dissolve the subsequently recited ingredients, dissolving in said sulfuric acid solution 20 to 150 parts by weight of a chelating sugar acid, 30 to 100 parts by weight of SnSO$_4$, and 0.5 to 1.1 mole Al$_2$(SO$_4$)$_3$ per mole SnSO$_4$, and adding water to the resulting solution to reduce the $\text{H}_2\text{SO}_4$ concentration therein to not more than 100 grams per liter.

7. A process for the electroplating or galvanic plating of tin on an electrically conductive cathodic substrate which comprises immersing a tin anode and said substrate in an aqueous plating solution containing (a) about 30 to about 100 grams SnSO$_4$ per liter, (b) about 0.5 to about 2 moles Al$_2$(SO$_4$)$_3$ per mole of SnSO$_4$, (c) about 30 to about 100 grams free $\text{H}_2\text{SO}_4$ per liter and (d) about 20 to 150 grams of a chelating sugar acid per liter and (e) about 20 to 150 grams of a chelating sugar acid per liter.

8. A process according to claim 7 wherein (i) said substrate comprises a surface of aluminum or aluminum alloy, (ii) electric current is set up between it and said tin anode to give a cathode current density of between about 10 and 100 amperes per square foot, and (iii) said plating solution contains 30 to 100 grams per liter SnSO$_4$, 0.5 to 1.1 mole Al$_2$(SO$_4$)$_3$ per mole of SnSO$_4$, 30 to 100 grams per liter $\text{H}_2\text{SO}_4$, and 20 to 60 grams of a chelating hexonic acid.

9. A process according to claim 8 wherein the hexonic acid in said plating solution is gluconic acid, wherein said solution additionally contains 0.2 to 2 grams per liter of polyethylene glycol of molecular weight between about 900 and 3000 and between 0.5 to 20 grams per liter of dimethylformamide or formamide, and cathode current density is maintained between about 10 and 40 amperes per square foot.

10. A process according to claim 8 wherein said aluminum-containing substrate is moved rapidly through said plating solution and cathode current density is maintained above 40 and below 60 amperes per square foot.

11. A process according to claim 8 wherein said substrate is an aluminum-containing metal wire and cathode current density is maintained above 40 and below 100 amperes per square foot.

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