

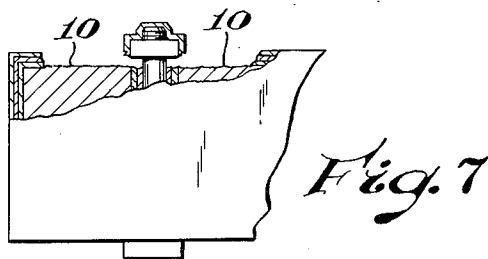
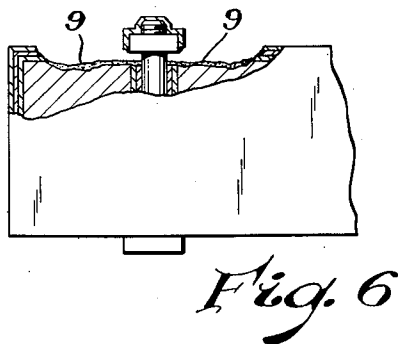
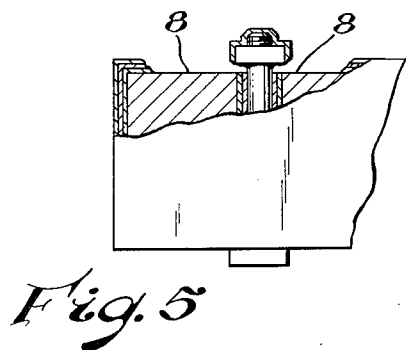
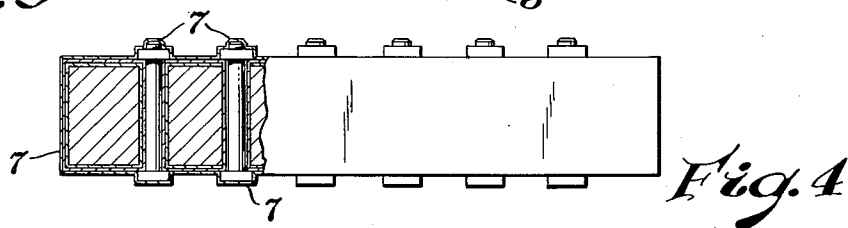
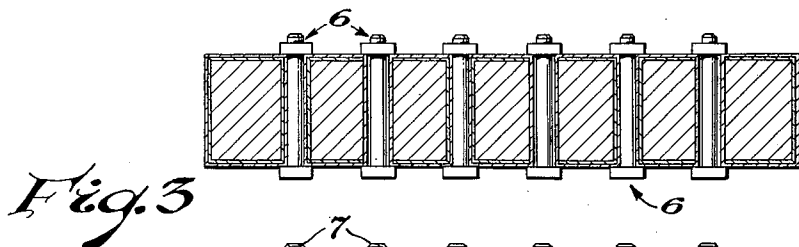
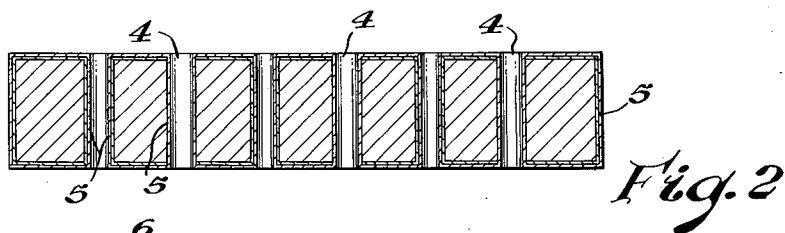
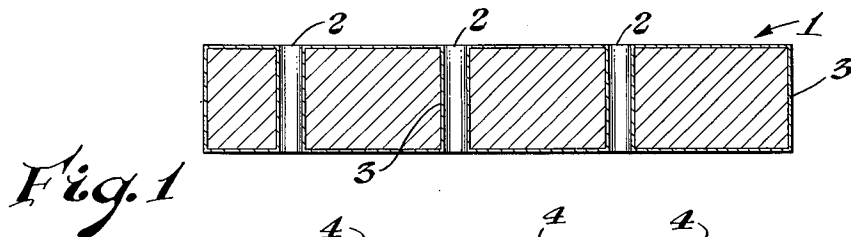
May 15, 1962

H. K. DE LONG

3,034,210

INHIBITION OF CORROSION OF MAGNESIUM

Filed Sept. 3, 1959



INVENTOR.  
Herbert K. DeLong  
BY  
C.W. Carlin  
ATTORNEY

1

3,034,210

**INHIBITION OF CORROSION OF MAGNESIUM**  
Herbert K. De Long, Clare, Mich., assignor to The Dow Chemical Company, Midland, Mich., a corporation of Delaware

Filed Sept. 3, 1959, Ser. No. 837,780

7 Claims. (Cl. 29-458)

The invention involves an improved method of inhibiting corrosion of magnesium metal and magnesium-base alloys when coupled by or to a less base, i.e., more noble metal, and exposed to a corrosive environment. By magnesium base alloys is meant herein an alloy containing at least about 65 percent by weight magnesium metal. Either magnesium metal or such an alloy thereof are sometimes referred to hereinafter as magnesium.

When dissimilar metals are placed in contact with each other or are coupled by a conductor and allowed to remain in such relationship, without specific protection, whether in the atmosphere, the sea, or the earth, at least one of the metals usually undergoes corrosive deterioration as a result of galvanic action between the dissimilar metals due to the presence of an electrolyte in the ambient contacting medium and the difference in the electropotential of the metals. Moisture and other gases suspended in or composing the air provide an electrolyte in the atmosphere. The water of the sea and the dissolved salts therein make sea water an exceptionally good electrolyte. The ground waters carrying dissolved minerals therein, particularly in soils of high organic content and, consequently of an acidic or sour nature, are effective electrolytes.

Metals employed commercially are seldom pure but nearly always contain traces of other metals because the procurement of a pure metal is either uneconomical or practically impossible or because an alloy is preferred due to its superior properties. Impure metals and alloys, therefore, as well as assemblies of manifestly dissimilar metals in contact with one another through an electrical conductor, are highly susceptible to galvanic action and the concomitant corrosion of the less noble metal. When different metals are in contact in a corrosive environment, whether in the same or in different metal pieces, galvanic currents are to be expected.

The metal which corrodes during galvanic action is that one which is higher in the electromotive series of the elements, referred to herein as less noble or more base. The less noble metal is sometimes said to be the anode of the galvanic pair and as such continues to give up electrons to the electrolyte and is thereby consumed.

Attempts to lessen corrosion of a metal due to the galvanic effect of its being anodic to another to which it is coupled has included the use of sacrificial metal pieces which provide a greater flow of electrons than a metal to be protected and which are thereby consumed in place of the metal sought to be protected. This method is meritorious in a large number of situations but entails the cost, installation, and replacement of the sacrificial metal, such metal being relatively expensive. Other known methods include the application, to the contacting surfaces of the dissimilar metals exposed to galvanic action, of coatings containing such compounds as metal dichromates and metal sulfates.

Known methods of this type however, have not been fully satisfactory to suppress sufficiently the galvanic action. A particular need for protection against corrosion occurs when magnesium metal or an alloy thereof is in contact with a more noble metal, e.g., an iron or copper alloy in a corrosive environment, e.g., the ocean or moist earth. In such case, the magnesium, being the less noble, is anodic to the more noble metal and is

2

therefore corroded away. A common situation in which magnesium is in contact with a more noble metal in a corrosive environment is that wherein magnesium pieces are secured by means of steel, copper or copper-base alloys, or aluminum rivets or bolts, or magnesium plates, sheets, or the like are otherwise in contact with steel, aluminum, copper, brass, or bronze plates, studs, conduits, or the like.

A particularly effective known method of protecting magnesium against corrosion by contact with a more noble metal connected thereto by an electrical conductor is the placement of tin metal or a tin-base alloy, containing at least about 40 percent tin, between the contacting surfaces of the metal. Such method is described in my copending application S.N. 718,027, filed February 27, 1958.

Positioning during fabrication, in an assembly comprising magnesium and a more noble metal, a layer or sheet of tin or tin alloy, or inserting between the dissimilar metals after fabrication such tin or tin alloy, is not always practical.

The method described in S.N. 718,027, although representing definite progress in the art, is not adaptable to conditions where it is not practical to interpose the tin or tin alloy sheet between the contacting or abutting surfaces of dissimilar metals. Furthermore, the method therein described is not adaptable to protecting against corrosion of the less noble magnesium due to the presence of more noble impurities contained within the same metal piece.

There is, accordingly, a need for a more convenient method of protecting magnesium metal or a magnesium base alloy coupled to a more noble metal or contaminated by more noble metal impurities or alloyed with a more noble metal against the corrosive effects induced by the more noble metal which method includes treatment of either the contacting areas or of the electrolyte-containing medium.

The present invention meets this need. The method of practicing the invention is made clear in the ensuing description and is specifically defined in the appended claims.

The present invention is a method of suppressing corrosion of magnesium metal or magnesium base alloys due to the galvanic effect produced by a more noble metal coupled thereto in an electrolytic medium which consists essentially of maintaining the magnesium metal or its alloy in the presence of a small but effective amount of a tin compound having a solubility in water of at least 0.05 weight percent at about 20° C.

The drawing illustrates, by a series of figures, the effectiveness of the invention as demonstrated by Example 3 set forth hereinafter.

The tin compounds suitable for use in the practice of the invention include organic tin compounds, e.g., tributyl tin oxide, dimethyl tin dichloride, stannous octoate, tributyl tin acetate, and inorganic tin compounds, e.g., sodium stannate, potassium stannate, and stannous fluoride.

The tin compound may be added directly to the electrolytic medium or it may be incorporated in a coating which is applied to the surface of either the magnesium metal or of the more noble metal or to both metal surfaces which are in electrical contact. Any coating material which is satisfactory as a more or less permanent coating to magnesium metal or to the more noble metal may be employed. Illustrative of such coatings are various paints, e.g., pigments dispersed in a suitable vehicle, e.g., zinc chromate, lead sulfate, lead oxide, or iron oxide, or the vehicle alone without the pigment, or a synthetic resin, e.g., a butyral, phenolic, or alkyl type resin, or shellac, a common varnish, enamel, or a rubber

or polyvinyl chloride coating in a suitable organic vehicle.

The organic tin compound or inorganic tin compound when added directly to the electrolytic medium according to the practice of this invention is employed in an amount of at least about 0.2 weight percent of the electrolyte. The maximum amount employed is not highly critical but in the interest of economy not more than 2 percent by weight of the electrolyte and usually not over 1 percent is recommended. When the tin compound is employed according to the invention by incorporating it into a coating material, between 1 and 25 percent by weight of the tin compound based on the weight of the coating material is employed and usually between 2 and 15 percent. The thickness of the coating material is not highly critical and varies with the composition of the material, method of application, and other considerations for determining the thickness of the coating desired.

The suppressing effect of the tin compound when used according to the invention is enhanced when there is added either to the electrolytic medium or to the coating material, dependent upon the mode of practicing the invention being employed, a soluble nitrate, e.g., an alkali metal or alkaline earth metal nitrate, illustrative of which are magnesium nitrate, calcium nitrate, and lithium nitrate. The nitrate is added in an amount between about 0.1 and 5 percent by weight of the electrolyte or coating composition containing the tin compounds. Lithium nitrate is the preferred nitrate to employ.

The following examples are illustrative of the practice of the invention:

#### Example 1

A sheet of a magnesium alloy designated AZ31B-O, comprising about 3 percent aluminum, about 1 percent zinc, about from 0.15 to 0.20 percent manganese, and balance magnesium was sanded and test panels 1 x 2 x 0.025 inch in size were cut therefrom.

Two holes were drilled in a test panel, thus prepared, of a suitable size to accommodate  $\frac{3}{16}$  inch diameter bolts. Threaded, round-headed steel bolts  $\frac{3}{16}$  inch in diameter and  $\frac{3}{4}$  inch long were then inserted into the holes and nuts applied to the threaded end thereof and firmly tightened so that a good electrical contact was made between the steel of the bolts and the magnesium metal of the panel. 250 milliliters of a 1 percent by weight sodium chloride brine was prepared. For comparative purposes, the magnesium panel containing the steel bolts was submerged in the brine at room temperature without further treatment of the brine and retained therein for 24 hours.

The panel was then removed from the brine, washed, and dried and found to be severely corroded in the area adjacent to and surrounding the steel bolts.

An arbitrary scale, ranging in lessening corrosion severity from 0 to 10, was then set up in which the corrosion induced on the magnesium panels containing the steel bolts (when thus submerged in the brine without inhibition) was rated 0 and no corrosion was given a rating of 10.

To contrast the corrosive effects of the steel bolts on the panel in the assembly prepared above to such effects, if any, when the invention was practiced, a second assembly was prepared as above and placed in a second solution of NaCl brine as above except that 0.5 percent by weight of sodium stannate hydrate,  $\text{Na}_2\text{SnO}_3 \cdot \text{H}_2\text{O}$ , was admixed with the NaCl brine prior to submerging the magnesium panel-steel bolt assembly therein. Sodium stannate is readily water-soluble. The panel containing the bolts was then submerged in the NaCl brine containing the sodium stannate and maintained therein at room temperature for 24 hours. The panel containing the steel bolts was then removed from the brine, washed, dried, and examined. Very little indication of corrosion could be detected on the panel surface adjacent to the

steel bolts. The panel was given a corrosion rating of 9 (10 representing absolutely no corrosion).

#### Example 2

Example 1 above was repeated except that 0.5 percent of  $\text{LiNO}_3 \cdot 3\text{H}_2\text{O}$  was dissolved in the NaCl and  $\text{Na}_2\text{SnO}_3 \cdot 3\text{H}_2\text{O}$  brine solution prior to submergence therein of the magnesium test panel containing the steel bolts. After submergence for 24 hours, the panel was removed, washed, dried, and examined as above. The corrosion of the panel about the steel bolts was even less than that of Example 1. The panel was given a corrosion rating of 9.5.

#### Example 3

The drawing is illustrative of this example, wherein a magnesium alloy panel is represented by numeral 1; three  $\frac{1}{4}$ " bolt holes, first drilled in the panel, by numeral 2; an anodized coating by numeral 3; three additional  $\frac{1}{4}$ " bolt holes made in the panel subsequent to the anodized coating by numeral 4; a resin-bodied coating, with or without a protective metallic compound suspended therein, by numeral 5; six  $\frac{1}{4}$ " bolts positioned in the six bolt holes and tightened firmly against the panel by numeral 6; a second resin-bodied coating, with or without a protective metallic compound therein, by numeral 7; a scraped away or bared portion at the junction of the magnesium alloy panel and the steel bolts by numeral 8; the corrosion effects of a salt spray test on the bared magnesium alloy surface, when no tin compound was present in the resin-bodied polymer coating, by numeral 9; a relatively uncorroded bared magnesium panel area, when a tin compound was present in the resin-bodied polymer coating in accordance with the invention, by numeral 10.

An AZ31B-O panel having a finished sanded size of 4 x 6 x 0.25 inch had a row of three substantially equispaced holes drilled therein to accommodate three  $\frac{1}{4}$  x 1 inch bolts, as shown in FIGURE 1. The magnesium panel containing the three holes was then given a standard paint base anodizing treatment designated H.A.E. Anodize according to Military Specification MIL-C-13335. Thereafter, another row of the three substantially equispaced holes, of the same size as the first three, were drilled in the anodized panel thereby presenting three holes protected by anodize treatment and three holes having the interior thereof unprotected by the anodize treatment as shown in FIGURE 2.

A standard vehicle of the type employed in the preparation of a primer known as Unichrome AP-10 chromate primer, but in this instance without the zinc chromate or other pigment, was obtained. The body of the vehicle consists of resin and shellac dispersed in an organic vehicle. The resin usually is polyvinyl butyral and is present in a weight ratio of about 62 parts to 38 parts of shellac. The suitable organic carrier is usually about a 50:50 volume ratio of toluol and isopropyl alcohol. The vehicle thus described was sprayed onto the panel including the interior of the six holes and dried. Thereafter six  $\frac{1}{4}$  x 1 inch threaded flat headed steel bolts were inserted into the holes, nuts screwed thereon, and the nuts tightened to make a firm contact between the steel heads of the bolts and the magnesium panel as shown in FIGURE 3. Thereafter a second coat of the Unichrome AP-10 primer, again without pigment therein, was sprayed onto the magnesium panel containing the six steel bolts, as shown in FIGURE 4. The coating was cured by forced air drying at 180° F. for 30 minutes. After drying, the coated surface of the panel containing the bolts was scratched through to bare the magnesium and steel surfaces at their junction, as shown in FIGURE 5. The panel was then subjected to a 20 percent salt spray fog test in accordance with Method 606.1 of Federal Specification TT-P-141-B for 85 hours. After this period of exposure to the salt spray, the panel was removed,

dried and examined. Both the exposed magnesium surface adjacent to the steel bolts and the magnesium surface coated with the bodied vehicle containing no zinc chromate or other inhibiting materials, were severely corroded, as shown in FIGURE 6. Both the unscratched and the bared magnesium surfaces were given a corrosion rating of 0.

For further comparative purposes the above test was repeated in exactly the same manner except that the Unichrome AP-10 bodied primer vehicle employed contained zinc chromate in the ordinary amount used to protect magnesium surfaces. The panel thus coated was subjected to the salt spray test described above. Examination of the thus treated magnesium panel following removal from the salt spray fog test showed severe corrosion in the area of the magnesium panel adjacent to the steel bolts, similarly as shown in FIGURE 6. The corrosion was of equal severity about each bolt showing that anodizing the interior of the holes had no beneficial effect upon the prevention of corrosion about the heads of the bolts. The corrosion, however, was almost, though not quite so severe on the thus treated panels as in the test above wherein no zinc chromate was present. The corroded panel was given a relative corrosion rating of 1.

The above test employing the Unichrome AP-10 bodied vehicle without pigment was repeated but, in accordance with the practice of the invention, there was incorporated into the primer vehicle (which contained no zinc chromate) 15 percent by weight of tributyl tin oxide. Tributyl tin oxide has a water-solubility of about 0.1 percent at room temperature. The thus treated vehicle was sprayed on the magnesium panel both prior to insertion of the bolts and following the insertion of the bolts and dried as above described and illustrated in FIGURES 1-5 of the drawing. Thereafter the panel containing the steel bolts was subjected to the salt spray test as above. The panel was then removed, washed, dried, and examined. Some corrosion was found on the magnesium panel surfaces adjacent to the steel bolts but it was clearly of definitely less extent than that shown in either of the above comparative tests. FIGURE 7 illustrates the comparative uncorroded area which occurs when the protective coating contains a tin compound in accordance with the invention in contrast to the corroded area which results when the protective coating does not contain a tin compound in accordance with the invention. There was no difference in the degree of corrosion of the magnesium panels about the steel bolts wherein the interior of the bolt holes had been anodized prior to being coated and wherein the bolt holes had not been anodized. The panel was given a corrosion rating of 7.

The tests were repeated employing decreasing percents of tributyl tin oxide. Some beneficial effect on inhibiting corrosion was observed down to 1 percent by weight of the tin compounds based on the weight of the coating composition. It was found that as much as 25 to 30 percent of the tin compound can be used but between 2 and 15 percent is recommended.

#### Example 4

Example 3 was repeated except that 15 percent by volume of stannous octoate instead of the tributyl tin oxide was admixed with the Unichrome AP-10 clear primer vehicle (no pigment therein) in coating a magnesium alloy panel containing the steel bolts. Stannous octoate has a water-solubility of about 0.05 weight percent at room temperature.

The magnesium panel and steel bolt assembly thus prepared was tested as in Example 3 according to the salt spray fog test. Some corrosion could be observed on the magnesium panel adjacent to the bolts. A rating of 8 was given to the panel according to the corrosion rating scale described above.

#### Example 5

Example 3 was again repeated except that 10 percent by volume of tributyl tin acetate, instead of the 15 percent tin compound there employed was admixed with the Unichrome AP-10 clear primer in coating the magnesium alloy panel containing the steel bolts. Tributyl tin acetate has a water solubility of about 0.06 weight percent at room temperature.

The magnesium alloy panel thus prepared was subjected to the salt spray fog test as above described. Examination of the panel containing the bolts showed some corrosion of the panel adjacent to the bolts. The panel was given a corrosion rating of 8 according to the scale described above.

To show that the tin compound must possess a minimum degree of solubility in water, Example 1 above was repeated except that 0.1 percent of magnesium stannate hydrate,  $\text{MgSnO}_3 \cdot \text{H}_2\text{O}$ , was admixed with a 3 percent sodium chloride aqueous solution. Magnesium stannate is substantially insoluble in water. After 24 hours of submergence in the salt solution, containing the magnesium stannate, the panel was removed, washed, dried, and examined. The examination of the panel which had been thus submerged, showed severe corrosion in the area of the panel adjacent to and surrounding the place of contact with the bolts. The panel was given a corrosion rating of 0. It is clearly apparent that unless some of the tin compound goes into solution, it does not inhibit the corrosion of the less noble metal of a bimetallic couple subjected to a corrosive environment.

An examination of the examples of the invention and test runs made for comparative purposes shows that a tin compound, having a water solubility of at least 0.05 weight percent, when admixed with an electrolyte in contact with magnesium or its alloy coupled to a more noble metal, markedly suppresses the corrosion of the magnesium due to galvanic action.

The examination of such examples and tests further shows that tin compounds, whose water solubility is at least 0.05 weight percent, when admixed with conventional coating compositions according to the invention in an amount of 1 percent by weight or more of the coating composition and the composition thus prepared applied to that surface of a magnesium piece or article which is subsequently brought into contact with the more noble metal, also markedly suppress the corrosion of the magnesium due to galvanic action.

The examples and tests also show that the suppression, in accordance with the method of the invention, of corrosion of magnesium when coupled to or in contact with a more noble metal is far superior to such known methods of suppressing as anodizing, applying resin coatings, and applying such resin coatings containing zinc chromate to the surface of either the magnesium or the more noble metal which may be brought in contact with each other.

Having described the invention what is claimed and desired to be protected by Letters Patent is:

1. The method of suppressing corrosion of magnesium metal when electrically coupled to a more noble metal in an electrolytic medium which consists of maintaining the magnesium metal in the presence of a small but effective amount of a tin compound having a water-solubility at 20° C. of at least 0.05 weight percent.

2. The method of suppressing corrosion of magnesium metal when electrically coupled to a more noble metal in an electrolytic medium which consists of dissolving in said electrolytic medium a tin compound having a water solubility of at least 0.05 weight percent at 20° C.

3. The method of claim 2 wherein the tin compound is present in an amount between 0.2 and 2.0 percent by weight of the electrolytic medium.

4. The method of claim 3 wherein a soluble nitrate is present in said electrolytic medium in an amount between 0.1 and 5.0 percent by weight of said electrolytic medium.

7

5. The method of suppressing the corrosion of an article composed of at least 60 percent magnesium metal when electrically coupled to a more noble metal in an electrolytic medium which consists of maintaining said magnesium article in the presence of small, but effective amounts of both a tin compound selected from the class consisting of tributyl tin acetate, tributyl tin oxide, dimethyl tin dichloride, stannous octoate, sodium stannate, potassium stannate, and stannous fluoride, and a metal nitrate.

6. The method of claim 5 wherein the metal nitrate is lithium nitrate.

7. The method of suppressing corrosion of an article composed of at least 60 percent magnesium when electrically coupled to a more noble metal in an electrolytic medium which consists of incorporating into a film-forming composition a tin compound having a water-solubility at about 20° C. of at least 0.05 weight percent in an amount of at least 1 percent and a soluble metal nitrate in an amount of between 0.1 and 5.0 percent, by weight

8

of the film-forming composition, applying said composition in an uncured state to at least one of the surfaces of the magnesium metal article and the more noble metal which will be in electrical contact when coupled together, coupling the magnesium and more noble metal, and curing said film in situ.

#### References Cited in the file of this patent

##### UNITED STATES PATENTS

|           |            |               |
|-----------|------------|---------------|
| 2,240,021 | Rutherford | Apr. 29, 1941 |
| 2,398,738 | Gilbert    | Apr. 6, 1946  |

##### FOREIGN PATENTS

|           |         |              |
|-----------|---------|--------------|
| 1,062,866 | Germany | Aug. 6, 1959 |
|-----------|---------|--------------|

##### OTHER REFERENCES

"Magnesium" (Pidgron et al.), published by American Society of Metals (Cleveland, Ohio). (Pages 200, 205, 240-244.)