

1

2,976,169

IMMERSION DEPOSITION OF TIN

Michael A. Streicher, Wilmington, Del., assignor to E. I. du Pont de Nemours and Company, Wilmington, Del., a corporation of Delaware

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This invention relates to the immersion deposition of tin and is more particularly directed to processes and compositions useful for applying tin coatings to selected areas of steel sheets so that such areas can be soldered.

The deposition of tin on steel by so-called replacement or immersion coating techniques has heretofore presented considerable difficulty. Some baths can be used but they coat the surface indiscriminately and cannot readily be used to coat selected areas. Many solutions, and particularly acidic solutions, which might be expected to deposit tin on steel are ineffective.

I have found that steel such as that used for making "tin" cans can be prepared for soldering by mechanically roughening selected areas which it will later be desired to solder and then applying tin to such roughened areas by applying a solution containing a stannous compound, sulfamic acid, and a polyalkylene oxide.

According to the invention, a steel sheet is first roughened mechanically. This mechanical treatment is required in order to obtain deposition of tin and only those areas which have been roughened will receive tin using the baths which will hereafter be described.

The mechanical roughening can be effected in any convenient way as by sanding, scraping, or grinding with abrasive materials. Much preferred is grinding with an abrasive which will leave the surface roughened without excessive removal of metal. Preferably the surface can be roughened as with an 80-grit sanding belt or its equivalent. Obviously considerable variation is permissible in the grit depending upon the surface to be treated and the speed of travel of a sanding belt or grinding wheel.

The surfaces to be coated with tin according to the invention should be clean in accordance with customary practices. They can be cleaned prior to roughening or after roughening. The surfaces can be cleaned using any conventional degreasing cleaning system followed by a conventional alkali cleaning. It is to be noted that if the surface is cleaned prior to mechanical roughening, then after such roughening any dust or grit remaining on the sheet should be removed by brushing or blowing.

If the immersion deposition of tin is to be effected at a rapid rate, which is a very desirable practice in the coating of sheet to be used in making "tin" cans, then the sheet ought to be preheated. This can be done by passing it through a hot water bath, by ending the cleaning cycle with a hot rinse, or of course the sheet can simply be passed through an area appropriately heated by dry heat.

The aqueous solutions employed according to the invention contain sulfamic acid and tin. The tin can conveniently be added as stannous sulfate. The bath can also be prepared using stannous sulfamate with a suitable excess of sulfamic acid.

While the proportions of the sulfamic acid and stan-

2

nous compound can be considerably varied it has been found for best results the solution can contain:

	Parts by weight
5 Sulfamic acid	27±50
Stannous sulfate	30±18
Water	2400

The amount of water can be considerably varied but the proportions shown will be found very satisfactory.

10 If the proportion of sulfamic acid is lowered much below the figure shown, the rate of deposition will fall off so that the process becomes undesirably slow. If the proportion of sulfamic acid is considerably raised above the figure shown, the efficiency of deposition drops and more hydrogen is evolved than is desired. About the same consequences result from raising or lowering the stannous sulfate content.

20 In the composition as shown, the stannous sulfate can be replaced by another soluble stannous salt such as stannous sulfamate, stannous hydroxy acetate, or stannous oxalate.

In addition to the components shown the composition must contain an "organic addition agent." The addition agent should be of the type shown in the Hoffman U.S. Patent 2,457,152. Any of the substituted or unsubstituted polyalkylene oxide addition agents there described can be employed, the amount in the above composition being 48±16 parts by weight. If less than the amount shown is used the effect will not be as great as may be desired while if a larger amount is used it has no great beneficial effect and is wasteful.

30 In addition to the polyalkylene oxide addition agents described in the Hoffman patent and in the references therein cited there can be used any of a number of more recently developed substituted or unsubstituted polyalkylene oxides of the same type. These will include an unsubstituted polyethylene oxide (now often called a polyethylene glycol) having a molecular weight ranging up from about 350 and will also include unsubstituted polyethylene oxides having molecular weights as high as 20,000.

40 Broadly there may be used any of the agents of the types described in the said Hoffman patent, but it is more specifically preferred to use an unsubstituted polyethylene oxide having a molecular weight between 350 and 20,000. It is still more preferred to use an unsubstituted polyethylene oxide having a molecular weight between 350 and 9000.

50 A detailed description of the substituted and unsubstituted polyalkylene oxides of the Hoffman patent will be found therein and need not be repeated in detail. The disclosure of the said patent is incorporated here by reference.

55 Preferred compositions of the invention are dry, or pasty, products containing an appropriate mixture of sulfamic acid with a tin compound and a polyalkylene oxide addition agent.

A preferred dry composition to be sold and to be used after dissolving in water is as follows:

	Parts by weight
60 Stannous sulfate	0.5-2
Sulfamic acid	10
Unsubstituted polyethylene oxide having a molecular weight between 6000 and 20,000	1.5-3

65 In this composition stannous sulfate can be replaced with another stannous compound in an amount to give an equivalent quantity of tin.

70 In use a customer can dissolve the dry, or pasty, products prepared as just above described in an appropriate amount of water. Alternatively a user can simply make the bath up at the point of use by dissolving the required

ingredients in water. It is preferred to make a bath as above generally described and preferably of about the following composition:

	Parts by wt.
Water	2400
Sulfamic acid	270±50
Stannous sulfate	30±18
Unsubstituted polyethylene oxide having a molecular weight between 350 and 20,000	48±16

In processes of the invention a strip of steel will ordinarily be roughened along one or several edges and a solution as described will be applied. This can be done by immersing the edge or the whole sheet in the solution to effect deposition without the application of an external electric current. Whichever is done, the tin will deposit only on the roughened areas so that the remainder of the sheet will not be coated. The solution can be applied in any other similar fashion as by flowing the solution on the strip, by spraying, and so forth.

The treating solutions of the invention should be used at elevated temperatures and temperatures are near to the boiling point will be used in practice. As has been noted earlier, the strip should also be treated so that there will be no undue cooling of the solution in use.

After a tin coating has been applied, the strip can be handled in conventional manner, rinsing off excess solution, drying, forming the strip and then soldering joints in conventional manner to form a "tin" can. The can will thereafter be enameled or otherwise treated in accordance with standard practices.

It will be seen that by coating only the edges or other selected areas of the strip it is possible to form cans which have tin only at the soldered joints. There need be no waste of tin and there need be no tin present where it would not be wanted.

In order that the invention may be better understood reference should be had to the following illustrative examples.

Example 1

Steel strip to be made into cans was first cleaned in the following sequence. It was first roughened along the edges in strips about one-half inch wide by grinding with an abrasive belt. The roughening was on opposite sides at the two edges, these sides being those which would be in contact in soldering of the side-seams of the can. The abrasive belt carried an 80-grit abrasive. After roughening the edges, the sheet was degreased in an organic solvent in conventional manner and dried in warm air.

The strip was then pre-heated in boiling water.

The strip was then immersed in a solution of the following composition:

	Parts by weight
Water	2400
Stannous sulfate	23.8
Sulfamic acid (crystalline)	268
Polyethylene oxide, 500-600 molecular weight	64

The solution was at the boiling point. The strip was in contact with the bath for one minute and received a satisfactory coat of tin on the roughened surfaces. There was no tin deposition on other areas.

The strip was then rinsed in weak sodium hydroxide solution (0.01 N). The strip was thereafter rinsed in warm water and dried.

The strip thereafter can be soldered readily to form a "tin" can.

Example 2

A procedure was followed as in Example 1 except that instead of polyethylene oxide above described there was used a polyethylene oxide of molecular weight 6000 in the same amount by weight.

Following all of the conditions as shown above there

was obtained a strip satisfactorily treated with tin only as its roughened edges and suitable for soldering to form a can.

Depending upon the amount of tin wanted on the strip the immersion time can be increased or lowered. Thus at the following immersion times the results obtained are as shown:

Immersion Time	mg. Sn/Sq. dm.	Plating Efficiency, Percent
5 sec.	5.0	47.1
15 sec.	12.6	75.1
30 sec.	24.8	66.6
1 min.	31.5	77.8
2 min.	57.5	74.5
5 min.	89.3	74.9

The plating efficiency is expressed as the percent of tin actually deposited as compared to that which is chemically equivalent to the iron dissolved from the strip. It will be understood that there is evolution of hydrogen during the immersion.

In the above examples other stannous compounds such as the hydroxy acetate, oxalate and sulfamate can be used instead of the sulfate in an amount to provide an equivalent quantity of tin, all other conditions remaining as shown, but with somewhat different rates of deposition with each solution.

Example 3

A procedure was followed as in Example 1 except that instead of the liquid polyethylene oxide there described there was used the same amount by weight of solid polyethylene oxide of 15000-20000 molecular weight. The results were the same as those in Example 1.

A procedure was followed as in Example 1 except that instead of the polyethylene oxide the same amount by weight of methoxy polyethylene oxide of 335-365 molecular weight was used. The results were the same as those in Example 1. It was found that after immersion for one minute the amount of tin deposited was 42 mg./sq. dm. and this amount was deposited at an efficiency of 59%, as defined in Example 2.

I claim:

1. In a process for making a selected area of a steel sheet amenable to soldering, the steps comprising mechanically roughening such area and effecting an immersion deposition of tin thereupon by applying thereto an aqueous bath consisting essentially of:

	Parts by weight
Water	2400
Stannous sulfate	30±18
Sulfamic acid	270±50
Polyalkylene oxide having a molecular weight between 350 and 20000	48±16

2. In a process for making a selected area of a steel sheet amenable to soldering, the steps comprising mechanically roughening such area and effecting an immersion deposition of tin thereupon by applying thereto an aqueous bath consisting essentially of:

	Parts by weight
Water	2400
Stannous sulfate	30±18
Sulfamic acid	270±50
Unsubstituted polyethylene oxide having a molecular weight between 350 and 9000	48±16

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