ABSTRACT OF THE DISCLOSURE

An aqueous acidic composition useful for forming a copper tin coating on a ferrous metal surface without the application of electric current, which comprises copper ions in the range of from about 0.01 to 30% by weight calculated as CuSO₄·5H₂O, tin ions within the range of about 0.01 to 30% by weight calculated as SnSO₄, and a long chain aliphatic amine in the range of about 0.01 to 10% by weight.

BACKGROUND OF THE INVENTION

Numerous treating solutions have been proposed for forming a copper-tin plate on metal surfaces without the use of electric current. Frequently, the solutions used have been aqueous acidic solutions of inorganic copper and tin salts, such as solutions of copper and tin sulfate, in combination with one or more additive materials which serve to enhance the deposition of the copper-tin plate and/or the characteristics of the plate which is produced.

While many of the compositions and processes which have heretofore been developed have been generally satisfactory, some difficulties have been encountered where different types and grades of ferrous metal surfaces have been treated. Frequently, with the compositions and processes of the prior art, variations in the type of ferrous metal being treated have resulted in similar variations in the quality of the copper-tin coating which has been produced. Moreover, where these copper-tin coating solutions have been used for treating steel wire, prior to wire drawing operations, it has often been found to be difficult to consistently obtain a bright, adherent coating. Additionally, the compositions of the prior art have had a relatively low tolerance for ferrous iron. With these solutions, as the quantity of ferrous iron in the bath has increased, the quality of the copper-tin coating produced has decreased. It has, therefore, been the practice to discard the electrosolvent copper-tin plating solution when the ferrous iron content has built up to about 3.5 to 4% Fe⁺⁺ and make-up a new plating bath. This, of course, is costly, both from the standpoint of the cost of the treating materials, as well as in the processing time lost while the line is shutdown for the building-up of a new treating bath. Additionally, this frequent discarding of the bath adds greatly to waste disposal problems.

It is, therefore, an object of the present invention to provide an improved coating solution from which bright adherent copper-tin coatings (bronze color) may be obtained on a ferrous metal surface, without the use of electric current.

It is a further object of the present invention to provide an improved process for forming a bright, adherent copper-tin coating on a variety of ferrous metal surfaces without the use of an electric current.

Another object of the present invention is to provide an improved composition and process for forming a bright, adherent copper-tin alloy coating on ferrous metal surfaces, which composition and process will tolerate the build-up of an appreciable quantity of ferrous ion in the coating solution without adversely effecting the quality of the copper-tin coating which is produced.

SUMMARY OF THE INVENTION

It has been found that various types of ferrous metal surfaces may be treated with the composition of the present invention without the use of electric current to form bright adherent copper-tin alloy coatings on ferrous metal surfaces. Moreover, these results were obtained even when ferrous ion content in the bath is at the saturation point. This method is found to be particularly suited for the treatment of steel wire, prior to subjecting the wire to a drawing operation as the copper-tin alloy coatings produced are found to retain their adhesion after the drawing operation.

More specifically, in the practice of the present invention, the novel bath compositions are aqueous acidic solutions containing copper ions in the range of about 0.01 to 30% by weight calculated as CuSO₄·5H₂O which solution desirably has a pH within the range of about 0 to 4, preferably within the range of about 0.2 to 2.0. The copper ions may be incorporated in the plating solutions at any suitable form, such as copper metal and/or various copper salts. The only requirements are that whatever form copper is used, it will produce in the aqueous acidic plating solution the desired copper ion content, within the desired pH range, and that the ions incorporated within the copper salt will not have any detrimental effect on either the solution in its operation or in the quality of the copper-tin plate which is produced.

In many instances, it has been found to be convenient to utilize copper sulfate as the source of copper ions in forming the aqueous acidic plating solutions. Additionally, with such baths, the bath pH may be maintained within the desired range by the addition of sulfuric acid. Where the aqueous acidic plating baths used contain such sulfate ions, they are typically present in amounts within the range of about 0.1 to 30% by weight of the solution. It is to be appreciated, of course, that other copper salts may also be used as the source of copper ions, such as copper metabolite, copper sulfamates, and the like, and that other acids may be used for the pH adjustment of the bath. It is to be appreciated, however, that in using such other salts or acids, care should be taken that the amounts of such latter ions introduced did not exceed the maximum amounts which can be present in the solution without detrimental effect.

The plating solution in the present invention also contains at least one long chain aliphatic amine having from 8 to 22 carbon atoms per aliphatic chain, preferably the number of carbon atoms is from about 12 to 20 and even more preferably about 12 to 18 carbon atoms. In general, the structure of the aliphatic amine is of the formula:

\[ \text{R1 (R2)} ] \]

wherein R may be hydrogen or lower alkyl; R1 is a long chain aliphatic group containing 8 to 22 carbon atoms and R2 may be R1 or R2.

Examples of R are methyl, ethyl, propyl, butyl, pentyl and hexyl; preferably, the R is methyl.
Examples of R₂ that may be employed in the present invention are the saturated alkyl groups, such as, octyl, nonyl, decyl, undecyl, dodecyl, lauryl, myristyl, stearyl, and the like, or the ethynlically unsaturated hydrocarbons having 8 to 22 carbon atoms.

Examples of aliphatic amines that may be employed in applicant's invention are listed below.

- H₂N-(C₈H₁₇)
- HN(CH₃)₂C₂H₅
- N(CH₃)₂C₆H₁₃
- N(C₆H₅)₂C₂H₅
- H₂N(C₆H₅)₂
- HN(CH₃)₂(C₆H₅)
- N(CH₃)₂C₁₀H₂₁
- N(CH₃)₂C₁₂H₂₅
- N(CH₃)₂C₁₄H₂₉

The aliphatic amine may be present in the bath in amounts ranging from about 0.01 to about 20%, preferably 0.1 to about 1% and even more preferably about 0.2%.

Acceptable bronze color coatings are obtained when a copper:tin ratio ranges from about 0.60:1.5 parts by weight to 1, preferably the ratio of copper to tin is in the range of 0.8 to 1.2:1 and even more preferably 1.1 parts by weight copper to 1 part of tin.

The tin may be introduced into the bath in a variety of means such as tin metal itself or as various salts. The source of tin ions may be tin benzoate, tin tartrate, tin sulfamate, and the like.

As has been indicated herein above, the aqueous acidic plating baths of the present invention are found to give excellent plating results even where the baths contain appreciable quantities of ferrous iron. As is recognized by those in the art, even though the baths are initially free of ferrous iron, where the baths are used to treat ferrous metal surfaces, the etching action of the bath results in the dissolution and eventual build-up of ferrous iron in the plating solution. Thus, the plating of the present invention may also contain ferrous ions in amounts up to the saturation point of the ferrous ion in the bath, with amounts of ferrous iron ions within the range of about 5 to 80 grams per liter being typical. Where such typical amounts of ferrous ions are present in the bath and even where the ferrous ion content is greater than the saturation point of the bath, it is still found that excellent quality copper-tin coatings can be produced.

It is to be appreciated that although certain particular preferred ranges have been given for the concentrations of the components of the plating solutions of the present invention, these concentrations are merely exemplary of those which may be used. Thus, in some instances, concentrations of these components which are outside of the ranges indicated may also be used to give satisfactory results. Accordingly, it is believed that those in the art will readily be able to determine the concentration of each of these components which should be used in each instance, depending upon the type of ferrous metal surface to be treated, the nature of the non-electrodeposited copper-tin coating which is desired, as well as the particular type and concentration of the other components in the treating solution.

In carrying out the method of the present invention, the ferrous metal surface to be treated, such as a length of steel wire, is first cleaned, using any suitable cleaning techniques. Where desired this cleaning may include acid pickling, such as with Muratic acid, alkaline cleaning, such as with alkali metal hydroxide and/or alkali metal permanganate containing cleaners and may include a combination of several of these cleaning or pre-treating steps. Following the cleaning or pre-treating of the steel surface, it is brought into contact with the copper-tin plating bath of the present invention. Depending upon the particular configuration of the ferrous surface to be treated, various contacting techniques may be utilized such as immersion, spraying, flooding, and the like. Where the ferrous surface treated is steel wire, it has generally been found to be preferable if the wire is immersed in the copper plating bath. During the immersion of the wire in the bath, the copper plating bath of the present invention is desirably maintained at a temperature within the range of about 15 to 85°C and preferably 24-66°C. And under these preferred conditions, immersion times of from about 10 seconds to 10 minutes are typical. After removal from the copper-tin plating solution, the ferrous metal surface may then be rinsed with water and dried.

When the ferrous surface treated in accordance with this process is steel wire, if desired following the application of the electroless copper-tin plate, a suitable lubricant may be applied to the coated wire to facilitate a subsequent drawing operation. Various lubricant materials as are known to those in the art, such as aluminum soap containing compositions may be applied to the copper-tin plated wire and this lubricant coating then dried thereon. The wire may then be subjected to the desired drawing operation and it is found that following the drawing, the copper-tin finish on the wire is very bright and uniform and shown good adhesion. Additionally, it is found that the solutions of the present invention may also be used to form a copper-tin coating which is useful as a lubricant material for warm forming operations, as well as a decorative copper-tin coating.

In order that those skilled in the art may better understand the present invention and the manner in which it may be practiced, the following specific examples are given. In these examples, unless otherwise indicated, parts and percent are by weight and temperatures are in degrees centigrade.

**Example I**

Three 4 I. baths were made up to contain 10 g./l. of SnSO₄, 15 g./l. CuSO₄·5H₂O, and 3.3 mL of H₂SO₄/l. To one of the baths was added 2 g./l. N,N (dimethyl) lauryl amine, to another 2 g./l. N,N (dimethyl) myristyl amine, and to the third ½ g/l. gelatin. Gelatin was used as a control (see U.S. 3,346,404). Two grades of cleaned mild steel wire were processed through each bath for one minute at 120°F. Both baths containing the aliphatic amines of this invention gave desirable bright gold colored coatings on both grades of wire. The gelatin bath had a good coating on only one of the grades of wire.

**Example II**

A test was conducted to compare N,N (dimethyl) myristyl amine with gelatin as to their effect on the coating color stability with changes in the Cu-Tin ratio. Two 4 I. baths were made up containing 13 mls. of H₂SO₄ and 15 g./l. of CuSO₄·5H₂O. To one bath was added 6 g./l. of gelatin and to the other 2 g./l. N,N (dimethyl) myristyl amine. Stannous sulfate was added to each bath and cleaned mild steel wire was processed in each at SnSO₄ concentrations of 1,3,5,7,10, and 15 g./l. The coatings were then checked for color. The coatings obtained from the bath containing gelatin got progressively lighter in color up to a SnSO₄ concentration of 10 g./l. Then the color change flattened out. However, the color of the coatings obtained from the bath containing N,N (dimethyl) myristyl amine has a flatter color response at SnSO₄ concentrations between 5 and 10 g./l. than
gelatin; thus allowing for lower operating concentrations and a more economical bath.

Example III

As a liquor coating bath is used in production, it tends to build-up iron in solution. This is iron that is removed from the work in the coating process and goes into solution as Fe^{2+}. Usual liquor baths tend to start giving yellow looking coatings when the iron builds-up to about 4\% Fe. An evaluation of N,N (dimethyl) myristyl amine was carried out in a high iron bath, comparing it with a gelatin control. A 4 liter bath was made-up to contain 13 mls. of H_2SO_4, 15 g./l. of CuSO_4·5H_2O, 10 g./l. SnSO_4, and 2 g./l. of N,N (dimethyl) myristyl amine. A second 4 liter bath was made-up with similar amounts of copper, tin, and sulfate ions and 2 g./l. gelatin. The two baths were artificially aged with FeSO_4·7H_2O and steel wire was processed through each bath at increments of 1% Fe^{2+}. At 4% Fe^{2+}, the gelatin bath started to give coatings of a yellower, less uniform color, while the bath containing N,N (dimethyl) myristyl amine showed no changes in coating color, even at 6% Fe^{2+}.

A particularly useful composition that may be employed in replenishing the active compounds of the present invention is a concentrate composition containing the following ingredients:

<table>
<thead>
<tr>
<th>Concentrations by weight, percent</th>
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<tbody>
<tr>
<td>Copper ions (calculated as CuSO_4·5H_2O)</td>
</tr>
<tr>
<td>Tin ions (calculated as SnSO_4)</td>
</tr>
<tr>
<td>Long chain aliphatic amine</td>
</tr>
</tbody>
</table>

What is claimed is:

1. An aqueous acidic composition of improved color stability useful for forming a copper-tin coating on a ferrous metal surface without the application of electric current which comprises copper ions in the range of about 0.10 to 30% by weight calculated as CuSO_4·5H_2O, tin ions within the range of about 0.01 to 30% by weight calculated as SnSO_4, and a long chain aliphatic amine of the formula:

$$N(R)(R_2)(R_3)$$

wherein R is independently selected from the group consisting of hydrogen and lower alkyl having 1 to 6 carbon atoms; R_2 is a long chain aliphatic group containing from 8 to 22 carbon atoms and R_3 is independently selected from the group consisting of R and R_2, in the range of about 0.01 to 10% by weight.

2. The composition of claim 1 wherein the ratio of copper to tin ranges from about 0.60 to 1.5:1 on a parts by weight basis.

3. The composition of claim 1 wherein R_1 ranges from 12 to 18 carbon atoms.

4. The composition of claim 3 wherein R and R_2 are both lower alkyl having 1 to 6 carbon atoms.

5. The composition of claim 1 wherein R and R_2 are both hydrogen.

6. The composition of claim 2 wherein the ratio of copper to tin is about 1:1.

7. A process for forming a copper-tin coating on ferrous metal surface which comprises treating the ferrous metal surface to be coated with a coating composition as claimed in claim 1 and maintaining this composition in contact with the ferrous metal surface for a period sufficient to effect the formation of the copper-tin coating.

8. A process for forming a copper-tin coating on ferrous metal surface which comprises treating the ferrous metal surface to be coated with a coating composition as claimed in claim 2 and maintaining this composition in contact with the ferrous metal surface for a period sufficient to effect the formation of the copper-tin coating.

9. A replenishing composition useful for forming an aqueous acidic copper-tin coating composition which coating composition is useful for forming a copper-tin coating on ferrous metal surfaces without the application of electric current comprising copper ions (calculated as CuSO_4·5H_2O) present in an amount ranging from 40 to 90% by weight, tin ions (calculated as SnSO_4) present in an amount ranging from 5 to 30% by weight and a long chain aliphatic amine of the formula:

$$N(R)(R_2)(R_3)$$

wherein R is independently selected from the group consisting of hydrogen and lower alkyl having 1 to 6 carbon atoms; R_2 is a long chain aliphatic group containing from 8 to 22 carbon atoms and R_3 is independently selected from the group consisting of R and R_2, present in an amount ranging from 0.5 to 10% by weight.

10. The composition of claim 1 containing greater than about 4% by weight Fe^{2+} ions.

References Cited

UNITED STATES PATENTS

<table>
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<th>Inventor(s)</th>
</tr>
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FOREIGN PATENTS

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<td>2/1965</td>
<td>Great Britain</td>
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</table>

LORENZO B. HAYES, Primary Examiner

U.S. Cl. X.R.

117—130 E
UNITED STATES PATENT AND TRADEMARK OFFICE
CERTIFICATE OF CORRECTION

PATENT NO. : 3,736,157
DATED : May 29, 1973
INVENTOR(S) : Kenneth J. Hacias

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Claim 1, in the formula, insert "N" before the first (R)
so that the formula reads:

\[ N(R)(R_1)(R_2) \]

Signed and Sealed this
Twenty-first Day of November 1978

[SEAL]

Attest:

RUTH C. MASON
Attesting Officer

DONALD W. BANNER
Commissioner of Patents and Trademarks