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METHOD OF PRODUCING PROTECTIVE LAYERS ON MAGNESIUM AND MAGNESIUM ALLOYS

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This invention relates to a method of producing protective layers on magnesium and magnesium alloys.

It is already known to produce protective layers on magnesium or magnesium alloys by immersing the article to be protected in aqueous solutions of chromate. The protective coatings thus obtainable are very sensitive to mechanical injury, since normally by injury of the very thin protective layer a local corrosion of the metallic work piece is started which is stronger than that occurring if the article would have been used without a protective layer obtained by corrosion. Stronger coatings, of course, can also be obtained by anodic treatment of the magnesium or its alloys in solutions of chromic acid. It was found out, however, that it is difficult to wash out the electrolyte absorbed in the oxide coating. On the other hand, residues of the electrolyte left in the protective coating obtained by corrosion may cause indirectly severe undesirable corrosions of the work piece in its use. The same drawbacks occur with protective coatings produced by immersing the work piece into molten salts, since also in this case the partly oxidized metal salts can never be perfectly removed again from the protective coating.

The present invention relates to a method for the production of protective coatings on articles consisting substantially of magnesium, such as, magnesium and magnesium alloys, in which the protective layers are produced with the aid of bifluorhydric or bi-hydrofluoric acids or its salts. Suitable acids of this kind are the silicofluoric or fluosilicic acid SiF_6H_2, the borofluoric acid BF_4H, the titanofluoric acid TiF_6H_2 and similar acids of this groups. As far as the corresponding metal salts are used in aqueous solution, at least the magnesium salts of these acids must be used, for example, $MgSiF_6$ or $MgTiF_6$ since the corresponding alkali salts would not produce a substantial or visible protective coating. The metal salts permit the production of coatings of an optimum quality. Where—when using salts of heavy metals—the corresponding heavy metal is also deposited, however, it can be easily removed from the protective coating lying thereunder, without detrimentally affecting the coating. Since some of the complex salts of the bifluoric acids are also sublimable, it is also possible to produce the protective layer on the article by sublimating. Especially magnesium silicofluorid $MgSiF_6$ is suitable for this purpose.

Some examples of practical processes for carrying out the invention will now be described in detail with respect to the salts of the silicofluoric acid SiF_6H_2 but we wish to make it quite clear that borofluoric acid salts or titanofluoric acid salts or mixtures of these substances may also be used for the production of protective layers.

Immersing a magnesium alloy known under the trade name electron into a concentrated aqueous solution of magnesium silicofluorid comprising 500 grams $MgSiF_6$ per 1 liter water, a fixedly adhering protective coating of light gray colour is formed on the metal. This protective coating offers already sufficient resistance against slighter corrosive attack and, moreover, forms an excellent base for varnish or lacquer. Cold varnish adheres better on this coating than on the corresponding coating obtained by chromic pickling. Moreover, while the known chromic pickling bath in case of combined work pieces comprising electron and, for instance, steel rings pressed into said electron, causes a chemical attack with respect to the steel, so that the same must be protected against such attack by special measures, such protection is not necessary when the said combined work pieces are treated in accordance with my novel method. Nevertheless, the action of our novel pickling bath with respect to magnesium and its alloys is so intensive that even die-cast work pieces of electron can be provided with the protective coating without any preliminary treatment, while the casting skin has to be removed from the work piece in order to produce thereon a coating by one of the conventional chromic pickles.

We have found that it is advantageous to immerse the metal article treated after my novel process into an alkaline solution, for example, lime water, after it has been taken out of the pickling bath, so as to neutralize or destroy any excessive $MgSiF_6$ still adhering to the article, unless the following after-treatment is used.

The protective coatings obtained by the action of concentrated aqueous magnesium silicofluorid on magnesium and its alloys can be rendered denser and more resistive in a mechanical respect by heating the metallic article treated in the pickling bath. In this case, the article is not washed off and not subsequently immersed in an alkaline solution. Advantageously, temperatures above 100° C up to a temperature somewhat under the softening temperature of the respective metal are applied. A temperature of 300° C. proved to be particularly suitable.

The whitish gray layer obtained by the said modification of the process according to the invention has optimum anticorrosive properties without any further treatment. First of all, however, it is more resistant mechanically. By reason of its greater thickness it is more suitable for the reception of impregnating substances than thinner protective layers. Thus, comparative tests between electron pickled by chromate and electron pickled in accordance with the invention have shown that our novel protective layer has a durability increased by 100 percent compared to the electron pickled by chromate, in case of a similar varnish coating.

We have found that a still greater density and reinforcement of the protective layer can be obtained by a repeated immersion treatment and subsequent heating.

The protective layer produced by our novel aqueous bath may be dyed, as the protective layer is being formed, by metallic compounds admixed additionally to the bath. For example, by the addition of potassium permanganate $KMnO_4$ a protective layer of a deep-black colour and by an addition of chromate e. g. Na_2CrO_4 a protective layer of a dark-gray colour can be obtained so that this colour is imparted to the metallic article proper. The work pieces so treated may be used for novel purposes.

A protective coating having a deep-black colour can be obtained on magnesium alloys, sheets of which are known on the market as "AZM" sheets, by immersing the article into a bath comprising:

Water	liters	1
$MgSiF_6$	grams	250
$KMnO_4$	do	30
H_1SiF_6 of a density of 1,3	cubic centimeters	150

The black coating obtained by said bath is also suitable as a base or ground layer for lacquer or varnish. Where the coating is oiled, instead of being varnished, its decorative effect and, moreover, its imperviousness to corrosion can be increased.

Reinforcement of the coating and making it denser is also possible with this blackening bath, by a repeated treatment of the metallic article.

The fact that the salts of the bi-fluorhydric acids are sublimable, this sublimation being possibly accompanied by a more or less intensive thermal decomposition, also offers the possibility of applying our novel process already in the casting operation of the magnesium and its alloys. In this case, the salts may be admixed to the moist sand or applied to the finished sand mould in the form of powder.

It is also possible to apply our novel protective coating on metal articles of magnesium and its alloys in an electrolytic process in which the work piece forms the cathode. Where a solution of magnesium silico-fluoride is used as an electrolyte, magnesium hydroxide is primarily produced on the cathode in the electrolytic operation which magnesium hydroxide is transformed into magnesium fluoride and silicic acid and forms a very dense layer on the cathode adhering very tightly thereto. In this manner it is also possible to obtain subsequently cathodically a greater density of the coatings obtained by our novel process in the above described manner.

The coatings produced by the metal salts of the bi-fluorhydric acids are generally more important than the protective layers obtained by action of the respective acid itself, except the coatings obtained by a cathodic treatment. Also, the acids proper are not suitable for the production of protective layers by sublimation.

The coatings produced in accordance with the invention form protective layers of relatively high imperviousness to corrosion, even if they are relatively thin, and the said imperviousness to corrosion can be increased to an optimum value by reinforcement and making denser of the coatings unless the maximum imperviousness is already present immediately by the production of the coating by the cathodic method or by sublimation. In the reinforced form the coatings show a high resistance in use against mechanical injury and that without an additional coating of varnish or the like being required, although the resistance against mechanical injury can be increased by oiling, lacquering, varnishing and the like. The coatings made in accordance with the invention show a great adhesion on the metal articles on which they are produced so that it is possible to deform the articles in cold condition after the production of the coating.

The method of the present invention has been described in detail with reference to specific embodiments. It is to be understood, however, that the invention is not limited by such specific reference but is broader in scope and capable of other embodiments than those specifically described.

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