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ELECTROLYTIC TIN PLATING BATHS

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This invention relates to electrolytic tin plating baths which embody improved addition agents.

In electrolytic processes for plating tin on steel strip, the strip is immersed in a plating bath from which a tin coating is electrolytically deposited on its surface. Such baths ordinarily consist of an aqueous solution of a tin salt, various acids or alkalies and various addition agents. Those with which the present invention is concerned consist of an acid, such as phenolsulfonic acid, benzene meta-disulfonic acid or sulphuric acid, and the corresponding stannous salt, besides the improved addition agent. Many substances have been used or tried as addition agents, perhaps the most common being glue, beta naphthol or sulfones, such as dihydroxy diphenyl sulfone. Their action is not fully understood, but satisfactory tin coatings cannot be produced in their absence.

After a tin coating has been deposited on a strip surface, the usual practice is to melt the coating to improve its luster. Nevertheless baths are known which are capable of depositing lustrous tin coatings directly without the need for melting, but those with which I am familiar produce coatings which are not sufficiently ductile or coherent and the processes are difficult to control. Consequently their use has been extremely limited and manufacturers continue to melt the coating.

An object of the present invention is to provide tin plating baths which embody improved addition agents and which are capable of depositing on strip ductile and coherent coatings that are lustrous even though not melted.

The addition agents of the present invention consist of complex condensation products formed by reacting aromatic amines with formaldehyde in an acid medium. The aromatic amines can be those having a primary amino group attached either to an unsubstituted benzene ring (aniline) or to a benzene ring substituted by one or more alkyl or halo groups in any of the ortho, meta or para positions with respect to the amino group (e. g. ortho, meta or para toluidine or chloraniline or xylidine). My present preference is para toluidine, which also contains the ortho and meta isomers to some extent. The amine is used in an amount of 2 to 6 grams per liter of bath solution. The formaldehyde can be either an aqueous formaldehyde solution or solid paraformaldehyde, and is used in an amount to form a ratio of 1 to 3 mols of formaldehyde to each mol of amine. Larger concentrations of formaldehyde seem harmless but of no benefit.

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First the amine is dissolved in an aqueous solution of an acid, such as sulphuric acid, phenolsulfonic acid or benzene meta-disulfonic acid. Next, with the solution maintained at a temperature within the range 40° C. to 60° C., aqueous formaldehyde or solid paraformaldehyde is added gradually over a period of at least five hours until the mol ratio is at least one mol of formaldehyde to each mol of amine. The resulting solution can be introduced to a plating bath until the desired concentration of addition agent is attained (2 to 6 grams of amine per liter of bath). However for simplicity I prefer to utilize the bath itself as the acid solution in which I dissolve the amine and then add the formaldehyde.

The usual sulphate, benzene meta-disulfonic or phenolsulfonic tin plating bath has a total free acid content expressed as the H_2SO_4 equivalent of 20 to 50 grams per liter. It contains 10 to 80 grams per liter of tin in the form of the corresponding stannous salt. Optionally benzene meta-disulfonic acid baths and phenolsulfonic acid baths can contain sulphate radicals from an effective amount to about 35 grams per liter and phenolsulfonic acid baths often contain phenol as an impurity in amount up to about 5 grams per liter.

When addition agents of the present invention are used in phenolsulfonic acid, benzene meta-disulfonic acid or sulphuric acid baths, the baths are capable of depositing bright, ductile and coherent coatings directly with a current density range of about 100 to 600 amperes per square foot, within a temperature range of about 90° F. to 140° F. and at strip speeds of about 50 to 600 feet per minute. The optimum current density, temperature, and strip speed must be determined individually for each plating line, as known in the art. Furthermore one must recognize that, while these variables normally are within the foregoing ranges, they cannot necessarily be varied at will within these ranges and still produce satisfactory coatings. Instead any significant variation in one ordinarily must be compensated by variations in others, also as known in the art. In general at a given operating temperature, the current density range widens as the strip speed increases, with the upper limit increasing more rapidly than the lower. In general the effect of raising the temperature is to shift the current density range upward, which effect becomes more pronounced at strip speeds greater than 300 feet per minute.

Specific examples of baths compounded in accordance with the present invention are as follows:

Example I

The bath was an aqueous solution containing the following ingredients:

	Grams/liter
Phenolsulfonic acid	130
Tin	35
Total sulphate radical	35
Toluidine	3

Formaldehyde sufficient to form a ratio of 3 mols per mol of toluidine.

At operating temperatures of about 90° F. to 110° F. and a strip speed of 100 feet per minute, this bath deposited coatings having satisfactory brightness or luster, ductility and coherence within a current density range of about 100 to 175 amperes per square foot. At the same temperature and a strip speed of 250 feet per minute the current density range for similarly satisfactory coatings was about 150 to 500 amperes per square foot.

Example II

The bath was an aqueous solution containing the following ingredients:

	Grams/liter
Phenolsulfonic acid	50
Stannous phenolsulfonate	137
Total sulphate radical	10
Toluidine	3

Formaldehyde sufficient to form a ratio of 1 mol per mol of toluidine.

The bath deposited satisfactory coatings at about the same operating conditions as the bath in Example I.

Example III

The bath was an aqueous solution containing the following ingredients:

	Grams/liter
Phenolsulfonic acid	53
Stannous phenolsulfonate	137
Toluidine	5

Formaldehyde sufficient to form a ratio of 2.5 mols per mol of toluidine.

The absence of sulphate ions caused the lower limit of the current density range to be considerably higher regardless of other factors (e. g. 250 amperes per square foot at a strip speed of 500 feet per minute).

Example IV

The bath was an aqueous solution containing the following ingredients:

	Grams/liter
Sulphuric acid	30
Stannous sulphate	64
Toluidine	6

Formaldehyde sufficient to form a ratio of 1 mol per mol of toluidine.

The bath does not have as wide a current density range as those of the other examples, but at current densities greater than 400 amperes per square foot deposits very bright tin coatings.

Example V

The bath was an aqueous solution containing the following ingredients:

	Grams/liter
Benzene meta-disulfonic acid	50
Stannous benzene meta-disulfonate	150
Total sulphate radical	10
Toluidine	5

Formaldehyde sufficient to form a ratio of 1 mol per mol of toluidine.

The bath deposited bright tin coatings at about the same operating conditions as the bath in Example I.

Example VI

The bath was an aqueous solution containing the following ingredients:

	Grams/liter
Phenolsulfonic acid	50
Stannous phenolsulfonate	137
Total sulphate radical	10
Aniline	4

Formaldehyde sufficient to form a ratio of 1 mol per mol of aniline.

This bath likewise deposited bright tin coatings at about the same operating conditions as the bath in Example I.

Example VII

The bath was an aqueous solution containing the following ingredients:

	Grams/liter
Phenolsulfonic acid	50
Stannous phenolsulfonate	137
Total sulphate radical	10
Xylidine	4

Formaldehyde sufficient to form a ratio of 1 mol per mol of xylidine.

This bath also deposited bright tin coatings at about the same operating conditions as the bath in Example I.

Example VIII

The bath was an aqueous solution containing the following ingredients:

	Grams/liter
Phenolsulfonic acid	50
Stannous phenolsulfonate	137
Total sulphate radical	10
Chloraniline	4

Formaldehyde sufficient to form a ratio of 1 mol per mol of chloraniline.

This bath again deposited bright tin coatings at about the same operating conditions as the bath of Example I.

From the foregoing description and examples it is seen that the present invention affords an easily prepared tin plating bath and one which deposits coatings that are ductile and coherent and bright although not melted. While I have described specific compositions by way of example, it is apparent modifications may arise. Therefore I do not wish to be limited to the disclosure set forth but only by the scope of the appended claims.

I claim:

1. An electrolytic tin plating bath consisting of an aqueous acid solution of 10 to 80 grams per liter of tin in the form of a stannous salt of an acid of the group consisting of phenolsulfonic acid, benzene meta-disulfonic acid and sulphuric acid, and the reaction product formed by dissolving an amine in said solution and gradually adding formaldehyde thereto at a temperature of 40° to 60° C., the amine being present in a concentration of 2 to 6 grams per liter and being of the group consisting of aniline, toluidine, xylidine and chloraniline, the formaldehyde being present in an amount of 1 to 3 mols of formaldehyde per mol of amine, said solution having a total free acid content expressed as the H_2SO_4 equivalent of 20 to 50 grams per liter.

2. An electrolytic tin plating bath consisting of an aqueous acid solution of 10 to 80 grams per

liter of tin in the form of stannous phenolsulfonate and the reaction product formed by dissolving an amine in said solution and gradually adding formaldehyde thereto at a temperature of 40° to 60° C., the amine being present in a concentration of 2 to 6 grams per liter and being of the group consisting of aniline, toluidine, xylidine and chloraniline, the formaldehyde being present in an amount of 1 to 3 mols of formaldehyde per mol of amine, said solution having a total free acid content expressed as the H_2SO_4 equivalent of 20 to 50 grams per liter.

3. An electrolytic tin plating bath as defined in claim 2 containing in addition sulphuric acid sufficient to furnish sulphate radicals in an amount up to about 35 grams per liter.

4. An electrolytic tin plating bath consisting of an aqueous acid solution of 10 to 80 grams per liter of tin in the form of a stannous salt of an acid of the group consisting of phenolsulfonic acid, benzene meta-disulfonic acid and sulphuric acid, and the reaction product formed by dissolving in said solution 2 to 6 grams per liter of toluidine and gradually adding formaldehyde at a temperature of 40° to 60° C. in an amount of 1 to 3 mols of formaldehyde per mol of toluidine, said solution having a total free acid content expressed as the H_2SO_4 equivalent of 20 to 50 grams per liter.

5. An electrolytic tin plating bath consisting of an aqueous acid solution of 10 to 80 grams per liter of tin in the form of a stannous phenolsulfonate, and the reaction product formed by dissolving in said solution 2 to 6 grams per liter of toluidine and gradually adding formaldehyde at a temperature of 40° to 60° C. in an amount of 1 to 3 mols of formaldehyde per mol of toluidine, said solution having a total free acid content expressed as the H_2SO_4 equivalent of 20 to 50 grams per liter.

6. An electrolytic tin plating bath consisting of an aqueous acid solution of 10 to 80 grams per liter of tin in the form of stannous sulphate and the reaction product formed by dissolving in said solution 2 to 6 grams per liter of an amine of the group consisting of aniline, toluidine, xylidine, and chloraniline and gradually adding formaldehyde at a temperature of 40° to 60° C. in an amount of 1 to 3 mols of formaldehyde per mol of amine, said solution having a total free acid content of 20 to 50 grams per liter H_2SO_4.

7. An electrolytic tin plating bath consisting of an aqueous acid solution of 10 to 80 grams per liter of tin in the form of stannous sulphate and the reaction product formed by dissolving in said solution 2 to 6 grams per liter of toluidine and gradually adding formaldehyde at a temperature of 40° to 60° C. in an amount of 1 to 3 mols of formaldehyde per mol of toluidine, said solution having a total free acid content of 20 to 50 grams per liter H_2SO_4.

8. An electrolytic tin plating bath consisting of an aqueous acid solution of 10 to 80 grams per liter of tin in the form of a stannous salt of an acid of the group consisting of phenolsulfonic acid, benzene meta-disulfonic acid and sulphuric acid, and the reaction product formed by dissolving in said solution 2 to 6 grams per liter of aniline and gradually adding formaldehyde at a temperature of 40° to 60° C. in an

amount of 1 to 3 mols of formaldehyde per mol of aniline, said solution having a total free acid content expressed as the H_2SO_4 equivalent of 20 to 50 grams per liter.

9. An electrolytic tin plating bath consisting of an aqueous acid solution of 10 to 80 grams per liter of tin in the form of a stannous salt of an acid of the group consisting of phenolsulfonic acid, benzene meta-disulfonic acid and sulphuric acid, and the reaction product of 2 to 6 grams per liter formed by dissolving in said solution xylidine and gradually adding formaldehyde at a temperature of 40° to 60° C. in an amount of 1 to 3 mols of formaldehyde per mol of xylidine, said solution having a total free acid content expressed as the H_2SO_4 equivalent of 20 to 50 grams per liter.

10. An electrolytic tin plating bath consisting of an aqueous acid solution of 10 to 80 grams per liter of tin in the form of a stannous salt of an acid of the group consisting of phenolsulfonic acid, benzene meta-disulfonic acid and sulphuric acid, and the reaction product formed by dissolving in said solution 2 to 6 grams per liter of chloraniline and gradually adding formaldehyde at a temperature of 40° to 60° C. in an amount of 1 to 3 mols of formaldehyde per mol of chloraniline, said solution having a total free acid content expressed as the H_2SO_4 equivalent of 20 to 50 grams per liter.

11. An electrolytic tin plating bath consisting of an aqueous acid solution of 10 to 80 grams per liter of tin in the form of a stannous salt of an acid of the group consisting of phenolsulfonic acid, benzene meta-disulfonic acid and sulphuric acid, and the reaction product formed by dissolving an amine in said solution and gradually adding formaldehyde thereto at a temperature of 40° to 60° C., the amine being present in a concentration of 2 to 6 grams per liter and being a primary aromatic amine having an amino group attached to one position on a benzene ring and groups of the class consisting of hydrogen, halogens, and alkyls attached to the other positions, the formaldehyde being present in an amount of 1 to 3 mols per mol of amine, said solution having a total free acid content expressed as the H_2SO_4 equivalent of 20 to 50 grams per liter.

12. An electrolytic tin plating bath consisting of an aqueous acid solution of 10 to 80 grams per liter of tin in the form of a stannous salt of an acid of the group consisting of phenolsulfonic acid, benzene meta-disulfonic acid and sulphuric acid, and the reaction product formed by dissolving in said solution 2 to 6 grams per liter of para toluidine and gradually adding formaledyhyde at a temperature of 40° to 60° C. in an amount of 1 to 3 mols of formaldehyde per mol of para toluidine, said solution having a total free acid content expressed as the H_2SO_4 equivalent of 20 to 50 grams per liter.

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