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PICKLING OF MAGNESIUM ALLOYS

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The invention is directed toward cleaning and brightening the surface of magnesium articles by the use of chemical solvents. It is particularly directed toward the removal from the surface of such articles of the adhering contaminants of an especially tenacious character which are acquired by such articles during hot mechanical working.

The term magnesium articles as used herein, refers to all pieces, shapes, and objects composed of magnesium metal or of at least about 85 percent by weight of magnesium metal alloyed with other materials.

Among the surface contaminants on magnesium articles are carbonized lubricants and rolled-on mill scale, consisting chiefly of oxides and hydroxides of magnesium and other metals and fragments of magnesium and of other metals and metal compounds, acquired during the forming or fabrication operations, e.g., hot rolling; such scale usually adheres tenaciously to the metal surface. Apart from the objectionable appearance caused by such contamination, particularly when the contamination includes heavy metal oxides, e.g., iron oxide, it can lead to accelerated and intensified corrosive attack of the magnesium article by functioning, in the presence of an electrolyte, as the cathode to the magnesium article surface as the anode. Therefore, the removal of such contamination from magnesium articles before they are put into service is highly important.

The removal of such surface contaminants by the chemical action of pickling solutions has been extensively used. Pickles which can be employed for this purpose are mineral acids. Such pickles have the disadvantage however, of violently attacking the magnesium metal and of causing stains and smut deposition, to produce surfaces of unacceptable appearance.

Acetic acid is also used with ammonium nitrate or an alkali or alkaline earth nitrate to reduce the rate of attack. The use of such acetic acid-nitrate compositions show some improvement over theretofore known methods of removing contaminants. However, certain drawbacks are associated with the use of acetic acid compositions: (1) vapor losses from the acetic acid are high which are costly, are a health hazard, and are a source of corrosion to nearby metal structures, particularly when the pickle is applied as a spray; and (2) in production spray pickle lines in which rubber-coated rollers are used to transfer magnesium alloy sheet through the acetic acid-nitrate pickle and rinse stages, slippage is frequently encountered which is associated with the undesirable low surface tension of the acetic acid-nitrate solution.

In view of the difficulties attendant upon the use of known chemical solvents for removing contaminants from the surface of magnesium articles, it is the principal object of the present invention to provide a more effective and economical method of removing such contaminants.

The foregoing and related objects are attained according to the invention by treating magnesium articles having contaminated surfaces with a solution consisting es-

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entially of glycolic acid and a nitrate of ammonium or of an alkali or alkaline earth metal, especially magnesium nitrate.

In the practice of the invention, the magnesium article to be treated is usually first degreased according to known practice, as by immersing the magnesium article in a suitable degreasing solution, e.g., one made by dissolving about 3 ounces of sodium carbonate and about 2 ounces of sodium hydroxide in sufficient water to make a gallon. The degreased magnesium article, which may be of any magnesium-base alloy in the form of rolled sheet, extruded rod or shape, forging, or the like, is then immersed in the solution according to the invention for a time sufficient to dissolve away the adhering contaminant. A period of time sufficient to remove about 0.00015 to 0.0005 inch from each exposed surface is usually used. However, for deeply embedded contaminants, it may be advisable to remove up to 0.003 inch of thickness from the exposed surface. This may be readily accomplished by the practice of the invention by merely immersing the magnesium article for a longer period of time; however, removal in excess of 0.001 inch from the surface of the magnesium article is seldom necessary. The period of time required is usually about 1 minute, although longer periods may sometimes be found desirable. In the interests of economical operation, the time should be as short as is commensurate with obtaining a bright surface.

The preferred mode of treating the magnesium article according to the invention is to pass it along a conveyor means between sprayers by which a spray of the glycolic acid-nitrate solution is sprayed onto the article. The article is thereafter water-rinsed and dried. Immersion or submersion of the magnesium articles in the glycolic acid-nitrate solution followed by water-rinsing and drying, however, is also effective as a mode of practicing the invention.

The glycolic acid concentration in the aqueous treating solution is from 10 to 40 percent by weight; a preferred concentration is about 25 percent. The ammonium, alkali or alkaline earth nitrate should be present in the treating solution in sufficient amount to provide a weight ratio of 1 of the nitrate component (NO_3) to between 3 and 10 of the glycolic acid i.e., from $\frac{1}{3}$ to $\frac{1}{10}$ as much (NO_3) as of glycolic acid by weight. Higher ratios of the nitrate increase the cost of the treating solution without advantages and higher ratios of glycolic acid tend to cause sludge formation, whereas no tendency to sludge formation occurs within the above recommended ratios. A preferred ratio of nitrate, i.e., (NO_3), to glycolic acid is about 1:5. For example, in a 25 percent solution of glycolic acid prepared by dissolving 250 grams of glycolic acid in enough water to make 1000 grams of solution, the preferred weight of (NO_3) to add thereto would be 50 grams. If the (NO_3) is added in the form of NaNO_3 , $\frac{85}{100} \times 50$ or about 68.5 grams of NaNO_3 would be added thereto.

Instead of employing an ammonium, alkali metal, or alkaline earth metal nitrate directly, the invention may be practiced by adding nitric acid and an alkali or alkaline earth metal hydroxide or carbonate or magnesium metal in suitable form such as trimmings or chips.

The invention lends itself well to the recovery of glycolic acid from the used glycolic acid-nitrate solution for reuse by passing the solution through an ion exchange resin bed and, moreover, vapor losses of the glycolic acid during practice of the invention either by spray or by immersion are negligible.

It has also been found that, in comparison to pickling solutions consisting of acetic acid-nitrate mixtures, the glycolic acid-nitrate solution of the invention causes less pinch roll slippage of sheet during its passage through a

spray pickle line. The effect of variations in the surface energy characteristics of the two solutions is not clear, but measurements taken of the surface tension of samples of each solution show that the glycolic acid-nitrate solution possesses higher surface tension than acetic acid-nitrate solutions. For example, the surface tensions of a 3.4 N solution of glycolic acid and a 3.4 N solution of acetic acid, each containing magnesium nitrate of 1.85 N were taken by the Traube Stalagmometer drop method at 30° C. The surface tension of the glycolic acid-nitrate solution was 64 dynes/cm. whereas that of the acetic acid-nitrate solution was 47 dynes/cm.

The following examples illustrate the practice of the invention.

Example 1

A solution was prepared by adding 228 milliliters of a technical grade 70 percent by weight aqueous solution of glycolic acid to 428 milliliters of water and thereafter adding 205 grams of $Mg(NO_3)_2 \cdot 6H_2O$. Since the specific gravity of 70 percent by weight glycolic is 1.25, there were present $228 \times 1.25 \times .70$ or 199.5 grams of glycolic acid and since about 24.2 percent of the magnesium nitrate hexahydrate is composed of the NO_3 component by weight, the ratio of the NO_3 component to the glycolic acid was about 1:4.

A piece of degreased rolled sheet of magnesium-base alloy composed of 3 percent aluminum, 1 percent zinc, 0.3 manganese, and the balance magnesium, having a gray coating of mill scale, produced by hot rolling, was gauged and immersed for a period of 1 minute at room temperature in the solution thus prepared. The magnesium article was then removed, water-rinsed, and dried. It was found that the sheet had been reduced in thickness a total of 0.0008 inch, i.e., 0.0004 inch of material was removed from each side of the sheet. The piece had an especially bright metallic luster and was entirely free from any stain, e.g., mottled or darkened areas.

Example 2

A solution was prepared according to the invention by dissolving 228 milliliters of a 70 percent aqueous solution of technical grade glycolic acid in 428 milliliters of water and thereafter 60 grams of $NaNO_3$ were admixed therewith, thereby producing a solution consisting of about 1 part by weight of (NO_3) to 4.5 parts by weight of glycolic acid. A piece of degreased rolled sheet of a magnesium-base alloy composed of 3 percent thorium, 1 percent zinc, and the balance magnesium, was gauged

and immersed for 1 minute in the solution thus prepared. It was then removed, rinsed with water, and dried. On gauging, it was found to be 0.00075 inch thinner. It had a bright metal luster and was entirely free from blemishes of any type.

Examination of the examples of the invention shows that contaminants can be removed from the surface of magnesium articles effectively, efficiently, and economically by practicing the invention. The use of the glycolic acid-nitrate composition employed represents a substantial saving over other compositions currently employed for brightening magnesium articles. The composition employed in the invention is easily stored and transported by pumping systems, exhibits a fast cleansing rate, lends itself well to ion exchange recovery means for the acid, has no objectionable odor associated with its use, effects a high luster with low metal loss, has negligible loss of acid by vaporization, and is compatible with other materials employed in the art of pickling magnesium articles.

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

1. The method of removing contaminants from the surface of a magnesium article which comprises subjecting the article to the action of an aqueous solution consisting by weight of between 10 and 40 percent of glycolic acid and from $\frac{1}{4}$ to $\frac{1}{10}$ as much of NO_3 , in the form of a soluble nitrate selected from the group consisting of ammonium and alkali and alkaline earth metal nitrates, as the weight of glycolic acid in said solution.

2. The method according to claim 1, wherein the soluble nitrate is $Mg(NO_3)_2$.

3. The method according to claim 1, wherein the soluble nitrate is $NaNO_3$.

4. The method according to claim 1, wherein the glycolic acid content is about 25 percent and the weight ratio of NO_3 to the glycolic acid is about 1 of the NO_3 to between 3 and 5 of the glycolic acid.

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