May 1, 1945. C. G. FINK 2,374,926

PROCESS OF COATING WITH TIN OR OTHER METALS

Filed Oct. 11, 1941

Fig. 1.

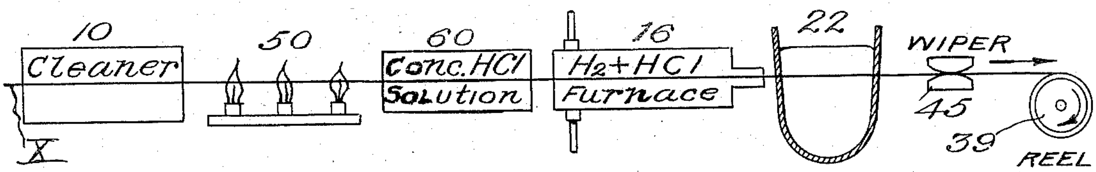


Fig. 2.

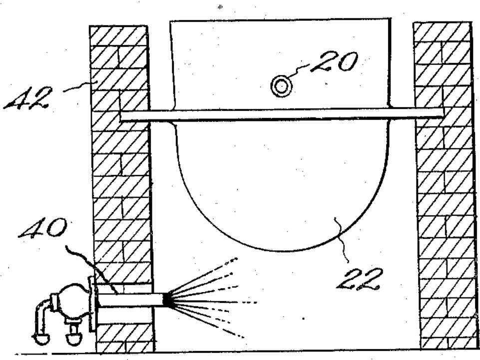


Fig. 3.

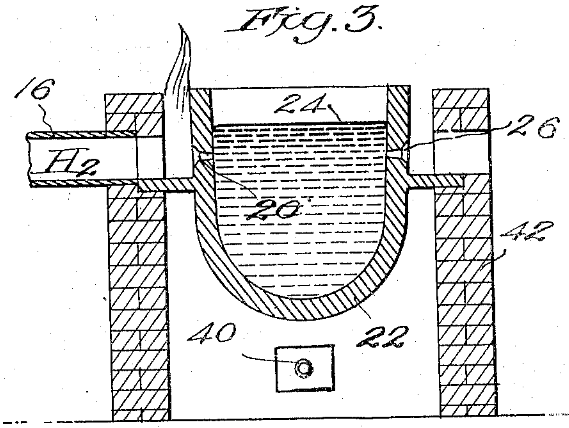
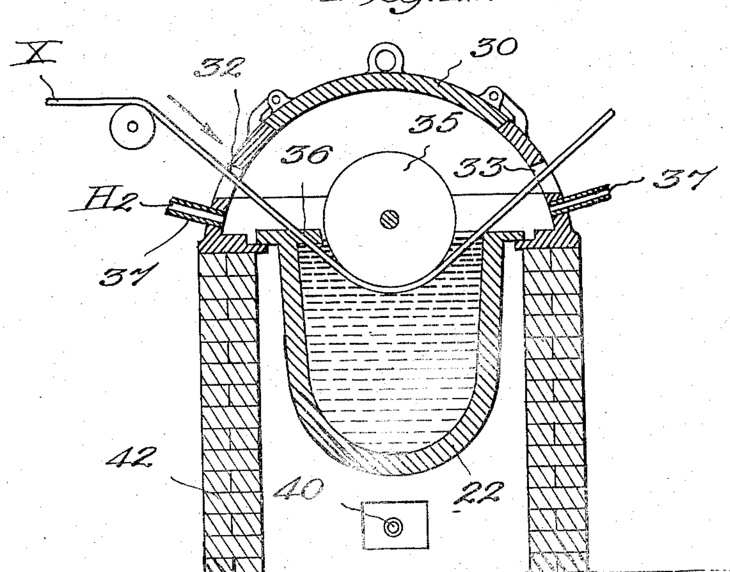


Fig. 4.



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PROCESS OF COATING WITH TIN OR OTHER METALS

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Application October 11, 1941, Serial No. 414,639

4 Claims. (Cl. 117—51)

This invention relates to a process of coating by dipping in a molten bath of tin, or other metals, among which have been used cadmium, zinc, lead, and beryllium, and provides improvements therein.

There is a recognized need for improvement of the product obtained by the generally used hot-dip process of producing tin-plate, sheets of metal and other shapes to be coated. In such generally used process, sheets of metal and other shapes are pickled, then run through a flux into the molten tin, and then out of the tin through a supernatant layer of palm oil.

In an article by D. J. Macnaughtan, S. G. Clarke and J. C. Prytherch in the Journal of the Iron & Steel Institute (British) vol. CXXV # 1, p. 159–74 (1932) entitled "The determination of the porosity of tin coatings on steel" it is stated "It has long been known that a thin tin coating—for instance, on tinplate—is seldom perfectly continuous, as even in the absence of obvious discontinuities the coating almost invariably contains minute holes. These small perforations cannot be seen by visual examination of the tinplate, but micro-examination reveals them as frequently taking the form of saucer-like craters at the bottom of which the basis metal is exposed," and the publication contains a table showing that the holes per square centimeter in tinplate having 1½ pounds of tin per base box thereon, averaged 12.78 (82½ per square inch). Tinplate used for cans often contains even less tin per base box than 1½ pounds, and the number of pin holes is much greater. It is probably because of this that lacquer on the inside of cans made of tin plate and used for food containers is now generally adopted by can-makers.

I have discovered that, by a process, involving a gas pre-treatment, metal may be coated with tin, or other metals and excellent coverage may be obtained. I eliminate the need of baths of molten fluxes and baths of molten metals, such as lead, used simply as heating baths, by my process.

The present invention provides a novel process for coating metals, especially ferrous-metal, with tin or other metals (cadmium, zinc, lead, beryllium for example) by means of which tenaciously adherent and substantially uniform, smooth, bright coatings may be obtained free from adhesions resulting from passage through molten flux and heating baths, suitable and satisfactory for the general uses of commerce and industry. It further provides a process which may be expeditiously carried on, with a speed and versatility capable of satisfying the manufacturing requirements of modern industry. It provides, in particular, a practical and satisfactory continuously working process for the manufacture of tin coated (or lead, zinc, cadmium, beryllium coated) wire, rods, bars, beams, sheets, and strips, such as may be used generally in the fabrication of coated metal products.

Embodiments of apparatus, and a diagram, illustrating modes of procedure in practicing the process are illustrated in the accompanying drawing, wherein:

Fig. 1 is a diagrammatic view illustrating one mode of procedure.

Figs. 2 and 3 are respectively a side view and a vertical section of a furnace for containing molten coating metal (tin) and in which articles are coated, embodying the present invention.

Fig. 4 is a vertical sectional view illustrating a second embodiment of a part of the apparatus according to the invention.

According to the present invention, I proceed in such manner as to remove oxygen, and such oxides as may remain after cleaning, from the article or object to be coated, and provide the article with a charge of reducing gas, together with hydrochloric acid which it carries with it into the molten tin bath (or a bath of another of the coating metals herein mentioned). This is accomplished by pre-treating or subjecting the article or object to be coated, for an adequate length of time, before passing into the tin bath, to the action of a reducing atmosphere containing hydrochloric acid to charge or pack the article or object with enough of the reducing gas and hydrochloric acid to bring about the complete union of the tin or other coating metal to the basis metal at the time of introduction into the tin bath.

Examples of reducing gases for obtaining the effects hereinbefore stated, are hydrogen, carbon-monoxide, nitrogen, and certain industrial gases containing mixtures of these, such as blast-furnace gas and blue water gas. Nitrogen is included as a reducing gas because in the present process its action is to remove oxygen and since it eliminates oxygen it may be regarded as a reducing gas. However, gases such as methane which are unstable and deposit foreign particles on the article to be coated and thereby interfere with the coating, should be eliminated.

The reducing gas is heated to increase its activity. The heat may be supplied either through the article itself, or through the gas, or through both. A wide choice of operating temperature appears to be available. Under ordinary operating conditions a temperature of from 300° to 800° C. is found to give good results with hydrogen containing hydrochloric acid.

The process is one by which the coating with tin, cadmium, lead, zinc, and beryllium can be carried on in a rapid and continuous manner, and is especially applicable to the coating of wire, rods, sheets and strips in a continuous manner. The process is also one by which a novel and superior product may be obtained.

In the case of tin, for example, by controlling the temperature of the molten tin and the length of time the article remains in contact with the tin bath, the alloy which is formed at the interface of the tin and the basis metal may be made of a substantially uniform thickness, it may be greatly limited as to its thickness, and the flow of crystals of the tin and of the basis metal may be limited to the alloy intermediate between the basis metal and the tin coating, so that stray crystals of the basis metal are kept out of the tin coating. The alloy which forms at said interface is of a ductile character, and this I attribute to the absence of oxygen and of oxidizing conditions, so that oxygen in the alloy is absent or in amounts that are inconsequential.

Now referring to the diagram, Fig. 1, a mode of procedure is substantially as follows:

Wire made of steel, designated by letter X, is taken as an example of an article to be coated. The wire X, if cleaning or removal of scale is required, is first passed through a pickler or cleaner 10 (which may be a vat containing a solution of hydrochloric acid, or an alkali bath, or any desired combination of cleaners), where its surface is cleaned of scale, oxides, grease, etc. After cleaning, or if cleaning is not required, the wire X is passed through a furnace 16 containing hydrogen and hydrochloric acid and subjected therein to a purely gas pretreatment. The hydrochloric acid may be introduced into the furnace 16 through a suitable duct along with the hydrogen. However, it is found advantageous to pass the wire through a concentrated solution of hydrochloric acid before entering the hydrogen furnace. Fifty percent and also thirty-five percent solutions of hydrochloric acid have been used. In some cases it may be desirable to slightly oxidize or activate the wire X before passing into the hydrochloric acid solution, for which purpose the wire may be passed through a flame as indicated at 50. Some or all of the hydrochloric acid solution carried by the wire into the furnace 16 is vaporized, is carried into the hydrogen furnace and provides a combined atmosphere of hydrogen and hydrochloric acid gases therein. Ferrous chloride formed by the action of the hydrochloric acid solution on the wire, is changed to hydrochloric acid in the presence of the hydrogen in furnace 16. Many other halogen salts would likewise be converted to the halogen acid in the furnace in the presence of hydrogen. Zinc chloride for example is changed to hydrochloric acid, and hence some of these salt solutions could be used as a source of the hydrochloric acid or other halogen acid in furnace 16.

After leaving the furnace 16, the wire X enters the bath 22 of the molten coating metal, as for example tin, the wire carrying with it, into the bath, hydrogen and hydrochloric acid.

The wire X after having been treated as just described, and after passing through the furnace 16 containing the hydrogen and hydrochloric acid, and after passing through the bath of molten tin, had a uniformly good adherent coating of tin which was mirror bright. The coating of tin which was applied was of a thickness corresponding to about 4 ounces of tin per base box.

The wire X is advantageously passed into the molten coating-metal bath in a manner to avoid passing through an oxide film, or a layer of scum, and without undesirable cooling. This has been accomplished by passing it into the bath of molten metal below the surface, as by passing it through a restricted orifice or opening 20 in a pot 22 containing the molten metal (tin for example), as shown in Figs. 2 and 3, the orifice 20 opening into the pot below the level 24 of the molten metal contained therein. The coated wire X may then be removed from the molten bath either through an orifice 26 (similar to 20) in the pot 20 below the level 24, or it may emerge through the surface of the bath in the top of the pot 22, and thence through a wiper.

A desideratum in arranging the entrance and exit opening or both, is to so restrict the exposed area of the bath, adjacent the point of entry and exit that oxidation is so restricted during operation of the process so as to be negligible so that oxide adhesions on the coated metal may be avoided.

The wire also may be passed into the molten tin in a manner to avoid passing through a tin oxide film by passing it into a bath of tin through a part 36 extending below the surface of the bath from above, and having a restricted passage or orifice for the wire, as illustrated in Fig. 4.

The surface of the molten coating metal (tin) may be protected against oxidation by covering it with an atmosphere of an inert or reducing gas substantially free from oxygen, etc., as for example, hydrogen, and the amount of oxide formed may be virtually eliminated by restricting the exposed area of the bath. As shown in Fig. 4, the pot 22 is provided with a hood or cover 30, provided with openings 32, 33, through which the wire passes in and out. A guide or roller 35 may be provided for guiding the wire in and out of the bath of molten metal. The hydrogen or other gas which is inert or reducing toward the coating metal may be supplied beneath the hood 30 by means of pipes 37.

Means, as a reel 39, may be provided for drawing the wire or other article continuously through the bath of molten metal and for collecting the coated wire. A drawning speed of 150 feet per minute has also been used in coating #28 gauge wire, in the work forming the basis of the mode of procedure herein given. Higher drawing speeds are obtained by lengthening the molten metal bath.

The coated article may, if desired, be wiped after leaving the bath of molten coating metal and while the coating metal on the article is still plastic, to remove surplus coating-metal and to regulate the thickness of the coating. A wiper is conventionally shown at 45.

The coating metal may be kept molten in the pot 22 by gas-burners 40 or by other suitable means, if found necessary, and the pot may be surrounded by walls 42. Heat from the wire may have an effect in maintaining the coating metal in the pot in molten condition. In most cases it is desirable not to exceed greatly the melting point of the coating metal, as there is, at very high temperatures, a tendency for crystals of the basis metal to migrate into the coating on the article.

The preferred temperature of the coating metal in the pot is 50° to 100° above the melting point of the metal. I have used in practice a temperature of 350–450° C. for tin; 450–550° C. for zinc; 350–450° C. for lead; 350–450° C. for cadmium; and 950°–1050° C. for beryllium.

When ferrous articles, for example, come into contact with the molten tin, an alloy bond of tin and iron is formed at the surface of the ferrous article, and in order that the thickness of this bond may be substantially uniform over individual articles, the articles are passed into and out of the tin bath in such manner that all parts are exposed to the bath for substantially the same length of time. This is accomplished by drawing wire, sheets, bars and the like through at a substantially uniform rate so that each part or spot enters and leaves the bath in the same time interval. Small articles are plunged into the bath so as to be submerged or immersed substantially all at once, and removed after a suitable interval. Moreover the time during which the articles remain exposed to the tin bath is preferably short.

For tin coated articles which are to be subjected to metal working processes usual in the fabrication of coated metal articles, bending, drawing, etc., the time of exposure to the tin bath is preferably such that only a thin alloy bond is formed between the basis metal of the article and the tin coating, and the bond is therefore kept thin so as to favor bending thereof with the basis metal without cracking or breaking.

Wire and flat strips coated with tin according to the present invention are smooth and bright; the tin coating is adherent and substantially uniform over the metal over which it is coated. The tin coating, inclusive of the alloy-bond between the tin coating and base, is substantially uniform in thickness.

The advantages obtained by coating articles with tin according to the present process, have also been found when zinc, cadmium, lead and beryllium have been used for the coating metal in place of tin. Coatings of the foregoing metals have been obtained on steel, copper, and nickel, as basis metals.

In place of hydrochloric acid, hydrobromic acid, hydroiodic and hydrofluoric acid can be used along with hydrogen, with results similar to those obtained with hydrochloric acid and hydrogen.

The process may be carried out by means of procedures other than that herein specifically described. For example, alloys of the coating metal may be used, and alloy coatings may be obtained by passing the metal through successive baths of coating metal, as for example successively through baths of tin and lead.

This application is a continuation in part of my application Serial No. 181,701, filed December 24, 1937.

What is claimed is:

1. A process of coating basis metals with a protecting coating, which comprises pretreating a basis metal of the group consisting of ferrous metal, copper and nickel, by charging it, at an elevated temperature, in and with a reducing gas, of the group consisting of hydrogen, carbon monoxide, nitrogen, blast furnace gas and blue water gas, and a halogen acid of the group consisting of hydrochloric, hydrobromic, hydroiodic and hydrofluoric acids, and, while carrying said charge, introducing the said basis metal to be coated into a normal molten bath of a coating metal of the group consisting of tin, cadmium, zinc, lead and beryllium, a wetting characteristic being imparted to said basis metal by its gas charge so that it takes a continuous and adherent coating of the coating metal.

2. A process according to claim 1, wherein the reaction between said basis metal and said coating metal is confined to the face portions in immediate contact.

3. A process according to claim 1 wherein said gaseous pretreatment of said basis metal is carried out at a temperature within the range 300° to 800° C.

4. A process of coating ferrous metal with tin, which comprises pretreating said ferrous metal by charging it, at an elevated temperature, in and with a reducing gas, of the group consisting of hydrogen, carbon monoxide, nitrogen, blast furnace gas and blue water gas, and a halogen acid of the group consisting of hydrochloric, hydrobromic, hydroiodic and hydrofluoric acids, and, while carrying said charge, introducing said ferrous metal into a normal molten bath of tin, a wetting characteristic being imparted to said ferrous metal by its gas charge so that it takes a continuous and adherent coating of tin.

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