

ALIEN PROPERTY CUSTODIAN

METHOD OF PRODUCING COATINGS ON MAGNESIUM OR ITS ALLOYS

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This invention relates to a method of producing coatings on magnesium or its alloys which are adapted to protect the same from corrosion.

Dips are known which are composed mainly of free acid and heavy metal salts, and by means of which good pickling effects can be produced on the surface of workpieces made of magnesium and its alloys. Owing to their high acidity however, such dips are but little suitable for the formation of protective coatings. Moreover, electrolytic methods have already been suggested for forming protective coatings by anodic oxidation, by means of current from an external source in alkali metal salt solutions usually having an alkaline reaction. The coatings thus produced are not sufficiently dense and hard to afford adequate protection against corrosion to the metal, and must therefore be compacted by known methods, or be provided with a coat of paint. Moreover the electrolytic method requires a much more complicated and expensive bath equipment than the dipping process and its use would only be justified if the coatings produced thereby are superior to the coatings produced by the dipping process.

The process of the present invention is based on the idea of producing protective coatings on magnesium and its alloys by employing the metal or alloys as an anode in a galvanic cell.

The invention accordingly contemplates making the workpiece under treatment the negative electrode of a galvanic cell having a positive electrode consisting of a metal, preferably steel, which is more electropositive than magnesium and which remains substantially unattacked by the electrolyte during treatment, and connecting the two electrodes through a conductor thereby generating an electric current.

The electrolyte preferably consists of an aqueous solution containing a substantial proportion of a compound or compounds adapted to furnish chromic acid ions together with a smaller proportion of a compound or compounds adapted to furnish ions of another acid or acids.

The invention has been successfully carried out with a pH value of the electrolyte during the treatment which is below 7 but not substantially below 3.5. The compound adapted to furnish chromic acid ions may consist of a chromate or dichromate of any suitable metal, preferably however of an alkali metal. Moreover chromic acid itself may be used in which case however the surface of the treated article is apt to become rough and pitted.

The compounds adapted to furnish the ions

of the other acid or acids may suitably be phosphates, borates, cyanates, sulphates, sulphites, selenates, selenites, tungstates, vanadates and molybdates of any suitable metal and are preferably used in the form of their alkali metal, magnesium or manganese salts, care being taken to adjust the pH value to the range above mentioned. The effectiveness of all the foregoing compounds can, in many cases, be materially improved by adding thereto a sulphate, a disulphate or a phosphate or a mixture of two or more of such salts.

In carrying out the invention, particularly favourable results have been obtained with electrolytes consisting of solutions of alkali metal chromates or dichromates containing between 5 and 12% and advantageously 10% of chromate or dichromate, to which 0.05 to 0.5% of an alkali metal bisulphate has been added in the case of dichromate solutions, and 5 to 15% of alkali metal bisulphate has been added in the case of chromate solutions. When using solutions consisting of a mixture of dichromate and chromate, the addition of alkali metal bisulphate should be adjusted in accordance with the ratio of dichromate to chromate. In cases where the electrolyte consists of a dichromate solution, the pH value should preferably be kept between 3.8 and 3.9, whereas when the electrolyte consists of a chromate solution, the same should preferably be kept between 4.5 and 6.0.

When the electrodes are connected together a current of about 0.5 volt and 3 to 4 amps. per sq. metre of electric surface is generated.

The period of treatment at room temperature should be about 30 minutes to 2 hours depending on the composition of the electrolyte and on the desired thickness of the protective layer.

After interrupting the current in the cell, the workpiece is removed from the electrolyte, preferably rinsed for 5 to 10 minutes in water at about 40° C., and then dried.

The hydrogen ion concentration of the electrolyte has a pronounced effect on the nature of the protective layer produced. When using less acid electrolytes, e. g. of a pH value of 4.5 to 6, the duration of the treatment for a coating of a given thickness is longer but the coatings produced are harder and denser. If, on the other hand, more acid electrolytes of a pH value of for example, 3.8 are employed, softer and more porous coatings are formed which are more suitable for certain purposes such as subsequent lacquering, painting or compacting and which moreover, are of a darker colour. It is therefore possible by

suitably controlling the composition of the electrolyte within the limits hereinbefore defined to produce coatings of any desired characteristics.

As has been shown by seawater spray tests, the protective coatings formed in accordance with the invention are greatly superior in their protective effect to those produced by immersion in the usual dips. Moreover the fact that no external source of current is required simplifies and cheapens the process.

The coatings produced in accordance with the invention, which by themselves furnish good surface protection, afford an excellent foundation for coatings of paint, lacquer or the like. If desired, the coatings can be further treated for the purpose of increasing their density and coherence, in any desired manner, for instance by immersing the coated article for about 20 minutes in a 5% waterglass solution at a temperature of 70 to 80° C. and subsequently washing and drying.

Example I

A bath was prepared which consisted of an aqueous solution containing 100 grms. of potassium dichromate and 0.8 gm. of potassium bisulphate per litre. A sheet consisting of an alloy containing 98% of magnesium and 2% of manganese and having dimensions 7 x 17 cm. and 2 mm. thickness was placed between two larger interconnected steel sheets at a distance of 4 cm. from each. The whole thus constituted a duplex galvanic cell. The magnesium alloy anode was connected to each steel sheet outside the bath by means of wires and a current of 0.5 volt and a mean amperage of 0.08 amp. was thus generated. After 75 minutes a black glossy and adherent layer had been formed on the magnesium alloy sheet. After removal from the bath the magnesium alloy sheet was rinsed in water at 40° C. for 5 to 10 minutes and then dried at room temperature.

For purposes of comparison the sheet provided with the protective coating was exposed for 700 hours to the seawater spray test together with a sheet of the same alloy that had been treated by immersion in an aqueous chromate solution of the usual composition (500 cc. of 40% HNO₃ and

180 grms. K₂Cr₂O₇ per litre). After this period the sheet merely treated by immersion had been attacked fairly severely and was even perforated at certain spots, whereas the sheet treated in accordance with the invention showed only very slight attack at isolated points.

Two further comparative test pieces (i. e. one treated by immersion and the other in accordance with the invention) were coated with a transparent cellulose lacquer and exposed to the seawater spray test. After 220 hours the lacquer had completely peeled off the sheet treated by immersion and the exposed surface showed strong signs of corrosion. At the end of the same period the lacquer coating on the sheet treated in accordance with the invention showed no tendency to peel; it adhered firmly to the base and only showed signs of slight pinhole attack at a few places.

Example II

A sheet of the same composition and having the same measurements as that described in Example I was treated in a bath consisting of an aqueous solution containing 100 grms. of sodium chromate and 80 grms. of potassium bisulphate per litre under the otherwise same conditions as those set forth in the preceding example. The voltage generated upon short circuiting the metal sheets serving as electrodes was 0.5 volt and the current density was 3 to 4 amp. per sq. metre surface of the magnesium alloy.

After rinsing and drying the magnesium sheet provided with the protective coating was coated with a cellulose lacquer and exposed to the seawater spray test, together with a sheet chromated by the immersion process hereinbefore referred to and likewise provided with a coating of the same lacquer. After 435 hours the chromated sheet had been badly attacked over its entire surface and the lacquer film had peeled off. At the end of the same period the lacquer coating on the sheet treated in accordance with the invention showed signs of slight attack only at the edges, that is to say, at obviously faulty spots, and still firmly adhered to the metal sheet.

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