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"ZINC GAS PLATING"

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IRON,
STEEL,
COPPER, ETC.

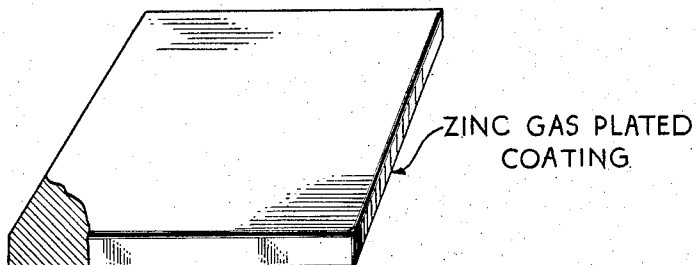


Fig. 1

CERAMIC

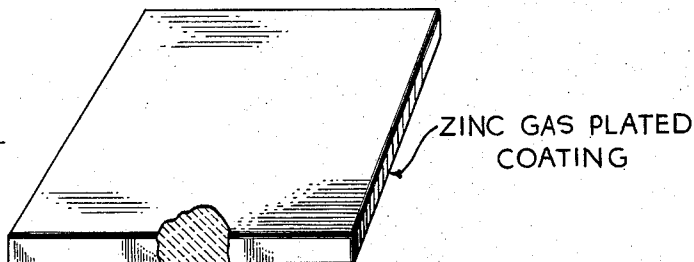


Fig. 2

GLASS FIBER

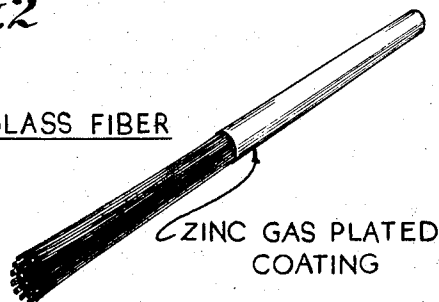


Fig. 3

PAPER,
WOOD

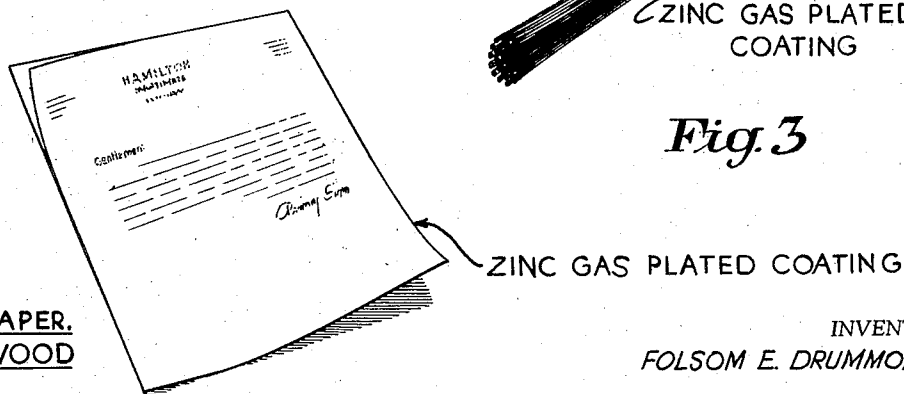


Fig. 4

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ZINC GAS PLATING

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2 Claims. (Cl. 117—47)

This invention relates to gas plating of zinc and zinc coated products.

In the production of many zinc coated products, as in the manufacture of galvanized iron, iron is cleaned and dipped into molten zinc to give it a protective covering of zinc to prevent rusting.

Another method for applying zinc, and known as sherardizing, consists in heating the metal to be zinc coated and spraying the surface with zinc dust. Electrolytic processes which are in general use commercially for the production of zinc comprise the electrolysis of solutions of zinc salts prepared from zinc ores.

Still another method consists in forming zinc films on a metal surface by applying a molten zinc halide thereto and reducing the compound to zinc metal in contact with the metal to be zinc plated.

While such methods are useful in the production and application of zinc coatings, they are slow and arduous to carry out as well as wasteful of the costly metal.

It is a principal object of the present invention to provide a high speed zinc plating method wherein zinc coatings are laid down on the surface to be zinc coated from a gaseous phase.

Another object of the invention is to provide a zinc coating process wherein different thickness coatings can be obtained. For example, in the production of corrosion resistant iron and steel products, zinc coatings of a desired thickness may be applied to suit the particular article and its intended use. The process of the invention provides a high speed method for applying uniform coatings of zinc on ferrous and non-ferrous substrates as desired. The process is particularly adapted for producing thin, continuous coatings of zinc at a high rate of speed and utilizing heat-decomposable compounds of zinc.

In accordance with this invention, a process of depositing zinc is provided which can be carried out at relatively low temperatures and pressures utilizing a heat-decomposable gaseous organo zinc compound. The material to be zinc plated is enclosed in a chamber and the air displaced with an inert gas such as carbon dioxide, argon, helium, or the like. The plating is carried out in the absence of oxygen and at a temperature below that at which zinc metal vaporizes.

To effect the deposition of zinc the base or substrate to be plated with zinc is heated to a temperature sufficient to cause a zinc bearing metal compound brought in contact therewith to be decomposed thus releasing zinc metal which is plated onto the surface of the article.

The present invention makes it possible to deposit uniformly thin coatings of zinc on the surfaces of various materials and such as will withstand the temperature used to bring about the decomposition of the gaseous zinc compound. Zinc plating of various articles may thus be accomplished by exposure of the article for a few seconds in such atmosphere. Articles of steel, iron, copper, magnesium, aluminum, or alloy metals as well as non-metal materials, for example, glass, ceramic tile, molded plastics, wood, paper and the like, may be thus zinc plated

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utilizing the process of this invention. Deposition of zinc metal on bearings and machine elements, hardware, utensils, and the like also may be accomplished by gas plating in accordance with this invention.

The invention permits a rapid deposition of zinc and while the article or sheet material is moved or conveyed through the plating chamber. A zinc metal film of one molecule thickness is initially deposited and which is increased to the desired thickness by lengthening the time of exposure of the substrate to the plating gas. Zinc metal is deposited in the microscopic pores and interstices in the surface of the substrate to form a tenacious, and continuous layer of zinc metal thereon.

In the use of gas plating to produce galvanized articles, the article or substrate to be zinc plated is thoroughly cleaned of foreign matter, and the resultant clean surface is then subjected to gas plating utilizing a suitable zinc bearing compound and which is heat decomposable at temperatures below the vaporization point of zinc (907° C.). The decomposition or disassociation of the gaseous zinc compound is made to take place in an atmosphere which is inert to the nascent zinc metal so that the formation of oxides or the like impure metal coatings is avoided. An atmosphere of dry helium gas is suitable for this purpose. Other gaseous mediums such as carbon dioxide, argon, nitrogen, hydrogen, or the like also may be used as a carrier for the zinc-bearing compound. An inert carrier gas preferably is used to control the movement of zinc plating and sweep away the gaseous by-products after plating has been effected. The carrier gas thus prevents the gaseous decomposition products, e.g. free radicals, as with the use of organozinc compounds, from reacting with the zinc metal deposited during the process.

In accordance with the preferred practice of this invention, the material or substrate to be zinc 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 helium or nitrogen. Thereafter a suitable zinc bearing gaseous compound is introduced into the plating chamber and which heat decomposes below 907° C. to deposit zinc onto the material to be zinc plated.

To bring about deposition of the zinc after introducing the zinc compound into the plating chamber, suitable heating means is provided to heat the material to a temperature high enough to cause the gaseous zinc compound to decompose and the zinc 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 may also be employed.

Where the deposition is effected at a temperature above the melting point of the zinc metal (419° C.) the deposited zinc coating is cooled to about 400–415° C. to solidify the zinc. The article or substrate material is coated with a thin coating of zinc after a few seconds exposure to the zinc plating gas. Long continuous lengths of material in the form of sheets, ribbons or the like may be thus zinc plated while the same is moved through the plating chamber from the inlet to the outlet.

Material or articles to be plated with zinc 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 cleaned to remove solid foreign matter. For degreasing surfaces the same may be washed with petroleum solvents such as toluol, solvent naphtha, trichloroethylene or the like. Last traces of moisture may be removed by heat-

ing the material at a temperature of 250° C. 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 gaseous zinc compound which is caused to decompose or disassociate and deposit zinc onto the article. After a desired thickness of zinc is deposited, the process is terminated and unused zinc material returned to storage or recirculated through the plating chamber.

The zinc compounds used for zinc gas plating comprises those which are gaseous and decompose to release the zinc metal at temperatures below the vapor point of zinc. At ordinary atmospheric pressure conditions (760 mm.) zinc vaporizes at about 907° C. Zinc carbonyls, carbonyl halides, hydrides, nitrides and organozinc compounds may be used.

Zinc alkyl compounds which may be utilized in carrying out the gas plating of zinc are listed as follows, along with their boiling points

Zinc diethyl, $\text{Zn}(\text{C}_2\text{H}_5)_2$, B.P. 118° C.
Zinc dimethyl, $\text{Zn}(\text{CH}_3)_2$, B.P. 46° C.
Zinc dipropyl, $\text{Zn}(\text{CH}_2\text{CH}_2\text{CH}_3)_2$, B.P. 146° C.
Zinc dibutyl, $\text{Zn}[(\text{CH}_2)_3\text{CH}_3]_2$, B.P. 81-2° C. at 9 mm.
Zinc di-isobutyl, $\text{Zn}[\text{CH}_2\text{CH}(\text{CH}_3)_2]_2$, B.P. 135° C.

The zinc alkyls can be made by heating zinc dust under ordinary atmospheric pressure with alkyl iodide at the boiling point of the latter. When the mass is converted into the alkyl zinc iodide, the temperature is raised and the zinc dialkyl distills off and is recovered.

A useful halide compound is zinc iodide (ZnI_2) which heat decomposes at about 625° C. to deposit zinc. Zinc acetylacetonate also may be employed as the organozinc compound. As an aromatic compound zinc diphenyl may be used which boils at 280° C. Zinc films under reduced pressures may be produced using zinc cyanide which decomposes at about 800° C. For producing adherent zinc films, the substrate is preferably heated above 419° C. at which zinc melts.

In the use of heat-decomposable zinc bearing compounds, the presence of oxygen and water vapor is avoided in order to prevent the formation of the oxides of zinc. The use of an inert carrier gas, and which preferably comprises 10% by volume of hydrogen, assists in carrying away decomposition gases and prevents the formation of blue powder and oxides of zinc. The temperature in the plating chamber is kept below that at which zinc metal is vaporized. The process is preferably carried out at atmospheric pressure but where it is desired to enhance the plating process, as when use is made of zinc bearing compounds requiring lower pressures, sub-atmospheric or vacuum pressures may be employed.

The flow rate of the zinc bearing gaseous compound to the plating chamber is suitably controlled to produce uniform and continuous film deposits of zinc. Optimum flow rates for the zinc bearing compound and carrier gas vary with different zinc compounds and in each instance is such as to quickly sweep away the gaseous by-products while contacting the substrate to be zinc gas plated with a sufficient concentration of zinc bearing vaporous compound to form a uniform, continuous coating of zinc on the substrate.

The following examples are illustrative of the process but are not intended to be restrictive thereof:

Example I

A steel panel 4" x 6" is wire brushed and suspended in a closed container or chamber. Dry helium gas is introduced into the chamber to sweep out the air. The panel is heated to 650° C. and then while thus heated gaseous vapors of zinc iodide are brought in contact therewith and decomposed depositing a film of zinc onto the surface of the heated panel. The zinc bearing compound is swept

across the heated panel in a current of helium containing 10% by volume of hydrogen to prevent redissolving of the zinc as the same is plated onto the surface of the panel.

Example II

In this instance the gas plating is carried out as described in Example I, using gaseous zinc dimethyl in helium carrier gas. The temperature of the panel is held at about 500° C. and a pressure of 2 mm. of mercury being maintained in the plating chamber to cause the gaseous zinc dimethyl to decompose or disassociate and deposit zinc metal on the surface of the panel.

Example III

In this example, the gas plating is carried out as in Example I, using zinc diethyl as the zinc plating compound.

Example IV

In this instance zinc gas plating is carried out as in Example I, using zinc dipropyl as the gas plating zinc bearing compound.

Example V

The gas plating in this instance is carried out using zinc dibutyl under a vacuum pressure of 9 mm. of mercury, and at 250° C. temperature.

Example VI

In this example, the gas plating is effected using zinc di-isobutyl at atmospheric pressure and employing a temperature of 350° C.

Example VII

In this instance the gas plating is carried out as in Example I, at atmospheric pressure using zinc diphenyl at temperature of 450° C.

Example VIII

In this example, zinc acetylacetonate is used as the metal bearing zinc compound and the process is carried out as in Example I with the panel heated to 375° C. or high enough to cause decomposition of the zinc acetylacetonate and release of the zinc metal to form a zinc deposit on the surface of the panel.

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

Inert carrier gas is admixed with the vapors of the zinc bearing compound and conducted to the plating chamber and into contact with the heated article to be plated as described. The carrier gas generally constitutes from 10% to 50% by volume of the gaseous mixture.

Articles to be zinc plated are heated in each instance to a predetermined temperature, being dependent upon the decomposition temperature of the zinc bearing compound used. Where desired the zinc plated article may be subjected to an annealing heat treatment to stabilize the metal deposit. Such heat treatment may consist of heating the zinc plated article at about 300 to 400° C. for an hour.

The invention provides a process for galvanizing articles and wherein zinc metal in an extremely pure state is deposited from the gaseous state by decomposition or disassociation of a gaseous zinc compound. The thickness of the zinc metal coating is suitably controlled by varying the time the zinc 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 proc-

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ess of this invention. A protective coating of zinc is thus provided which renders metal articles resistant to corrosion.

The process further makes it possible to carry out the galvanizing 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 zinc while same is moved along through a plating chamber. The invention is particularly useful in galvanizing articles to provide the same with a thin uniform coating of metal and which is diffused into the pores and interstices of the material forming a substantial integral outer layer of corrosion resistant zinc 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.

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What is claimed is:

1. A method of gas plating objects with zinc metal which consists in heating the object to be zinc plated to the decomposition temperature of a heat-decomposable gaseous zinc metal compound, and contacting said heated object with said gaseous zinc compound contained in carbon dioxide carrier gas to cause thermal decomposition of said zinc metal compound and deposition of zinc onto the surface of said object, said zinc metal compound being zinc acetylacetonate.

2. As an article of manufacture, a zinc plated object gas plated in accordance with the process of claim 1.

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