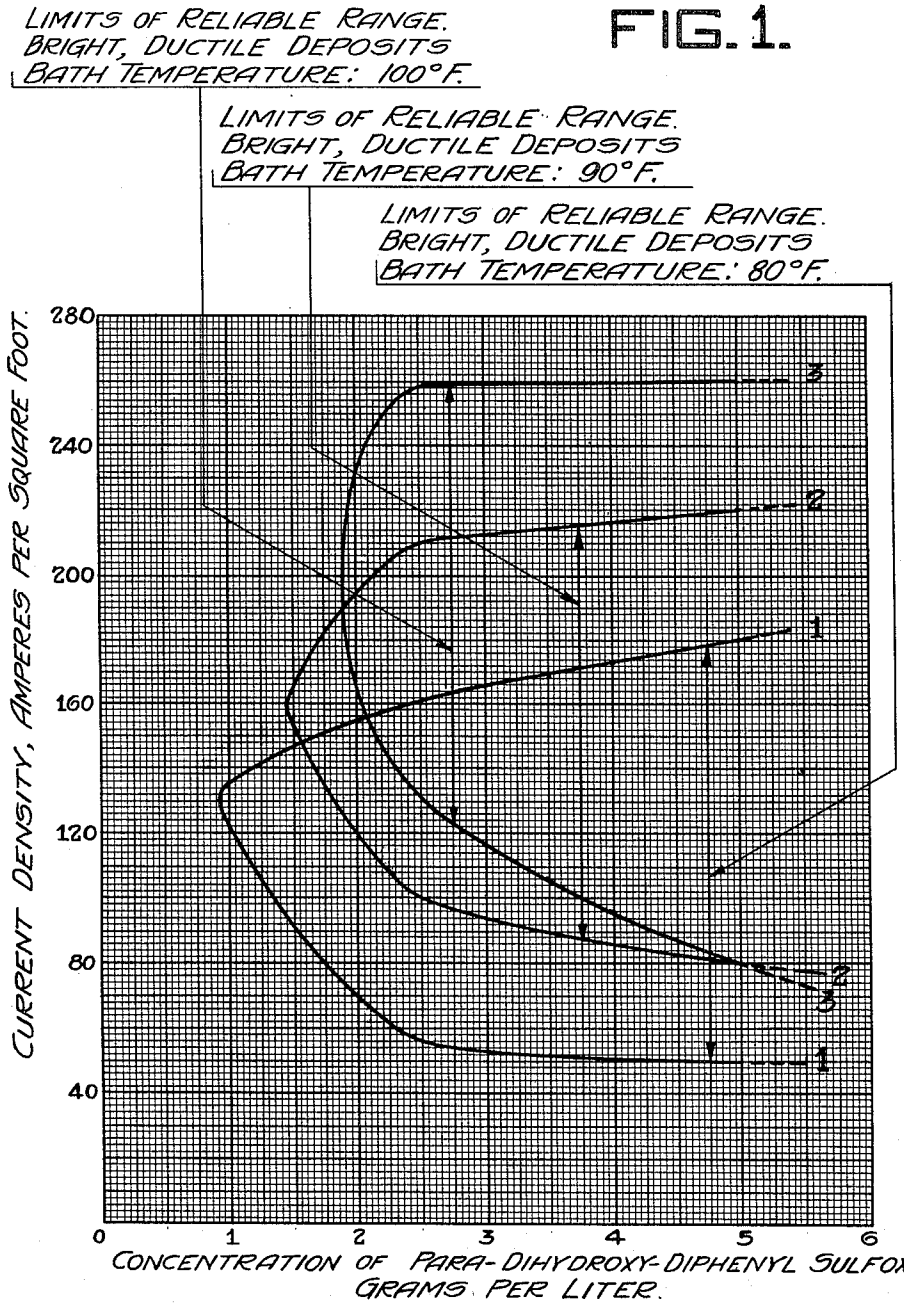
April 30, 1946. J. W. ANDREWS 2,399,194

PROCESS FOR ELECTRODEPOSITION OF TIN

Filed Nov. 19, 1941 2 Sheets-Sheet 1

FIG. 1.



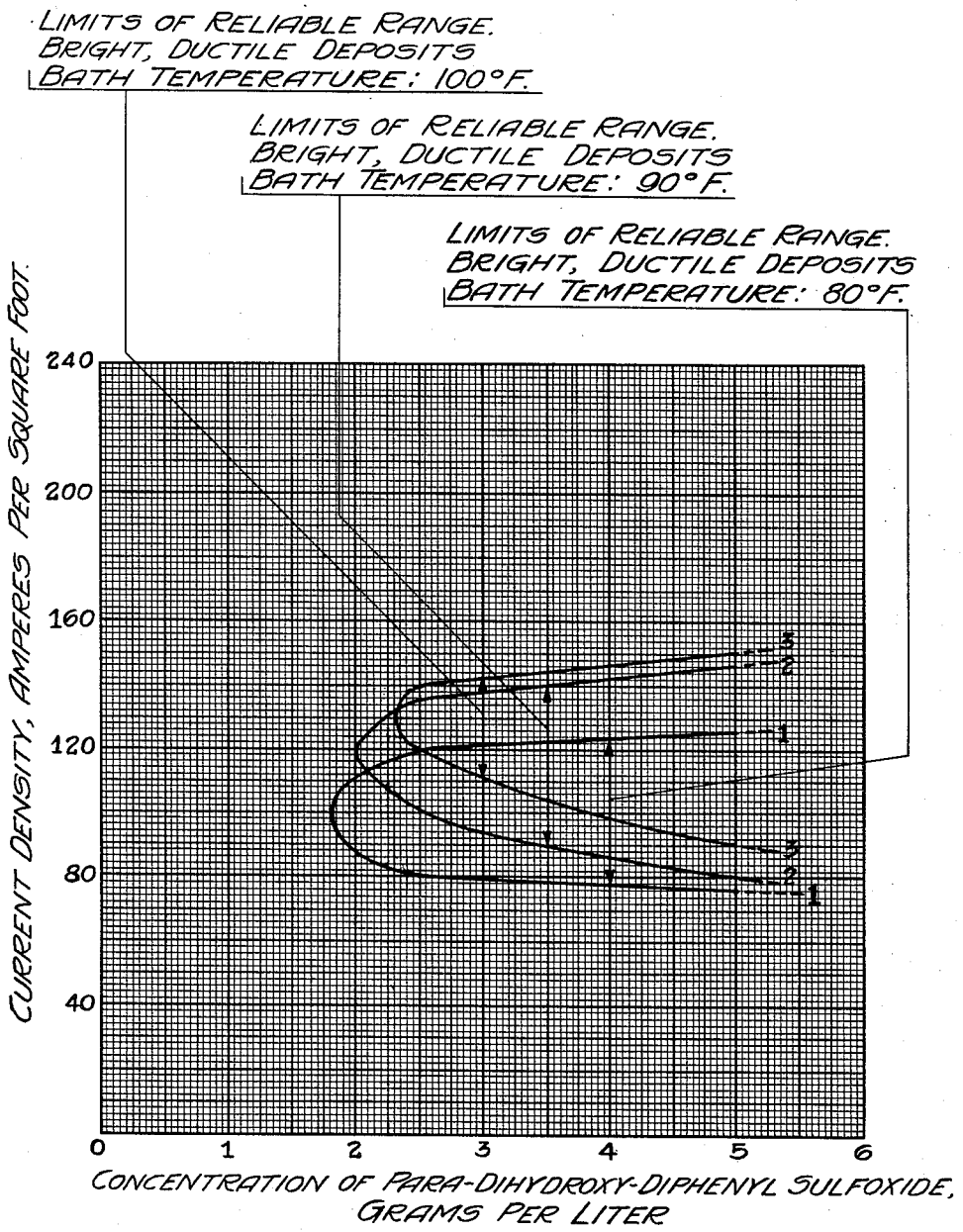
Inventor:
JOHN W. ANDREWS,
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FIG. 2.



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2,399,194

UNITED STATES PATENT OFFICE

2,399,194

PROCESS FOR ELECTRODEPOSITION OF TIN

John W. Andrews, Pittsburgh, Pa., assignor to Carnegie-Illinois Steel Corporation, a corporation of New Jersey

Application November 19, 1941, Serial No. 419,781

10 Claims. (Cl. 204—54)

In accordance with the present invention there are provided certain improvements in the electrodeposition of metals, especially the electrodeposition of tin where it is desired to obtain a thin metal deposit or plating such as a tinplating which is lustrous, highly coherent, and possesses a high degree of ductility.

That the electrodeposition of a metal from a solution of its salts in many instances results in unsatisfactory deposits is well known. Consequently in the deposition of metals, particularly tin, copper, cadmium, lead and zinc, it has been common practice to add to the electrolyte one or more compounds known as addition agents. These materials, although only minor constituents of the solution, have a very definite effect on the deposit of metal obtained. Their function is to make the deposit more dense and adherent, that is prevent spongy or powdery deposits; to make smoother deposits, that is, to inhibit the natural tendency of crystal growth which results in treed or granular deposits; in some cases, to regulate the hardness and ductility of the deposit; and in certain instances to provide a degree of brightness to the plated article.

The materials which have been used as addition agents comprise a wide variety of different substances. They are for the most part organic compounds of an indefinite nature—that is, they are vegetable products or extracts from vegetable products such as gum arabic, or aloes, or animal products such as glue or gelatin, or organic waste materials such as the residues from the distillation of coal or wood. Such materials vary in composition according to their source and even from batch to batch. In some cases the exact analysis is not definitely known. This indefiniteness of composition makes the exact control of plating conditions difficult and variations in results are inevitably encountered.

The present invention relates to improved addition agents which are useful particularly in tinplating operations, which improved agents being definite organic chemical compounds eliminate the aforementioned difficulties and the use of which result in the tin deposits being lustrous, substantially more ductile and substantially more coherent than those obtainable heretofore.

The improved addition agents of the present invention belong to a class of organic compounds termed sulfoxides. However, only those sulfoxides that can be designated by the general structural formula OH—R—SO—R'—OH, where R and R' represent a benzene or a naphthalene group, may be employed.

The above formula covers the hydroxy-sulfoxides of phenol and naphthol, of which group the most easily prepared and, therefore, the most important are:

(1) The para-dihydroxy-diphenyl-sulfoxide, and
(2) The beta-dihydroxy-dinaphthyl-sulfoxide.

The remaining members of the group are ring isomers of these two compounds. It is preferred to use the phenyl compound.

The theory of addition agents is a highly controversial subject. However, the effect of their presence rather than the mechanism of their action is the important practical feature. Therefore, it will not be attempted to explain the action of the improved agents except to note that on continued electrolysis, their concentration gradually diminishes, indicating that minute amounts are consumed during the metal deposition.

This diminution of concentration proceeds with all addition agents for some reason. However, the rate of depletion of the sulfoxides agents is much less than that of material previously used. Consequently, since less frequent replenishment is required, fluctuation of bath composition is lessened and a greater uniformity of product is obtained.

Moreover with many of the agents used heretofore the decrease of concentration proceeds even when the bath is standing idle. This is not true of the sulfoxide agents and constitutes a marked advantage accruing in their use.

An additional advantage of the present improved addition agents is that they are best operated without the addition of any other addition agent to the bath. In fact, if a lustrous, ductile, coherent deposit is desired, the co-use of glue and similar materials with the present improved addition agents is to be avoided. However, glue may be used in conjunction with the sulfoxide agent if a "white" deposit is desired; and all deposits obtained by the use of the sulfoxide agents of this invention are much more ductile than any deposit resulting from the use of glue alone.

So far as it has been able to be determined the new agents are equally effective in all the common acid tinplating electrolytes; and while the data presented hereinafter refers specifically to the use of para-dihydroxy-diphenyl-sulfoxide in a sulphonic acid tin bath, nevertheless, the said data are characteristic of the other sulfoxide agents, and depict with reasonable accuracy the behavior of any of the new agents in this and other acid tinplating baths.

In practicing the present invention the quantity of sulfoxide agent used depends to a great extent on the conditions under which it is decided to conduct the plating; that is, the acidity of the bath, the bath temperature, and the current density.

The relationship of the above factors is shown in the accompanying drawings wherein:

Fig. 1 shows graphically the relationship of

para-dihydroxy-diphenyl-sulfoxide concentration, current density, and bath temperature when plating from an agitated sulphonic acid solution of a certain tin content and acidity;

Fig. 2 shows graphically similar relationships when the bath contains the same tin content as Fig. 1, but with high acidity.

In the drawings, Fig. 1 shows the relationship, as has been said before, of para-dihydroxy-diphenyl-sulfoxide concentration, current density, and bath temperature. Such indicated relationships hold when the plating is done from an agitated sulphonic acid solution containing 35 gm. per liter of tin and 62 gm. per liter of phenolsulphonic acid.

The relationship shown by Fig. 2 obtains when the bath contains 35 gm. per liter of tin and 110 gm. per liter of phenolsulphonic acid.

In the drawings, curves 1—1 define the limits at which acceptable deposits are obtained reliably when the bath temperature is 80° F.; curves 2—2 limits at 90° F.; and curves 3—3 define the limits when the temperature is 100° F.

The area between any pair of curves bearing the same reference number defines the conditions of current density and sulfoxide concentration at which coherent, ductile and lustrous deposits are reliably obtained.

A study of the curves of the drawings show:

(1) For given bath composition and operating temperature the current density range over which acceptable deposits are obtained widens as the concentration of sulfoxide is increased;

(2) The effect of increasing acidity, other factors constant, is to narrow the lustrous range as will be seen by comparing Figs. 1 and 2. That is to say, the temperature increases the effectiveness of the sulfoxide addition while increasing the acidity decreases the effectiveness of the addition.

It is to be emphasized that the curves in the drawings define the limits at which lustrous, coherent, ductile deposits can be reliably obtained. Lustrous deposits are obtainable outside the illustrated range but such attainment can not be duplicated with any degree of certainty.

The minimum concentration of the sulfoxide agents commensurate with good results is about one gram per liter. However, as shown in Fig. 1, this minimum imposes certain limitations of plating conditions which are avoided by using larger quantities of the agent. Reference to Figs. 1 and 2 will show that the effect of increasing the sulfoxide agent concentration, other factors constant, is to widen the current density range through which acceptable deposits are obtained. This effect continues until the solubility limit of the agent in the plating bath is reached; the effect becoming less and less pronounced as this limit is approached. Increasing the concentration beyond the solubility limit while not detrimental serves no useful purpose.

In view of the above the concentration limits may be set at: minimum—1 g./l.; maximum— the solubility limit of the agent which is about 10 g./l. (the exact value depending on the agent, the acidity and the temperature of the bath). For most purposes, however, it is recommended that not less than 2½ g./l. be used and it is preferred to use 4 to 5 g./l.

The following specific examples show the use of the improved addition agents of the present invention.

Example I

Plating bath composition:	G./l.
Phenolsulphonic acid	62
Stannous phenolsulphonate	136
Para-dihydroxy-diphenyl-sulphoxide	4

At room temperature this bath may be operated at a current density of anywhere from about 55 to about 165 amp. per square foot. The operating current density range can be widened and shifted upward by increasing the temperature as will be seen by reference to Fig. 1.

The tin deposits produced under the above conditions are characterized by a lustre and they are more ductile and more coherent so far as is known than any of the commercial tinplating deposits heretofore normally obtained.

Example II

Bath composition:	G./l.
Sulphuric acid	40
Stannous sulphate	63
Beta - dihydroxy - dinaphthyl - sulphoxide	0.5

This bath does not have a wide current density range, but if operated around 100° F. and at a current density of 50–60 amp. per sq. ft., brighter tin deposits than ordinary are obtained.

Example III

Bath composition:	G./l.
Para-cresol sulphonic acid	70
Stannous cresol sulphonate	145
Para - dihydroxy - diphenyl - sulphoxide	4

This bath compares in effectiveness with that of Example I; at room temperature the lustrous current density range is around 50–150 amp. per sq. ft. The solubility of the sulphoxide is somewhat greater in this bath (15–20 g./l.), although there apparently is no increase in its activity.

Example IV

Bath composition:	G./l.
Hydrofluoboric acid	108
Stannous fluoborate	86
Para-dihydroxy-diphenyl-sulphoxide	5

When this bath is thoroughly agitated and kept at 120° F., lustrous ductile and coherent tin deposits may be obtained over a current density range of 100–200 amp./sq. ft.

Examples show the use of the improved agents in three types of acid bath, namely, two organic electrolytes, the phenol-sulphonic acid bath and the cresol-sulphonic acid bath containing, respectively, stannous phenolsulphonate and stannous cresol sulphonate, and two inorganic electrolytes, the sulfate and fluoborate. The examples are not intended as limitations but merely to substantiate the earlier statement that the new agents are applicable in all the commonly used acid tin electrolytes. It will be understood that either the beta-dihydroxy-dinaphthyl sulphoxide addition agent or the para-dihydroxy-diphenyl sulphoxide addition agent is adapted to be used, and is intended to be used, in the foregoing examples.

We wish to call attention to the fact that the data presented in the drawings and the operating conditions recited in the examples were derived using an agitated solution. This condition was chosen since it duplicates commercial strip plating operations, and therefore represents the conditions under which the present agents will find their widest use.

It is recognized by those skilled in the art of plating that agitation is a prime factor influencing the character of tinplate deposits. That is,

1. Agitation raises the upper current density limit at which deposits of optimum quality can be obtained from a given solution; the increase in current density limit depending on the degree of agitation,

2. Agitation results in improved deposits from any given solution; the effect of agitation appears to be independent of the other factors affecting deposit quality.

In other words, regardless of the bath composition, the addition agent or agents chosen, or other expedients used to enhance the quality of results, the use of agitation is generally preferred since other factors being equal, the optimum in results will be achieved. The data presented in the graphs was obtained at a degree of agitation which is the equivalent of that prevailing when strip moves through the bath at a lineal speed of 150 ft./min. The agitation was accomplished by pumping the solution through the plating apparatus.

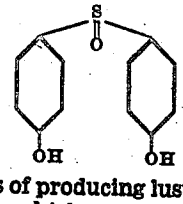
It may be noted again for emphasis that it is common practice to use addition agents of many kinds in electrodepositing tin. For the most part, however, commercial addition agents are complex mixtures or compounds of indefinite composition. Consequently, exact control of plating conditions is difficult to attain and variations in results inevitably are encountered.

In contra-distinction to such indefinite materials the sulphoxide addition agents of the present invention are definite chemical compounds which can be prepared synthetically. They can be made to definite specifications of purity. This uniformity of composition permits improved plating practices and ready duplication of results.

I claim:

1. The process of electrodepositing tin which comprises electrolyzing an aqueous acidic tin plating solution of a tin aryl-sulphonate in the presence of a sulphoxide addition agent in an amount not less than about 1 gm. per liter, and which is designated by the general structural formula OH—R—SO—R'—OH where R and R' represent a ring selected from the group consisting of benzene and naphthalene, the sulphoxide addition agent being in solution.

2. The process of producing lustrous and ductile deposits of tin which comprises electrolyzing an aqueous acid tin plating bath consisting essentially of a solution of approximately 62 gm. per liter of phenol-sulphonic acid, 136 gm. per liter of stannous phenolsulphonate and about 4 gm. per liter of para-dihydroxy-diphenyl-sulphoxide, using a current density of from approximately 55 to approximately 165 amp. per square foot at room temperature, the said para-dihydroxy-diphenyl sulphoxide having the structural formula

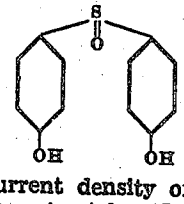


3. The process of producing lustrous and ductile deposits of tin, which comprises electrolyzing, with a current density of from substantially 55 to 165 amps. per square foot, an aqueous acid tin plating bath containing essentially in solution approximately 62 gm. per liter of phenolsulphonic acid, 136 gm. per liter of tin phenolsulphonate and a sulphoxide addition agent which is designated by the general structural formula OH—R—SO—R'—OH where R and R' represent a ring selected from the group consisting of benzene and naphthalene, the addition agent being present in an amount of not less than about 1 gm. per liter.

4. The process of producing lustrous and ductile deposits of tin, which comprises electrolyzing, with a current density of from substantially 55 to 165 amps. per square foot an aqueous acidic tin plating bath consisting essentially of a solution of a tin salt and from 2.5 gm. per liter to approximately 5 gm. per liter of a sulphoxide addition agent which is designated by the general structural formula OH—R—SO—R'—OH where R and R' represent a ring selected from the group consisting of benzene and naphthalene.

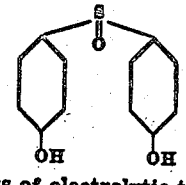
5. The process of electrodepositing lustrous, ductile deposits of tin, which comprises electrolyzing an aqueous acidic tin plating bath comprising essentially a tin aromatic sulphonate and an addition agent selected from the group consisting of para-dihydroxy-diphenyl sulphoxide and beta - dihydroxy - dinaphthyl sulphoxide, which addition agent is present in an amount not less than about 1 gm. per liter, and which is designated by the general structural formula OH—R—SO—R'—OH, where R and R' represent a ring selected from the group consisting of benzene and naphthalene, the said bath being electrolyzed using a current density of from approximately 55 to approximately 165 amps. per square foot at room temperature.

6. The process of producing lustrous, ductile, and adherent tin deposits, which comprises electrolyzing an aqueous acidic tin plating bath consisting essentially of a solution of a tin salt and from approximately 2.5 gm. per liter to approximately 5 gm. per liter of para-dihydroxy-diphenyl sulphoxide as addition agent, the said addition agent being represented by the structural formula



and using a current density of from approximately 55 to approximately 165 amps. per square foot at room temperature.

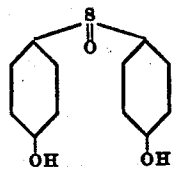
7. In the production of lustrous, ductile, and coherent tin deposits, the improvements which consist in electrolyzing an aqueous acidic stannous tin electrolyte in the presence of not less than about 1 gm. per liter of para-dihydroxy-diphenyl sulphoxide as addition agent, and using a current density of from approximately 55 to approximately 165 amps. per square foot at room temperature, the said addition agent being represented by the structural formula



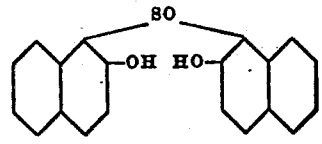
8. The process of electrolytic tin plating which comprises electrolyzing an electrolyte comprising

essentially an aqueous acid tin solution and not less than about 1 gm. per liter of a sulphoxide addition agent, which is designated by the general structural formula OH—R—SO—R'—OH where R and R' represent a ring selected from the group consisting of benzene and naphthalene.

9. The process of electrolytic tin plating as claimed in claim 8, wherein the addition agent is para-dihydroxy-diphenyl-sulphoxide having the structural formula



10. The process of electrolytic tin coating as claimed in claim 8, wherein the addition agent is beta-dihydroxy dinaphthyl sulphoxide having the structural formula



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