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## PROCEDURE FOR BRIGHTENING TIN COATINGS

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This invention pertains to procedure for brightening products electroplated with tin or tin alloys, and particularly, to the brightening of stannous coatings on metal base stock such as strip, sheet, and wire.

Another aspect of my invention deals with the provision of a continuous brightening process; it also deals with the bright conditioning of electroplated tin coatings. In order to simplify the description of the invention, when I herein-after speak of base metal strip, I have reference to a suitable base metal stock material such as steel strip, sheet, or wire, or a suitable metal article.

Tin and tin alloys when electrically deposited from a solution containing tin salts have a somewhat dull or matte appearance. This is true whether the plating is performed in an acid or an alkaline solution. That is, a stannous deposit of suitable ductility has a so-called matte-like appearance. For this reason, it has been customary to brighten the coating by scratch-brushing or polishing. However, I have determined that this practice has definite disadvantageous features. In the first place, it is practically impossible to thus polish a very thin deposit as the base metal becomes exposed. In the case of heavier coatings, the loss of weight must be considered. In addition, the porosity of the coating may be increased.

Although clean, bright-appearing, and smooth surface coatings are required in many cases, the heretofore objectionable results have limited the usefulness and applicable field of electroplated tin coatings, particularly in the food lines.

In view of the above considerations, I have endeavored to develop a new method of brightening that will eliminate the above-mentioned disadvantageous features of the so-called brushing operations. I have passed the coated strip through hot oil baths having a suitable mineral or vegetable oil content to effect a brightening of the coating. But the relatively low flash point of such a type of oil and its relatively unsaturated condition have made the operation rather dangerous and critical. Furthermore, in introducing acids into more stable non-acid oil baths, the question arose as to objectionable reactions taking place between the acid and the oil; and, spangles tended to appear upon cooling in the case of such a type of bath.

I experimented with the use of a mineral oil which is relatively stable at high temperatures and which has a relatively high flash point. By mineral oil I have reference to a paraffinic or

naphthenic base oil such as produced by the distillation of residual oil. I prefer paraffinic base mineral oils to the naphthenic oils as a brightening medium because of their greater stability. Mineral oils as here employed may also include those that are solids at room temperatures such as waxes or semi-solid oils such as vaseline or paraffin. In carrying out this treatment, I preferably move the coated strip through a hot mineral oil bath having a temperature above the melting point of the tin coating. I found that this step brightens the so-called matte deposit, but leaves what I have termed a very thin fog-like film. Then the question arose as to whether this so-called fog-like film was due to the mineral oil treatment or due to the presence of oil insoluble material present before the hot oil treatment. After considerable experimentation and study, I believe that the latter is the case, in that: Soluble tin salts are subjected to hydrolysis when diluted with water, and thus, after the coating operation and during the water rinsing, there may be a subsequent precipitation of the basic water insoluble tin salts. Both acidic and alkaline tin solutions employ suitable organic addition agents to obtain a satisfactory adherent and ductile tin deposit. Some of these products are possibly deposited with the stannous metal during the plating operation. At least one of the organic agents is generally a colloid or a colloid-forming material, and as such, it can travel to the cathode carrying a definite electrical charge under the influence of the electrolysis. Metallic and non-metallic impurities present in the stannous bath may also be co-deposited. Also, stannous tin salts even when present in acidic plating solutions are subject to oxidation under atmospheric conditions and some of these salts of oxidized form may be deposited upon the surface of the stannous metal.

In view of the possible diversity of causes of the film on the matte-like surface of the coatings, the question arose as to how to successfully effect a removal of the film without objectionably affecting the surface of the coating and without a wasteful or material loss of its thickness.

I found that favorable results could be obtained by immersing the coated strip after the plating application in a suitable type of hot acidic solution, and preferably, a hot acidic-reducing solution for a sufficient length of time. After washing off the acid solution and drying, I then subjected the coated strip to a hot min-

eral oil bath treatment. In this manner, the coated strip is brightened to effect a highly lustrous, reflective, and non-porous surface condition. It is preferably passed through an oil bath having a temperature at or above the melting point of the tin coating, and then subsequently, quickly, without exposing it to the atmosphere, quenched in a cold oil bath.

Also as previously intimated, I determined that a mineral oil can be successfully employed and is preferable, due to its stability at the high temperatures involved, namely, 460-550° F., as vegetable or animal oil breaks down very rapidly at these temperatures from oxidation.

I found the above order preferable for producing the desired results. In other words, as now carried out, surface oxides, metal compounds, etc., are changed into pure metal or dissolved before the oil bath treatment, and the subsequent melting of the coating will not bury or imbed surface impurities. The mineral oil bath in effect completes the operation by fusing and changing the crystal structure of the surface, producing a bright lustrous coating, and alloying such coating to the base metal strip. The resultant article is so brightly lustrous that a comparison with the so-called brushed type of surface places the latter in the category of having a semi-bright surface appearance.

It has been an object of my invention to provide new and improved procedure for brightening tin coatings.

Another object of my invention has been to eliminate the disadvantageous features of the so-called brushing type of brightening operation.

A further object has been to provide a strip brightening treatment such that new and improved results are effected, especially as applied to a stannous coating.

A still further object has been to provide an improved type of hot oil brightening treatment.

These and many other objects of my invention will appear to those skilled in the art from the specification and claims.

The product produced by the present invention is ductile, has a low porosity, and is easily soldered. As previously intimated, the strip is passed successively (and preferably continuously) from an electroplating bath, after it has been washed by a suitable means, to a hot acid treatment bath where the metallic surface is substantially restored without increasing the porosity of the coating and with a minimum loss in thickness of the coating as compared to the high percentage loss in the case of a brushing treatment. After the acid treatment step, the strip is then rinsed and successively subjected, without exposing it to the atmosphere, to a hot and then a cold oil treatment bath. The oil treatment first fuses and then solidifies the coating, producing a highly lustrous product having a high adherency without the production of spangles and other objectionable defects.

It will be appreciated that the matte film which is originally produced by the electroplating operation has a rather infinitesimal thickness, since the coating, itself, may be only .00005" in thickness. I preferably use and have determined the need for hot solution treatments. The materials employed in the so-called hot acid bath may be generally classified as follows: (1) Hot solutions of water soluble organic or inorganic acids preferably having neutral or reducing properties when used in hot solutions; (2) hot solutions as in (1) with the addition of strong inor-

ganic or organic reducing agents of a water soluble type; (3) molten baths of low melting point organic acids or acid salts of either a water soluble or water insoluble type, preferably the former.

In early experiments on dips for the removal of the adherent film, it was found that hot baths of organic acidic products of high molecular weight would substantially remove the film if used at suitable high temperatures, such as 400° F., for a suitable period of time. In this connection, I successfully employed palmitic and stearic acids. It is my opinion that the free acid in such materials has a solvent and reducing action on the materials. Later, I employed acids soluble in water which could be easily removed by rinsing to prevent the formation of spangles. The acids included inorganic acids such as diluted sulphuric acid, hydrochloric acid, and organic acids such as citric, oxalic, and tartaric; the organic acids being employed in a water solution at a temperature near the boiling point of water.

I discovered that reducing agents introduced into the water soluble acid solutions shortened the dipping time for the removal of the film. In this connection, stannous chloride, hydrazing hydrochloride, or hydroxylamine hydrochloride were successfully employed. I also successfully used a solution of perchloric and acetic acids.

I have determined that guanidine, its salts, alkyl or aryl guanidine, or salts of alkyl or aryl substituted guanidine may be used alternately for hydrazine or hydrazine hydrochloride, see the above example. That is, guanidine or salts thereof, has a strong reducing action comparable with hydrazine. Specific examples are: guanidine carbonate, guanidine hydrochloride, methyl guanidine hydrochloride, etc.

The following are specific examples of dips successfully employed in carrying out the invention:

1. A hot bath of palmitic acid used at 400° F. for 7 sec.
2. A hot bath of stearic acid at 400° F. for 10 sec.

Per cent by weight

- |                        |    |
|------------------------|----|
| 3. Tartaric acid ..... | 4  |
| Water .....            | 96 |

Used for 15 sec. at 200° F.

- |                      |    |
|----------------------|----|
| 4. Citric acid ..... | 8  |
| Water .....          | 92 |

Used for 15 sec. at 200° F.

- |                      |    |
|----------------------|----|
| 5. Oxalic acid ..... | 4  |
| Water .....          | 96 |

Used for 10 sec. at 200° F.

- |                      |    |
|----------------------|----|
| 6. Lactic acid ..... | 85 |
| Water .....          | 15 |

Used for 10 sec. at 200° F.

7. Molten tartaric acid at 355° F. for 7 sec.
8. Concentrated solution of an alkyl naphthalene sulfonic acid sold under the trade name of "Dupont Neomerpin N" at 200° F. for 5 sec.
9. Hot bath of triethanolamine at 400° F. for 15 sec.

Per cent by weight

- |                           |    |
|---------------------------|----|
| 10. Perchloric acid ..... | 28 |
| Water .....               | 72 |

Used at 200° F. for 15 sec.

- |                                     |      |
|-------------------------------------|------|
| 11. Calcium chloride (anhyd.) ..... | 30   |
| Hydrochloric acid .....             | 2.5  |
| Water .....                         | 67.5 |

Used at 200° F. for 10 sec.—the action of this solution was good, but hard to control.

	Per cent by weight
12. Perchloric acid.....	63
Acetic acid.....	10
Water.....	27

Used at 170° F. for 15 sec.

13. Zinc chloride—200 gm/100 cc. of water used at 350° F. for 15 sec.

	Per cent by weight
14. Citric acid.....	20
Sulfamic acid.....	20
Stannous chloride.....	2
Water.....	58

Used at 200° F. for 8 sec.

15. Hydroxylamine dihydrochloride.....	3 1/3
Stannous chloride.....	2
Citric acid.....	5
Water.....	89 2/3

Used at 200° F. for 8-10 sec.

16. Citric acid.....	20
Stannous chloride.....	2
Hydrochloric acid.....	3 to 9
Water.....	69 to 75

Used at 180-200° F. for 10 sec.

17. The preferred dip for the shortest possible dipping time was the following:

	Per cent by weight
Hydrazine dihydrochloride.....	1 to 3 1/3
Stannous chloride.....	5
Citric acid.....	5
Water.....	86 2/3 to 89

With the addition of a small quantity of metallic tin.

Used at 190-210° F. for 6 sec.

I determined that the proportions of the various components given in the above examples could be varied over suitable ranges with comparable results, and that the water soluble components of the example may be also interchanged with good results. For the shortest possible dipping time, it is desirable to provide a dipping solution of both acidic and strongly reducing properties; I determined that dips of this type have a long life without the addition of further chemicals and that there were no deleterious resultant reactions. Although in the description I have particular reference to the conditioning of acid-plated coatings, the invention also applies to alkaline coating baths and in such case there is an added advantage in that the acid dip removes the alkali from the surface of the coating by neutralization. I also found that hot anhydrous amines were practical, for example, triethyltetramine, ethylolamine, and triethylolamine at 400° F.

I prefer the present procedure to a so-called acid-hot oil bath in that the useful application is much wider and acids of low molecular weight may be successfully employed. I later determined that solutions evolving chlorine gas in small quantities within the solution are beneficial for removing the film, as chlorine gas in an acid medium, as set forth in Example 11, effectively dissolves film.

Although for the purpose of illustrating my invention, I have shown and illustrated certain embodiments thereof, it will be apparent to those skilled in the art that other suitable modifications, subtractions, additions, and substitutions may be made without departing from the spirit and scope thereof as indicated by the appended claims.

I claim:

1. A process for brightening an electro-deposited stannous metal coating on a metal strip, said stannous metal coating having a substan-

tially dull, film or matte-like surface appearance produced by the electroplating operation; including the steps of immersing the strip in a hot bath of an aqueous solution of an acid having neutral or reducing properties when used in hot solutions at least 3% by weight and a reducing agent maintained at a temperature of from 170° F. to 210° F. to remove said film, rinsing the coating to remove the bath solution, and then subjecting the thus treated coating to the action of a hot mineral oil bath to melt the coating and provide a mirror-like surface appearance.

2. A process for brightening an electro-deposited stannous metal coating on a metal strip, said stannous metal coating having a substantially dull, film or matte-like surface appearance produced by the electroplating operation; including the steps of immersing the strip in a hot bath of an aqueous solution of an acid having neutral or reducing properties when used in hot solutions at least 3% by weight and a reducing agent maintained at a temperature of from 170° F. to 210° F. to remove said film, rinsing the coating to remove the bath solution, then heating the strip to melt the coating and then cooling the strip to solidify the coating and provide a mirror-like surface appearance.

3. In a process of melting an electro-deposited stannous metal coating on a metal strip for providing a mirror-like melted surface, said stannous metal coating as electro-deposited having a substantially dull, film or matte-like surface appearance produced by the electroplating operation; the steps after electroplating and prior to melting of removing the film by immersing the strip in a hot bath of an aqueous solution of an acid having neutral or reducing properties when used in hot solutions at least 3% by weight and a reducing agent maintained at a temperature of from 170° F. to 210° F., and then rinsing the coating to remove the bath solution.

4. A process for brightening an electro-deposited stannous metal coating on a metal strip, said stannous metal coating having a substantially dull, film or matte-like surface appearance produced by the electroplating operation; including the steps of immersing the strip in a hot bath of an aqueous solution of an organic acid at least 5% by weight and a reducing agent maintained at a temperature of from 170° F. to 210° F. to remove said film, rinsing the coating to remove the bath solution, and then subjecting the thus treated coating to the action of a hot mineral oil bath to melt the coating and provide a mirror-like surface appearance.

5. A process for brightening an electro-deposited stannous metal coating on a metal strip, said stannous metal coating having a substantially dull, film or matte-like surface appearance produced by the electroplating operation; including the steps of immersing the strip in a hot bath of an aqueous solution of an organic acid at least 5% by weight and a reducing agent maintained at a temperature of from 170° F. to 210° F. to remove said film, rinsing the coating to remove the bath solution, then heating the strip to melt the coating and then cooling the strip to solidify the coating and provide a mirror-like surface appearance.

6. In a process of melting an electro-deposited stannous metal coating on a metal strip for providing a mirror-like melted surface, said stannous metal coating as electro-deposited having a substantially dull, film or matte-like surface appearance produced by the electroplating

operation; the steps after electroplating and prior to melting of removing the film by immersing the strip in a hot bath of an aqueous solution of an organic acid at least 5% by weight and a reducing agent maintained at a temperature of from 170° F. to 210° F., and then rinsing the coating to remove the bath solution.

7. A process for brightening an electro-deposited stannous metal coating on a metal strip, said stannous metal coating having a substantially dull, film or matte-like surface appearance produced by the electroplating operation; including the steps of immersing the strip in a hot bath of an aqueous solution of at least 4% by weight of an organic reducing acid maintained at a temperature of from 170° F. to 210° F. to remove said film, rinsing the coating to remove the bath solution, and then subjecting the thus treated coating to the action of a hot mineral oil bath to melt the coating and provide a mirror-like surface appearance.

8. A process for brightening an electro-deposited stannous metal coating on a metal strip, said stannous metal coating having a substantially dull, film or matte-like surface appearance produced by the electroplating operation; including the steps of immersing the strip in a hot bath of an aqueous solution of at least 4% by weight of an organic reducing acid maintained at a temperature of from 170° F. to 210° F. to remove said film, rinsing the coating to remove the bath solution, then heating the strip to melt the coating and then cooling the strip to solidify the coating and provide a mirror-like surface appearance.

9. In a process of melting an electro-deposited stannous metal coating on a metal strip for providing a mirror-like melted surface, said stannous metal coating as electro-deposited having a sub-

stantially dull, film or matte-like surface appearance produced by the electroplating operation; the steps after electroplating and prior to melting of removing the film by immersing the strip in a hot bath of an aqueous solution of at least 4% by weight of an organic reducing acid maintained at a temperature of from 170° F. to 210° F., and then rinsing the coating to remove the bath solution.

10. A process for brightening an electro-deposited stannous metal coating on a metal strip, said stannous metal coating having a substantially dull, film or matte-like surface appearance produced by the electroplating operation; including the steps of immersing the strip in a hot bath of an aqueous solution of an acid at least 2.5% by weight of an acid having neutral or reducing properties when used in hot solutions maintained at a temperature of from 170° F. to 210° F. for up to 15 seconds to remove said film, rinsing the coating to remove the bath solution, then heating the strip to melt the coating and then cooling the strip to solidify the coating and provide a mirror-like surface appearance.

11. In a process of melting an electro-deposited stannous metal coating on a metal strip for providing a mirror-like melted surface, said stannous metal coating as electro-deposited having a substantially dull, film or matte-like surface appearance produced by the electroplating operation; the steps after electroplating and prior to melting of removing the film by immersing the strip for about 6 seconds in a hot bath comprising by weight, hydrazine dihydrochloride 1 to 3 1/3%, stannous chloride 5%, citric acid 5%, and the balance water; maintaining said bath at a temperature of 190° to 210° F., and then rinsing the coating to remove the bath solution.

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