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GAS PLATING WITH TIN

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Fig. 1

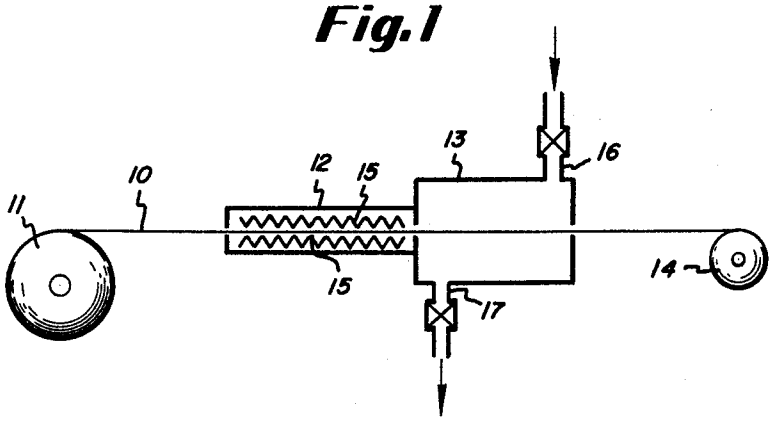
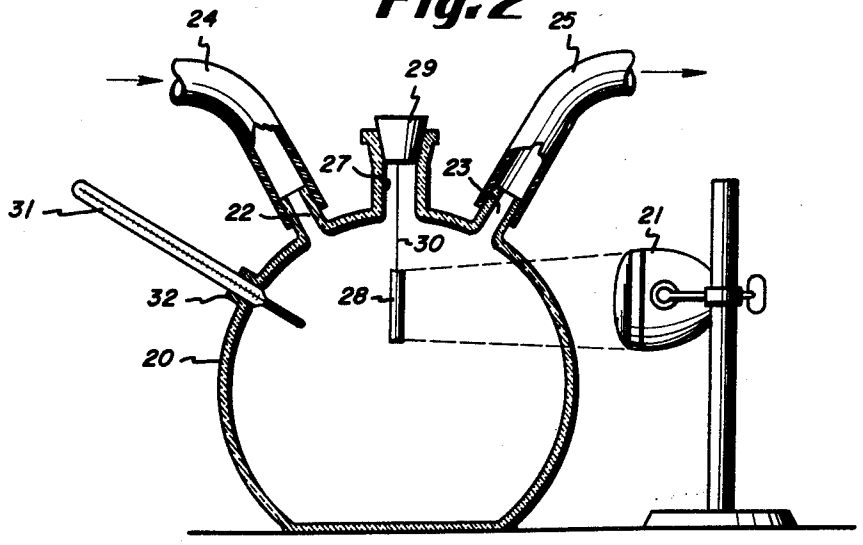



Fig. 2




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# GAS PLATING WITH TIN

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2 Claims. (Cl. 117—107)

This invention relates to the gas plating of tin and products produced thereby.

In the production of tin-coated products, for example tinplate for cans, it has been the universal practice to employ electro-tinning processes. While such methods are useful in the production of these tin-coated articles, such electrolytic tinplating methods involve the use and handling of large quantities of electrolyte solutions and washing liquids and auxiliary equipment which renders the process costly and arduous to carry out.

Another method consists of hot-dip tinplating. Utilizing this tinning method, it is difficult to produce coatings of uniform thickness and the process is wasteful of the costly metal. Moreover, it is desired to provide a higher speed tinning process than presently attainable by conventional processes.

In tinning, it is often desired to apply coatings of different thickness. For example, in the production of tin cans, as aforementioned, different thickness of coatings of tin are generally applied to the cans. The inside, for instance, may be coated with sixty millionths of an inch thickness of tin and the outside as low as fifteen millionths of an inch. Heavy coatings of 0.0005 to 0.0010 inch thick are applied to steel, cast iron and copper articles that come in contact with foods. A high speed process for applying uniform tin coatings of predetermined thickness on steel, iron, copper and the like is accordingly of great importance commercialy. The process of the present invention is particularly adapted for producing thin, uniform, thickness coatings of tin on supporting surfaces or substrate.

In accordance with this invention, a tinning process is provided which can be carried out at a high rate of speed for production of tinplated sheets and articles. The process is carried out at relatively low temperatures and pressures utilizing a heat-decomposable gaseous organotin compound. The material to be tinplated is enclosed in a chamber and the air displaced with an inert gas such as nitrogen, carbon dioxide, argon, helium, or the like, and the tinning carried out in the absence of oxygen.

To effect the deposition of tin, the base or material to be tinned is heated to a temperature sufficient to cause the organotin compound brought in contact therewith to be decomposed thus releasing tin metal which is plated onto the surface of the article.

The present invention makes it possible to deposit uniformly thin coatings of tin on the surfaces of various materials and such as will withstand the temperature used to bring about the decomposition of the gaseous organotin compound. Tinning of various articles may thus be accomplished by exposure to the article for a few seconds in such an atmosphere. Articles of steel, iron, copper, magnesium, aluminum, or alloy metals as well as nonmetal materials, for example, glass, ceramic tile, molded plastics, wood, paper and the like, may be tinned utilizing the process of this invention. Gas plating of tin on bearings and machine elements, hardware, utensils, and the like also may be readily achieved.



The invention permits a rapid deposition of tin while the article or sheet material is moved or conveyed through the plating chamber. A tin metal film of one molecule thickness is initially deposited and this built up to the desired thickness by lenghtening the time of exposure to the tin plating gas. Tin is deposited in the microscopic pores and interstices in the surface of the substrate to form a tenacious layer of tin thereon.

In carrying out the tin gas plating to produce tinned articles, the article or surface to be tinned is thoroughly cleaned of foreign matter, and the resultant cleaned surface is then subjected to gas plating utilizing a suitable organotin compound which is heat decomposable at temperatures substantially below the vaporization point of tin. The decomposition or disassociation of the gaseous organotin compound is made to take place in an atmosphere which is inert to the nascent metal so that the formation of oxides or the like impure tin metal coatings is avoided. An atmosphere of dry nitrogen gas has been found suitable for this purpose. Other inert gaseous mediums such as carbon dioxide, argon, helium, or the like also may be used. An inert carrier gas preferably is used to control the movement of tinplating gas in contact with the article to be plated. Nitrogen, argon, helium, or carbon dioxide likewise may be used for this purpose.

In carrying out the tin plating process in accordance with the preferred practice of this invention, the material to be plated is placed in a closed container or chamber having an inlet and outlet opening. Air and water vapor are then suitably displaced from the plating chamber by filling the same with nitrogen. Thereafter an organotin compound such as tin tetramethyl is introduced into the plating chamber and heat decomposed to deposit tin onto the material to be tinned.

To bring about deposition of the tin after introducing the organotin compound into the plating chamber, suitable heating means is provided to heat the material to a temperature high enough to cause the gaseous tin compound to decompose and the tin metal constituent deposited onto the surface of the material. Heating of the material may be accomplished in any suitable manner.

Where the plating chamber is made of glass, clear plastic, or light transparent material, the heating may be effected by the use of infra-red rays as produced by lamps arranged about the plating chamber. Electrical resistance heating means, e.g., dielectric or induction heating may also be employed. Heating of the tin plating gaseous compound in the plating chamber is carefully controlled by means of heat insulating baffles and the like to prevent tin from being deposited on the walls of the plating chamber. The article or substrate material is coated with a thin coating of tin after the heated substrate is exposed a few seconds to the tin plating gas. Long continuous lengths of material in the form of sheets, ribbons or the like thus may be tin-plated while the material is moved through the plating chamber from the inlet to the outlet.

Material or articles to be tinned are freed of foreign matter and moisture prior to plating as aforementioned. Such cleaning may be accomplished by chemical or mechanical means or suitable combination thereof. Metal surfaces may be sandblasted or wire brush cleaned to remove solid foreign matter. For degreasing surfaces the same may be washed with petroleum solvents such as toluol, solvent naphtha or the like. Last traces of moisture may be removed by heating the material at a temperature of 250° to 300° C. for a sufficient time to drive off residual moisture and volatile cleaning solvents.

After the article has been thoroughly cleaned the same is introduced into the plating chamber and while heated brought in contact with the heat decomposable organotin

compound and tin deposited onto the article. After a desired thickness of the tin is deposited, the process is terminated and unused organotin material returned to storage or recirculated through the plating chamber.

The organotin compounds found useful for gas plating tin are the tin tetraalkyls, e.g., tin tetramethyl and tin tetraethyl. Such compounds may be prepared by the action of zinc, dialkyls or alkyl magnesium salts on stannic chloride. Mixtures of tin alkyls may also be used where desired. Other organotin compounds which can be used include particularly the tin hydrides or stannanes, e.g., $SnH_4$ which will decompose or dissociate to plate tin below 0° F. Substituted stannanes, such as $CH_3SnH_3$, $(CH_3)_2SnH_2$, $(CH_3)_3SnH$, etc. also may be employed for gas plating tin. Using stannanes provides a relative temperature range for gas plating from 0° F. or below up to 1000° F. The stannanes are suitably produced by reducing the corresponding halide, e.g., chloride with a reducing agent such as lithium borohydride.

The decomposition and boiling point temperature of a number of organotin compounds useful in gas plating tin on substrates are shown in the table below.

| Compound | Decomposition Temp., ° F. | Boiling Point, ° F. |
|---|---|---|
| $Sn(CH_3)_4$ | 1,000 | 172 |
| $(CH_3)\ SnH_3$ | 650 | 138 |
| $(CH_3)_2\ SnH_2$ | 400 | 95 |
| $SnH_4$ | 0 | −62 |

Apparatus suitable for carrying out the process is illustrated on the accompanying drawings, wherein

Figure 1 illustrates an embodiment for gas plating tin on continuous strips of metal, e.g., a long continuous length sheet or ribbon of material which is drawn through the plating chamber, the apparatus being illustrated diagrammatically;

Figure 2 illustrates a modified apparatus wherein the plating chamber comprises light transparent side walls, the article to be tin-coated being arranged therein and heated by infra-red lamps.

Referring more particularly to the apparatus shown in Figure 1, a continuous length of previously cleaned metal strip, generally designated **10**, is suitably drawn from a storage roll **11** and passed through a preheating chamber **12** and thence through a plating chamber **13** and after being tinned is suitably stored on roll **14**. A flexible coating of tin is deposited onto the strip so that the same can be rolled up on a storage roll as shown.

Heating of the strip is suitably effected by the use of electrically heated resistance coils **15** arranged in the heating chamber **12**, the strip **10** being moved along therebetween and heated.

The tin plating chamber **13** is provided with inlet opening **16** and outlet opening **17** through which the strip **10** is moved. Organotin compounds, for example tin tetramethyl, is introduced into the plating chamber through the inlet **16** and waste gas products are drawn off through the outlet **17**. Tin tetramethyl which vaporizes at a temperature of approximately 1000° F. is admixed with a carbon dioxide carrier gas and circulated through the plating chamber **13** to effect the tinning of material arranged therein.

In the modified illustration in Figure 2, a plating enclosure or chamber **20** is provided which has transparent walls for transmission of infra-red heat rays therethrough, and such as emitted by lamps **21**. The plating chamber or container **20** comprises an inlet opening **22** and an outlet opening **23**. A conduit **24** is connected to the inlet opening **22** through which the organotin gaseous compound is conducted into the plating chamber, waste gases being withdrawn therefrom through a conduit **25** connected to the outlet opening **23**. The arrows in Figure 2 illustrate the directional flow of tinplating vapors through the plating chamber. Articles to be tinplated are introduced through an opening **27**, the article being suitably suspended from a closure member **29** as by means of a wire or cord member **30**. A thermometer **31** is suitably inserted in an opening **32** in the plating chamber **20** for use in indicating temperatures therein. Waste gases discharged from the plating chamber may be conducted to a suitable condenser, not shown, and the excess or unused organotin compound recovered for re-use.

Carbon dioxide carrier gas is admixed with organotin vapors and conducted to the plating chamber and into contact with the heated article to be tinplated as described. The carrier gas generally constitutes from 10% to 50% by volume of the gaseous mixture.

The following examples are illustrative of the invention but are not intended to be restrictive of the process of gas plating tin onto articles or materials in accordance with this invention.

*Example I*

A steel panel 4 x 6" is wire brushed and suspended in a closed container such as illustrated in Figure 2. Nitrogen gas is introduced to sweep out the air and the panel is heated to 1000° F. Thereafter vapors of tin tetramethyl are admitted into the container until the fumes of the organotin compound fill the container. Deposition of tin begins immediately as soon as the fumes reach the hot steel panel depositing a thin film of tin thereon.

*Example II*

A thin ribbon of copper is heated to 1000° F. and conveyed through a chamber, as illustrated in Figure 1, in which is circulated vapors of tin tetramethyl. The rate of flow of the gaseous medium to the plating chamber was controlled to approximate 20 cubic feet per hour per cubic foot of space of the plating chamber, the organotin vapors being present in the ratio of about 10 ounces of tin tetramethyl per cubic foot of carbon dioxide carrier gas. A one-minute exposure produces a coating of tin on the order of 0.0001 inch thick. When the exposure is increased corresponding increased coatings of tin are produced.

*Example III*

In the example gas plating of tin was carried out as described in Example II, utilizing tin tetraisobutyl to produce a tinned copper strip. In this instance a vacuum pressure of about ½ atmosphere is maintained in the plating chamber.

*Example IV*

In the instance continuous length steel strip is tinplated as described in Example II, using tin hexaphenyl and heating the steel strip to 750° F. under partial vacuum as in Example III to bring about the decomposition of the organotin vapors and deposition of tin.

*Example V*

Glass fibers are tinned as described in Example I, using tin tetramethyl vapors and bringing the same in contact with the fibers while heated to approximately 1000° F.

*Example VI*

In this example the tinning of glass fibers is carried out as in Example II, the fibers being tinned as the same are drawn and attenuated from a molten mass of glass, and utilizing the residual heat of the congealed molten glass of the fibers or filaments to bring about decomposition of the tin tetramethyl and deposition of a thin film of tin onto the surface of the fibers of glass.

Organotin compounds which may be utilized in carrying out the gas plating of tin in accordance with this in-

vention are listed as follows along with their boiling points:

| Organo Compound | Physical State | B.P., °F., at 760 mm. |
|---|---|---|
| Tin tetramethyl $(CH_3)_4Sn$ | Liquid | 172 |
| Tin tetraethyl $(C_2H_5)_4Sn$ | do | 350 |
| Tin tetraisobutyl $(C_4H_9)_4Sn$ | do | 512 |
| Tin tetrapropyl $(C_3H_7)_4$ | do | 432 |
| Tin hexaethyl $[(C_2H_5)_3Sn]_2$ | do | 518 |
| Tin hexaphenyl $[(C_6H_5)_3Sn]_2$ | do | 536 |
| Tin tetraphenyl $(C_6H_5)_4Sn$ | Solid (M.P. 439°). | 788 |

These alkyl and aryl organotin compounds may be prepared utilizing conventional Grignard synthesis and such as described in U.S. Patent No. 2,675,397.

The minimum flow rate of organotin vapors into the plating chamber is suitably controlled to produce an even uniform deposit of tin. The optimum rate of flow of tin vapors varies with the different organotin compounds used and in each instance is high enough to keep the plating chamber uniformly filled with fumes of the organotin compound so that a substantially uniform even deposit of tin is formed on the articles being plated.

A temperature of 172° F. vaporizes tin tetramethyl and 350° F. is required for vaporizing tin tetraethyl. The organotin compound employed is suitably heated in a container, not shown, which is connected to a source of carbon dioxide, and the vapors picked up and conveyed into the plating chamber. Articles to be tinned are heated to a temperature high enough to cause the organotin vapors brought in contact therewith to decompose and release the tin. The temperature in each instance is, of course, dependent upon the decomposition temperature of the organotin compound used. Where desired, the tinned article after gas plating may be subjected to an annealing heat treatment to stabilize the tin metal deposit. Such heat treatment may consist of heating the tin plated article at about 750 to 1200° F. for an hour.

The invention provides a process for tinning articles and wherein the tin is deposited from the gaseous state by decomposition or disassociation of an organotin gaseous compound. The thickness of the tin metal coating is suitably controlled by varying the time the metal-bearing gas is maintained in contact with the material or article to be plated. A coating of one molecular thickness up to several thousandths of an inch may be produced utilizing the process of this invention. A protective coating of tin is thus provided which renders the article resistant to corrosion.

The process further makes it possible to carry out the tinning of articles at high speeds and as an adjunct to the production of steel strip, for example, as produced in high speed rolling mills. Screens and the like also may be gas plated with tin while same is moved along through a plating chamber. The invention is particularly useful in tinning articles to provide the same with a thin uniform coating of metal and which is deposited into the pores and interstices of the material forming a substantial integral outer layer of corrosion resistant tin metal.

It will be understood that while there has been described and set forth certain specific embodiments and examples of the invention, it is not intended that the same be restricted specifically thereto. Various substitutions and changes accordingly may be made by those skilled in the art and to which the invention is readily susceptible without departing from the spirit and scope thereof, the invention being more particularly set forth in the appended claims.

What is claimed is:

1. A method of tin plating material by gas plating which comprises establishing a source of gaseous tin tetraisobutyl, providing a source of dry nitrogen gas, enclosing said material to be tinned, displacing the air from said enclosure by the introduction of said nitrogen, introducing vapors of said tin tetraisobutyl compound into said enclosure and in contact with said material, and heating said material to a temperature to cause thermal decomposition of said tin compound and deposition of tin onto the surface of said material, said gaseous tin compound being admixed with carbon dioxide carrier gas and conducted into said enclosure and in contact with said heated material.

2. As an article of manufacture, material gas plated to tin plate the same as set forth in claim 1.

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