

PATENT SPECIFICATION

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(54) TIN ELECTROPLATING BATHS

(71) We, KENVERT INTERNATIONAL CORPORATION, a corporation organized and existing under the laws of the State of Connecticut, United States of America, of 210 East Main Street, Rockville, Connecticut, 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 baths for the electrodeposition of tin and electroplating methods using such baths.

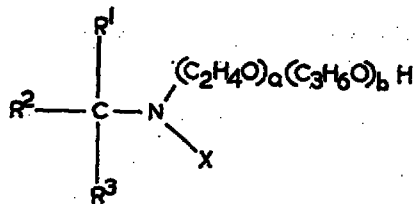
A variety of baths have been employed for electrodepositing tin upon metallic substrates, possibly the most widely used of which are the stannous fluoborate and caustic stannate solutions. Although these baths have proven generally satisfactory and have been widely used they are usually deficient in 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, uniformity and stability against 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. Krijji 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.

Various baths which are operable with varying degrees of efficiency and effectiveness are described in the literature and in patents. Excellent deposits are produced under most circumstances by the acid tin sulphate electroplating compositions described in our copending applications Nos. 50950/69 and 54688/69. Nevertheless, there remains a need for a bath capable of producing smooth, bright, dense, adherent deposits which exhibit desirable soldering properties, which resist ageing, and

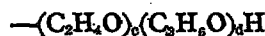
which avoid step plating when holes are present in the workpiece.

It is an object of the present invention to provide an improved electroplating bath for the electrodeposition of tin.

According to the invention there is provided an aqueous acid electroplating bath comprising from 35.0 to 85.0 grams per litre of stannous ion, from 70.0 to 250.0 grams per litre of sulphate radical; from 0.25 to 25.0 grams per litre of a surface active imidazoline derivative, from 0.0 to 5.0 grams per litre of a condensate of an alkylphenol having an alkyl chain containing 6 to 12 carbon atoms with ethylene oxide and/or propylene oxide, from 0.15 to 15.0 grams per litre of a tert-carbinamine polyoxyalkylene compound, from 0.005 to 1.0 gram per litre of a brightener which is a cyclic ketone and/or cyclic aldehyde, and from 0.9 to 4.5 grams per litre of hydrogen ion. The carbinamine compound has the general formula:



in which R_1 , R_2 and R_3 are each alkyl groups which together contain from 7 to 23 carbon atoms; and X is a hydrogen atom and a is an integer from 15 to 45 b is a number from 15 to 67.5 and the ratio $b:a$ is from 1.0:1.0—1.5:1.0, or X is a group



and $a+c$ is an integer from 15 to 45, $b+d$ is a number from 15 to 67.5 and the ratio $(b+d):(a+c)$ is from 1.0:1.0 to 1.5:1.0.

The preferred bath comprises from 55.0 to 75.0 grams per litre of stannous ion, from 125.0 to 200.0 grams per litre of sulphate radical, from 1.0 to 15.0 grams per litre of the imidazoline derivative, from 0.1 to 1.0 gram

per litre of the alkylphenol condensate, from 0.5 to 10.0 grams per litre of the carbinamine compound, from 0.05 to 0.5 grams per litre of the brightener and from 1.5 to 3.0 grams per litre of hydrogen ion. Most desirably, the imidazoline derivative and the carbinamine compound are present in concentrations of from 5.0 to 10.0 and from 2.0 to 5.0 grams per litre respectively.

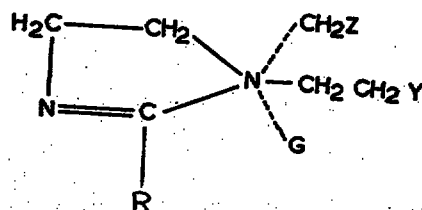
In accordance with the electroplating method of the invention an aqueous acid bath having the above composition defined is first prepared and maintained at a temperature of from 45° to 135°F. A workpiece having a metallic surface and a tin anode are immersed in the bath, and a voltage is applied thereacross to deposit tin on the metallic surface, the voltage providing a current density of from 10.0 to 200.0 amperes per square foot at the workpiece. In the preferred method, the bath is maintained at a temperature of from 60° to 90° Fahrenheit and the voltage provides a current density of from 50.0 to 100.0 amperes per square foot at the workpiece. Most desirably, the ratio of the area of the anode to that of the workpiece is from 1.5:1.0 to 3.0:1.0, and the current density at the anode is less than 40.0 amperes per square foot.

For proper operation, the acid baths of the present invention require the stannous ion, the sulphate radical, an imidazoline derivative, a carbinamine polyoxyalkylene compound, and a cyclic aldehyde and/or cyclic ketone brightener. The stannous ion and the sulphate radical may be furnished 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 this purpose. Less desirably, a tin compound other than stannous sulphate, e.g. stannous fluoborate, may be employed; and, when used, they are preferably present in concentrations of not more than 50.0 per cent by weight of the sulphate compound, and more preferably they provide less than 20.0 per cent by weight thereof.

Although the amount of stannous ion present in the baths can vary from 35.0 to 85.0 grams per litre, it is preferably from 55.0 to 75.0 grams per litre. Similarly, although the concentration of sulphate ion is from 70.0 to 250.0 grams per litre it is preferably from 125.0 to 200.0 grams per litre. A broad range of from 0.9 to 4.5 grams per litre is permitted for the hydrogen ion concentration; however,

it is most desirably maintained at from 1.5 to 3.0 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 low current densities, and burning will be apparent at the high end of the current density range. On the other hand, although desirable deposits are obtained at higher current densities with relatively high concentrations of stannous ion, too great an amount will tend to produce a very poor deposit at low current densities and to adversely effect brightness and other qualities of the deposit. Maintaining the sulphate radical and the hydrogen ion within the ranges of concentrations specified will ensure that the bath operates efficiently to produce the quality of deposit required.

In addition to the stannous ion and sulphate radical, the acid baths of the present invention contain an imidazoline derivative and a carbinamine polyoxyalkylene compound, and preferably, but optionally, they may contain a condensate of an alkyl phenol with an alkylene oxide. The imidazoline derivative corresponds to the formula:



in which R is an alkyl radical having from 5 to 24 carbon atoms; G is an —OH ion, an acid salt radical, an anionic surface-active sulphate salt radical (such as preferably a radical —OSO₂—OR), or 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 a group —OR' or a group —N(R')₃A group (in which each R' is a hydrogen atom an alkali metal atom or a group —(CH₂)_nCOOM; A is an anionic monovalent radical and n is an 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 indicates that these substituents are optionally present, but it should be understood that they are either both present or both absent. Desirable components are provided when, in the foregoing formula, G represents the radical —OSO₂—OR (particularly when R is a C₁₀ to C₁₈ alkyl group), and Z is a —COOM radical in which M is preferably an alkali metal cation.

Exemplary of the compounds corresponding to the foregoing formula which are satisfactory for use in the baths described herein are 2-

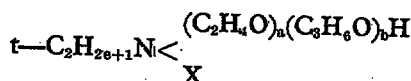
alkyl - 1 - (ethyl - beta - oxypropanoic acid) imidazolines wherein the alkyl group is capryl, undecyl or a mixture of C_7 - C_{11} chains, and the disodium salt of lauroyl-cycloimidinium-1-ethoxyethanoic acid-2-ethanoic acid. Moreover, it may be found that the best results are obtained by using combinations of the imidazoline derivatives. Particularly significant benefits may be obtained with a mixture of (A) an imidazoline derivative wherein the groups G and CH_2Z are both omitted and Y is $-N(CH_2)_n-COOH)_2Cl$ (n being an integer of from 1 to 4), and (B) an imidazoline derivative wherein G is $-OH$, Y is

$-O(CH_2)_mCOOM$ and Z is $-(CH_2)_nCOOM$ n being an integer from 1 to 4, m being 0 or 1 and M being an alkali metal). A second beneficial system may be a mixture of an imidazoline 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

$-N(CH_2CH_2COOH)_2(CH_2COOH)_2Cl$.

The first-mentioned imidazoline derivative is suitably provided in a weight ratio of from 1.0:1.0 to 8.0:1.0 relative to the second-mentioned imidazoline derivative and preferably in a ratio of from 4.5:1.0 to 6.5:1.0.

The carbinamine compound employed is that as above defined. Preferably, however, it has the general formula:



wherein e is an integer of from 12 to 15; most desirably, X is $-H$ and a and b each represent numbers from 15 to 20. The carbinamine compounds are described in United States Patent No. 3,117,999. For effective results, the carbinamine compound (of mixture thereof) should be used in a concentration of from 0.15 to 15.0 grams per litre. Preferably, the amount of carbinamine is from 0.5 to 10.0 grams per litre, and most desirably is from 2.0 to 5.0 grams per litre.

Although the carbinamine compound and the imidazoline derivative are generally adequate, as the only surface active agents, to attain the objects of the present invention, most often the best deposits will be produced by use of the combination along with the alkyl-phenol/alkylene oxide condensate. The molar ratio of alkylene oxide to alkylphenol is suitably from 8.0 to 25.0:1.0. The alkyl substituent of the phenol has a carbon chain 6 to 12 carbon atoms and preferably from 8 to 10 carbon atoms. Exemplary of the alkyl phenol condensates are octyl phenoxy polyethoxy ethanols and nonyl phenoxy polyethoxy ethanols, with the preferred agents being nonyl phenoxy poly-

ethoxy ethanols having an oxide:phenol molar ratio of from 10.0:1.0 to 20.0:1.0.

The remaining essential component of the bath is a brightener which is cyclic aldehyde, cyclic ketone or mixture thereof. Any suitable compounds of these types may be employed and the carbonyl groups may be attached directly to the ring or connected through one or more atoms. Specific examples of the cyclic ketones that may be appropriate in a particular bath are benzylideneacetone, methyl phenyl ketone, isopropyl phenyl ketone, 4-(2-furyl)-3-butene-2-one, 4-*p*-sulphophenyl-3-butene-2-one, 1,5-di-*p*-sulphophenyl-1,4-pentadiene-3-one, 4-hydroxy-3-methoxy-benzylideneacetone, 4-(pyridyl-2)-3-butene-2-one, furylideneacetone and pyridylideneacetone. Exemplary of the cyclic aldehydes that are suitable as brighteners are 2-pentyl-3-phenyl-propenal, *o*-anisaldehyde, *p*-anisaldehyde bisulphite, furfural, glutaraldehyde, cinnamaldehyde, veratraldehyde, benzaldehyde, *o*-chlorobenzaldehyde and *p*-chlorobenzaldehyde. Preferably, the aldehyde has a five-membered heterocyclic ring, and most desirably the aldehyde group is attached to one of the carbons in the ring, which generally will be that in the 2-position. Although longer carbon chain aldehydes may be used, the particular preferred compounds are those which contain a simple aldehyde group ($-CHO$), and the aldehydes may be ring- or chain substituted. Particularly good results are attained by the use of aldehydes based upon thiophene, furan and pyrrole, and specific heterocyclic carboxaldehydes which have proven highly effective are furfural (2-furaldehyde), 2-thiophene carboxaldehyde and 2-pyrrole carboxaldehyde.

Although beneficial results have been obtained by the incorporation of the brightener in amounts of as little as 0.005 grams per litre it is preferably included in amounts of at least 0.05 grams per litre. As the concentration of brightener is increased above 0.5 grams per litre, it becomes increasingly difficult to control operation of the bath, and above 1.0 gram per litre pitting and burning become quite evident and the level of brightness at low current densities is diminished significantly. Accordingly, the baths preferably employ the aldehyde or ketone compounds in amounts of from 0.05 to 0.5 gram per litre.

Since some of the suitable brighteners demonstrate relatively low solubility in the acid bath, it may be necessary to employ a solvent solution thereof to facilitate formulation of the bath. Among the various solvents which may be employed, depending upon the particular brightener involved, are the low molecular weight alkanols e.g. methanol, ethanol and propanol) and the low molecular weight glycol ethers e.g. ethylene glycol monoethyl ether). Generally, the brightener is added to the sol-

vent in amounts of from 1.0 to 50.0 preferably from 5.0 to 25.0 grams per litre thereof, so as to obtain a stable solvent solution which may be readily dispersed in the acid bath.

5 Although it has generally been found that the bath desirably operates without additional components, other additives may be included to modify the operation of the present bath, such as surface-active agents, chelating agents and auxiliary brighteners. Exemplarily of such auxiliary brighteners are the polyvinyl alcohols, which should usually be added in amounts of less than 1.0 gram per litre and preferably less than 0.2 gram per litre. Although little or no tendency for metal sludge and precipitate formation 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 and the aminopolyacetic acids, e.g. ethylene-diamine 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.

25 As has been indicated previously, the baths of the present invention are operable over a wide range of cathode current density depending upon other factors such as temperature and agitation. More specifically, the operable range is from 10.0 to 200.0 amperes per square foot (ASF) and preferably from 25.0 to 150.0 ASF, with a narrower range of from 50.0 to 100.0 ASF being most desirable. The plating efficiency is generally quite high and will range up to about 95 percent based upon the theoretical rate of deposition under optimum conditions, and bright deposits of excellent quality can normally be produced at a bath efficiency in excess of 70 percent. In order to obtain optimum results, the anode:cathode ratio should be from 1.5:1.0 to 3.0:1.0, and preferably about 2.0:1.0. Moreover, the anode current density should not exceed 40 ASF since there is an apparent density for inefficient operation, excessive sludging and rough deposits to be formed at higher anode current densities. The applied voltage should be from 0.2 to 5.0 volts and preferably from 0.5 to 4.0 volts.

50 The baths should be operated at temperatures between 45 and 135° Fahrenheit, and preferably from 60° to 90° 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, and the bath is consumed at an excessive rate.

60 Any metallic substrate or metal-surface 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, but alloy anodes may also be feasible.

Agitation is highly desirable to obtain high quality, uniform deposits and to avoid development of sludge or film, and plating at high current densities and temperatures is improved by more intense agitation. However, excessively high rates of agitation are undesirable because they can cause excessive consumption of the bath and impose limitations upon the current densities at which brightness is achieved. Not only is agitation of the bath itself desirable but agitation of the cathode may be beneficial in obtaining a uniform plate and enabling extension of the range of satisfactory current density.

The process is adapted to still plating and barrel plating apparatus with equal efficacy, and may be used for strip, wire and connector strip. Use of the bath and process is particularly significant with respect to connector strip because of the excellent solderability of the plate produced and the avoidance of step plating (i.e., due to upsetting of polarization) thereby. 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; preferably, it will be effected on a continuous basis. 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 a 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 prepared containing 120.0 grams per litre of stannous sulphate, 92.0 grams per litre of sulphuric acid; 4.5 grams per litre of a commercial imidazoline derivative of the above formula wherein groups G and CH₂Z are omitted and Y is —N(CH₂CH₂COOH)₂(CH₂COOH)Cl; 0.75

- gram per litre of a second commercial imidazoline derivative of the above formula wherein Z is $-\text{COONa}$, G is $-\text{OH}$, and Y is OCH_2COONa ; 0.93 gram per litre of an ethylene oxide/octyl phenol condensate having an ethylene oxide/octyl phenol molar ratio of about 10.0:1.0; 4.1 grams per litre of a commercial mixture of carbinamine compounds having the formula
- 10 $t-\text{C}_6\text{H}_{2e+1}\text{NH}(\text{C}_2\text{H}_4\text{O})_a(\text{C}_8\text{H}_8\text{O})_b\text{H}$ (wherein e is an integer from 12 to 15 and a and b each represent numbers of from 15 to 20); and 0.08 gram per litre of thiophene aldehyde. The bath is introduced into strip plating apparatus and maintained at a temperature of about 68° Fahrenheit.
- 15 A punched steel connector strip and a pure tin anode are introduced into the bath. A potential of about 3 volts is impressed across the strip and the anode, providing a current density at the cathode of about 80 ASF and at the anode of less than 40 ASF. The strip is agitated and plated for a period of about 2 minutes in the bath. Upon inspection of the strip after removal from the bath, rinsing and drying, a bright dense, adherent deposit of tin is found to be present, which deposit is smooth and free of pitting and is uniform throughout,
- even about the holes. Solderability as plated and after prolonged ageing is found to be excellent. 30
- Example 2
- A tin solution is prepared by dissolving in water 132.0 grams per litre of stannous sulphate, 55.0 millimetres per litre of sulphuric acid and about 0.1 gram per litre of thiophene aldehyde. A first aqueous stock solution (A) is prepared by admixing the octylphenol condensate and the imidazoline derivative first mentioned in Example One, in concentrations of 20.0 and 80.0 grams per litre, respectively. A second stock solution (B) is prepared by dissolving in water 100.0 grams per litre of the same mixture of carbinamine compounds as used in Example One. A series of tests is run using steel panels in Hull cells which contain baths formed from different proportions of the three solutions. The baths are operated at 75° Fahrenheit with 5 amperes applied for 3 minutes; agitation is provided by a stirring rod moved across the face of the panel. In the following table are shown the volumes of the stock solutions in the several baths, the bright plating range (in amperes per square foot) and a visual description of the deposit produced. 35 40 45 50 55

TABLE ONE

Test No.	Tin Solution, Parts	Solution "A", Parts	Solution "B", Parts	Bright Range (ASF)	Description of Deposit
1	250	12	2.5	20-200	Cloudy Bright
2	250	12	5	30-200	Cloudy Bright Better than No. 1
3	250	12	10	20-150	Bright
4	250	12	20	20-200	Cloudy Bright
5	250	24	5	20-150	Very Bright
6	250	24	10	20-200	Very Bright
7	250	24	20	20-175	Very Bright

Thus, it can be seen that the present invention provides a bath and method for producing a smooth, adherent, dense, bright and relatively nonporous deposit of tin, pitting is minimized, step plating about holes in the workpiece is avoided and relatively smooth deposits may be produced upon relatively rough surfaces. There is no need for a high level of control of the concentration of the components of the bath within critical limits, and the bath is capable of producing a deposit that does not tarnish, is highly resistant to staining, and that exhibits high corrosion protection and excellent

solderability, both as plated and after prolonged ageing.

WHAT WE CLAIM IS:—

1. An aqueous acid electroplating bath for the electrodeposition of tin comprising: from 35.0 to 85.0 grams per litre of stannous ion; from 70.0 to 250.0 grams per litre of sulphate radical; from 0.25 to 25.0 grams per litre of a surface active imidazoline derivative; from 0.0 to 5.0 grams per litre of a condensate of an alkylphenol having an alkyl chain containing from 6 to 12 carbon atoms with ethylene

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5	250	24	5	20—150	Very Bright
6	250	24	10	20—200	Very Bright
7	250	24	20	20—175	Very Bright

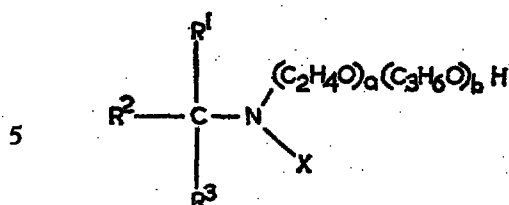
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$$\begin{array}{c}
 \text{H}_2\text{C} - \text{CH}_2 \\
 | \quad \diagup \\
 \text{N} = \text{C} - \text{N} \\
 | \quad \diagdown \quad \diagup \quad \diagdown \\
 \text{R} \quad \text{CH}_2\text{Z} \\
 \quad \quad \text{CH}_2\text{CH}_2\text{Y} \\
 \quad \quad \text{G}
 \end{array}$$


in which R is an alkyl group containing from 5 to 24 carbon atoms; G is a hydroxyl ion, an acid salt radical, an anionic surface-active sulphate salt radical or an anionic surface active sulphonate salt radical; Z is a group


$$\text{—COOM, —CH}_2\text{COOM, or —CHOH—CH}_2\text{SO}_3\text{M}$$

(in which M is hydrogen or alkali metal and or organic base) Y is a group $-\text{OR}'$ or $-\text{N}(\text{R}')_3\text{A}$ (in which each R' is hydrogen or alkali metal, or a group $-(\text{CH}_2)_n-\text{COOM}$; A is an anionic monovalent radical and n is an integer from 1 to 4); and both the groups G and CH_2Z are present or absent.

12. A bath as claimed in claim 11, in which G is an anionic surface active sulphate salt radical of the formula $-\text{OSO}_2-\text{OR}$ (in which R is an alkyl group containing from 10 to 18 carbon atoms) and Z is a group COOM (in which M is an alkali metal cation).

13. A bath as claimed in claim 11, in which the imidazoline derivative is a 2 - alkyl - 1 - (ethyl - beta - oxypropanoic acid) - imidazoline (in which the alkyl group is capryl, undecyl or a mixture of C_7 — C_{17} chains) or the disodium salt of lauroylcyclo - imidinium - 1 - ethoxy - ethanoic acid - 2 - ethanoic acid.

14. A bath as claimed in claim 11, in which the imidazoline derivative is a mixture of (A) an imidazoline derivative in which the groups G and CH_2Z are both absent and Y is a group $-\text{N}(\text{CH}_2)_n-\text{COOH}$ (in which n is an integer from 1 to 4); and (B) an imidazoline derivative (in which G is $-\text{OH}$, Y is a group $-\text{O}(\text{CH}_2)_n\text{COOM}$ and Z is a group $-(\text{CH}_2)_m\text{COOM}$ (in which n is an integer from 1 to 4, m is 0 or 1 and M is an alkali metal)).

15. A bath as claimed in claim 14, in which weight ratio of (A) to (B) is from 1.0:1.0 to 8.0:1.0.

16. A bath as claimed in claim 15, in which the weight ratio of (A) to (B) is from 4.5:1.0 to 6.5:1.0.

17. A bath as claimed in any one of the preceding claims, in which the carbinamine compound has the formula:

$$t-C_2H_{26+1}N \begin{matrix} (C_2H_4O)_a(C_3H_6O)_bH \\ \times \end{matrix}$$
$$t-C_2H_{2e+1}N \leq \frac{(C_2H_4O)_a(C_3H_5O)_bH}{X}$$

11. A bath as claimed in any one of the preceding claims, in which the imidazoline derivative has the formula:



in which a, b and X have the meaning defined in claim 1, and e is an integer from 12 to 15.

18. A bath as claimed in claim 17, in which X is a hydrogen atom and a and b are both numbers from 15 to 20.

19. A bath as claimed in any one of the preceding claims, in which the molar ratio of alkylene oxide to alkyl phenol in the alkyl phenol condensate is from 8.0:1.0 to 25.0:1.0.

20. A bath as claimed in any one of the preceding claims, in which the alkyl substituent on the alkyl phenol of the alkyl phenol condensate contains from 8 to 10 carbon atoms.

21. A bath as claimed in claim 20, in which the said alkyl substituent is a nonyl or octyl group.

22. A bath as claimed in claim 21, in which the alkyl substituent is a nonyl group and the molar ratio of alkylene oxide to phenol is from 10.0:1.0 to 20.0:1.0.

23. A bath as claimed in any one of the preceding claims in which the brightener has a heterocyclic ring and an aldehyde group is attached directly to a carbon atom in the ring.

24. A bath as claimed in claim 23, in which the heterocyclic ring contains five members.

25. A bath as claimed in claim 24, in which the aldehyde brightener is thiopene aldehyde.

26. A bath as claimed in any one of the preceding claims, in which at least the predominant portion of the stannous ion is provided by stannous sulphate and wherein a portion of the sulphate radical is furnished by sulphuric acid.

27. A bath as claimed in any one of the preceding claims, containing up to 1.0 gram per litre of polyvinyl alcohol as an auxiliary brightener.

28. A bath as claimed in claim 27, containing up to 0.2 grams per litre of polyvinyl alcohol.

29. A bath as claimed in any one of the preceding claims, containing, as chelating agent, citric acid, malic acid or an amino-polyacetic acid.

30. A bath as claimed in claim 29, containing from 5.0 to 20.0 grams per litre of chelating agent.

31. A bath as claimed in claim 1, substantially as hereinbefore described with reference to the Examples.

32. A method of electroplating tin upon a workpiece which has a metallic surface which comprises immersing the 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 the anode and workpiece to deposit tin upon the metallic surface, the voltage giving a current density of from 10.0 to 200.0 amperes per square foot at the workpiece.

33. A method as claimed in claim 32, in which the bath is maintained at a temperature of from 60° to 90° Fahrenheit and the voltage provides a current density of 50 to 100 amperes per square foot at the workpiece.

34. A method as claimed in claim 33, in which the ratio of the area of the anode to that of the workpiece is from 1.5:1.0 to 3.0:1.0, and the current density at the anode is less than 40 amperes per square foot.

35. A method as claimed in claim 32 substantially as hereinbefore described with reference to the Examples.

36. Workpieces when plated by a method as claimed in any one of claims 33 to 35.

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