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Nitrate Salt
Carboxylic Acid
With

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CLEANING MAGNESIUM ARTICLES

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The invention relates to the method of cleaning metal articles composed of magnesium metal or a magnesium-base alloy. It particularly relates to a method of cleaning such articles which imparts a mirror-like luster to the articles thus cleaned.

The term magnesium-base alloy refers herein to an alloy containing at least 75 percent magnesium metal. Hereinafter the term magnesium will sometimes be used to refer to either magnesium metal or such alloy thereof.

Magnesium articles, e.g., those formed by extrusion, rolling, molding, casting, or by the fabrication of magnesium shapes, frequently acquire an objectionable tarnish or scale which is extremely diffcult to remove from the magnesium surface.

The removal of the tarnish or scale from such surfaces has long presented a problem. Numerous attempts have been made to attain the removal thereof and leave a bright smooth surface, none of which, however, has been fully satisfactory. Scraping and scalping to remove the scale or tarnish is time-consuming, wasteful of metal, and often not possible in the case of intricately formed articles.

Subjecting the magnesium article to be treated to the action of a chemical solution has been more successful than the actual cutting away of the tarnished portion, but a number of disadvantages associated with the use of chemical solutions has not been overcome. Among such disadvantages are excessive attack on the metal by the chemical solution being used, rapid deterioration of the solution requiring frequent replacement, relative ineffectiveness of the solution employed, unadaptability of the solution to revivification, and formation on the magnesium article treated of various types of blemishes including objectionable blotches, discolorations, and smut depositions.

Furthermore, the use of known compositions for cleaning the surface of a magnesium article have not imparted to the article thus cleaned a bright mirror-like luster during the cleaning process without loss of an objectionable amount of magnesium metal.

In view of the difficulties attendant upon the use of known chemical solvents for cleaning the surface of magnesium articles and the desirability of imparting a mirror-like luster to the magnesium article thus cleaned, the principal object of the invention is to provide a more effective and economical method of cleaning magnesium and magnesium alloy articles and imparting during such treating a mirror-like luster.

The foregoing and related objects are attained according to the invention by subjecting a magnesium base article to an aqueous solution consisting of (1) nitric acid, (2) ammonium nitrate, an alkali metal nitrate, or alkaline earth nitrate or mixtures thereof, and (3) a water-soluble carboxylic or hydroxycarboxylic acid or a water-soluble salt thereof, and (4) the balance water.

In the practice of the invention, the cleaning solution employed may consist of between about 0.1 and 2.0 N HNO_3, between about 0.3 and 5.0 N of the nitrate salt and between about 0.5 and 5 N of the organic compound. The preferred nitrate to employ is $Mg(NO_3)_2$ and the preferred organic compound is glycolic acid, sometimes referred to as hydroxyacetic acid. The above normalities, when employing HNO_3, $Mg(NO_3)_2$ (calculated as the anhydrous salt), and glycolic acid expressed in grams per liter are: between about 6 and 126 grams of HNO_3, between about 22 and 375 grams $Mg(NO_3)_2$, and between about 38 and 380 grams of glycolic acid. The components of the cleaning solution of the invention are usually employed in amounts sufficient to provide a solution consisting of between 0.3 and 0.8 N HNO_3, between 0.5 and 2.0 N nitrate salt, between 1 and 2 N of the organic compound, and balance water.

Attempts to use nitric acid in a cleaning or pickling solution for magnesium has heretofore been unsuccessful among other reasons, because of the redeposition of heavy metals, thereby giving rise to poor corrosion of the thus cleaned article due to galvanic action when subsequently put in use.

The invention is carried out by admixing the ingredients of the treating solution, which may be referred to broadly as a pickle bath, in a suitable vessel or vat. The order of addition of ingredients is unimportant.

One mode of carrying out the invention is to fill the vat partially with a measured volume of water and admix therewith sufficient concentrated nitric acid (usually 68 to 70 percent HNO_3 in water) to give the desired concentration of HNO_3 and then admixing with the acidified bath sufficient nitrate salt, e.g., $Mg(NO_3)_2 \cdot 6H_2O$, to provide the required concentration of the NO_3 radical, and then admixing the carboxylic or hydroxycarboxylic acid or salt thereof to provide the desired amount of the organic compound in the bath. The magnesium or magnesium-base alloy article to be treated is first degreased, if necessary, as by immersing it in an aqueous alkaline solution, e.g., one containing between 2 and 4 ounces of sodium hydroxide and between 3 and 4 ounces of sodium carbonate per gallon of water at between 180° and 200° F. for from 10 to 15 minutes, removing it therefrom, an drinsing with water. The thus degreased magnesium or magnesium-base alloy article is then immersed in the aqueous treating composition of the invention for from 0.1 to about 10 minutes at a temperature between about 65° and 150° F., removed therefrom, and water rinsed.

Organic compounds useful in the practice of the invention include any carboxylic or hydroxycarboxylic acid or an ammonium or alkali metal salt thereof having a water-solubility of at least 38 grams per liter. Among such acids are acetic, propionic, butyric, oxalic, malonic, succinic, glutaric, glycolic, lactic, malic, tartaric, citric, water-soluble methyl, ethyl, or propyl-substituted branched-chain derivatives of such acids, and ammonium, sodium, and potassium salts of such acids. The organic compound recommended is an hydroxy-carboxylic acid. Glycolic acid is most commonly used.

The invention lends itself readily to a continuous operation, one mode of continuous operation being to pass the magnesium or magnesium-base alloy article to be treated according to the invention through a vat or tank, generally of an elongated shape, containing the composition of the invention, as by means of a conveyor belt, and then continuously conveying the thus treated article from the vat through water sprays which rinse the adhering treating bath therefrom and thence conveying the rinsed article into a drying oven or subjecting it to air jets which cause air at high velocity to impinge on the article and strip any adhering liquid therefrom. Various modifications of such continuous operation are apparent to those skilled in the art.

The time required for subjecting the magnesium article being treated to the action of the bath is relatively short, 0.2 to 1 minute being a preferred range and 0.5 minute being commonly employed. The thus treated article may be immediately rinsed after leaving the bath and is ready for use. Thus, in accordance with the invention, a blotched discolored or otherwise blemished magnesium or magnesium-base article may be converted within a

matter of seconds to a highly atttractive article having bright mirror-like surfaces. It is customary, however, to dry the thus treated and rinsed article prior to storage or for further use although the drying step is optiontal.

The amount of magnesium or magnesium-base alloy to be removed from the surface of the treated article during treatment is extremely small. In a continuous operation, for example, during a period of days wherein hundreds of such articles are treated, the average depth of metal removal per surface exposed is less than 0.5 mil (0.0005 inch).

The treating bath of the invention may be used for an indefinite period of time because it lends itself readily to revivification at periodic intervals. Since the percent of nitrate salt is increased in the bath during the use thereof in treating magnesium metal because of the formation of $Mg(NO_3)_2$, a periodic or automatic recording of the normality of the nitrate content of the bath is taken. The preferred range, stated in normality of the nitrate salt is between 1 and 2 N. In an elongated treating vat, the normality will vary from the input end to the output end, being greater at the output end. When the concentration at the outlet end of the vat reaches about 2 N, the bath is then revivified. Revivification is preferably carried out by passing the bath through an ion exchange resin which replaces at least a substantial portion of the metal ions present with hydrogen ions thereby replenishing the bath with nitric acid as well as removing the excess metal, usually magnesium, ions. A periodic test for the nitric acid content of the bath is also made as well and the treated magnesium articles gauged to ascertain the depth of metal being removed. The nitric acid content of the bath is adjusted to remove about 0.5 mil of the metal from each surface of the article being treated, that concentration being found optimum for thorough cleaning without excess loss of metal. The concentration of nitric acid in the bath to attain this objective has been found to be about 0.5 to 1 N, i.e., 31.5 to 63 grams per liter.

The following example is illustrative of the practice of the invention:

A panel composed of AZ31B magnesium alloy consisting of about 3 percent aluminum, 1 percent zinc, 0.4 percent manganese, and balance magnesium, was degreased by immersing in the aqueous $NaOH\text{-}Na_2CO_3$ cleaning solution referred to above for a period of 2 minutes at a temperature of 180° F., removed therefrom, and water-rinsed. The panel thus degreased was then immersed in the cleaning bath of the invention at 100° F. for 1 minute. The bath was prepared by adding sufficient concentrated nitric acid, dry $Mg(NO_3)_2 \cdot 6H_2O$ and dry glycolic acid to provide a concentration of 31.5 grams of HNO_3, 128 grams of $Mg(NO_3)_2 \cdot 6H_2O$, and 152 grams of glycolic acid per liter of the bath. The respective normality of the ingredients of the bath, it will be observed, were about 0.5 N for each of HNO_3 and $Mg(NO_3)_2$ and about 2 N for the glycolic acid.

The magnesium alloy thus treated had a bright mirror-like luster, entirely free from any residual tarnish or any discoloration due to deposition on the thus treated panel due to the presence of such heavy metals as iron in the bath. The depth of metal removed was less than 0.5 mil per side of the panel thus treated.

The advantages to be realized from the practice of the invention are clearly outstanding. Among such advantages are: the use of a readily available and low-cost acid, viz., nitric acid; simple and effective revivification of the bath by periodic addition thereto of nitric acid and the exchange of the magnesium or other positive metal ions formed in the cleaning process for the hydrogen ion to reduce the nitrate therein to the desirable nitrate range and by the same step replace at least a portion of the HNO_3 desired; the lack of deterioration or impairment of the more expensive organic acid or salt employed in the bath since it is not consumed in the cleaning process; imparting a bright mirror-like finish to magnesium metal heretofore unattained by a nitric acid-containing bath; producing a surface free, not only from any unremoved tarnish, but also from any redeposition due to the presence of such heavy metals as iron or nickel in the bath, the presence of which is highly objectionable both from the standpoint of appearance and because of the ensuing galvanic action which, as a result thereof, greatly accelerates the corrosion of the magnesium in use.

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

1. The liquid composition for cleaning and brightening the surfaces of metal articles composed of at least about 75 perecnt magnesium metal which consists of a solution comprising between about 0.1 and 2 N HNO_3, between about 0.3 and 5.0 N nitrate salt selected from the class consisting of ammonium, alkali metal and alkaline earth metal nitrates, between about 0.5 and 5 N glycolic acid, and the balance water.

2. The method of cleaning a metal article containing at least 75 percent magnesium consisting essentially of subjecting said article to the action of an aqueous solution comprising between about 0.1 and 2.0 N HNO_3, between about 0.3 and 5.0 N nitrate salt selected from the class consisting of ammonium, alkali metal, and alkaline earth nitrates, between 0.5 and 5.0 N glycolic acid, and balance water, for between 0.1 and 10 minutes at a temperature between about 65° and 150° F.

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