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PROCESS OF ZINC COATING MAGNESIUM ARTICLES

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This invention relates as indicated to a process for providing zinc coatings on magnesium work surfaces and the articles which may be produced by such process.

The provision of zinc coatings on magnesium bodies has been under investigation for quite some time. The process of the present invention differs from the prior art proposals in the procedural steps employed by which there is produced a final adherent film of zinc on the magnesium base material which is characterized by smoothness and adherence which has not been secured heretofore.

It is a principal object of this invention to provide a process of the character described which is relatively inexpensive and easy to control and thus easy to use on a commercial scale.

It is a further object to provide a process which will produce coatings of zinc on magnesium and magnesium base alloys, which coatings have a smoothness and adherence to the base metal not possessed by the coatings produced heretofore.

It is a further object to provide products resulting from this process which are useful for a wide variety of purposes for which zinc-coated magnesium bodies as produced heretofore were not suitable.

Other objects of the invention will appear as the description proceeds.

To the accomplishment of the foregoing and related ends, said invention then comprises the features hereinafter fully described and particularly pointed out in the claims, the following description setting forth in detail certain illustrative embodiments of the invention these being indicative, however, of but a few of the various ways in which the principle of the invention may be employed.

Broadly stated the process of the present invention comprises the steps of first chemically plating onto the previously cleaned and prepared work piece a superficial layer of zinc and then electrodepositing thereover a smooth continuous layer of zinc having a thickness of not more than about .0008 inch.

The process of this invention as thus broadly defined may be best understood by giving a detailed description of each of the steps which are performed in sequence in practicing such process.

The base metal

The base metal to which this invention is applicable is the broad class of metals which includes magnesium and its alloys. Throughout the ensuing description and in the claims the base metal will be referred to as magnesium. By such terminology we intend to include not only pure or substantially pure magnesium but also those alloys thereof of which magnesium is the principal constituent.

Generally, the magnesium articles which may be subjected to my process will be in the form of sheets or plates, especially when the ultimate use thereof requires that form or slight modifications thereof since it has been

found that the coating produced by our process will not be adversely affected when the body to which the same has been applied is deformed. One particular use of the coated products produced by this process is as printing plates and these, of course, will be of the physical size and configuration which has now become standard for printing plates composed entirely of zinc.

The process of this invention is applicable not only to magnesium which has been produced by working such as rolling but also by casting. The present process has been found useful in the application of a bright corrosion resistant coating on cast machine parts made of magnesium.

Surface preparation

The initial work piece regardless of whether it is in the form of a rolled or cast article and regardless of its size and shape should be first thoroughly cleaned and this can be best accomplished by first immersing the work piece in an alkaline cleaner bath such as is commonly used in industry for the purpose of removing adherent grease and dirt. Such alkaline cleaning baths are not effective however to remove coatings which are chemically combined as for example the oxides and other films which may have been formed on the work piece due to reaction of the same with the air or other substances with which the same may have been in contact. This type of adherent film can best be removed and the work surface desirably brightened by immersing the work piece which was previously cleaned in the alkaline cleaning bath and then washed with water, in an aqueous solution of nitric acid containing about 10% nitric acid and which bath is maintained at a temperature of from room temperature to about 100° F. and sometimes as high as 120° F. It will be found that a dip for a period of about 10 to about 30 seconds will be sufficient after which the work is removed and rinsed in water. Instead of chemically removing such tightly adherent surface films, it is possible also to remove the same chemically as by polishing and buffing or by combination of a chemical means. If such combination is used then the chemical treatment such as the nitric acid bath should be used last in order to insure the greatest possible freedom of deleterious deposits on the work surface.

After the work surface has been freed of its adherent films and in the manner just described and thoroughly rinsed with clean water, it is then preferably pickled in either of two solutions such as the following:

Phosphoric acid (85%)	gal.	0.2
Sodium bifluoride	oz.	13.3
Water to make 1 gal.		

The cleaned magnesium article is immersed in this solution for 1.5 minutes with mild agitation, removed and rinsed in cold water. A second pickle that gives fair to good results is composed of:

Hydrochloric acid	fl. oz.	1
Sodium sulfate	oz.	0.1
Water to make 1 gal.		

The magnesium article is immersed in this solution for 0.5 to 1 minute with mild agitation. The above bath suffers two deficiencies, first, its chemical activity is short, and second, results are not always consistent. The first bath on the other hand is deactivated slowly, and results are uniform.

It will be found that this pickle step has the effect of activating the surface of the magnesium work piece so that it more uniformly and efficiently accepts and has deposited thereon the chemical plating of zinc which is then applied thereto in carrying out my process. The last pickling step just referred to is believed also to remove from the work surface those magnesium salts

which may be formed in the nitric acid pickling step which was employed for the purpose of removing the tightly adherent film such as the oxides and assists also in providing a desirably bright work surface.

After being removed from this activating pickle bath the object is again thoroughly rinsed in water and then within a period of less than 10 minutes so as to prevent the occurrence of contamination or deterioration of the surface, the work is subjected to the chemical plating step which is the next step in my process.

The thus freshly cleaned and prepared work piece then has deposited thereon a superficial coating of zinc from a bath such as any of those known in the art as a zincate bath of which the following is representative:

	Oz.
Tetrasodium pyrophosphate	16
Zinc sulphate monohydrate	4
Sodium fluoride	0.67
Sodium carbonate	0.67

Water to make 1 gal.
pH, 10.2–10.4 (paper).

The immersion dip is operated at a temperature of from 160 to 190° F. and the magnesium article is immersed in the bath from 0.5 to 2 minutes with mild agitation. Inadequate polishing and buffing of the magnesium metal will be evidenced at this point by the appearance of discolored areas. Those areas will be the centers of rough and nodular deposits when subsequent electrodeposits are applied. Inadequate pickling will result in a streaky appearance in the immersion plate, but this condition is not always detrimental to further deposition by electrolysis.

Another type of bath which may be used in providing the necessary initial superficial coat of chemically deposited zinc has a composition as follows:

	Oz.
Tetrasodium ethylenediamine tetracetate	30
Zinc carbonate	4.5
Boric acid	6.0

Water to make 1 gal.

This bath can be operated at a temperature of from 70 to about 120° F. Best results will be secured if the bath is mildly agitated during use. The necessary coating is produced by the immersion of the work piece in this bath at the temperature stated for a period from about ½ to about 3 minutes.

The coating chemically deposited by this first step is extremely thin. The work piece should be maintained in this first bath for a time interval within the limits given above just sufficient to produce a substantially uniform and substantially completely continuous coating of zinc. At this point it should be observed, however, that since the operation of baths of this character referred to above depend on an ion exchange between the base metal and the bath components, some of the base metal will always remain uncoated. It is for this reason that best results will be secured if the work piece is removed from the bath at the earliest possible moment after the deposited coating has the appearance to the naked eye of being a continuous coating. The factors which determine the length of time the article should be kept in this chemical plating bath are the temperature of the bath, the concentration of its components, and to a certain extent the composition of the work to which it is applied. An entirely practical test and one which will yield consistently good results is to remove the work piece from the bath as soon as it appears to the naked eye to have a continuous coating thereon of zinc.

After the work piece is removed from the chemical deposition bath it should be rinsed in cold water before being subjected to the next step.

The electrode position step

The thus prepared and superficially zinc coated magnesium work piece is then given a coating of electrodeposited zinc, which coating has a thickness of not more than about .001 inch and preferably not more than about .0008 inch. The minimum thickness of coating which will generally be found to be sufficient is that which upon critical inspection is shown to be a truly continuous plate over the entire work surface. The upper limit of thickness given above is critical since it has been found that if an electrodeposited film of greater thickness is utilized, such film rapidly loses its adherence and uniformity in thickness. The following is a representative bath and conditions of operation thereof for the deposition of the electroplating:

Zinc metal	oz.	4
Total sodium cyanide	oz.	9.6
Sodium hydroxide	oz.	12
Brightening agent	gm.	1 to 8

Water to make 1 gal.

The bath is operated at room temperature (from 70 to 95° F.) without agitation at a current density of from 15 to 30 amp./ft.^{2}. Since the apparent conductivity of both zinc or magnesium is not of the highest order in the electroplating solution, uncoated portions of a highly conductive rack tend to rob the magnesium metal of plate, for this reason it has been found desirable to use steel racking tips. Resinous types of brightening agents permit the application of bright, dense and adherent deposits of zinc. For example a condensation product composed of 3 moles of monoethanol amine, one mole of hydrogen sulfide and one mole of acetaldehyde produces a very bright zinc deposit.

While the composition of the cyanide zinc electrolyte used in depositing the electroplate as given above is representative of a composition which gives good results, the concentration thereof may be varied within the limits given below:

	Oz./gal.
Zinc metal	3.5 to 5.5
Sodium cyanide	8.4 to 13.2
Caustic soda	10 to 12

Certain basic factors should be observed in compounding an electrolyte within the limits given above. Zinc metal higher than 5.5 oz. per gal. tends to produce deposits of poor adhesion, a caustic content lower than 10 oz./gal. tends to produce deposits of inferior color and structure. Anode corrosion is also inhibited by low caustic concentration. The cyanide concentration is governed by the concentration of zinc metal. An M ratio (calculated as total NaCN/Zn) of 2.4 is preferred, but may vary from 2 to 2.8.

As indicated previously, the process of this invention has been used in a highly successful manner in the production of zinc-coated magnesium plates which can be used as a superior substitute for solid zinc plates heretofore used as printing plates. It has been found that a printing plate produced in accordance with the present invention may be employed with the same processes heretofore utilized in the preparation of printing plates made entirely of zinc with the result, however, that a vastly superior printing plate is produced. It is believed that by the use of the present process there was produced the first commercially successful printing plate composed of a zinc-coated magnesium sheet.

Composite printing plates made by our process have been found to be superior to those produced from solid zinc sheets. The surface of the printing plate which is composed of magnesium or magnesium alloys, the same having been exposed by the acid etching process employed in producing the plate, is superior to a surface composed of zinc. Microscopic examination of such magnesium surface has shown that its physical structure as a result

of the acid etching process is quite different from a zinc surface similarly etched.

The nature of the physical superficial coating of zinc is an important factor of the present invention. Efforts have been made to produce zinc-coated magnesium printing plates by electrodepositing all of the zinc on the magnesium base metal. Those attempts have not been successful in that the printing plate was not satisfactory. It appears that the fact that the superficial coating is discontinuous, i. e., in the form of a lattice leaving a minor proportion of the magnesium exposed is the key to the success of the printing plates made by our process. Thus, this superficial layer can and should be produced by means of a zinc bath wherein there is an ion exchange between the bath and the work so as to insure the generation of a lattice structure deposit of zinc on the magnesium. When the finish coat of zinc of the thickness within the ranges specified above is then applied, an entirely satisfactory plate is produced which is not only sufficiently adherent to the work piece, but which has the smoothness and other properties necessary for the production of articles such as printing plates.

Other modes of applying the principle of the invention may be employed, change being made as regards the details described, provided the features stated in any of the following claims or the equivalent of such be employed.

We, therefore, particularly point out and distinctly claim as our invention:

1. The process of making a bi-metal plate consisting of a magnesium base plate having a surface coated with a smooth thin continuous adherent coating of zinc which comprises chemically depositing a superficial uniformly discontinuous layer of zinc onto the thoroughly cleaned surface of a magnesium plate by contacting said cleaned surface with an aqueous alkaline solution comprising zinc ions having ion exchange with the magnesium plate and then directly upon such chemically deposited zinc, electrodepositing from a cyanide bath a continuous layer of zinc having a thickness of not over about .0008 inch.

2. The process of making a magnesium work piece consisting of a magesium base having a surface coated with a smooth thin continuous adherent coating of zinc which comprises chemically depositing a superficial uniformly discontinuous layer of zinc onto the thoroughly cleaned surface of a magnesium base by contacting said cleaned surface with an aqueous alkaline solution comprising zinc ions having ion exchange with the magnesium base and then directly upon such chemically deposited zinc, electrodepositing from a cyanide bath a continuous layer of zinc having a thickness of not over about .001 inch.

3. The process of making a magnesium work piece consisting of a magnesium base having a surface coated with a smooth continuous adherent coating of zinc which comprises chemically depositing a superficial uniformly discontinuous layer of zinc onto the thoroughly cleaned surface of a magnesium base by contacting said cleaned surface with an aqueous alkaline solution comprising zinc ions having ion exchange of zinc for the magnesium of said base and then directly upon such chemically deposited zinc-coated structure, electrodepositing from a cyanide bath in which the ratio of cyanide to zinc is between about 2 and 2.8 a continuous layer of zinc completely covering the superficially zinc-coated base, said electrodeposited zinc layer having a thickness of not over about .001 inch.

4. The process of making a bi-metal plate consisting of a magnesium base plate having a surface coated with a smooth continuous adherent coating of zinc which comprises chemically depositing a superficial uniformly discontinuous layer of zinc onto the thoroughly cleaned surface of a magnesium plate by contacting said cleaned surface with an aqueous alkaline solution comprising zinc ions having ion exchange of zinc for the magnesium of said plate and then directly upon such chemically deposited zinc-coated structure, electrodepositing from a cyanide bath in which the ratio of cyanide to zinc is between about 2 and 2.8 a continuous layer of zinc completely covering the superficially zinc-coated plate, said electrodeposited zinc layer having a thickness of not over about .001 inch.

5. The process of making a bi-metal plate of a magnesium base plate having thereon a thin adherent smooth continuous coating of zinc adapted for use in making a photoengraving printing plate which comprises chemically depositing a superficial uniformly discontinuous layer of zinc onto the thoroughly cleaned surface of a magnesium plate by contacting said cleaned plate surface with an alkaline zincate bath having ion exchange of zinc with the magnesium of said plate and then directly upon such chemically deposited zinc, electrodepositing from a cyanide bath a continuous layer of zinc having a thickness of not over about .0008 inch.

6. The process of making a magnesium base plate having a zinc-coated surface consisting of two zinc layers, with the combined zinc coating being so smooth, thin and adherent that the plate may be used as a photoengraving printing plate, which comprises chemically depositing onto the thoroughly cleaned surface of a magnesium plate, by contacting said cleaned surface with an aqueous alkaline solution comprising zinc ions having ion exchange of zinc for the magnesium of said plate, a uniformly discontinuous superficial coating of zinc, and then directly upon such chemically deposited zinc coating, electrodepositing from a cyanide bath in which the ratio of cyanide to zinc is between about 2 and 2.8 a continuous layer of zinc completely covering the superficially zinc-coated magnesium plate, said electrodeposited zinc layer having a thickness of not over about .0008 inch.

7. The process of providing a magnesium work piece with a smooth adherent continuous coating of zinc which comprises chemically depositing a superficial uniformly discontinuous layer of zinc onto the thoroughly cleaned surface of a magnesium base by contacting said cleaned surface for between about 0.5 and 2 minutes with a zincate bath having a pH of between about 10.2 and 10.4 maintained at a temperature of between about 160° and 190° F. and then directly upon said superficially zinc-coated surface, electrodepositing from a cyanide bath in which the cyanide to zinc ratio is between about 2 and 2.8 a continuous layer of zinc having a thickness of not over about .0008 inch.

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