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ELECTRODEPOSITION OF TIN

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This invention relates to the electrodeposition of tin and more particularly to a novel method of electrodepositing tin and to an electrolyte by which said method may be carried out.

The invention has among its objects the provision of a novel method of electrodepositing tin, particularly as a coating on products such as strip metal, by which a dense, compact, adherent deposit may be secured under broader ranges of current density, temperature agitation, and other bath conditions than was formerly possible.

Another object of the invention resides in the provision of an electrolyte for the electrodeposition of tin which gives denser and more uniform coatings at high current densities.

These and further objects of the invention will become more fully apparent in the following description.

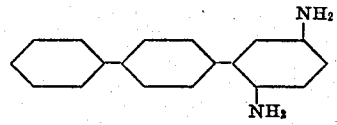
Broadly stated, the invention consists in the addition to acid or neutral electrolytes for tin plating, that is those with a pH value of 7 or less or those having a maximum upper limit in the pH value of 7, an addition agent which broadens the plating conditions, such as temperature of the bath, degree of agitation, and current density, under which satisfactory coatings are secured. The effect of the agent added by the present invention to the plating bath is particularly noticeable in the higher current density ranges, the resulting bath making deposition possible at much higher current densities than formerly could be used. As a result, satisfactory coatings are secured even though plating conditions in the bath are not maintained so accurately as was heretofore necessary.

In the electroplating of continuous strip metal, such as thin strip steel, in connection with which the invention will be described for purposes of illustration, the strip is usually fed continuously to the electrocoating line from coils. In one such practice, the strip after being uncoiled is continuously cleaned and then coated with tin in an electrolytic bath. The coated strip is washed and dried, after which the coating is melted by running the strip through a furnace, to bring the coating to a bright condition and to improve its bond to the base metal. Such procedure is most conveniently carried out with the strip continuously in motion, the leading end of one supply coil of strip metal being joined to the trailing end of an exhausted coil, as by being welded thereto. Such joining of coils end to end, and other conditions which may arise in the cleaning, electroplating, and melting line cause at least an occasional variation in speed of the strip through

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the plating bath. Such variations in speed are compensated for to some extent at least by varying the current density of the depositing current in order to maintain a substantially uniform thickness of coating metal on the strip. When tin plating electrolytes heretofore known are employed in the coating method above described, however, it has been found that there are certain critical current densities between which the current has to be maintained to insure the deposition of a satisfactory coating. In one such prior electrolyte, the permissible plating range of current density is from 140 to 300 amperes per square foot. Current densities above and below such upper and lower limits, respectively, have been found to yield porous, non-uniform coatings which, even after the melting step, were not so satisfactory as could be desired.

In the practice of the present invention there is added to acid or neutral tin electrodepositing electrolytes a relatively small quantity of diphenyl-para-phenylene-diamine, which has the chemical formula $C_6H_5 \cdot C_6H_4 \cdot C_6H_3(NH_2)_2$ or structurally



Specifically, such added material may range in quantities from .02 to 50 parts by weight of the pure material per million of the electrolyte. The addition of diphenyl - paraphenylene - diamine broadens the current density range which may be used to obtain a satisfactory coating so that electrolytes in accordance with the description to follow may be satisfactorily operated through current density ranges as high as 600 amperes per square foot. Diphenyl-para-phenylene-diamine does not appear to affect the lower current density range; thus one modification of the electrolyte of the present invention has a current density range of from 140 to 600 amperes per square foot of the material to be plated in the electrolyte, and another has a permissible current density range of 20 to 600 amperes per square foot.

The term "diphenyl-para-phenylene-diamine" as employed in this specification and the appended claims refers to the commercial material having the formula $C_6H_5 \cdot C_6H_4 \cdot C_6H_3(NH_2)_2$. The quantities stated in each instance in the specification and claims are in terms of parts by weight of the pure material.

As is disclosed in the copending application Serial No. 620,639, filed of even date, now Patent

No. 2 450,794, diphenyl-para-phenylene-diamine may also be added to tin plating electrolytes containing small quantities of monobutyl phenylphenol sodium monosulphonate. Monobutyl phenylphenol sodium monosulphonate has been found to broaden the permissible current density range in its lower portion. When the two such addition agents, that is, diphenyl-para-phenylene-diamine and monobutyl phenylphenol sodium monosulphonate, are employed in an electrolyte of the type disclosed they appear to have no adverse effect on each other, the resulting electrolyte being broadened in permissible current density range on both the lower and upper ends of the range.

It has been found that the addition of diphenyl-paraphenylene-diamine within the above range broadens the upper limit of the permissible current density range in the cases of a wide variety of acid and neutral electrolytes. As an example of a solution, which has been used to advantage, there is given the following:

Example I

Tin (Sn^{++})	grams per liter	10–60
Phenolsulphonic acid (ortho, meta or para)	do	35–110
Dihydroxy diphenyl sulphone	do	1–9
Diphenyl - para - phenylene - diamine	parts per million by weight	.02–50

Although electrolytes within the above ranges of components give satisfactory results, it is generally preferred to restrict the components to somewhat narrower ranges which are given in the following Example II:

Example II

Tin (Sn^{++})	grams per liter	28–37
Phenol sulphonic acid (ortho, meta or para)	do	65–90
Dihydroxy diphenyl sulphone	do	4–6½
Diphenyl - para - phenylene - diamine	parts per million by weight	.02–50

The electrolytes disclosed in the above Examples I and II may be made by dissolving phenol sulphonic acid, stannous sulphate, and dihydroxy diphenyl sulphone in water in sufficient quantities to provide a solution containing the specified amounts of free acid and dihydroxy diphenyl sulphone. To such electrolyte is then added diphenyl-para-phenylene-diamine in the amounts specified. By the use of the above electrolytes not only is satisfactory deposition under less critical conditions of temperature and agitation possible, but as above disclosed, the current density range on the upper side is broadened to as high as 600 amperes per square foot. As a further result the diphenyl-para-phenylene-diamine has been found to promote a brighter and better deposit by increasing the compactness of deposit at all usable current densities, to reduce the tendency for treeing and looseness of deposit at high current densities, and to reduce the tendency of the surface of the electroplated deposit to oxidize before it is melted.

The dihydroxy diphenyl sulphone ordinarily employed is the reaction product of phenol and sulphuric acid and consists principally of 4-4' dihydroxy diphenyl sulphone and 4-2' dihydroxy diphenyl sulphone. For convenience this material is sometimes referred to as phenol sulphone.

Although in the electrolytes set out in the above examples phenol sulphonic acid is employed, the addition of diphenyl-para-phenylene-diamine displays advantages when employed with neutral electrolytes and with electrolytes containing other acids singly or together. Typical of such other acids are sulphuric acid, fluosilicic acid, benzene sulphonic acid, cresol-sulphonic acid chlorobenzene sulphonic acid and nitrobenzene sulphonic acid. All of such acids readily dissolve tin from the anodes, and are cheap and easily obtainable. The sulphonic acids are particularly suitable, however, because they form extremely soluble salts of tin. When acids other than phenol sulphonic are employed, the quantities are calculated on the basis of the weight of the acid molecularly equivalent to the range stated for phenol sulphonic acid.

Furthermore, although the electrolyte in the above examples contain phenol sulphone, it is to be understood that other soluble aromatic sulphones may also be used, such as the sulphones of cresol, resorcinol, and naphthol.

As above indicated, diphenyl-para-phenylene-diamine may be employed in electrolytes containing another or other addition agents useful in broadening the lower current density range where the diphenyl-para-phenylene-diamine is not materially adversely effected by the presence of such other addition agent in the electrolyte. Typical of such other addition agent for broadening the lower limit of the current density range is monobutyl phenylphenol sodium monosulphonate. A typical electrolyte containing both monobutyl phenylphenol sodium monosulphonate and diphenyl-para-phenylene-diamine is given in the following Example III:

Example III

Tin (Sn^{++})	grams per liter	28–37
Phenol sulphonic acid (ortho, meta or para)	grams per liter	65–90
Dihydroxy diphenyl sulphone	do	4–6½
Monobutyl phenyphenol sodium monosulphonate	parts per million by weight	5–2000
Diphenyl-para-phenylene diamine	parts per million by weight	.02–50

The addition of the monobutyl phenylphenol sodium monosulphonate broadens the current density range on the lower side to as low as 20 amperes per square foot and thus satisfactory plating may be obtained by use of the electrolyte in Example III of from 20 to 600 amperes per square foot. Electrolytes comprising monobutyl phenylphenol sodium monosulphonate as an addition agent, and methods of electrodeposition with such electrolytes, are the subject matter of application Serial No. 620,639 above referred to.

Having thus fully disclosed my invention in connection with the novel method of electrodeposition and preferred examples of electrolytes for use therein, I desire to claim as new the following.

I claim:

1. An electrolyte for deposition of tin consisting of an aqueous solution of 10 to 60 grams per liter of tin, an acid of the group consisting of phenol sulphonic acid, sulphuric acid, fluosilicic acid, benzene sulphonic acid, cresol sulphonic acid, chlorobenzene sulphonic acid, and nitrobenzene sulphonic acid, the range of acid being 35 to 110 grams per liter for phenol sulphonic acid and the molecular equivalent for the other acids, 1 to 9 grams per liter of dihydroxy diphenyl sulphone, and 0.02 to 50 parts per million by weight of diphenyl-para-phenylene-diamine.

2. An electrolyte for deposition of tin consisting of an aqueous solution, having a maximum upper limit in the pH value of 7, of 10 to 60 grams

per liter of tin, 1 to 9 grams per liter of a sulphone of a substance of the group consisting of phenol, cresol, resorcinol, and naphthol, and 0.02 to 50 parts per million by weight of diphenyl-para-phenylene-diamine.

3. An electrolyte for deposition of tin which consists of an aqueous solution of the following ingredients:

Tin	grams per liter	10–60
Phenol sulphonic acid	do	35–110
Dihydroxy diphenyl sulphone	do	1–9
Diphenyl-para-phenylene-diamine	parts per million by weight	0.02–50

4. An electrolyte for deposition of tin which consists of an aqueous solution of the following ingredients:

Tin	grams per liter	28–37
Phenol sulphonic acid	do	65–90
Dihydroxy diphenyl sulphone	do	4–6½
Diphenyl-para-phenylene-diamine	parts per million by weight	0.02–50

5. An electrolyte for deposition of tin consisting of an aqueous solution, having a maximum upper limit in the pH value of 7, of 10 to 60 grams per liter of tin, 1 to 9 grams per liter of a sulphone of a substance of the group consisting of phenol, cresol, resorcinol, and naphthol, 5 to 2000 parts per million by weight of monobutyl phenylphenol sodium monosulphonate, and 0.02 to 50 parts per million by weight of diphenyl-para-phenylene-diamine.

6. An electrolyte for deposition of tin which consists of an aqueous solution of the following ingredients:

Tin	grams per liter	28–37
Phenol sulphonic acid	do	65–90
Dihydroxy diphenyl sulphone	do	4–6½
Monobutyl phenylpheonl sodium monosulphonate	parts per million by weight	5–2000
Diphenyl-para-phenylene-diamine	parts per million by weight	0.02–50

7. An electrolyte for deposition of tin consisting of an aqueous solution of 10 to 60 grams per liter of tin in the form of a soluble tin salt, 1 to 9 grams per liter of dihydroxy diphenyl sulphonic, and 0.02 to 50 parts per million by weight of diphenyl-para-phenylene-diamine, the maximum upper limit in the pH value of the electrolyte being 7.

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