A New Inorganic Coating for Magnesium Alloys with Superior Corrosion Resistance

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INTRODUCTION

Magnesium, the sixth most abundant element in the earth's crust, is the lightest of all commonly used structural metals. Having a density of only 1.74 g/cm^3, it is one and one-half times lighter than aluminum, approximately four times lighter than zinc or steel and is comparable in weight to perhalogenated or mica and asbestos filled plastics. Although pure magnesium is too soft for structural use, the addition of other elements such as aluminum, zinc, manganese and rare earths have produced alloys with enhanced chemical and physical properties. Alloys of magnesium have found considerable use in applications where weight saving is important. The automotive industry has been looking increasingly towards magnesium for reducing vehicle weight, thus improving fuel economy, and is currently the major user of magnesium die cast parts. For example, a weight reduction of 125 lb. will yield a fuel economy improvement of 0.2 to 0.5 miles per gallon in the EPA Combined City-Highway test.[1] In a recent perspective of magnesium in automobiles more than forty production applications of magnesium alloys on US cars are listed.[2] Other industries which benefit from magnesium's low weight include power tools, computers, recreational equipment and aerospace. In addition to it's low weight other advantageous properties include a high-strength-to-weight ratio, excellent dimensional stability, high impact resistance, good creep strength as well as high thermal and electrical conductivity. In addition, magnesium and its alloys are recyclable and present no toxicity hazard.[3]

Pure magnesium metal is a reactive metal and thus is easily oxidized. This oxidation or corrosion, galvanic as well as surface, is often the major obstacle against the use of magnesium in aggressive corrosive environments. However, through the use of high purity alloys with a low content of iron, nickel and copper, satisfactory performance may be achieved with respect to surface corrosion.[4,5] For example, the corrosion rate in salt spray (ASTM B117) of high purity AZ91D[6] and AM60[7], both die cast alloys, range from 1-12 mpy and less than 20 mpy, respectively, while two sand cast alloys, AZ91E and WE43, exhibit similar rates of 5 mpy[8] and 8-16 mpy[9], respectively. Other commonly used alloys, such as ZE41A, demonstrate considerably higher corrosion rates. The corrosion rate of ZE41A has been reported to be greater than 400 mpy.[10] The utilization of these alloys, particularly in aggressive environments, will require the application of surface treatments to provide additional protection against surface corrosion. In contrast, alloy composition will have a limited influence on galvanic corrosion; however, in this case, the service performance will depend on the proper design, assembly and surface treatments as well as the metal purity.[11]

In terms of aerospace applications, magnesium alloys, including ZE41A, QE22A and AZ91E, are currently used to fabricate main transmission housings and other gear boxes for several helicopters which are used for commercial and military purposes. Other parts, which are cast using these alloys, include intakes and intermediate casing for aircraft engines, housing for auxiliary power units, canopy frames and speed brakes. In many cases, extremely corrosive environments are encountered and, as a result, high performance coatings are required to produce maximum protection against surface and galvanic corrosion while minimizing maintenance.

The surface treatment processes for magnesium alloys which serve as a paint base and a barrier towards corrosion can be grouped into two types. The first type is the chemical conversion coatings which are applied either by immersion, brush on or spray-type processes while the second type involves an electrochemical anodic process. Table I provides a list of the more commonly employed surface treatments.[12] Though many of the conversion coatings do produce a surface that provides some corrosion protection and can act as a paint base, they are limited in applications on the more reactive sand cast alloys. In addition, the abrasion resistance of these coatings, including the anodic processes, are not particularly high. It is interesting to note that most of the treatments shown in Table I also utilize chromates in the primary coating or sealing bath. The utilization of chromates plus other materials such as cadmium, zinc, lead, copper and many volatile organic compounds (VOCs) has resulted in the EPA identifying the metal finishing industry as one of the most significant contributors to environmental pollution.[13] As a result, there is a critical need for new coating technologies which will reduce or eliminate chromate based systems yet provide adequate corrosion resistance, abrasion resistance and paint adhesion.

Table I. Common Inorganic Surface Treatments for Magnesium Alloys.

Chemical Treatment	Type	Solution Constituents
#1	Conversion	Sodium dichromate, nitric acid
#7	Conversion	Sodium dichromate, calcium or magnesium fluoride
#17	Anodic	Ammonium bifluoride, sodium chromate, phosphoric acid
#19	Conversion	Chromic acid, calcium sulfate
#21	Conversion	Chromic acid, ferric nitrate, potassium fluoride
HAE	Anodic	Potassium hydroxide, potassium fluoride, aluminum hydroxide, sodium phosphate, potassium manganate
Iridite No. 15	Conversion	Chromic acid, chloride, nitrate solution
Bonderite 1000	Conversion	Iron phosphate

Recently, a new high performance coating for magnesium alloys has been developed which exhibits improved corrosion protection and abrasion resistance as well as providing an excellent paint base. The coating has been given the trademark, TAGNITE™, and is produced by an electrochemical process that does not employ chromates. The process and coating characteristics are described herein.

products which may be present on the alloys through the use of the mild alkaline etch. This solution, commonly used to brighten die cast alloys, shows an insignificant metal loss after a ten minute treatment. The coating process itself consists of two steps. The first step is a simple chemical process in which the magnesium alloy is immersed into a heated solution containing the fluoride ion. This solution applies a layer containing a mixture of magnesium fluoride and oxofluorides and magnesium oxide and serves as a base for the step second. The second step is an electrochemical process in which the magnesium alloy is made the anode in an electrolytic cell.

The electrolytic process is accomplished using a relatively high voltage rectifier which supplies a combination AC/DC signal to the electrochemical cell. As in other anodization processes, the magnesium alloy is the anode while the stainless coating tank serves as the cathode. The electrolytic process involves the concurrent anodization or oxidation of the metal substrate and deposition of inorganic species from the silicate containing electrolyte. As a result of the relatively high voltages, greater than 150V, a spark process develops during the deposition. The sparking action is the result of the applied voltage being greater than the dielectric breakdown voltage of the layer produced in the first chemical step and the developing coating in the electrolytic step and produces temperatures which have been estimated to be greater than 1000°C. These localized high temperatures result in the fusion of silicate and oxide species onto the metal surface. Although the heat generated from the spark is localized on the surface, the resistive heating of the solution requires a cooling system to maintain the electrolyte temperature between 10-20°C. Figure 2 is a photograph of a magnesium AZ91D panel during the deposition process with the sparks visible on the panel surface. The lifetime of these sparks is typically less than a millisecond.

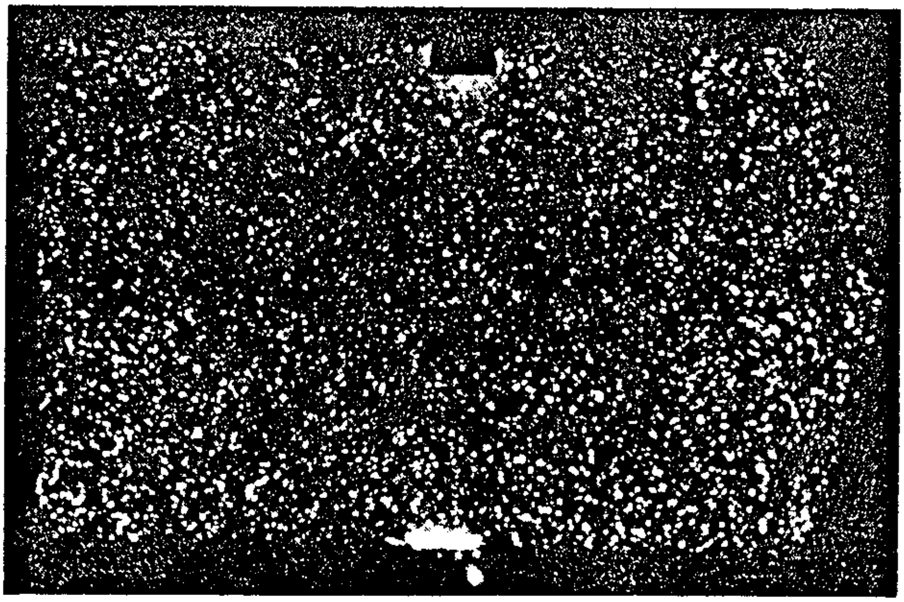

Figure 2. A photograph of a 4" x 6" test panel of magnesium alloy AZ91D during the Tagnite anodic spark deposition process.

Surface and near surface elemental analysis of the coating by ESCA indicates the

EXPERIMENTAL

Evaluation of coating performances was conducted on two magnesium alloys, AZ91D, a die cast alloy, and ZE41A, a sand cast alloy. All panels used to evaluate corrosion resistance were from the same melt so as to eliminate any variation in base corrosion rate for the bare metal due to variations in alloy composition. All coatings were applied as per specifications either in-house for the Tagnite coating or by an aerospace approved metal coating facility. In addition, all panels were entered into the salt spray chamber together to eliminate variation in chamber conditions.

Coating thicknesses were measured by an eddy current technique using an EMI International EM-2000E instrument which was calibrated with two plastic sheets of certified thickness on an alloy base of similar surface roughness as the panel tested. The arithmetic average roughness height, R_a, was measured using a Sheffield type QE profilometer amplimeter which was calibrated using a precision reference specimen. Five measurements were made across the surface of each panel using a 0.03" cut off width and 1.5" piloter stroke length. The five readings were averaged to yield the R_a value. Abrasion resistance testing were conducted using a Taber Model 5130 abraser using two C-17 abrading wheels with 1000 grams of load (ASTM D4060). The C-17 wheels were refaced before each test and after every 1000 cycles using a S-11 refacing disk. Results are reported as a Taber Wear Index (TWI) and number of cycles achieved. Corrosion performance testing was performed using a Singleton Model 20 corrosion test chamber operating as per ASTM B117. Panel evaluation was conducted as specified in ASTM D1654, method A and B. Scanning electron photomicrographs were obtained on a Hitachi S-800 scanning electron microscope.

THE COATING PROCESS

The application of the TAGNITE coating, as is the case with other coating processes, requires good cleaning practices such as those specified in MIL-M-3171.[14] Typically, the cleaning procedure shown in the process flow diagram of Figure 1 is sufficient to degrease and clean the surface. In addition, this method is capable of removing minor corrosion

Figure 1. Process Flow Diagram for TAGNITE Treatment of Magnesium Alloys.

Degreaser, aqueous based
40-50°C, 1-15 min., Rinse

Alkaline Etch
70-80°C, 1-10 min., Rinse

Fluoride Pretreatment
70-95°C, 5-90 min., Rinse

TAGNITE-8200
10-15°C, Rinse

Surface Neutralization
Post-Treatment
50°C, 30-120 seconds, Rinse

major constituents include magnesium, silicon, oxygen and fluorine for the coating on both the AZ91D and ZE41A alloys with a very minor quantity of potassium. For the ZE41A alloy, a minor percentage of cerium was detected, a result of the 1% rare earth composition of the alloy. The measured bonding energies indicate that the silicon atom is present in the form of silicate, not as silica, and the fluorine atom exists in its ionic form. This presence of magnesium in the coating indicates the electrolytic process involve the oxidation of the magnesium alloy substrate with the concurrent spark deposition of silicate and oxide species on the surface of the magnesium alloy. The oxidation and deposition process also results in a dimensional change for the magnesium alloy part. Cross-sections of panels which were partially masked, then coated and subsequently examined by SEM indicate that a dimensional increase of approximately 54% of the coating thickness occurs for the AZ91D alloy as compared to 46% for the ZE41A. These values are similar to those reported for the other two anodic processes. For example, chemical treatment 17 and HAE show an increase of approximately 65 to 75% and 50 to 75%, respectively.[15]

The thickness of the coating can be varied from two to thirty micrometers by controlling the current density and the time of the coating process. Typically, the process is performed at a constant current density in the range of 5 to 15 A/ft^2 with coating times of 10 to 20 minutes for a five to ten micrometer (0.2 to 0.4 mil, type I) thickness and 45 to 75 minutes for a 20 to 25 micrometer (0.8 to 1.0 mil, type II) thickness. The final voltage, though dependent upon the current density and bath composition, typically ranges from 280 to 320 volts for a type I and 320 to 340 volts for a type II with power requirements of approximately 0.4 and 1.6 kW hr/ft^2, respectively.

COATING MORPHOLOGY

The coating produced during the electrochemical process yields a surface with a finite amount of porosity. The porosity is a result of the evolution of oxygen gas from the oxidation of water or hydroxide ion with the concurrent generation of sparks at the surface. Figure 3A is a scanning electron photomicrograph representing the top view of a 5 micrometer thick Tagnite coating on a AZ91D test panel at a magnification of 2000 while Figure 4A represents a 22 micrometer thick coating on a ZE41A test panel. The maximum size of the pores is typically in the range of one to five micrometers for a type I thickness and one to ten micrometers for a type II thickness with the size dependent on the electrolyte composition, concentration and the time of coating process. The increase in pore size with coating thickness may be attributed to a similar increase in spark size resulting from a greater dielectric breakdown voltage as the deposition process proceeds. Though the surface is porous, the surface texture as measured by profilometer indicates the arithmetic average roughness height (R_a) ranges from 25 to 85 microinches for coatings between 2 to 25 micrometers (0.1 to 1.0 mil) thick. The value of R_a is dependent on the time of deposition or the thickness, only marginally dependent on the current density or the rate of deposition, and is essentially independent of the substrate alloy. For example, a coating thickness of 12.5 micrometers produces a surface with a value of R_a from 48 to 53 microinches for current densities between 3 and 15 A/ft^2.

Finally, it should be noted that although the coating has a porous microstructure,

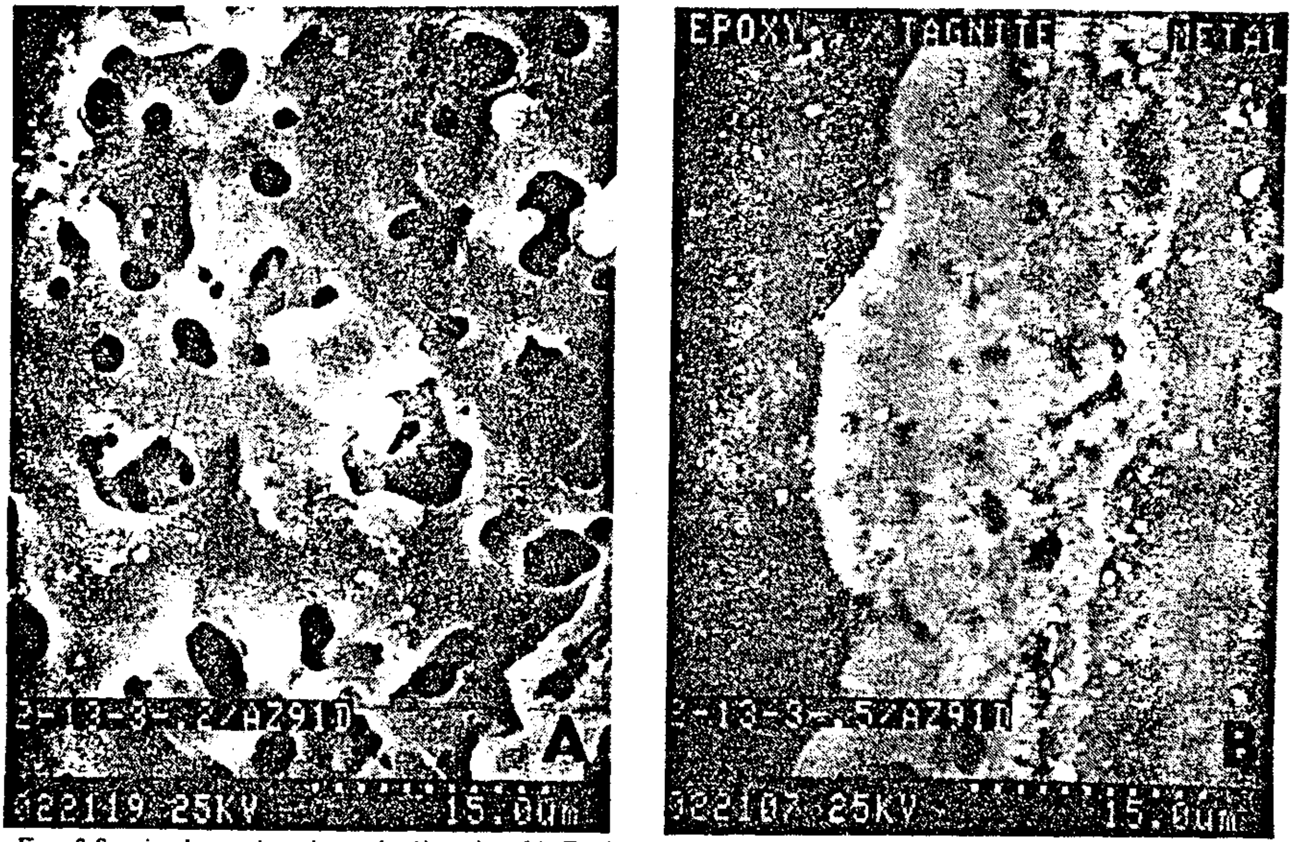

Figure 3. Scanning electron photomicrographs: A) top view of the Tagnite coating on AZ91D (200x), B) cross-section view of the Tagnite coating on AZ91D (2000x).

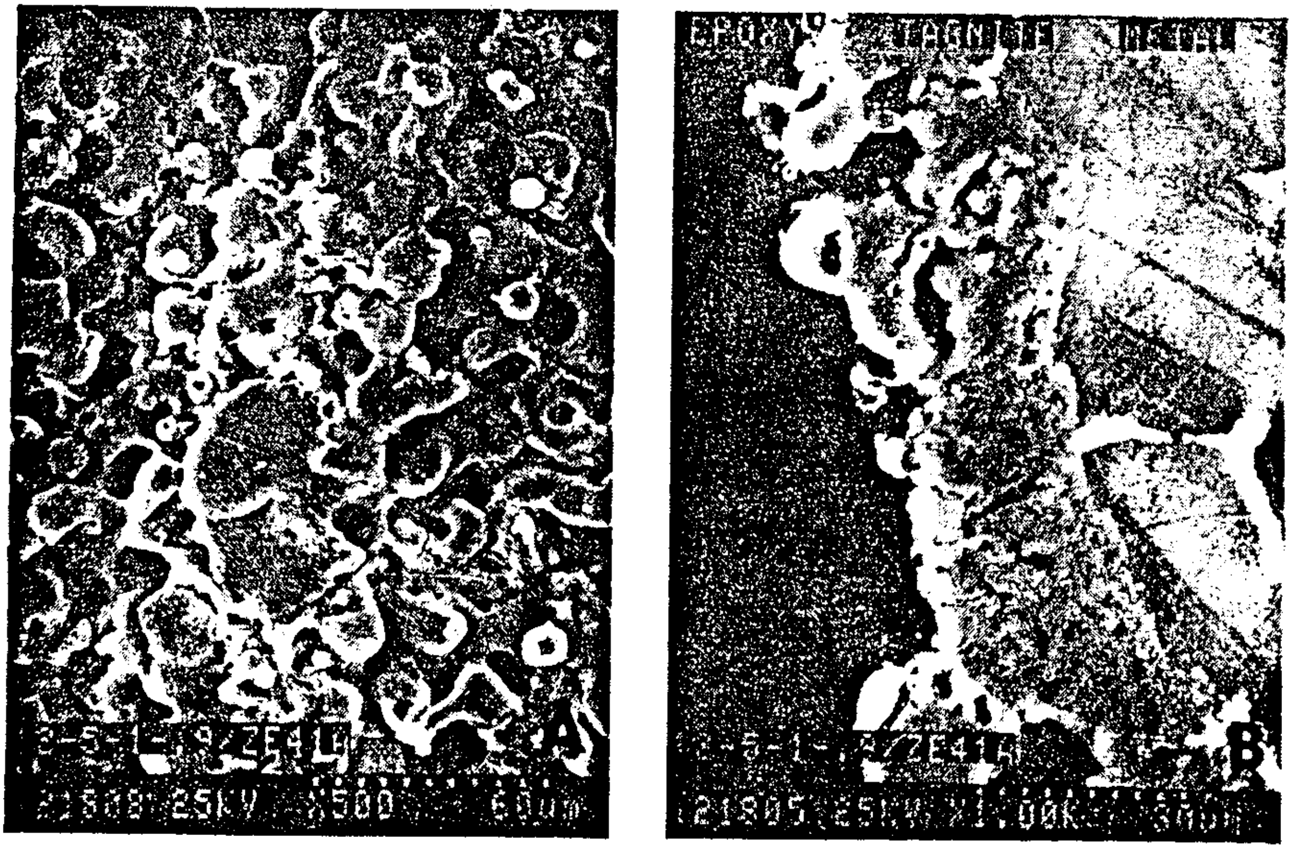

Figure 4. Scanning electron photomicrographs: A) top view of the Tagnite coating on ZE41A (500x), B) cross-section view of the Tagnite coating on ZE41A (1000x).

cross-sectional views of the coating indicate that the pores do not completely transverse the coating. Figure 3B and 4B are SEM photomicrographs of cross-sections of the TAGNITE coatings on the same alloys as shown in Figures 3A and 4A, respectively. As can be seen, the coating interface with the metal is quite good with no passageways occurring between the exterior and the base metal. Thus, the coating has the effect of preventing an aggressive environment from contacting the reactive metal substrate which would result in extensive corrosion.

CORROSION PROTECTION AND PAINT ADHESION

With the advent of high purity magnesium alloys, the corrosion rate for the base metal has been significantly reduced as compared to pure magnesium metal. In aggressive environments, however, additional corrosion protection is required and provided by the application of surface coatings. In addition, these coatings also serve as a base for painting. To test for corrosion resistance and paint adhesion, accelerated testing is performed using a salt spray chamber (ASTM B117). Table III illustrates some representative data for salt spray testing on the AZ91D and ZE41A alloys which have been treated with the Tagnite, HAE and chemical treatment 17 coatings. As can be seen, the Tagnite coating provides increased corrosion protection as compared to HAE and chemical treatment 17. For example, the Tagnite coating on AZ91D with a thickness of 5 to 10 micrometers (Type I) yields an ASTM D1654 (procedure B) rating of 8 after 28 days in salt spray while both HAE and treatment 17 are rated at 5 after just 14 days. It should be noted that the rating is based on the percentage of the total surface area that has failed due to corrosion pits, blisters or any other type of failure present. A rating of 8 represents a 2 to 3% failed area and a 5 denotes 11 to 20% of the area has failed. The best rating is a 10 which corresponds to no failures. The application of a thicker coating provides improved protection as indicated by a rating of 10 for a Type II Tagnite coating after 28 days in salt spray. The ZE41A alloy also benefits from a Tagnite coating and, as shown in table III, a type II coating typically gives a rating of 9 on panels exposed to salt spray for 14 days while treatment 17 affords only minor protection with over 75% of the area having failed (a rating of zero) after only 2 days. It should be noted that the duration of the corrosion test will be less for the ZE41A alloy than the AZ91D alloy due to the difference in corrosion rates for the base alloys.

Table III. ASTM D1654 Ratings on AZ91D Panels Subjected to Salt Spray.

Coating/Alloy	Thickness	Time	Unscribed Area (Procedure B)
Tagnite[1]/AZ91D	Type I	28 days	8
Tagnite[1]/AZ91D	Type II	28 days	10
Tagnite[1]/ZE41A	Type II	14 days	9
Dow 17/AZ91D	Type I	14 days	5
Dow 17/AZ91D	Type II	14 days	5
Dow 17/ZE41A	Type II	2 days	0
HAE[2]/AZ91D	Type I	14 days	5

[1] Post-treated using sodium dihydrogen phosphate

[2] Post-treated using sodium dichromate and ammonium bifluoride

A comparison of the coating morphologies offers a possible explanation for the greater effectiveness of the Tagnite coating over HAE and treatment 17 towards corrosion. Cross-sections and surface examination of the coatings by SEM indicate the pores in the Tagnite coating are smaller and more uniform in size and distribution as compared to the other two anodic processes. Further, the Tagnite coating shows considerably fewer interconnecting pores which completely transverse the coating to the base metal substrate. In contrast, the coating from treatment 17 typically produces the deepest pores with a high degree of interconnectivity. As a result, the Tagnite coating effectively isolates the magnesium metal substrate from the corrosive environment.

The corrosion resistance of the magnesium alloys may be further improved by sealing the coatings with paints. In this case, test panels of the AZ91D alloy which were coated with 10 to 25 micrometers of the Tagnite coating were primed with a melamine polyester primer and then painted with a thermosetting acrylic enamel top coat. The panels after being scribed were placed into salt spray for 28 days, with an evaluation of each leg of the scribe being performed every seven days. The data, shown in Table IV, indicate consistently high ratings with no corrosion migration under the scribe or corrosion in the unscribed areas. The lack of corrosion creepage from scribe is indicative of the good paint adhesion characteristics of the coating and may be attributed to its surface morphology.

Table IV. ASTM D1654 Ratings on AZ91D Panels with Tagnite, Painted and Scribed.[1]

Sample No.	Scribed Area (Procedure A) 7 day	 14 day	 21 day	 28 day	Unscribed Area (Procedure B) 28 day
10-22-3	10	10	10	10	10
10-23-3	10	10	10	10	10
10-24-1	9	10	10	10	10
10-25-2	9	10	10	10	10
10-29-6	10	10	10	10	9

[1] Testing (ASTM) and evaluation (ASTM D1654) was carried out by R.W. Murray, The Dow Chemical Company, Technical Service and Development, Lake Jackson Center, Texas.

The effect of primer and top coat on the corrosion resistance and paint adhesion was also examined on the ZE41A alloy. When panels of this alloy, treated with the Tagnite and treatment 17 coatings, are painted with one coat of primer (MIL-M-23377E) and subjected to salt spray for 28 days, extensive corrosion occurs for the treatment 17 coated panels with typical ratings of 3 (procedure B). In contrast, the Tagnite coated panels are rated as 10 (procedure B). Additionally, panels were also coated with the Tagnite and treatment 17 coatings, painted with one coat of primer (MIL-M-23377E) and a top coat (MIL-C-46168D). In this case, the paint adhesion characteristics were tested by scribing the panels before placing them together in salt spray for 28 days. Due to the higher corrosion rate of this alloy, corrosion pits develop on the scribe for both coating systems; however, the extent of corrosion migration under the scribe or the degree of paint adhesion to the anodic coatings is considerably better with the Tagnite coating than with treatment 17. Ratings (procedure A) of 5A and 9A (with a single low value of 7A) are typically obtained for treatment 17 and Tagnite coatings, respectively.

ABRASION RESISTANCE

Abrasion resistance has been determined on Tagnite, treatment 17 and HAE coatings on AZ91D as well as the Tagnite coating on ZE41A. Table V illustrates representative data in the form of the number of cycles and a Taber Wear Index (TWI). As can been seen from the data, the Tagnite coating on both AZ91D and ZE41A is considerably more wear resistant than either HAE or treatment 17. Though the abrasion resistance will largely be dependent upon the chemical nature of the coating, the significant increase in resistance may be partially attributed to the coating process in which the localized high temperature, occurring during the spark deposition, fuses the silicate and oxide species onto the metal substrate surface.

Table V. Abrasion Test Results.

Sample	TWI[1]	Cycle	Comments
AZ91D, TAGNITE, 0.3 mil	9	5000	< 10% metal exposed
AZ91D, TAGNITE, 0.6 mil	8	7000	< 10% metal exposed
AZ91D, TAGNITE, 0.8 mil	7	5000	< 10% metal exposed
AZ91D, TAGNITE, 0.9 mil	6	6000	< 10% metal exposed
AZ91D, HAE, Type I (0.2 mil)	142	75	10% metal exposed, coating gone after 200 cycles
AZ91D, HAE, Type II (2.6 mil)	142	1800	10% metal exposed; coating gone after 3000 cycles
ZE41A, TAGNITE, 0.2 mil	6	1000	10% metal exposed
ZE41A, TAGNITE, 0.5 mil	7	5000	10% metal exposed
ZE41A, TAGNITE, 0.6 mil	14	5000	10% metal exposed
ZE41A, TAGNITE, 0.8 mil	12	7000	10% metal exposed
ZE41A, TAGNITE, 1.0 mil	14	9000	10% metal exposed
AZ91D, TAGNITE, 0.5 mil	14	3000	bare metal starting to show[2]
AZ91D, Treatment 17, 1.0 mil	37	1000	coating gone after 500 cycles[2]
AZ91D, HAE, 1.0 mil	104	1000	coating gone after 500 cycles[2]

[1] Taber Wear Index (TWI) defined as TWI=(A-B)x1000/C where A is the weight of the test specimen before abrasion in milligrams, B is the weight of the test specimen after abrasion in milligram and C is the number of cycles of abrasion recorded.

[2] Data provided by R.W. Murray, The Dow Chemical Company, Lake Jackson Research Center, Freeport, Texas.

ENVIRONMENT

Over the last several years, concern has been raised regarding the impact the metal finishing industry has on the environment. When one considers that the commonly used materials include chromium, cadmium, zinc, lead, copper, nickel, cyanides and VOCs, it is not surprising that the EPA has listed the metal finishing industry as a major contributor to environment pollution.[13] Due to the demanding environment in which their products function, the aerospace industry has become a major user of metal finishing systems, and have recently expressed concerns regarding VOC emissions, utilization of 1,1,1-trichloroethane, hexavalent chromium emissions, the land ban and hazardous waste disposal costs, OSHA compliance and source reduction and recycling. As a result of the increasing inevitable government regulation of hazardous wastes, the industry will be required to become more environmentally responsible through the implementation of waste minimization programs and/or the utilization of less hazardous materials.

Chromates are one of the principal chemicals used in metal finishing industry, particularly those dealing with magnesium based alloys. The chromate ion is an excellent corrosion inhibitor. It is used as a paint pigment, employed in chromate conversion coatings, as well as in anodizing baths for aluminum based and magnesium based alloys and as a post-treatment for sealing anodized surfaces. However, chromates are known to be highly toxic and carcinogenic.[16] The oral ingestion of 1-2 grams of chromic acid or 6-8 grams of potassium dichromate is reported to cause kidney failure, liver damage, blood disorders and even death.[17] In addition, exposure of chromates to the skin for prolong periods may cause rashes, blisters and ulcers while inhalation may cause lung cancer. Due to these health risks, OSHA limits insoluble chromates in the air space to 1mg/m^3 per 8 hour day per 40 hour week and has specified that chromate containing paints must be labelled with a lung cancer warning.[18]

There are several approaches to the chromium issue. One option is to improve the handling procedures in the work place so as to comply with the allowable chromate exposure limits. Since it is likely that the regulations will only become more restrictive, this alternative will serve only as a temporary basis. Another alternative is to reduce or eliminate chromate containing waste by the application of new technologies. For example, a study by VanCleave[19] has resulted in a significant chromium reduction in which chemical treatment 21 was found to be a suitable replacement for treatment 1, both chromate containing solutions, thus permitting the elimination of a planned 7600 gallon treatment 1 tank in their new finishing facility.

Though the implementation of chromium reduction programs is clearly needed, the best alternative is the utilization of chromium free materials. Recently, Hinton[20,21] has presented several alternatives to chromate conversion coatings and paint pigments for aluminum based alloys. For magnesium alloy users the elimination of chromate may be more difficult, partly due to the greater chemical reactivity of magnesium. Many of the commonly employed conversion coatings are chromate based (see Table I) while the common cleaning solution for removing corrosion products and old finishes is chromic acid. Further, current specifications such as MIL-M-3171 require the application of chemical treatment 1 to sand cast magnesium alloys for corrosion protection during shipment and storage.

As discussed earlier chemical treatment 17 and HAE are routinely applied to magnesium alloys when increased corrosion protection is required. Treatment 17 contains approximately 8% by weight sodium dichromate and, although it is reported that the solution is only infrequently disposed, thus generating only small volumes of chromium containing waste water through dragout, the presence of large processing tanks still results in employee exposure and the potential for environmental damage should a spill occur. In addition, even though disposal is infrequent, chromium is introduced directly into the environment from the coating itself. Based on the operational parameters for treatment 17 approximately 0.1 to 0.2

oz of chromium would be introduced into the environment per square foot of metal coated.[22] Although HAE is not a chromate containing solution, the coating requires a post-treatment in ammonium bifluoride and sodium dichromate for all grades except grade 1[15] and thus utilizes chromium compounds in the overall process.

A significant chromate reduction may be made by first replacing chromate conversion coatings which are used for temporary protection with oil. It has been reported that magnesium components may be stored from 1 to 5 years if the alloy is oiled and sealed in a polythene bag containing a desiccant.[23] Furthermore, the use of oil instead of the conversion coatings will allow the metal surface to be cleaned using alkaline cleaners without relying on chromic acid. Finally, the application of a chromium free coating system such as the Tagnite coating will eliminate chromates in the anodizing and/or post-treatment baths.

CONCLUSIONS

Reduction and elimination of chromium based systems will be a major endeavor in the metal finishing industry as the governmental regulation of chromium becomes more and more restrictive. For magnesium based alloys chromium reduction may be achieved by replacing the conversion coating used for temporary storage with oil and by the application of chromium free coating systems such as Tagnite. The Tagnite system provides greater corrosion protection, enhanced paint adhesion and better abrasion resistance than either chemical treatment 17 or HAE.

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REFERENCES

1. Davis, J. The Potential for Vehicle Weight Reduction Using Magnesium, Society of Automatic Engineers, Paper 910551, 11991. pp. 71-85.

2. Mezoff, J. G. Magnesium in Automobiles, in Perspective, Society of Automotive Engineers, Paper 800417, 1980. pp. 1-14.

3. Murray, R. W., and J. E. Hillis. Magnesium Finishing: Chemical Treatment and Coating Practices, SAE, Paper 900791, 1990. pp. 1-10.

4. Aume, T.K. Minimizing Base Metal Corrosion on Magnesium Products. The Effect of Element Distribution (Structures) on Corrosion Behavior, Proceedings of the 40th World Magnesium Conference, Toronto, 1983.

5. Hillis, J.E. The Effects of Heavy Metal Contamination on Magnesium Corrosion

Performance, SAE, Paper 830523, 1983. pp. 1-7.

6. Reichek, K.N., K.J. Clark, and J.E. Hillis. Controlling the Salt Water Corrosion Performance of Magnesium AZ91 Alloy, SAE, Paper 850417, 1985.

7. Hillis, J.E. and Reichek, K.N. High Purity Magnesium AM60 Alloy: The Critical Containment Limits and the Salt Water Corrosion Performance, SAE, Paper 860288, 1986, pp. 1-8.

8. The Dow Chemical Company. Heat Treating Sand and Permanent Mold Magnesium Castings. No. 141-552-87. Midland, Michigan, 1987. 10 pp.

9. Magnesium Elektron, Inc. WE43 A Corrosion Resistant Magnesium Casting Alloy for Use up to 570°F. No. 467A. Lakehurst, New Jersey, 1991. 4 pp.

10. Stevenson, A. Metals J., 39 (5): 16-19, 1987.

11. Hawke, D.L., J.E. Hillis, and W. Unsworth. Preventive Practices for Controlling the Galvanic Corrosion of Magnesium Alloys, IMA Technical Committee Report, 1988.

12. The Dow Chemical Company. Magnesium : Operations in Magnesium Finishing. No. 141-479-86R. Midland, Michigan, 1990. 56 pp.

13. Holmes, J. Metal Finishing, 87 (11): 65, 1989.

14. Military Specification. MIL-M-3171C. Magnesium Alloy, Processes for Pretreatment and Prevention of Corrosion on, U.S. Government Printing Office, No. 713-153/4659, March 1974. 44 pp.

15. Military Specification. MIL-M-45202C. Magnesium Alloys, Anodic Treatment of, U.S. Government Printing Office, No. 703-023/2048, April 1981. 31 pp.

16. McCoy, D.J. Proc. Second AESF/EPA Chromium Colloquium. Miami, Florida, 1990.

17. Toxicological Profile for Chromium, Agency for Toxic Substances. U.S. Public Health Services. Report No. ATSDR/TP-88/10, July, 1989.

18. Bittner, A. Surface Coatings Australia, 27 (5): 6, 1990.

19. VanCleave, T.E. Evaluation of Dow 21 to Replace Dow 1: Chromium Reduction Using Process Consolidation. 7th Annual Aerospace Hazardous Waste Minimization Conference, St. Louis, Missouri, 1992.

20. Hinton, B.R.W. Metal Finishing, 89 (9): 55, 1991.

21. Hinton, B.R.W. Metal Finishing, 89 (10): 15, 1991.

22. Treatment 17 typically requires revivification after 20 ft^2/gal have been treated with the recommended concentration of 6.7 to 16 oz/gal of sodium dichromate (the preferred concentration being 13.3 oz/gal). If one assumes the bath contains 6.7 oz/gal of sodium dichromate after 20 ft^2/gal have been processed and that all the loss chromate occurs in the coating, then 6.6 oz/gal of sodium dichromate will be needed to return the solution to the preferred concentration or 0.1 oz of chromium per square foot of metal treated would be loss to the coating.

23. Magnesium Elektron Ltd. Surface Treatments for Magnesium Alloys in Aerospace and Defence. Twickenham, England. 14pp.