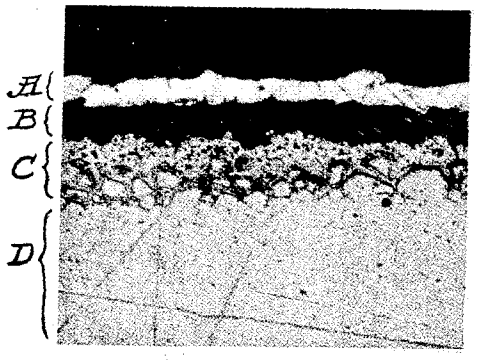
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PROCESS FOR ELECTROLYTICALLY ZINC PLATING MAGNESIUM AND MAGNESIUM BASE ALLOYS

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PROCESS FOR ELECTROLYTICALLY ZINC PLATING MAGNESIUM AND MAGNESIUM BASE ALLOYS

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The present invention relates to a method for producing zinc coated magnesium articles and more particularly to a process for providing magnesium and magnesium alloy articles with a corrosion resistant coating of electrodeposited zinc and the product thereof.

It has long been recognized that the use of magnesium and magnesium alloy articles has been restricted because of their tendency to corrode, particularly in the presence of chlorides. Thus, in a paper presented before the Institute of Metals, in September, 1931, by H. Sutton and L. F. Le Brocq., scientific officers of the Royal Aircraft Establishment, Great Britain, the following statements were made in a discussion of the protection of magnesium alloys against corrosion. (J. I. M., vol. XLVI, 1931, pp. 53–80):

"The use of magnesium alloys in engineering construction has, up to the present, been considerably restricted on account of their tendency to corrode, particularly in the presence of water-soluble chlorides. If this tendency could be overcome a large field would be opened to the use of these alloys, particularly where rigidity coupled with lightness is a necessity, as, for example, in aircraft construction. Various methods have been suggested from time to time for combating the tendency of magnesium alloys to corrode. These methods may be classified as follows:

"(I) Addition to magnesium of a metal or metals, also producing an alloy having useful mechanical properties;

"(II) Coating with other metals by such processes as shearardizing, calorizing, the Schoop metal-spraying process, etc.;

"(III) Production of a protective film by chemical means (dipping processes);

"(IV) Production of a coating by anodic or cathodic treatment; and

"(V) Painting or enamelling.

"For many purposes, notably for parts exposed to marine atmospheres, both commercially pure magnesium and the magnesium-manganese alloy require protection against corrosion in order to obtain reasonably long life of the parts.

"Samples of magnesium bar, previously lightly sand-blasted, were sherardized by heating with various mixtures of zinc metal powder and zinc oxide. After 1 month's exposure to the sea-water-spray test all the samples showed marked corrosion. Similar experiments in which cadmium metal powder replaced zinc metal powder yielded slightly less favorable results.

"Samples as calorized appeared to offer no appreciable resistance to corrosion by sea-water spray.

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"Attempts to oxidize several of the calorized samples anodically in an aqueous solution of chromic acid were unsuccessful."

These authorities also state that sprayed coatings of metallic aluminum and anodic oxidation by the Bengough process did not provide satisfactory results. The same source is an authority for the statement that protection of magnesium and its alloys by means of a chromate treatment likewise is not satisfactory for severe conditions of service.

Attempts to provide a protective coating on magnesium and its alloys by electrodeposition of zinc from a zinc cyanide-sodium cyanide electrolyte containing 59 grams per liter of zinc cyanide and 37 grams per liter of sodium cyanide likewise failed. These authorities state this fact in the following words:

"The plated bar was washed with distilled water and exposed to the sea-water-spray test without lanolining. After one week, practically the whole of the zinc deposit had been separated from the base metal by the products of corrosion."

From the foregoing it is apparent that these experts did not consider that any of the methods then available gave satisfactory results for increasing the corrosion resistance of magnesium and its alloys. Even in 1936 authorities held the same opinion as is clearly shown by the following statement found in "Corrosion Resistance of Metals and Alloys," McKay and Worthington, Reinhold Publishing Corporation (1936), pp. 108 and 109:

"Metallic coatings do not seem to have virtue. From the standpoint of two-metal galvanic relations, zinc—and possibly cadmium—alone might have virtue, if they could be satisfactorily deposited though even this is somewhat doubtful. There are technical obstacles, seemingly impossible to avoid, in coating magnesium electrolytically. Nor has anodic oxidation been found to be of any use with magnesium alloys."

That the problem of electrolytically coating magnesium has not been solved even as late as 1939 is evident from the statements in a booklet published by the Dow Chemical Company, Midland, Michigan, August 1, 1939. On pages 57 and 58 the following statement is made:

"Electroplating: Some success has been attained in the experimental electroplating on Dowmetal. Coatings applied by this method offer the possibility of bright, non-tarnishing finishes for

in-door service. Although production methods have not been fully worked out . . ."

The U. S. Patent No. 1,801,629 likewise points out that although in a handbook entitled "Magnesium," published by American Magnesium Corporation it is indicated that saisfactory results can be obtained by thus electroplating with alkaline, neutral or cyanide solutions provided the surface to be plated has been properly prepared, "As a matter of fact, careful investigation has disclosed that a closely adherent electrodeposited coating cannot be obtained with any of the solutions named nor is the method of preparing the surface a satisfactory one."

The foregoing discussion makes it manifest that magnesium and its alloys do not have satisfactory corrosion resistance, that a successful method of electrodepositing corrosion resistant coatings has not been provided and that the failure of the art to discover such a method has restricted the use of magnesium and magnesium alloys where exposed to corrosive mediums especially water-soluble chlorides. Although it is apparent that many attempts have been made to solve this vexatious problem none, so far as I am aware, has provided a process satisfactory on an industrial scale for providing magnesium and magnesium alloys with a corrosion resistant coating.

I have discovered that magnesium and magnesium alloys can be provided with a corrosion resistant coating of electrodeposited zinc.

It is an object of the present invention to provide a process for electrodepositing a corrosion resistant zinc coating on magnesium and magnesium alloys.

It is another object of the present invention to provide a process for electrodepositing on magnesium and magnesium alloys a zinc coating of relatively low porosity having a higher corrosion resistance than the basis metal.

It is a further object of the present invention to provide a process whereby magnesium and magnesium alloys are provided with an electrolytically deposited coating of zinc bonded to the basis metal by an alloy bond.

The present invention also contemplates the provision of a process whereby magnesium and magnesium alloys are provided with a heat treated electrolytically deposited zinc coating having greater surface hardness and wear-resistance than the basis metal. The special heat treatment is applied in such a manner that the yield point of the basis metal remains substantially unimpaired.

Other objects and advantages of the present invention will become apparent from the following description in which the single figure is a reproduction of a photomicrograph taken at 250 diameters of magnesium containing material having a layer of electrodeposited zinc thereon bonded to the basis magnesium containing material by a zinc-magnesium alloy intermediate layer after heat treatment.

Broadly stated the present invention contemplates the use of a specially treated cyanide bath for the electrodeposition of zinc on especially treated magnesium or magnesium alloys to provide a magnesium or magnesium alloy article having an electrodeposited zinc coating. The zinc coated magnesium or magnesium alloy article is then subjected to a special heat treatment for critical periods of time to provide an alloy bond and to reduce the relative porosity of the zinc coating to a satisfactory value.

While Kenaga in U. S. Patent No. 1,801,629 has taught that no cyanide zinc bath is satisfactory for electrodepositing zinc on magnesium and its alloys and teaches the use of a solution of a halide in anhydrous solvent, I have discovered that an aqueous electrolyte having the following composition

Constituent	Normality
[Zn]	1.0
[CN] radical	2.1
[Free Alkali]*	1.45
[CO_3] radical	0.56
[F]	0.18
[Total Alkali]	2.3

*The free alkali concentration is that which would exist as sodium hydroxide in solution if no complexes were formed.

gives satisfactory results provided the bath is pre-treated in a critical manner as described hereinafter.

Another important feature of the present invention is the discovery that the electrolyte hereinbefore described may be used for long periods of time after pretreatment without staining of the cathode occurring. This is in distinct contrast to the statements made in Trans. Electro-chemical Society, vol. XL (1921), 263, wherein C. J. Wernlund makes the following statements:

"Almost any sodium-zinc cyanide solution which contains excess of sodium cyanide will give a smooth, gray-white deposit of zinc on iron cathodes when first made up."

"Every such solution after a period of electrolysis varying from 1 to 10 hours and usually after about 2 or 3 hours gave only darkened or stained deposits."

Aqueous solutions previously employed in electro-depositing zinc comprise, generally speaking, acid type and alkaline type of electrolytes. The acid type electrolytes include, for instance, chloride and sulphate solutions while the alkaline type of electrolytes contain cyanide as one of their principal constituents.

Exhaustive tests have shown that no adherent and uniform plate can be obtained on magnesium alloys by using conventional acid type electrolytes of the foregoing types. The zinc deposited from such acid type electrolytes is spongy and dark in colour, lacks adherence (it falls off the cathodes when touched or rubbed) and at the same time the magnesium alloy cathode is heavily corroded.

Under certain conditions, specified more fully hereinafter, alkaline, or cyanide electrolytes can be used to deposit zinc or magnesium alloys. The conditions governing the quality of the electroplate include

1. The composition of the electrolyte.
2. Pre-treatment of the electrolyte.
3. Operating conditions during electroplating.
4. Heat treatment.

1. The Quality of the Plate Varies With Composition of Electrolyte

All of the alkaline, or cyanide, electrolytes investigated produce electrodeposits of zinc on magnesium alloy. However, not all electrolytes of the alkaline, or cyanide, type produce continuous, uniform and sufficiently adherent plates of good zinc colour, and the electrodeposits obtained on a variety of such electrolytes vary from bright and very sketchy, i. e., thin and discontinuous plates to dark, coarse, heavy but very blistery zinc coatings. It has become apparent

that the composition of cyanide type electrolytes is limited insofar as the quality of the plate produced is concerned.

Some cyanide type electrolytes produce a fairly light-colour plate but the adherence of such plates requires special care in handling after plating. An electrolyte of this type (B–2) has for example the following compositions:

Zn concentration—1.0 normal;
CN radical concentration—0.7 normal;
Alkaline concentration—2.2 normal;
Acetic acid concentration—1.0 normal.

Another cyanide type electrolyte (B–5) produces a rather dark and coarse plate which has fairly good adherence but has a strong tendency to form blisters. In this type of electrolyte, of all the types investigated, gassing at the cathode is strongest. An electrolyte of this type has, for example, the following composition:

Zn concentration—1.0 normal;
CN radical concentration—1.5 normal;
Alkaline concentration—1.8 normal.

An electrolyte of the cyanide type (B–6 which produces satisfactory plates has for example, the following composition:

Zn concentration—1.0 normal;
CN radical concentration—2.1 normal;
Free alkaline concentration*—1.45 normal;
CO_3 radical concentration—0.56 normal;
Fluoride concentration—0.18 normal.
Total alkaline concentration—2.2 normal.

In addition, the foregoing type (B–6) of electrolyte contains organic material. However, not all organic addition agents suggested in the prior art can be used. For instance, organic compounds used in commercial plating operations, such as sodium sulfate derivatives of 2-ethylhexanol produce unsatisfactory results, while an addition of small amounts of gum arabic and dextrose appear to have a beneficial effect on the plate produced from such (B–6) electrolytes.

It is important to note that even the "B–6" type of electrolyte does not produce satisfactory plates on magnesium alloys, particularly not under continual plating operations, unless it has been subjected to a special pre-treatment and unless certain specific operating conditions are maintained. These requirements are in contradiction to plating specifications taught by the prior art, e. g., in the literature for commercial zinc plating on iron and steel. These critical pre-treatment and operating conditions are discused more fully hereinafter.

In conjunction with the three alkaline type electrolytes discussed above, the observation has been made consistently that, under comparable operating conditions, the B–2 type of electrolyte produces very little gassing at the cathode. The B–5 type electrolyte produces very strong gassing at the cathode and a coarse dark plate having numerous blisters. Comparing the ratio of the free alkaline concentration to that of zinc of the three electrolytes, the following is of interest:

Electrolyte B–2—1.2 little gassing;
Electrolyte B–5—1.8—heavy gassing;
Electrolyte B–6—1.45—medium gassing.

2. Pre-Treatment of Electrolyte Required

As mentioned hereinabove, the preferred electrolyte B–6 has the following composition:

Zn concentration—1.0 normal;
CN radical concentration—2.1 normal;

Free alkaline concentration*—1.45 normal;
CO_3 radical concentration—0.56 normal;
Fluoride concentration—0.18 normal;
Total alkaline concentration—2.2 normal; and small amounts of organic material like gum arabic and dextrose.

Statements in the literature to the effect that this electrolyte produces a continuous, uniform and fully adherent zinc plate on steel could be confirmed fully, particularly if the stated preferred temperature range (40–50° C.) and the stated preferred current density (approximately 37–40 amp./sq. ft.) were employed.

However, this electrolyte does not produce a continuous uniform and adherent plate of zinc on magnesium alloy if used at the current density specified for iron and steel or at lower or higher current densities (10–100 amp./sq. ft.). Likewise a variation of the specified operating temperature does not produce any notable improvement.

In order to obtain a continuous, uniform and sufficiently adherent zinc plate on magnesium alloy, the electrolyte has to be subjected to a pre-treatment. This pre-treatment is carried out at current densities ranging from 35–400 amp./sq. ft. and at temperatures ranging from 20–80 degrees C. The duration of such pre-treatment depends to some extent on the current density applied, in other words, higher current densities require less time. It has been found that current densities in excess of 50 amp./sq. ft. up to approximately 250 amp./sq. ft. will put the electrolyte in satisfactory operating condition if applied for approximately ½ hour or until a test plate, plated under preferred conditions is provided with a continuous, uniform layer of electrodeposited zinc which adheres well enough to be handled.

Extensive investigations have shown that the sludging of the anodes, which is more fully discussed hereinbelow, should preferably be avoided during the step of the pre-treatment, since it has been noted that the sludging of the anodes during the pre-treatment often shortens the life of the electrolyte for regular plating operations.

Furthermore, the colour of the electrolyte has been found to be a criterion, an amber or dark amber colour of the electrolyte indicating poor plating qualities or a short life of the electrolyte during plating operations. On the other hand, electrolytes possessing a light amber to light yellow colour or even no colour at all possess superior plating qualities and their useful life increases in proportion as the electrolyte becomes lighter in colour, or colourless.

The total wattage alone or the amount of watt-hours alone consumed in the treatment do not provide a sufficiently accurate specification for suitable operating conditions of the pre-treatment. Thus electrolytes subjected to a low amperage pre-treatment over an extended period of time, such as 10 amp./sq. ft. for a period of 10–50 hours, do not put the electrolyte in a satisfactory condition for plating. A high amperage pre-treatment of the order of 300–400 amp./sq. ft. for a period of from 20 to 30 minutes when associated with elevated temperatures of about 70° C. to about 80° C. or higher produces erratic results, and the colour of the electrolyte usually changes from colourless or light amber to an amber or dark amber.

* The free alkaline concentration is that which would exist as sodium hydroxide in solution if no complexes were formed.

After an electrolyte has been subjected to the pre-treatment at a low current density for an extended period of time it is seldom possible to revive the electrolyte by subjecting it to a pre-treatment under the above stated optimum conditions. If the operating conditions for the pre-treatment are controlled in such a manner that the preferred current range of current densities is maintained and at the same the voltage adjusted in the manner described hereinafter to prevent the occurrence of sludging the electrolyte has invariably served for extended periods of time for continual plating, producing plates which are satisfactory with respect to their colour, smoothness, fine grain, density and adherence. It is also possible after a satisfactory pre-treatment to store the electrolyte for days, weeks and even months without apparent loss of its efficiency in continual plating operations.

In such instances, where the voltage and amperage conditions were within the preferred range, but the time allowed for the pre-treatment not sufficiently long, the quality of the plates obtained in regular continual plating operations falls off after a shorter or longer period of time, and it is possible to restore such electrolytes to full efficiency by subjecting them to another pre-treatment under the preferred conditions described hereinabove.

It is important to note that in most instances where an electrolyte showed signs of deteriorating quality of the plate or did not produce satisfactory plates, check plates were run on steel, giving invariably good plates which possessed perfect adherence even under repeated bending tests.

The foregoing remarks are supplemented and summarized in the following tabulations:

Table I

A. Condition of the electrolyte	Quality of plate		
	Good	Fair	Unsatisfactory
1. Fresh			X
2. Aged 1 to 30 days and tested at frequent intervals			X
3. After pre-treatment (any)	X	X	X
4. After pre-treatment: approx. 550–2,000 watt hrs./sq. ft.; voltage not below 6, preferably not below 6 to 8; current density 75–275 amp. sq. ft	X		
5. Same as (4), stored and tested at frequent intervals over period of 3 months	X		
6. After pre-treatment: below approx. 500 watt hrs./sq. ft., voltage below 5, current density averaging 10 amp./sq. ft. ranging from 3–30 amp./sq. ft		(some) X	(most) X
7. Same as (6), stored and tested at frequent intervals over period of several weeks			X

B. Operating conditions	Condition of plate	
	"Dow"	"Steel"
1. (*a*) Electrolyte freshly prepared, (*b*) Electrolyte stored for 1–10 days: Approx. 40° C., 40 amp./sq. ft.	N. G.	O. K.
Approx. 20° C., 20 amp./sq. ft.	N. G.	O. K.
2. After pre-treatment: Approx. 40° C., 40 amp./sq. ft.	N. G.	O. K.
Approx. 20° C., 20 amp./sq. ft.	O. K.	O. K.

3. Operating Conditions During Electroplating

After the pre-treatment has been properly applied, the preferred operating conditions are as follows:

Temperature—below 35° C. and preferably room temperature (approximately 15–25° C.).
Current density—below 40 amp./sq. ft.
Voltage—above about 6 volts and preferably above about 6 to about 8.

Although the first plate or two may not be satisfactory in all respects, the following plates will possess all requirements of a good and satisfactory electroplate.

It has been noted that at constant current density an increase in voltage occurs if the voltage is held below a range of 6 to 8 volts. This increase in voltage occurs sooner if the pre-treatment has not been carried on for a sufficient period of time and/or at sufficiently high voltages and amperages. However, after the pre-treatment has been carried out in accordance with the best procedure developed, eventually an increase in voltage at constant current density will occur if the voltage during plating operations is not high enough to prevent sludging. Apparently the aforesaid increase in voltage occurring at constant current density is caused by an increase in the resistance of the bath which in due time usually can be traced to a gradually growing film covering the anodes (sludging).

4. Heat Treatment

A heat treatment is necessary to produce a superior bond between basis metal and electroplate. Alkaline-cyanide electrolytes, recommended in the literature for the commercial application of zinc plating, particularly the B–6 type, produce a zinc plate on steel which not only is satisfactory in appearance but also possesses perfect adherence, as for instance demonstrated by "twisting" and "repeated bending tests." This is not so in the case of zinc plating on magnesium alloy. There, even the most satisfactory type of electrolyte investigated (B–6), which produces a zinc plate of satisfactory adherence, does not produce a satisfactory bond between the plate and the basis metal. The zinc plate is sufficiently adherent to prevent its scaling or removal by mere handling, but upon repeated bending and subjection to ordinary wear, the plate will crack or flake off. It is for this reason that a special process had to be developed which produces a perfect bond as shown by metallographical investigation and as proven by repeated bending tests as well as by extended scratch brushing and buffing operations.

After the magnesium or magnesium alloy article has been coated with an electro deposit of zinc of suitable thickness the plated article is then subjected to a heat treatment at a temperature of about 645° F. to a temperature not exceeding the temperature at which the magnesium basis metal begins to move toward the warping temperature. Temperatures of about 645° F. to about 805° F. have been used with satisfactory results. It is preferred, however, to employ temperatures above about 680° F. Within the preferred range a substantially perfect bond between the electro deposited zinc and the basis magnesium metal may be obtained with heating cycles as low as one minute per heat treatment. The heat treatment need not be carried out at substantially constant temperature but may be carried out under conditions involving a rise in

temperature provided that the final temperature attained by the heat treated article does not exceed the warping temperature of the basis magnesium article.

Typical of the conditions under which the heat treatment of electro plated magnesium or magnesium alloy articles may take place will be readily appreciated by those skilled in the art from a study of the following tabulation:

Table II

	Time	Number of specimens	Character of bonding	Approximate temp. range
HEATING AT CONSTANT TEMPERATURE				
	Min.			° *F.*
1	60	8	Poor	600–645
2	30	1	do	640–650
3	30	1	do	655–665
4	30	1	Fair	675–685
5	30	1	do	685–695
6	30	2	Good	745–755
7	10	1	do	745–755
8	10	1	do	725–735
9	3	2	Good-Fair	719–729
10	4	1	do	702–712
11	3	1	Good	675–685
12	1	1	do	795–805
13	1	18	do	780–800
14	1¼			
15	1¼	1	do	745–755
16	1	1	do	745–755
HEATING AT INCREASING TEMPERATURE				
A	14	1	Good	600–760
B	12	1	do	700–760
C	5	1	do	700–760

Anode Sludging

In the literature frequent reference is made to the sludging of anodes in cyanide type electrolytes used for zinc plating. This phenomenon has been observed also in the course of this development and gave rise to difficulties which have been overcome. These difficulties comprise mainly the coating of the anodes with a brownish or black deposit resulting in an increase of the resistance of the bath which in time becomes so great that less and less current passes through the bath and the anodes have to be replaced by clean ones. Simultaneously the quality of the plate gradually deteriorates.

Among the various methods and means investigated regarding the elimination of the anode sludging phenomenon, one practical method found comprises the application of a comparatively higher current density at the anodes. In the beginning of the development, an anode surface area two to four times larger than that of the cathode surface area was considered desirable. Later it was observed that an increased anode surface in reality only serves to postpone the complete blackening and final usefulness of the anodes. The sludging of the anodes is completely overcome by reducing the anode surface area to a fraction of that of the cathode surface area, and anode surfaces having ½ to ⅓, or ¼, or ⅛ of the area of the cathodes have been used in continual operations without any noticeable sludging of the anodes. Another method of overcoming the sludging of the anodes comprises increasing the voltage of the bath above 6–8 volts, e. g., by increasing the distance from anodes to cathodes. All methods eliminating the anode sludging during the pre-treatment as well as in continual operations necessitate an increase in electric energy consumption.

The sludging of the anodes caused considerable trouble not only during regular plating operations but also in the course of the pre-treatment. By applying the same principle used in the plating operation to the pre-treatment also, the sludging of the anodes during the pre-treatment has been practically eliminated, thus producing electrolytes possessing longer life for regular plating operations.

In order that those skilled in the art may have a better understanding of the present invention, the following illustrative example of the preparation of a zinc plated magnesium article having greater corrosion resistance than the basis magnesium alloy and having a yield point substantially the same as that of the basis magnesium article is provided.

An aqueous electrolyte is prepared containing sufficient zinc that the normality of the zinc concentration is about 1.0; sufficient cyanide that the cyanide concentration is about 2.1 normal; sufficient alkali that the total alkali concentration is about 2.2 normal and the free alkali concentration is about 1.45 normal; sufficient carbonate that the [CO_3] radical concentration is about 0.56 normal and sufficient fluoride that the fluorine concentration is about 0.18 normal. The electrolyte also contains about 7.5 grams per liter of dextrose and about 1.1 grams per liter of gum arabic. Of course it will be understood by those skilled in the art that I prefer to employ zinc cyanide as the source of zinc, and alkali metal salts as the source of the alkali, additional cyanide ion and the carbonate and fluorine ions. As is customary the aqueous electrolyte is filtered. After filtration a check-plate may be prepared when desired. Such a check-plate when deposited on steel is good. However, when deposited on magnesium-containing material the plate is sketchy.

A pre-treatment is then applied to the filtered electrolyte. The current being turned on the bath at sufficient pressure to provide an increase in anode current density from zero to about 35 to about 400 amperes per square foot. A total amount of current for the period of the pre-treatment of from 300 to 2000 watt hours, preferably 1200, plus or minus about 30%, watt hours per square foot of cathode area is passed through the bath. The passage of this amount of current through the bath is associated with a temperature rise from about 20° C. to about 80° C., preferably about 30° C. to about 70° C. unless the bath is cooled artificially. Pre-treatments at constant temperatures, particularly low temperatures of about room temperature or below, have been noted to be especially beneficial. The anode area should be equal to that of the cathode area, or preferably about ¼ to about ⅛ the area of the cathode. During the pre-treatment the temperature of the bath rises to about 30° to about 80° C. and preferably to about 50° to about 70° C. The pretreated bath is then cooled to about room temperature, say about 15° to about 25° C. and strips, sheets, castings or other forms of magnesium-containing material electroplated in the pretreated electrolyte preferably at a cathode current density of about 5 to about 25 amperes per square foot at a temperature of about 18–25° C. for about 3 to about 10 minutes, preferably about 5 minutes, until an electroplate of zinc of desired thickness is obtained.

As pointed out hereinbefore, sludging of commercially pure zinc anodes may be eliminated by employing a cathode area which is a multiple of the anode area. It has been discovered that

a cathode area equal to and up to about 3 times that of the anode area will eliminate sludging of commercially pure zinc anodes in cyanide baths. Also, without regard to the respective electrode surface areas, the bath voltage may be adjusted so that no sludging occurs, preferably above a range of from 6 to 8 volts. Thus the conditions for pre-treatment involve the use of a cathode area of about 5 times the anode area and an anode current density of about 50 to about 400 amperes per square foot, or the application of a comparatively higher voltage, or both, for a period of time long enough to pass through the bath from 500–2000 watt hours per square foot of cathode.

After the electrodeposit of zinc of desired thickness is obtained the plate is washed, rinsed and dried. Thereafter the zinc plated magnesium containing article is subjected to a heat treatment in an inert atmosphere, in vacuum or in hydrogen in accordance with the Table II. It will be appreciated that the drying of the electroplate obviates the possibility that any moisture remains between the grains or crystals of the electrodeposit which in the subsequent heat treatment might be converted into steam with sufficient force to disrupt the electrodeposited layer. After the heat treatment the heat treated magnesium-containing article having an electrodeposited zinc layer is allowed to cool.

A transverse section of magnesium containing material which had been provided with an electrodeposited coating of zinc and thereafter heat treated as described hereinbefore, after polishing and etching, was photographed at a magnification of 250 times. This photomicrograph has been reproduced as the drawing and clearly shows the nature of the bond which seems to have formed an alloy at the junction of the base metal and the zinc. In the drawing area A is a film of electrodeposited copper applied to the zinc surface of the heat treated material to protect the zinc coating during metallographic treatment. Area B is the zinc-rich surface coating of the heat treated material and area C is the area in which the zinc-magnesium alloy exists. Area D is the magnesium containing basis metal. It will be appreciated from the drawing that the heat treated magnesium-containing article comprises a core of magnesium or magnesium alloy, a bond of magnesium-zinc alloy of interlocking crystals of the eutectic type and a surface layer of zinc. The bond between the surface layer of zinc and the basis material is so firm that the zinc plated article may be bent on small radii without flaking of the electrodeposited zinc. The physical properties of the magnesium-containing material remain about the same. For example, the yield point of the heat treated zinc coated magnesium material is about the same as that of the uncoated magnesium material. However, the corrosion resistance of the heat treated zinc coated material is far superior to that of the uncoated material.

The heat treated, zinc plated magnesium article thus produced was then subjected to corrosion resistance tests together with chromated magnesium metal known as "Dowmetal" under the following conditions: to steam for 24 hours at a substantially constant temperature of about 212° F.; to the equivalent of sea water, i. e., water containing 3.55% sea salt for 24 hours at room temperature; and to industrial seaboard atmosphere for 20 weeks. Under these conditions the heat treated zinc plated magnesium article withstood the corroding effects of steam as well as chromated "Dowmetal" and withstood the corrosive effects of sea water and the industrial seaboard atmosphere better than chromated Dowmetal.

In the foregoing a product and a process have been described in which the anodes and cathodes have been cleaned and roughened by means of rough and fine emery paper, following which the electrodes have been wiped with cotton or the like and then washed with a degreasing agent such as benzene. After all of the more important data and observations had been obtained with this procedure, certain changes regarding the preparation of the electrodes as well as of the electrolyte have been investigated which have led to further improvements.

The preparation, particularly of the cathode surface, in the manner described hereinabove served a very important and practical purpose. The roughened but still comparatively even surface of the cathode thus prepared lends itself to macroscopical as well as microscopical surface examination, enabling the investigator to determine quickly the condition and quality of the electroplate produced at each single test of the investigation. After the fundamental characteristics governing the pre-treatment, the anode sludging, the electroplating and the heat treatment had been determined, other methods which provide a more satisfactory surface and which would be applicable under industrial conditions were investigated. Among such methods of surface preparation the sand blasting of cathodes as well as anodes appears to be superior to other chemical or etching treatments investigated. As a precaution the sand blasting of the articles to be plated is followed by a degreasing thereof using, e. g., benzene as a degreasing agent. After drying in air, the articles are ready for use and installed in the electrolytic bath.

The principal beneficial effect of the sand blasting of the anodes appears to be uniform corrosion and a uniformly clean surface.

The comparatively soft magnesium alloys have, after sand-blasting, a surface composed of a great number of finer or larger indentations depending on the grain size of the material used in the sand blast. It has been noted that the cleanliness of the cathodes appears to be quite satisfactory, but owing to the great number of indentations produced by the sand blast the surface area of the cathode has been considerably increased, and it has been found necessary to increase the current density specified for rather even surfaces, as described hereinabove, from two to four times in order to electro-deposit a surface layer of approximately the same thickness as obtained by the method previously employed. A five minute electroplate under the conditions described hereinabove (15–25 amp./sq. ft.) results in a comparatively thin plate while higher current densities of the order of 40 to 80 amp./sq. ft. result in a uniform and even electro-plate. If the current density is considerably increased above 80 amperes per square foot a tendency towards treeing has been observed.

Electroplated cathodes, the surface of which has been prepared by sand blasting, possess a markedly increased adherence of the electroplate as compared with the method described hereinabove. This marked increase in adherence becomes apparent if strip specimens prepared by emerying and by sand blasting are electroplated and then subjected to the same amount of twist-

ing. While the electroplate deposited on the emery specimen will show signs of cracking or flaking off, no surface defects become visible on the sand blasted specimens upon macroscopical or microscopical surface examination.

In all other respects, particularly as related to the pre-treatment and the overcoming of the anode sludging, the earlier findings have been fully confirmed when using sand blasted cathodes.

An improved method of preparing the electrolyte B-6 has been developed.

Place ¾ of the H_2O volume in a beaker and dissolve in following order and manner:

$Zn(CN)_2$
NaCn
NaOH
Na_2CO_3

Heat solution to 40–50° C.; add NaF. Keep at 40–50° C. for 10 minutes. Turn off heat. Allow to cool and stand for at least 12–16 hrs. Filter solution and wash precipitate (collect wash in solution). Measure volume of filtrate. Slightly less H_2O than the difference in volume between filtrate and desired volume is used to dissolve the organic material in the following order and manner:

Dextrose
Heat solution to 40–50° C.
Gum arabic

This solution is then poured directly into the main solution. The solution is then agitated a little to insure complete mixing.

The solution may then be used immediately.

All dissolving operations are carried out using mechanical agitation.

This method of preparing the electrolyte makes it possible to use a freshly prepared electrolyte for electroplating a satisfactory zinc coating on magnesium alloys. However, upon standing overnight or for some length of time or even after short interruption of continual plating operations which commenced immediately after the preparation of the electrolyte, the electrolyte becomes as poor and as unusable regarding its plating qualities as electrolytes prepared in the manner described hereinabove.

It appears therefore important that the fundamental results and observations recorded hereinabove as relating to the pre-treatment, sludging of the anodes, and operating conditions during regular and continual plating operations have been fully substantiated and confirmed when using the improved method of preparing the electrolyte.

Examinations of photomicrographs of cross-sections of the novel heat treated zinc plated magnesium articles show that the composite article has three distinct areas. The core of magnesium or magnesium alloy, an intermediate zone of magnesium-zinc alloy and an outer or surface zone of electrodeposited zinc. This structure is clearly evident from the reproduction of a photomicrograph of magnesium material plated with zinc and subsequently heat treated as indicated hereinbefore in Fig. 1. As can readily be seen in Fig. 1, the bond between the electrodeposited zinc and the basis magnesium article is of the alloy type and provides good adherence of the zinc electroplate to the base material.

The heat treated zinc plated magnesium article of the present invention not only is superior to conventional magnesium or magnesium alloys in its corrosion resistance but has a slightly higher scratch hardness, equivalent tensile strength, yield point and elongation.

In all cases, the heat-treated, zinc-coated magnesium alloy article can be subjected to finishing operations such as scratch-brushing or buffing, which may be followed up by electrolytic polishing for the purpose of improving its appearance and corrosion resistance. These finishing operations remove a dull gray surface film. Further improvements with respect to the wear and corrosion resistance can be obtained by subjecting the magnesium alloy article which has been zinc-coated in the manner described hereinabove to a second coating operation; in this case preferably a comparatively light zinc coating is applied in the first plating operation, and the operating conditions for the second step including surface preparation and finishing operations are carried out in accordance with the process described hereinabove. That is to say after the plated article has been heat treated as described hereinbefore the surface thereof is roughened in any suitable manner such as by attrition by scratch brushing, buffing, with emery, by sandblasting or electrolytic polishing followed by degreasing and a second electroplate of zinc deposited in the manner described hereinbefore.

Although the present invention has been described in conjunction with certain preferred embodiments thereof, it is to be understood that variations and modifications may be made as those skilled in the art will readily understand. Such variations and modifications are to be considered within the purview of the present specification and the scope of the appended claims. Thus, the terms "magnesium-containing material" or "metallic magnesium-containing material" as employed herein define metallic materials containing at least 51% magnesium. Furthermore, it will be appreciated that the otherwise plane surfaces of a magnesium-containing article which has been cleaned by sand blasting or similar means provide a cathode area greater than the area determined by the calculation thereof from the measurement of the width and length. For example, a sheet of magnesium-containing material which measures one foot in width and one foot in length when cleaned by emery paper or the like may be considered to have an area of one square foot. However, when cleaned by sand-blasting or similar means creating furrows or pits or the like in the otherwise plane surfaces of the article, a magnesium-containing article one foot wide and one foot in length provides a cathode area greater than one square foot. Therefore the limiting cathode current density of about 80 amperes per square foot of cathode area for magnesium-containing articles which have been cleaned by sand-blasting or similar means is to be considered equivalent to the limiting cathode current density of about 40 amperes per square foot for magnesium-containing articles which have been cleaned by emery paper or the like.

I claim:

1. A process for providing metallic magnesium and alloys thereof containing at least 51% magnesium with corrosion-resistant surface which comprises establishing an aqueous electrolyte about 1.0 normal to zinc, about 2.1 normal to CN radical, about 0.56 normal to CO_3 radical, about 0.18 normal to fluoride, about 1.45 normal to "free" alkali, and about 2.2 normal to total alkali, pretreating said aqueous electrolyte by

electrolyzing said electrolyte using a magnesium test cathode at about 35 to about 400 amperes per square foot at temperatures of about 20° to about 80° C. until about 300 to about 2000 watt hours per square foot of cathode area have passed through said aqueous electrolyte and until said magnesium test cathode is provided with a continuous and adherent coating of electro-deposited zinc whereby a modified aqueous electrolyte is produced, immersing metallic magnesium as cathode in said modified electrolyte, passing an electric current through said aqueous electrolyte at a current density of less than about 40 amperes per square foot at temperatures below 35° C. and voltages exceeding 6 volts until said magnesium is provided with a coating of electro-deposited zinc and zinc-coated magnesium is obtained, and subjecting said zinc-coated magnesium to heat treatment in an inert atmosphere at temperatures above about 600° F. until at least a portion of said zinc coating has diffused into said magnesium and said zinc coating is firmly bonded to said magnesium.

2. A process for providing metallic magnesium and alloys thereof containing at least 51% magnesium with corrosion-resistant surface which comprises establishing an aqueous electrolyte about 1.0 normal to zinc, about 2.1 normal to CN radical, about 0.56 normal to CO_3 radical, about 0.18 normal to fluoride, about 1.45 normal to "free" alkali and about 2.2 normal to total alkali, pretreating said aqueous electrolyte by electrolyzing said electrolyte using a magnesium test cathode with a current density of about 35 to about 400 amperes per square foot until about 300 to about 2000 watt hours per square foot of cathode area have passed through said aqueous electrolyte whereby a modified aqueous electrolyte is produced and said test cathode is provided with a continuous adherent coating of zinc, conducting said pretreating electrolyzing at temperatures between 20° and 80° C., immersing magnesium as cathode in said modified electrolyte, passing an electric current through said aqueous electrolyte at a current density of less than about 40 amperes per square foot, and at temperatures below 35° C. and voltages exceeding 6 volts until said magnesium cathode is provided with a coating of electro-deposited zinc and zinc-coated magnesium is obtained, and subjecting said zinc-coated magnesium to heat treatment in an inert atmosphere at temperatures of about 675° F. to about 800° F. for about 4 minutes to about 1 minute.

3. A process for providing metallic magnesium and alloys thereof containing at least 51% magnesium with corrosion-resistant surface which comprises establishing an aqueous electrolyte about 1.0 normal to zinc, about 2.1 normal to CN radical, about 0.56 normal to CO_3 radical, about 0.18 normal to fluoride, about 1.45 normal to "free" alkali, about 2.2 normal to total alkali and containing small amounts of gum arabic and dextrose, pretreating said aqueous electrolyte by electrolyzing said electrolyte using a magnesium test cathode at a current density of about 35 to about 400 amperes per square foot until about 300 to about 2000 watt hours per square foot of cathode area have passed through said aqueous electrolyte, conducting said pretreating-electrolyzing at temperatures below about 80° C., whereby a modified aqueous electrolyte is produced, and said test cathode is provided with a continuous adherent coating of zinc, immersing magnesium as cathode in said modified electrolyte, passing an electric current through said aqueous electrolyte at a current density of less than about 40 amperes per square foot, at temperatures below about 35° C. and voltages exceeding 6 volts, until said magnesium cathode is provided with a coating of electro-deposited zinc and zinc-coated magnesium is obtained, and subjecting said zinc-coated magnesium to heat treatment in an inert atmosphere at temperatures of about 675° F. to about 800° F. for about 4 minutes to about 1 minute.

4. A process for providing metallic magnesium and alloys thereof containing at least 51% magnesium with corrosion-resistant surface which comprises establishing an aqueous electrolyte about 1.0 normal to zinc, about 2.1 normal to CN radical, about 0.56 normal to CO_3 radical, about 0.18 normal to fluoride, about 1.45 normal to "free" alkali, about 2.2 normal to total alkali and containing about 7.5 grams of dextrose per liter and about 1.1 grams of gum arabic per liter, pretreating said aqueous electrolyte by electrolyzing said electrolyte using a magnesium test cathode at a current density of about 35 to about 400 amperes per square foot until about 300 to about 2000 watt hours per square foot of cathode area have passed through said aqueous electrolyte, at temperatures between about 20° C. and about 80° C., whereby a modified aqueous electrolyte is produced, and said test cathode is provided with a continuous adherent coating of zinc, immersing magnesium as cathode in said modified electrolyte, passing an electric current through said aqueous electrolyte at a current density of less than about 40 amperes per square foot, and at temperatures preferably below 35° C. and voltages exceeding 6 volts, until said magnesium cathode is provided with a coating of electro-deposited zinc and zinc-coated magnesium is obtained, and subjecting said zinc-coated magnesium to heat treatment in an inert atmosphere at temperatures of about 675° F. to about 800° F. for about 4 minutes to about 1 minute.

5. A process for providing metallic magnesium and alloys thereof containing at least 51% magnesium with corrosion-resistant surface which comprises establishing an aqeous electrolyte about 1.0 normal to zinc, about 2.1 normal to CN radical, about 0.56 normal to CO_3 radical, about 0.18 normal to fluoride, about 1.45 normal to "free" alkali, about 2.2 normal to total alkali and containing about 7.5 grams of dextrose per liter and about 1.1 grams of gum arabic per liter, pretreating said aqueous electrolyte by electrolyzing said electrolyte using a magnesium test cathode at a current density of about 35 to about 400 amperes per square foot until about 840 to about 1560 watt hours per square foot of cathode area have passed through said aqueous electrolyte at temperatures of about 20° to about 80° C. whereby a modified aqueous electrolyte is produced, and said test cathode is provided with a continuous adherent coating of zinc, cooling said modified electrolyte to a temperature below about 35° C., immersing degreased magnesium from which surface film has been removed in said modified electrolyte as cathode, passing an electric current through said aqueous electrolyte at a cathode current density below about 40 amperes per square foot for about 3 to about 20 minutes at temperatures below 35° C. and voltages exceeding 6 volts, employing an anode area of about ¼ to about ⅛ that of the cathode to obtain zinc-coated magnesium, rinsing said zinc-coated magnesium, drying said zinc-coated magnesium and subjecting said zinc-coated magnesium to heat

treatment in an inert atmosphere at temperatures of about 675° F. to about 800° F. for about 4 minutes to about 1 minute.

6. A process for providing metallic magnesium and alloys thereof containing at least 51% magnesium with corrosion-resistant surface which comprises establishing an aqueous electrolyte about 1.0 normal to zinc, about 2.1 normal to CN radical, about 0.56 normal to CO_3 radical, about 0.18 normal to fluoride, about 1.45 normal to "free" alkali, about 2.2 normal to total alkali and containing about 7.5 grams of dextrose per liter and about 1.1 grams of gum arabic per liter, pretreating said aqueous electrolyte by electrolyzing said electrolyte using a magnesium test cathode at a current density of about 35 to about 400 amperes per square foot until about 840 to about 1560 watt hours per square foot of cathode area have passed through said aqueous electrolyte at temperatures of about 20° to about 80° C. whereby a modified aqueous electrolyte is produced and said test cathode is provided with a continous adherent coating of zinc, cooling said modified electrolyte to a temperature of about 35° C. or below, sand-blasting magnesium to remove surface film and to provide an increased effective cathode area and degreasing said magnesium, immersing said

treated magnesium as cathode in said cooled modified aqueous electrolyte, passing at a temperature below 35° C. an electric current through said aqueous electrolyte at a voltage greater than about 6 to about 8 volts and at a cathode current density of not more than about 80 amperes per square foot of cathode area for about 3 to about 20 minutes to obtain zinc-coated metallic magnesium, said cathode area being computed from the linear dimensions of the cathode, rinsing said zinc-coated magnesium, drying said zinc-coated magnesium, and subjecting said zinc-coated magnesium to heat treatment in an inert atmosphere at temperatures of about 675° F. to about 800° F. for about 4 minutes to about 1 minute.

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