

1

3,100,170

PICKLING MAGNESIUM ARTICLES

Donald Jack Levy, Olivette, Mo., assignor to The Dow Chemical Company, Midland, Mich., a corporation of Delaware

No Drawing. Filed Jan. 4, 1960, Ser. No. 83
11 Claims. (Cl. 156-20)

The invention pertains to cleaning or pickling metal articles composed of at least about 75 percent magnesium, hereinafter sometimes referred to as magnesium articles.

Such magnesium articles, usually contain contaminants on the surface thereof which stimulate corrosion thereof following working, shaping, or fabrication. Corrosion of the surface contaminated magnesium articles manifests itself by the formation of a tarnish and/or tenaciously adhering scale during storage and use at a rate which is deteriorating and destructive to the metal unless such contaminants are removed.

A number of attempts have been made to remove such contaminants and thereby lessen the corrosion of magnesium articles. Among such attempts are scalping away the contaminated outer layer and by subjecting the contaminated article to the action of a chemical composition usually consisting of dipping or otherwise applying the composition as an aqueous solution followed by water-rinsing, and usually, thereafter, by drying. The chemical treating solution, usually being acidic, is commonly called a pickle bath and the treatment therein, pickling. Pickling of magnesium articles has been successful to some extent to remove the contaminants from the surface of the article thus treated to lessen subsequent corrosion and is widely practiced. A number of pickling compositions have been employed in attempts to attain this purpose, some of which have been found useful to attain such contaminant removal from magnesium articles and provide improved resistance against corrosion to magnesium articles. There are nevertheless one or more difficulties attendant upon the use thereof. Among such difficulties are: excessive attack of the composition on a magnesium article resulting in uneconomical loss of magnesium metal; relatively short life of the composition and/or impracticality or impossibility of revivifying the composition periodically for continued use; the failure of the composition to remove adequately the contaminating tarnish and scale; the tendency of the composition to form on the treated magnesium article mottled or streaked blemishes often due to the presence of heavy metal compounds such as those of iron, copper or zinc; expense or unavailability of the ingredients of the composition; and ineffectiveness in improving the corrosion resistance of the article so treated.

Relatively concentrated solutions of sulfuric acid, having a normality of at least about 20 N have recently been found to be especially effective for removing tarnish and scale from some magnesium-base alloy articles. However, when such articles are composed of certain magnesium-base alloys, and especially magnesium-base alloys containing over 0.5 percent zinc, a black discoloration appears upon such sulfuric acid-treated magnesium-zinc articles. Since a large percent of magnesium-base alloys contain between 0.5 and 1.5 percent zinc, there is clearly a desideratum in the art of treating magnesium-base alloy articles to provide a method of treatment by which to obtain a bright surface thereon as well as impart thereto good resistance to corrosion when such articles contain more than 0.5 percent zinc.

I have now found that a bright lustrous surface having high corrosion resistance can be obtained by subjecting a magnesium-base alloy article containing not more than 2.0 percent zinc to the action of an aqueous composition

2

prepared by admixing with an aqueous sulfuric acid solution, of at least 20 N but not over 25 N, one or more of a halogen ion- or nitrate ion-yielding compound wherein the halogen is chlorine or iodine. Illustrative of such compounds are: HNO_3 , a soluble nitrate salt, HCl , a soluble chloride salt, a soluble iodide salt, HI , an oxychloride salt, an oxyiodide salt, or a halogen-substituted ionizable organic compound such as monochloroacetic acid, for a time sufficient to remove the contaminants or scale therefrom, water-rinsing, and preferably drying the magnesium article so treated.

When aqueous sulfuric acid of less than 20 N is employed, in the practice of the invention, the reaction rate is undesirably fast and the extent of corrosion resistance imparted to the article is unsatisfactory even though an excessive amount of metal is removed from the magnesium article during treatment. When the acid normality is greater than 25 N, the reaction rate is undesirably slow and more of the halide ion- or nitrate ion-yielding addition is required to attain satisfactory cleaning and corrosion protection.

In the practice of the invention the halide ion- or nitrate ion-yielding compound is admixed with the sulfuric acid solution in an amount sufficient to yield a weight of between 5 and 250 grams of the (NO_3) or halogen fraction or portion of the compound per liter of the sulfuric acid-treating composition so made.

The practice of the invention is applicable to brightening and providing corrosion resistance to any magnesium or magnesium-base alloy article including those containing zinc alloyed therein up to 2 percent thereof. Articles thus treated are free from undesirable blotches or streaks which form on certain extensively used magnesium-base alloy articles when sulfuric acid alone is used. The composition containing any of the above named acids or salts as an adjuvant to sulfuric acid of the required normality for pickling magnesium articles exerts a minimum attack on the magnesium article being pickled and is relatively low in cost. The article so pickled shows a particularly high resistance to corrosion in relation to the depth of the layer of metal removed during pickling. The improved composition employed in the invention requires no sequestering or buffering agent as do most compositions presently employed in pickling magnesium-base alloys. Such sequestering or buffering agents are relatively expensive and sometimes prevent a satisfactory removal of the tarnish or scale during the pickling operation.

The preferred mode of treating the article to be cleaned and given protection against corrosion in accordance with the invention is to employ a bath of the aqueous acid or salt and sulfuric acid of a suitable normality and immerse the article to be treated therein. The temperature of the bath may be any temperature less than the boiling point thereof but it is preferred that it be between 80° and 150° F. The period of immersion of the article being treated in the bath depends upon the concentration and the temperature of the bath, the composition of magnesium alloy being treated, and the severity of tarnish or scale on the article. Immersion in the bath should be sufficiently long to provide the necessary corrosion resistance desired. A minimum of 0.1 mil of metal should be removed per side and generally 0.2 to 0.3 mil is usually removed per side from the commercial coil-rolled magnesium alloy strip metal to remove, substantially, the surface contamination in accordance with the invention. Not only are there extensive material savings by removing a lesser amount of metal than heretofore has been commonly required, and the treating bath, therefore, less contaminated, but the bright lustrous surface attained on the metal is equally as good when only enough metal

is removed to rid the article being treated of the tarnished layer as when more metal is removed. Treating times usually vary between about 1 and 10 minutes although shorter or longer periods are sometimes employed in the practice of the invention.

The reason why less metal need be removed in the practice of the invention to rid the article being treated of all tarnish and scale and provide especially good resistance against corrosion is not fully known but it appears that the pickling composition employed in the practice of the invention attacks the contaminants on the mag-

the period of exposure to air is 2 minutes. The duration of the test was 7 days. The thus treated article is cleaned, as by dipping in a chromic acid solution and rinsing in water, and thereafter reweighed and the metal loss calculated.

Table I below sets out pickling compositions illustrative of the practice of the invention wherein the recommended minimum weight of a nitrate, chloride, or iodide portion or fraction of a nitrate ion-, chloride ion- or iodide ion-yielding compound is added to the sulfuric acid solution having the normality shown.

Table I

Normality of H_2SO_4	Minimum recommended weight of NO_3 , Cl , or I fraction of compound added in grams per liter									
	Weight of NO_3 added as—			Weight of Cl added as—					Weight of I added as—	
	HNO_3	$NaNO_3$	NH_4NO_3	HCl	$NaCl$	KCl	$HClO_4$	MCA^1	NaI	KIO_3
25	25			20	10					
23			50							
20		35	50	5		5	20	5	5	5

¹ Monochloroacetic acid.

nesium alloy preferentially to the metal itself and as one of the concomitant effects thereof, it is unnecessary to undercut the contaminants to the extent necessary when employing known methods of cleaning, brightening, and providing protection against corrosion to magnesium-base alloy articles.

When the magnesium article is removed from the treating bath it has a liquid film of the bath adhering thereto. Best results are attained in the practice of the invention when the film of bath is water-rinsed off shortly after such removal, e.g., within 15 and preferably within 5 seconds. It is recommended that the water be applied during the rinsing operation generously to flush the adhering acid from the entire surface of the article rather rapidly. The temperature of the rinse water is unimportant, water at room temperature commonly being employed. The article thus treated is preferably thereafter dried, as in a forced-air drier.

The pickling composition employed in the practice of the invention may be revived conveniently as required. Periodic tests thereof show when the acid normality and/or the concentration of the halide ion or nitrate ion concentration thereof require adjustment. Such adjustment is readily done by adding sufficient sulfuric acid and/or the halide ion- or nitrate ion-yielding material to bring the concentration thereof within the ranges thereof set out hereinabove. Since some magnesium sulfate and other salts are formed during the pickling operation in accordance with the invention, and such salts largely settle to the bottom of the bath as a precipitate, the bath may be separated therefrom by merely filtering, decanting, siphoning, or otherwise drawing off the supernatant liquid pickling composition therefrom.

The corrosion rate of a magnesium or magnesium-base alloy article is commonly measured by a standard alternate brine immersion and air exposure test and, therefore, such test is applicable for determining the effectiveness of pickling compositions and methods. Such a test was employed to ascertain corrosion rates of magnesium or magnesium-base alloys when treated according to the invention and when not so treated for purposes of comparison. The test employed herein is designated A.S.T.M. B192-44T as described in American Society for Testing Materials Standards, 1958, page 243. The test broadly consists of alternately immersing a previously weighed magnesium article in a sodium chloride brine and exposing it to the air at fixed intervals for a specified testing period at a temperature of 80° F. The sodium chloride brine was a 3 percent by weight solution. The length of each immersion period is 0.5 minute and

Any of the compositions set forth in Table I produce a bright lustrous finish and a high resistance to corrosion on a magnesium-alloy article, having a Zn content of not more than 2 percent, which is subjected to the action thereof as by immersion therein.

In the practice of the invention it is recommended that the magnesium article to be treated be first degreased by subjecting it to the action of a conventional alkaline cleaner, e.g., by immersing the article in such cleaner for from 3 to 10 minutes at from 100° to 200° F. to remove oil, grease, and other organic substances therefrom. A common aqueous alkaline cleaner employed is one prepared by dissolving 3 ounces of $Na_2CO_3 \cdot 10H_2O$ and 2 ounces of $NaOH$ in sufficient water to make a gallon. After immersing the article to be cleaned in such alkaline cleaner and removing it therefrom, it is water-rinsed. Thereafter the magnesium article is subjected to the action of the pickle bath in accordance with the method of the invention.

The following examples are illustrative of the practice of the invention:

Convenient size magnesium alloy sheet panels of between 0.05 and 0.06 inch thick were degreased by immersion in an alkaline degreasing bath for about 5 minutes at about 190° F., removed therefrom, and rinsed. Solutions of aqueous sulfuric acid were prepared having a normality of either 25 or 23. Pickle baths were then prepared by admixing with portions of such normality sulfuric acid, sufficient weights of a nitrate ion-, chloride ion-, or iodide ion-yielding compound, to provide the desired weight of NO_3 , Cl , or I fraction thereof per liter of the aqueous sulfuric acid solutions. The degreased panels were then immersed in the pickling bath thus prepared and agitated moderately therein until 0.5 mil thickness of metal had been removed per side of the panel being pickled. The thus treated panels were then removed, water-rinsed promptly, and air-dried. The articles treated were composed of either an extensively-used magnesium-base alloy consisting of 3 percent aluminum, 1 percent zinc, and about 0.4 percent manganese, and balance magnesium, or the more special magnesium-base alloy consisting of 0.7 percent zirconium, 3 percent thorium, and balance magnesium. Table II sets out the alloy treated, the normality of the H_2SO_4 solution and the grams of NO_3 , Cl , or I present per liter of H_2SO_4 solution, and the compounds added to yield the NO_3 , Cl , or I ions. Table II also sets out the temperature of the bath, the length of immersion, and the corrosion rate as determined by subjecting both unpickled panels and panels pickled according to the invention to A.S.T.M. test B192-44T. Each of

the magnesium alloy panels tested showed a very bright lustrous surface after treatment in accordance with the invention whereas those not treated had a dull tarnished surface due to unremoved contaminants thereon.

Table II

Magnesium alloy, percent by weight	Normality of H ₂ SO ₄ solution	Grams of NO ₃ , Cl, or I ions present/liter	Compound added	Temp., ° F.	Time, minutes	Corrosion, mg./cm. ² /day	
						Untreated	Treated
3 Al, 1 Zn, 0.4 Mn, and balance Mg	25	25 NO ₃	NaNO ₃	80	5.0	2.7	0.46
Do.	25	25 NO ₃	HNO ₃	80	3.7	2.7	0.43
Do.	25	25 NO ₃	HNO ₃	180	20.0	2.7	0.37
Do.	25	200 NO ₃	HNO ₃	80	5.0	2.7	0.45
Do.	25	50 NO ₃	NH ₄ NO ₃	80	1.0	2.7	0.45
Do.	25	20 Cl	HCl	80	0.7	2.7	0.62
Do.	23	18 Cl	KCl	80	0.8	2.7	0.38
Do.	23	16 Cl	MCA*	80	3.0	2.7	0.42
Do.	23	20 Cl	HClO ₄	80	2.5	2.7	0.39
Do.	23	5 I	NaI	80	3.0	64.0	0.20
0.7 Zr, 3.0 Th, and balance Mg	25	20 Cl	HClO ₄	80			

*Monochloroacetic acid.

An examination of the results of Table II shows that the corrosion resistance of the magnesium panels treated according to the invention, wherein 0.5 mil thickness of metal was removed per side, had a corrosion rate which was markedly less than the corrosion rate of the panels which were not treated.

It is obvious that the practice of the invention offers a number of advantages heretofore not attained by the employment of known methods of pickling magnesium-base alloy articles. It has been noted particularly that the zinc content does not result in a discolored surface after pickling. It is also to be noted that the zirconium-thorium magnesium-base alloy, which has a particularly high corrosion rate when it is not pickled, had a particularly low corrosion rate when pickled in accordance with the practice of the invention. Among the advantages of the invention are the consistently and outstandingly good resistance to corrosion and bright finish obtained at room temperature at a relatively fast but easily controlled pickling rate accompanied by unusually low metal loss.

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

1. The method of pickling a magnesium article containing at least about 75 percent magnesium and not over 2 percent zinc to remove contaminating tarnish and scale therefrom and to improve the corrosion resistance thereof which consists of subjecting the article to the action of an aqueous composition pickle composition consisting essentially of H₂SO₄ having an acid normality of at least 20 but not over 25 and having dissolved therein a compound selected from the class consisting of soluble nitrates, halides, oxyhalides, halogen-substituted organic acids, and mixtures thereof, capable of yielding nitrate and halogen-containing ions in solution, wherein the halogen is chlorine or iodine, in sufficient amount to provide between 5 and 250 grams of the nitrate and halogen fractions of said compounds per liter of said aqueous composition.

2. The method according to claim 1 wherein the length

of the immersion of said article in said aqueous pickle composition is between 0.1 and 90 minutes.

3. The method according to claim 1 wherein the article being pickled is immersed in the aqueous pickle com-

position for a time sufficient to remove substantially all foreign contaminating materials from the surface thereof, removed therefrom, and water-rinsed.

4. The method according to claim 3 wherein the magnesium alloy article being treated is immersed in the aqueous pickle composition for a time sufficient to remove metal to a depth of at least 0.1 mil per side.

5. The method according to claim 3 wherein the magnesium metal article being treated is water-rinsed within 15 seconds after its removal from the aqueous pickle composition.

6. The method according to claim 3 wherein the aqueous pickle composition and the magnesium alloy article immersed therein are maintained in motion relative to each other.

7. The method according to claim 3 wherein the temperature of the aqueous pickle bath is between about 80° F. and 300° F.

8. The method according to claim 3 wherein the soluble halogen-containing ion is chlorine.

9. The method according to claim 3 wherein the soluble halogen-containing ion is iodine.

10. The method according to claim 3 wherein the soluble nitrate ion-yielding compound is nitric acid.

11. The method according to claim 3 wherein the soluble nitrate ion-yielding compound is a nitrate salt.

References Cited in the file of this patent

UNITED STATES PATENTS

1,918,545	Hoy	July 18, 1933
2,287,050	Miller	June 23, 1942
2,411,532	Escoffery	Nov. 26, 1946
2,511,988	Myers et al.	June 20, 1950
2,574,049	Mayhew	Nov. 6, 1951
2,751,342	Guggenberger	June 19, 1956
2,762,728	Hahn	Sept. 11, 1956
2,864,730	Kinder et al.	Dec. 16, 1958
2,894,883	Walker et al.	July 14, 1959
2,967,136	Cybirowsky et al.	Jan. 3, 1961