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PROCESS FOR THE PROTECTION OF MAGNESIUM AND ITS ALLOYS

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This invention relates to a process for the treatment of magnesium and its alloys in order to protect their surface with a film resistant to corrosion.

The inventor has made the surprising discovery that if one causes an acid solution containing manganese in the form of ions to act upon magnesium or magnesium-base alloys, an adherent deposit of an oxide or oxides of manganese is formed on the magnesium under certain conditions.

In carrying out my process, the magnesium-base metal is first of all immersed in an acid bath, whose P_H is below 7, contalning manganese in the ionised state, preferably either as Mn^{++} or MnO^{-}_{4}, and also preferably the ion of an oxidising acid such as CrO_4 or Cr_2O_7.

These ions may be added separately, the manganese either in the form of an acid such as $HMnO_4$ or of a salt containing certain soluble anions, as for example $MnSO_4$; or they may also advantageously be added together in the form of $MnCr_2O_7$.

The magnesium-base metal which it is desired to protect may simply be subjected to chemical action in such a bath or it may be submitted to electrolytic action, preferably by the application of alternating current, the composition of the bath being modified to suit the circumstances.

If only chemical action is employed, one obtains a very thin deposit of oxides which only afford a relatively slight protection, for the reaction quickly comes to a stand still. In order to convert this layer into one which will adequately protect the metal, it is necessary to protect the film by a further coating such as for example by means of painting.

In general it is more advantageous to deposit the film of oxides electrolytically which permits of forming thicker and more adherent deposits. The brown film of manganese oxides thus obtained can be submitted to a further treatment in an alkaline solution or in boiling water, which changes the composition of the oxides. One can also submit the aforesaid brown film to a subsequent treatment in a bath of soluble silicates, or apply an exterior coating of paint.

By way of example one may proceed in putting my invention into effect according to one of the modes of procedure subsequently described.

The solutions serving for the bath are prepared by adding to a solution of chromic acid of known strength definite quantities of $MnCO_3$ (or MnO_2) and have a P_H inferior to 7.

The electrodes are constituted by objects in magnesium-base metals it is desired to treat, and one causes an alternating current of from 2 to 12 amp/dm^2 to pass across the bath under a voltage of from 4 to 40 volts. The current is maintained for a period of time varying from 5 to 15 minutes. The bath is kept at room temperature.

The results obtained vary with the relative concentrations of CrO_4 and Nn ions. Thus if one investigates solutions with increasing content of Mn ions, while keeping the CrO_4 ion content constant, the reactions obtained show the following surprising variations.

(*a*) *Bath composition.*—10% H_2CrO_4, 1 to 2% $MnCO_3$.

The CO_2 contained in the $MnCO_3$ (or the oxygen of the MnO_2 is this latter is employed) is evolved with formation of $MnCr_2O_7$.

If one restricts the protection to purely chemical action one obtains a good pickling action. If one passes alternating current, its action deposits a film of black oxide of chromium showing traces of brown oxide of manganese, more particularly in the central portions some distance from the edges.

(*b*) *Bath Composition.*—10% H_2CrO_4, 3% $MnCO_3$.

Chemically one obtains pickling and electrolytically a dissolution of the magnesium. There is in neither case any appreciable deposit formed on the magnesium-base metal.

(*c*) *Bath composition.*—10% H_2CrO_4, 4 to 5% $MnCO_3$.

Chemical action gives a very thin film varying from gold to pale yellow, resembling in appearance the film produced by treatment with a solution of $K_2Cr_2O_7$ and HNO_3. If SO_4 ions are present, as in a solution containing H_2CrO_4 and $MnSO_4$, the thickness of the film is considerably increased.

Electrolytic action gives instead of a yellow film a deposit containing a mixture of black oxide of chromium and brown oxide of manganese.

(*d*) *Bath composition.*—10% H_2CrO_4, 6 to 10% $MnCO_3$.

Chemical treatment shows no apparent action. On passing an electric current, a very adherent deposit of brown oxide of manganese is formed, more or less mixed with oxides of chromium according to the quantity of free CrO_3.

The protective action against corrosion of this last film is excellent. One can still further increase the protection it affords by applying a fin-

ishing coating of paint or by treating it in a silicate solution. In the latter case there is a simultaneous modification of the superficial layer of oxides due to the formation of other oxides of Mn and a deposit of silica which forms an external protective coating.

These modes of procedure and the results they afford are given merely by way of example and should not in any way be deemed as limitative in their scope. Thus, for example, the concentrations of chromic acid may also be varied within certain limits, the $MnCO_3$ replaced by an equivalent quantity of MnO_2, $MnSO_4$ be substituted entirely or in part as the desired source of Mn^{++} ions, or MnO^{+}_{4} substituted in certain cases for the Nn^{++} ions in question.

The invention also covers, as new products of industrial value, all objects in magnesium-base metals covered with a protective coating constituted either by oxide or oxides of manganese alone or by a mixture of these oxides with oxides of chromium. Objects so protected may be of course be still further protected by an exterior coating of paint or one produced by subsequent treatment in a bath of soluble silicates.

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