

PATENT SPECIFICATION

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(54) TIN ELECTROPLATING BATHS

(71) We, KENVERT INTERNATIONAL CORPORATION, a Corporation organised and existing under the laws of the State of Connecticut, United States of America, of 210 East Main Street, Rockville, Connecticut 06066, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to electroplating and more particularly it relates to an aqueous bath for electroplating tin upon various conductive substrates and electroplating processes using such a bath.

A variety of baths have been proposed for electrodepositing tin upon metallic substrates, possibly the most widely used of which are the stannous fluoborate and caustic stannate solutions. Although these proposed baths have proved generally satisfactory and have been widely utilized, they are usually deficient in one or more desirable operating characteristics and the deposits which they produce frequently fail to provide a desirable balance of brightness, smoothness, ductility, adherence, solderability, porosity and stability, to ageing. Some of the baths are relatively expensive and many tend to be difficult to maintain since fairly critical control of the concentrations of the components thereof is normally required. Recent efforts to provide bright tin deposits are described by P. Baeyens and G. Krijl in "Philips Formaldehyde Bright Tin", in TRANSACTIONS OF THE INSTITUTE OF METAL FINISHING, 1967, Volume 45, at Pages 115—121, and in United States Patent No. 3,361,562.

Although various of the baths which have been proposed are operable with varying degrees of efficiency and effectiveness, there has, nevertheless, remained a need to develop a bath capable of producing smooth adherent deposits which exhibit spectral brightness and in which there is considerable stability of the components. Moreover, there has been a continuing need to provide baths which are relatively economical in that the primary

and secondary brighteners or surface active agents employed therein are not excessively consumed.

It is an object of the present invention to provide an improved aqueous bath for electrodepositing tin upon a conductive substrate.

According to the present invention there is provided an aqueous acid bath containing from 10.0 to 50.0 grams per litre of stannous ion; from 100.0 to 250.0 grams per litre of sulphate radical; from 0.2 to 20.0 grams per litre of a surface active agent which is one or more imidazoline derivatives or a mixture of one or more imidazoline derivatives with a condensate of an alkyl phenol having an alkyl chain of 6 to 12 carbon atoms with ethylene oxide and/or propylene oxide; and from 0.005 to 1.0 gram per litre of a heterocyclic carboxaldehyde wherein the heterocyclic ring has five members and the carboxaldehyde group is attached to a carbon atom in the ring. The bath is highly acid and contains from 1.5 to 4.5 grams per litre of hydrogen ion.

The preferred baths contain an imidazoline derivative in combination with the alkyl phenol-alkylene oxide condensate since such a combination makes possible electrodeposits exhibiting spectral brightness over a wide range of current density. The baths are useful for still and barrel plating and are operable over a fairly wide range of current density.

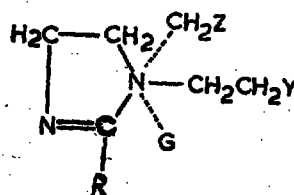
The aqueous bath is suitably prepared and maintained at a temperature of from 45 to 135° Fahrenheit. The workpiece which has a conductive surface and a suitable high-purity tin anode are immersed in the bath and a voltage is applied to provide a current density from 0.5 to 150.0 amperes per square foot at the surface of the workpiece. As a result, a smooth, adherent, ductile deposit of tin is produced which may vary from bright to spectral bright depending upon the current density and whether the optimum formulation is employed for a given set of conditions, as will be pointed out more fully hereinafter.

The acid baths of the present invention

require the stannous ion, the sulphate radical, an imidazoline derivative and the heterocyclic aldehyde for proper operation. The stannous ion and the sulphate radical may be supplied to the bath by any combination of compounds suitable for use in tin plating solutions, but to avoid the presence of unnecessary and possibly interfering ions, these components are desirably introduced in the form of stannous sulphate and sulphuric acid. As is apparent, the former compound will provide both the stannous ion and the sulphate radical, whereas the latter compound provides additional sulphate radical which is present in the bath. The use of sulphuric acid is also desirable from the standpoint of control of the hydrogen ion concentration, although other acids providing non-interfering radicals may also be used for that purpose. Tin compounds other than stannous sulphate, e.g. stannous fluoborate, may be employed, but preferably they are used in amounts of not more than 50 per cent by weight of the sulphate compound, and preferably less than 20 per cent by weight thereof.

Although the amount of stannous ion present in the baths can vary from 10.0 to 50.0 grams per litre, it is preferably from 12.0 to 20.0 grams per litre. Similarly, although the concentration of sulphate ion can normally be from 100.0 to 250.0 grams per litre, it is preferably from 175.0 to 225.0 grams per litre. Although a broad range of from 1.5 to 4.5 grams per litre is suitable for the hydrogen ion concentration, it is most desirably maintained at from 2.5 to 3.5 grams per litre. If the concentration of stannous ion in the bath is too low, the efficiency of plating and the quality of the deposit produced will be unsatisfactory at the low current density area and burning will be apparent at the high density area. On the other hand, although high levels of this ion permit desirable deposits to be obtained at higher current densities, too high a stannous ion concentration tends to result in the formation of a very poor deposit at low current density and to minimize the benefit afforded by the brightener system. Maintaining the sulphate radical and the hydrogen ion within the ranges of concentrations specified will ensure that the bath operates efficiently to produce the type of deposits desired.

In addition to the stannous ion and sulphate radical, the acid baths of the present invention require an effective amount of a surface-active agent which may be one or more imidazoline derivatives alone or, preferably, a combination of imidazoline derivative with the condensate of an alkyl phenol and the alkylene oxide. The imidazoline derivatives employed are of the general formula:



in which R is an alkyl radical having from 5 to 24 carbon atoms; G is —OH ion, an acid salt radical, an anionic surface-active sulphate salt radical (such as, preferably, the radical —OSO₂—OR), of an anionic surface-active sulphonate salt radical; Z is a group —COOM, —CH₂COOM, or —CHOH—CH₂SO₃M (in which M is a hydrogen atom, an alkali metal atom or an organic base); and Y is either a group —OR' or a group —N(R')_nA in which each R' substituent is a hydrogen or alkali metal atom or a group —(CH₂)_nCOOM, A is an anionic monovalent radical and n is a integer from 1 to 4).

The use of the dotted line representation for the bonds connecting the substituents G and CH₂Z to the nitrogen atom in the formula indicates that these substituents are optionally present or absent, but it should be understood that they are either both present or both absent. Desirable compounds are provided when, in accordance with the foregoing formula, G represents a radical —O—SO₂—OR, (particularly one in which R is a C₁₈ to C₁₀ alkyl group) and Z is a —COOM radical in which M is preferably an alkali metal atom.

Examples of the compounds corresponding to the foregoing formula which are satisfactory for use in the baths of the invention are 2 - alkyl - 1 - (ethyl - beta - oxy - propanoic acid) imidazolines wherein the alkyl group is capryl, undecyl or a mixture of C₇—C₁₇ chains, and the disodium salt of lauroyl - cycloimidinium - 1 - ethoxyethanoic acid-2-ethanoic acid.

Although the imidazoline derivatives provide a desirable degree of brightening when used alone, generally the full advantages of the present invention can be attained only by use of imidazoline derivatives in combination with the condensate of an alkyl phenol and the alkylene oxide. The alkylene oxide will suitably be present in a molar ratio relative to the alkyl phenol of from 8:1 to 25:1 and is ethylene oxide, propylene oxide or a mixture thereof. The alkyl substituent on the phenol has a carbon chain of 6 to 12 carbon atoms and preferably of 8 to 10 carbon atoms.

Examples of the alkyl phenol/alkylene oxide condensates include octyl phenoxy

polyethoxy ethanols and nonyl phenoxy polyethoxy ethanols with the preferred agents being nonyl phenoxy polyethoxy ethanols having a molar ratio of ethylene oxide to nonyl phenol of from 9:1 to 20:1.

The total concentration of the surface-active agent can vary from 0.2 to 20.0 grams per litre and is preferably from 1.0 to 4.0 grams per litre. As indicated above, the preferred surface-active agents are, in fact, a combination of the imidazoline derivative and the alkyl phenol/alkylene oxide condensate. Particularly beneficial results have been obtained by the use of the imidazoline derivative in an amount of from 1.0 to 2.5 grams per litre and the alkyl phenol/alkylene oxide condensate in an amount of from 0.1 to 1.0 grams per litre.

It has further been found that the best results with the imidazoline derivatives are obtained by using combinations of such derivatives. Particularly significant benefits are obtained by a mixture of (A) an imidazoline derivative of the above formula wherein the groups $-G$ and $-CH_2Z$ are both omitted and Y is $-N[(CH_2)_n-COOH]_2Cl$, n being from 1 to 4; and (B) an imidazoline derivative wherein $-G$ is OH , $-Y$ is $-O(CH_2)_mCOOM$ and Z is $-(CH_2)_mCOOM$; n being from 1 to 4 and m being 0 or 1 and M being an alkali metal atom. A highly beneficial system is that obtained by a mixture of an imidazoline derivative corresponding to the aforementioned general formula wherein Z is $COONa$, $-G$ is OH , and Y is OCH_2COONa ; and a second imidazoline wherein the groups G and $-CH_2Z$ are omitted and Y is $-N(CH_2CH_2COOH)_2(CH_2COOH)Cl$. The first-mentioned imidazoline derivative is suitably provided in a weight ratio of from 1:1 to 8:1 relative to the second-mentioned imidazoline derivative and preferably in a ratio of from 4.5:1 to 6.5:1.

The other essential component in the baths of the invention is the heterocyclic carboxaldehyde which acts as a primary brightener. As indicated hereinbefore, the heterocyclic ring is five membered and may be based upon thiophene, furan and pyrroles. The carboxaldehyde group is attached to one of the carbons in the ring which generally will be in the 2-position, and the preferred compounds are those in which a simple carboxaldehyde group ($-CHO$) is employed although longer carbon chain carboxaldehydes may also be employed; in addition, the carboxaldehydes may be ring- or chain-substituted materials. Specific heterocyclic carboxaldehydes which have proved highly effective are furfural (2-furaldehyde), 2-thiophene carboxaldehyde and 2-pyrrole carboxaldehyde.

Although beneficial results have been obtained by the incorporation of the heterocyclic carboxaldehydes in amounts as little

as 0.005 grams per litre, the brightener is preferably included in amounts of at least 0.01 and desirably at least 0.05 grams per litre. As the amount of aldehyde is increased above 0.5 gram per liter, there is a greater difficulty in controlling the operation of the bath. Above 1.0 gram per litre, pitting and burning become quite evident and the low current density area on a test panel is no longer bright. Accordingly, the baths preferably contain the aldehyde compounds in amounts of from 0.05 to 0.5 gram per litre.

Since some of the heterocyclic carboxaldehydes have a relatively low solubility in the acid bath, it may be necessary to employ an organic solvent solution thereof to facilitate formation of the bath composition. Among the various solvents which may be employed, depending upon the particular aldehyde selected, are the low molecular weight alkalons containing up to 4 carbon atoms (e.g. methanol, ethanol and propanol) and the low molecular weight glycol ethers containing up to 10 carbon atoms (e.g. ethylene glycol monoethyl ether). Generally, the aldehyde is added to the solvent in amounts of from 1.0 to 50.0 grams per litre thereof and preferably in amounts of from 5.0 to 25.0 grams per litre thereof and preferably in amounts of from 5.0 to 25.0 grams per litre, so as to obtain a stable solvent solution which may be readily dispersed in the acid bath.

In addition to the components described hereinbefore, other additives may be included in the bath to modify the operation thereof, such as auxiliary brighteners, surface-active agents and chelating agents. However, it has generally been found that the bath desirably operates without such additional components.

Examples of the auxiliary brighteners which may be added are the aryl aldehydes (e.g. benzaldehyde and cinnamaldehyde), polyvinyl alcohol and carbocyclic and heterocyclic ketones (e.g. benzylideneacetone, furylideneacetone and pyridylideneacetone). Generally, such auxiliary brighteners should be added in amounts of less than 1.0 gram per litre and preferably less than 0.2 gram per litre.

Although no apparent tendency for the formation of metal sludge and precipitate has been noted in properly operated baths, for some applications it may be desirable to incorporate a chelating agent such as citric acid, malic acid or an aminopolyacetic acid (e.g. ethylenediamine tetraacetic acid, diethylenetriamine pentaacetic acid and nitrilotriacetic acid). Such chelating agents, when employed, are generally included in an amount of from 5.0 to 20.0 grams per litre.

As has been indicated previously, the baths of the present invention are operable over a relatively wide range of cathode current density. More specifically, the operable range is

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generally from 0.5 to 150 amperes per square foot (ASF) and preferably from 1 to 45 ASF, with a narrower range of from 10 to 30 ASF being most desirable for barrel plating operation. The plating efficiency is generally quite high and will range up to 98 per cent, based upon the theoretical rate of deposition, at current densities below 15 amperes per square foot. In order to obtain optimum results, the anode:cathode area ratio is suitably from 1.0:1.0 to 3.0:1.0, and is preferably about 2.0:1.0. Moreover, the anode current density should not exceed 15 ASF since there is an apparent tendency for polarization of the anode, for the brightener to become unstable and for formation of tetravalent tin. The applied voltage is preferably from 0.2 to 5.0 volts and is preferably from 0.5 to 4.0 volts.

The baths should suitably be operated at a temperature from 45 to 135° Fahrenheit, and preferably from 55 to 85° Fahrenheit. Operation below 45° Fahrenheit tends to be inefficient and to produce undesirable deposits, whereas temperatures higher than 135° Fahrenheit tend to produce dull, rough and generally unacceptable deposits.

Any metallic substrate or metal-surfaced article which can be plated with tin using prior art baths may be coated in accordance with the present invention. For example, good deposits of tin may be produced upon articles of copper, nickel, iron and steel. The best results are obtainable with these baths if relatively pure tin anodes are employed.

Agitation is desirable to obtain deposits which are uniform and of high quality and to avoid development of sludge or film. Not only is agitation of the bath itself desirable but agitation of the cathode may be desirable to obtain a uniform plate and to enable extension of the range of satisfactory current density to higher levels.

The process is adapted to both still plating and barrel plating apparatus with equal efficacy. Filtration of the bath is not essential but will normally be beneficial when contamination of the bath is encountered due to airborne impurities and carryover from other finishing operations. Various filtering media may be utilized including fabric, porous stoneware and other conventional filtering materials.

The depletion of the various components of the bath is best corrected by analysis for the several components on a periodic basis which can be established for a given facility. To determine the necessity for the addition of a surface-active agent, the best procedure is to evaluate a sample of the bath in a suitable test cell, and a suitable schedule may be established for a given facility and workpiece. To determine the amounts of stannous salt required, a 0.1 N potassium iodate solution and an 1.0 per cent solution

of starch may be used for titration. The free sulphuric acid concentration may be determined by simple titration procedures with a suitable indicator such as thymolphthalein. The amount of brightener required is best evaluated by testing a sample of the bath in a suitable test cell.

In order that the invention may be well understood the following Examples are given by way of illustration only. In the Examples all parts are parts by weight unless otherwise indicated.

EXAMPLE 1

An aqueous bath is required containing 30.0 grams per litre of stannous sulphate, 108.0 millilitres per litre of sulphuric acid (specific gravity 1.84), 0.6 gram per litre of an imidazoline derivative of the formula above wherein the groups —G and —CH₂Z are omitted and Y is a group —N(CH₂CH₂COOH)₂(CH₂COOH)Cl, 0.1 gram per litre of an imidazoline derivative wherein Z is —COONa, —G is —OH, and —Y is —OCH₂COONa, and 0.25 gram per litre of an ethylene oxide/octyl phenol condensate having a molar ratio of about 10.0:1.0, and 0.08 gram per litre of thiophene aldehyde. The bath was introduced into a barrel plating apparatus and maintained at a temperature of about 68° Fahrenheit.

Into the bath were introduced small integrated circuit packages fabricated of a ferrous alloy containing cobalt, nickel and manganese. The packages had a length of about 3/4 inch and a cross-section of about 1/2 inch by 1/2 inch. A pure tin anode providing an anode to cathode ratio of about 1.0:1.0 was used and a potential of 2 volts was applied across the plating barrel with a current of about 25.0 amperes. The average cathode current density was estimated at about 7.5 ASF because of the complexity of the part.

After about 12.5 minutes the printed circuit packages were removed from the bath and were found to have an electroplated tin deposit of about 0.3 mil. thick. The deposit was spectral bright in all current density areas of the parts and was free from burning. The deposit was also found to be highly adherent.

EXAMPLE 2

The procedure of Example 1 was substantially repeated utilizing transistors with wire leads. The cathode current density was calculated to average about 15 ASF. Upon removal from the bath, the transistors and the wire leads were found to be plated with a spectral bright tin deposit of about 0.3 mil. thick. Flexing of the leads did not produce any evidence of cracking of the plated deposit or of lack of adherence of the deposit to the substrate.

EXAMPLE 3

The procedure of Example 1 was again repeated utilizing as the parts being treated sheet metal and wood screw fasteners fabricated from a steel alloy. The average cathode current density was calculated at about 15 ASF and the parts were found to have a spectral bright, adherent tin deposit of about 0.3 mil thick over their entire surface area.

EXAMPLE 4

In a rack plating tank were placed bearings fabricated of steel with a bonded aluminium backing. The bath was that of Example 1 and in this instance was maintained at a temperature of about 60° Fahrenheit and the current applied across the tank was calculated to produce an average cathode current density of about 25 ASF. After 12 minutes, the parts were removed and were found to have a spectral bright tin deposit of about 0.5 mils thick. The deposit was ductile and highly adherent to the steel portion of the bearings although adherence to the aluminium backing was typically poor as can be anticipated for an electroplated tin deposit on aluminium.

EXAMPLE 5

The procedure of Example 4 was repeated utilizing printed circuit boards fabricated of copper with a screened resist pattern. The temperature of the bath was maintained at about 68° Fahrenheit and the cathode current density was calculated to average 15 ASF. After 11.5 minutes, the parts were removed from the bath and found to have a spectral bright, highly adherent tin deposit of about 0.3 mil thick over the resist-free areas.

EXAMPLE 6

Part A
The bath of Example 1 was tested in a rotary test cell manufactured by Conversion Chemical Corporation of Rockville, Connecticut in accordance with United States Patent No. 3,215,609. The test panels were cleaned steel and the potential applied across the cell was 1.0 volt developing an amperage of about 1.5. The temperature was maintained at about 68° Fahrenheit and after plating for 6 minutes, the test panels were removed and found to be bright over the entire range of 0.5 to 100.0 amperes per square foot.

Part B

The procedure of Example 6A was repeated substituting for the thiophene aldehyde an equal amount of pyrrole aldehyde. Again, the test panels were found to be spectral bright throughout the current density range of 5.0 to 100.0 ASF, but a slight foginess tending to reduce the otherwise brilliant

lustre was apparent in the area below 5.0 ASF.

Part C

The procedure of Example 6A was again repeated substituting furfural for the thiophene aldehyde. Again, the test panels were bright over the plating range of 0.5 to 100.0 amperes per square foot but a slight fog in the entire plating range tended to reduce the otherwise brilliant lustre.

EXAMPLE 7

The procedure of Example 6A was repeated omitting the ethylene oxide/octyl phenol condensate. In this instance, the test panels were found to have a spectral bright tin deposit in the range of 25.0 to 100.0 ASF. Below 25.0 ASF, there were portions of the test panels which were unplated indicating a tendency toward skip plating in the lower current density areas. However, the plated deposits were spectral bright. This and related tests indicate the very significant benefits to be obtained by combining the imidazoline derivatives with the alkyl phenol/alkylene oxide condensates.

EXAMPLE 8

The procedure of Example 6A was repeated omitting from the bath the second-mentioned imidazoline derivative. In this instance, the plated deposit was uniform and adherent throughout the current density range of 1.0 to 100.0 ASF. Although the deposit was bright or non-matte in character, it was not so spectral bright as that obtained by the combination of the imidazoline derivatives in the preferred bath of Example 1.

EXAMPLE 9

The procedure of Example 6A was repeated utilizing a standard Hull cell. The temperature of the bath was maintained at about 90° Fahrenheit and a voltage of about 3.0 was applied across the cell. After plating for about 3.0 minutes, the test panels were found to have a spectral bright, adherent tin deposit over a range of about 25.0 to 135.0 ASF.

Thus, it can be seen that the present invention provides a highly effective bath for electroplating tin on various metallic substrates. The deposits are adherent and ductile and may vary from bright to spectral bright depending upon whether the optimum formulations are employed. Various types of parts may be readily plated over a relatively wide range of current density.

WHAT WE CLAIM IS:—

1. An aqueous acid electroplating bath for producing an adherent electroplated tin deposit comprising from 10.0 to 50.0 grams per litre of stannous ion; from 100.0 to 250.0

**EXAMPLE 3**

The procedure of Example 1 was again repeated utilizing as the parts being treated sheet metal and wood screw fasteners fabricated from a steel alloy. The average cathode current density was calculated at about 15 ASF and the parts were found to have a spectral bright, adherent tin deposit of about 0.3 mil thick over their entire surface area.

EXAMPLE 4

In a rack plating tank were placed bearings fabricated of steel with a bonded aluminium backing. The bath was that of Example 1 and in this instance was maintained at a temperature of about 60° Fahrenheit and the current applied across the tank was calculated to produce an average cathode current density of about 25 ASF. After 12 minutes, the parts were removed and were found to have a spectral bright tin deposit of about 0.5 mils thick. The deposit was ductile and highly adherent to the steel portion of the bearings although adherence to the aluminium backing was typically poor as can be anticipated for an electroplated tin deposit on aluminium.

EXAMPLE 5

The procedure of Example 4 was repeated utilizing printed circuit boards fabricated of copper with a screened resist pattern. The temperature of the bath was maintained at about 68° Fahrenheit and the cathode current density was calculated to average 15 ASF. After 11.5 minutes, the parts were removed from the bath and found to have a spectral bright, highly adherent tin deposit of about 0.3 mil thick over the resist-free areas.

EXAMPLE 6**Part A**

The bath of Example 1 was tested in a rotary test cell manufactured by Conversion Chemical Corporation of Rockville, Connecticut in accordance with United States Patent No. 3,215,609. The test panels were cleaned steel and the potential applied across the cell was 1.0 volt developing an amperage of about 1.5. The temperature was maintained at about 68° Fahrenheit and after plating for 6 minutes, the test panels were removed and found to be bright over the entire range of 0.5 to 100.0 amperes per square foot.

Part B

The procedure of Example 6A was repeated substituting for the thiophene aldehyde an equal amount of pyrrole aldehyde. Again, the test panels were found to be spectral bright throughout the current density range of 5.0 to 100.0 ASF, but a slight fog-giness tending to reduce the otherwise brilli-

ant lustre was apparent in the area below 5.0 ASF.

Part C

The procedure of Example 6A was again repeated substituting furfural for the thiophene aldehyde. Again, the test panels were bright over the plating range of 0.5 to 100.0 amperes per square foot but a slight fog in the entire plating range tended to reduce the otherwise brilliant lustre.

EXAMPLE 7

The procedure of Example 6A was repeated omitting the ethylene oxide/octyl phenol condensate. In this instance, the test panels were found to have a spectral bright tin deposit in the range of 25.0 to 100.0 ASF. Below 25.0 ASF, there were portions of the test panels which were unplated indicating a tendency toward skip plating in the lower current density areas. However, the plated deposits were spectral bright. This and related tests indicate the very significant benefits to be obtained by combining the imidazoline derivatives with the alkyl phenol/alkylene oxide condensates.

EXAMPLE 8

The procedure of Example 6A was repeated omitting from the bath the second-mentioned imidazoline derivative. In this instance, the plated deposit was uniform and adherent throughout the current density range of 1.0 to 100.0 ASF. Although the deposit was bright or non-matte in character, it was not so spectral bright as that obtained by the combination of the imidazoline derivatives in the preferred bath of Example 1.

EXAMPLE 9

The procedure of Example 6A was repeated utilizing a standard Hull cell. The temperature of the bath was maintained at about 90° Fahrenheit and a voltage of about 3.0 was applied across the cell. After plating for about 3.0 minutes, the test panels were found to have a spectral bright, adherent tin deposit over a range of about 25.0 to 135.0 ASF.

Thus, it can be seen that the present invention provides a highly effective bath for electroplating tin on various metallic substrates. The deposits are adherent and ductile and may vary from bright to spectral bright depending upon whether the optimum formulations are employed. Various types of parts may be readily plated over a relatively wide range of current density.

WHAT WE CLAIM IS:—

1. An aqueous acid electroplating bath for producing an adherent electroplated tin deposit comprising from 10.0 to 50.0 grams per litre of stannous ion; from 100.0 to 250.0



- grams per litre of sulphate radical; from 0.2 to 20.0 grams per litre of a surface-active agent which is one or more imidazoline derivatives or a mixture of one or more imidazoline derivatives with a condensate of an alkyl phenol, having an alkyl chain of from 6 to 12 carbon atoms, with an alkylene oxide which is ethylene oxide or propylene oxide or a mixture thereof; from 0.005 to 1.0 gram per litre of a heterocyclic carboxaldehyde wherein the heterocyclic ring has five members and the carboxaldehyde group is attached to a carbon atom in the ring; and from 1.5 to 4.5 grams per litre of hydrogen ion.
2. A bath as claimed in claim 1 which contains from 12.0 to 20.0 grams per litre of stannous ion.
3. A bath as claimed in claim 1 or claim 2 which contains from 175.0 to 225.0 grams per litre of sulphate ion.
4. A bath as claimed in any one of the preceding claims which contains from 1.0 to 4.0 grams per litre of the surface-active agent.
5. A bath as claimed in claim 4 in which the surface active agent is a mixture of an imidazoline derivative and the alkyl phenol/alkylene oxide condensate and contains from 1.0 to 2.5 grams per litre of imidazoline derivative and from 0.1 to 1.0 grams per litre of alkyl phenol/alkylene oxide condensate.
6. A bath as claimed in any one of the preceding claims which contains at least 0.01 grams per litre of the heterocyclic carboxaldehyde.
7. A bath as claimed in claim 6 which contains at least 0.05 gram per litre of the heterocyclic carboxaldehyde.
8. A bath as claimed in claim 7 which contains from 0.05 to 0.5 gram per litre of the heterocyclic carboxaldehyde.
9. A bath as claimed in any one of the preceding claims which contains from 2.5 to 3.5 grams per litre of hydrogen ion.
10. A bath as claimed in any one of the preceding claims in which the imidazoline derivative has the formula:
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- in which
- R is an alkyl radical having from 5 to 24 carbon atoms;
- G is an —OH radical, an acid salt radical, an anionic surface active sulphate salt radical, or an anionic surface active sulphate salt radical;
- Z is a group —COOM, —CH₂COOM, or —CHOH CH₂SO₃M; (in which M is a hydrogen or alkali metal atom or an organic base); and
- Y is either a group —OR' or a group —N(R')₃A (in which each R' substituent is a hydrogen or alkali metal atom, or a group —(CH₂)_n—COOM; 'A is an anionic monovalent radical, and n is an integer from 1 to 4); and the groups G and CH₂Z both being present or both absent.
11. A bath as claimed in claim 10 in which G is an anionic surface-active sulphate radical of the formula —SO₃—OR and Z is a group —COOM.
12. A bath as claimed in claim 11 in which R is an alkyl radical group containing 10 to 18 carbon atoms and M is an alkali metal atom.
13. A bath as claimed in claim 10 in which the imidazoline derivative is a 2-alkyl-1-(ethyl-beta-oxy-propanoic acid) imidazoline (in which the alkyl group is a capryl or undecyl group or a mixture of C₇—C₁₇ chains) or the disodium salt of lauroyl-cycloimidinium-1-ethoxyethanoic acid-2-ethanoic acid.
14. A bath as claimed in claim 10 in which the imidazoline component is a mixture of (A) an imidazoline derivative wherein the groups —G and —CH₂Z are both omitted and Y is —N[(CH₂)_n—COOH]₂Cl, n being from 1 to 4; and (B) an imidazoline derivative wherein —G is —OH, Y is —O(CH₂)_nCOOM and Z is —(CH₂)_mCOOM, n being from 1 to 4, m being 0 or 1 and M being an alkali metal atom.
15. A bath as claimed in claim 14 in which Y in said derivative (A) is a group —N(CH₂.CH₂COOH)₂ (CH₂COOH)Cl and, in said derivative (B) Z is a group —COONa and Y is a group —OCH₂COONa.
16. A bath as claimed in claim 14 or claim 15 in which weight ratio of derivative (B) to derivative (A) is from 1:1 to 8:1.
17. A bath as claimed in claim 16 in which the weight ratio of derivative (B) to derivative (A) is from 4.5:1 to 6.5:1.
18. A bath as claimed in any one of the preceding claims in which the surface active agent is a mixture of an imidazoline derivative and the alkyl phenol/alkylene oxide condensate and the mole ratio of alkylene oxide to alkyl phenol in the condensate is from 8:1 to 25:1.
19. A bath as claimed in any one of the preceding claims in which the surface active agent is a mixture of an imidazoline derivative and the alkyl phenol/alkylene oxide condensate and the alkyl substituent on the phenol has a carbon chain of from 8 to 10 carbon atoms.
20. A bath as claimed in claim 19 in which the alkyl phenol/alkylene oxide condensate is an octyl phenoxy polyethoxy



ethanol or a nonyl phenoxy polyethoxy ethanol.

21. A bath as claimed in claim 20 in which the alkyl phenol/alkylene oxide condensate is a nonyl phenoxy polyethoxy ethanol wherein the mole ratio of ethylene oxide to nonyl phenol is from 9:1 to 20:1.

22. A bath as claimed in any one of the preceding groups wherein the carboxaldehyde group in the heterocyclic carboxaldehyde is attached at the 2-position of the heterocyclic ring.

23. A bath as claimed in claim 22 in which the heterocyclic carboxaldehyde is furfural, 2-thiophene carboxaldehyde or 2-pyrrole carboxaldehyde.

24. A bath as claimed in any one of the preceding claims in which the heterocyclic carboxaldehyde is incorporated in the bath in the form of a solution thereof in an organic solvent.

25. A bath as claimed in claim 24 in which the organic solvent is a lower alkanol or lower glycol ether.

26. A bath as claimed in any one of the preceding claims in which the major proportion of the stannous ion is provided by stannous sulphate and a portion of the sulphate radical is provided by sulphuric acid.

27. A bath as claimed in any one of the preceding claims also containing one or more other auxiliary brighteners, surface active agents and/or chelating agents.

28. A bath as claimed in claim 27 in which the auxiliary brightener is an aryl aldehyde, polyvinyl alcohol or a carbocyclic or heterocyclic ketone.

29. A bath as claimed in claim 28 in which said auxiliary brightener is present in an amount of less than 1.0 gram per litre.

30. A bath as claimed in claim 29 in which said auxiliary brightener is present in an amount of less than 0.2 gram per litre.

31. A bath as claimed in claim 27 in which said chelating agent is citric acid, malic acid or an aminopolyacetic acid.

32. A bath as claimed in claim 31 in which the chelating agent is present in an amount of from 5.0 to 20.0 grams per litre.

33. A bath as claimed in claim 1 substantially as hereinbefore described with reference to any of the Examples.

34. A method of electroplating tin upon a conductive substrate which comprises immersing the substrate, as cathodic, workpiece and a tin anode in a bath as claimed in any one of the preceding claims maintained at a temperature of from 45 to 135° F. and applying a voltage across said anode and workpiece to deposit tin upon the substrate, the voltage providing a current density of from 0.5 to 150.0 amperes per square foot at the workpiece.

35. A method as claimed in claim 34 in which the current density is from 1 to 45 amperes per square foot.

36. A method as claimed in claim 35 in which the plating is carried out as a barrel plating operation and the current density is from 10 to 30 amperes per square foot.

37. A method as claimed in any one of claims 34—36 in which the anode:cathode area ratio is from 1.0:1.0 to 3.0:1.0.

38. A method as claimed in claim 37 in which the anode:cathode area ratio is about 2:1.

39. A method as claimed in any one of claims 34—38 in which the applied voltage is from 0.2 to 5.0 volts.

40. A method as claimed in claim 39 in which the applied voltage is from 0.5 to 4.0 volts.

41. A method as claimed in any one of claims 34—40 in which the bath is maintained at a temperature of from 55 to 85°F.

42. A method as claimed in any one of claims 34—41 in which the bath is agitated.

43. A method as claimed in claim 42 in which the workpiece is also agitated.

44. A method as claimed in claim 34 substantially as hereinbefore described with reference to any of the Examples.

45. Workpieces when plated by a method as claimed in any one of claims 34—44.

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