

NOTICE: When government or other drawings, specifications or other data are used for any purpose other than in connection with a definitely related government procurement operation, the U.S. Government thereby incurs no responsibility, nor any obligation thatsoever; and the fact that the Government may have formulated, furnished, or in any way supplied the said drawingt, specifications, or other data is not to be regarded by implication or otherwise as in any manner licensing the holder or any other person or corporation, or conveying any rights or permission to manufacture, use or sell any putented invention that may in any way be related thereto.

63-2-3

COATING and CHEMICAL



CCL REPORT NO. 136

EXPLORATION OF NEW METHODS FOR PREVENTING GALVANIC

CORROSION BETWEEN MAGNESIUM AND STEEL

BY

LT. DONALD K. STELLING

AMCMS CODE NO. 5026.11.84205 DA PROJECT 593-32-007

8 JANUARY 1963



ABERDEEN PROVING GROUND MARYLAND

DESTROY; DO NOT RETURN

2

CATALOGED BY ASTIA AS AD No.

ASTIA AVAILABILITY NOTICE

-

1

Qualified requesters may obtain copies of this report from the Armed Services Technical information Agency, Arlington Hall Station, Arlington 12, Virginia.

Copies available at Office of Technical Services, \$ 0.50

Contraction of the

Standin St

THE FINDINGS IN THIS REPORT ARE NOT TO BE CONSTRUED AS AN OFFICIAL DEPARTMENT OF THE ARMY POSITION.

TABLE OF CONTENTS

	Paga No.
TITLE PAGE	11
ABSTRACT	611
INTRODUCTION	1 - 2
DETAILS OF TEST	2 - 3
DISCUSSION	3
SUMMARY	3 - 4
REFERENCES	4
APPEND IX	5
Tables - V	6 - 8
DISTRIBUTION LIST	9 - 10

i

UNCLASSIFIED

Report No. CCL # 136

Copy Number_

EXPLORATION OF NEW METHODS FOR PREVENTING GALVANIC

CORROSION BETWEEN MAGNESIUM AND STEEL

By

Lt. Donald K. Stelling

8 January 1963

AMCMS Cude No. 5026.11.84205

Dept of the Army Project No. 593-32-007

Coating and Chemical Laboratory Aberdeen Proving Ground Maryland

UNCLASSIFIED

AUTHOR:

or the second second

CONALD K. STELLING, Chenist 2nd Lt. Ord. Corps Paint, Varnish & Lacquer Branch

REVIEWED BY: Meln

Ilu

MELVIN H. SANDLER Chief, Paint, Varnish & Lacquer Branch

APPROVED BY:

/17

C. F. PICKETT, Technical Director Coating and Chemical Laboratory

المراجع والمتعار ويعجون العام والعام والمراجع والمراجع

ASTRACT

An investigation was conducted to explore new methods of treating magnesium-steel couples after the two metals had been assembled and placed in electrical contact 'th each other. A phosphate anodizing treatment, prepared with this objective in mind, proved to be ineffective when applied to such couples. The treatment swemed to offer considerable corrosion resistance to magnesium alone when the operating conditions of the treatment were controlled within close limits.

A

I. INTRODUCT:UN

The accelerated corrosion rate observed with magnesium when coupled to a dissimilar metal is a problem of great concern to the defense industry. With missile systems and lightweight airborne equipment becoming increasingly more complex, design requirements oftentimes call for an assembly of dissimilar metals, such as magnesium and steel. Electrical contact between the two metals is oftentimes established and because of the difference in the relative positions of the two metals in the EMF series, a gaivanic cell is created. When the assembly is exposed to moisture and electrolyte, as in a saline atmosphere, galvanic corrosion results. The most effective method of preventing galvanic corrosion is to insulate the faying surfaces of the two metals to prevent the formation of the galvanic cell. However, when press fits between dissimilar metals are required, this is not possible. There is a need for an effective treatment that can be applied to dissimilar metal couples (particularly magnesium and steel) after assembly that will prevent or appreciably retard the affects of galvanic corrosion. A recently duveloped stannate treatment offers a step in this direction. The treatment involves immersing a magnesium-steel assembly for a minimum of twenty minutes in a bath containing potassium stannate (K_2SnO_3), sodium hydroride (NaOH), sodium acetate (NaC₂H₃O₂), and tetrasodium pyrophosphate (Na4P207) maintained between 180°F and 212°F. Although the treatment affords some protection against galvanic corrosion, it has not provided the desired degree of protection.

A hypothesis exists stating the rate of corrosion of a metal depends, in most cases, on the permeability of the surface film to the reactants. The porosity of the film appears to depend on the relative volume of the film compared to the volume of the metal from which it is formed, i.e., Wd/awD where:

- W = molecular weight of the metallic compound forming the film (of formula MaXb)
- D = density of the compound forming the film
- W = atomic weight of metal
- d = density of the metal
- M = metal anion of the compound forming the film
- X = cation of the compound forming the film
- a = number of anions per molecule of film compound
- b = number of cations per molecule of film compound

If this ratio is greater than one, the film tends to be protective; if the ratio is less than one, the film is porous and non-protective. The ratio for magnesium oxide (MgO), formed on a magnesium surface when exposed to molsture, is 0.64 and thereby accounts for the non-protective character of the film formed by corrosion product. On the other hand, magnesium treated with chromic acid forms a corrosion resistant film composed of magnesium chromate (MgCrO₄, $7H_2O$) for which the ratio is 11.3. Similarly, the film of magnesium fluoride (MgF₂) formed when magnesium is treated by hydrofluoric acid produces a ratio of 1.49 indicating the film to be protective, which indeed it is.

If this hypothesis is valid for all films, then a magnesium surface film of magnesium phosphate $(Mg_3(PO_4)_2)$, resulting from treatment with a $PO_4 \equiv$ solution, or a magnesium surface film of magnesium pyrophesphate $(Mg_2P_2O_7)$, resulting from treatment with $P_2O_7^{m}$ solution, should be protective since their ratios are 4.0 and 3.9 respectively. Therefore, it was decided to conduct a number of laboratory tests whereby magnesium panels would be treated by phosphate and pyrophosphate solutions under various operating conditions including the application of an external EMF. If, a treatment could be developed that would successfully protect magnesium alone, it would then be tested on magnesium-steel couples since the phosphate and pyrophosphate treatments should also produce protective films on steel because the ratios for ferrous phosphate (Fe₃(PO₄)₂) and (Fe₄(P₂O₇)₃) are 8.9 and 12.0 respectively.

11. DETAILS OF TEST

These studies were conducted testing the applicability of various phosphating procedures on magnesium. After treatment, the panels were coated with 0.001 inch dry film of Hilitary Specification MiL-P-15930 (Primer, Vinyl Zinc Chromete Type, Formula No. 120) air dried 72 hours, scored, and then exposed to 20% sait spray (operated according to Federal Test Method Standard No. 141, method 6061). The test panels were examined every 24 hours and evaluated for corrosion resistance.

Initially, three series of AZ31B magnesium alloy panels were given a light zinc phosphating treatment according to Military Specification TT-C-490, type 1. For each series of panels, the application procedure was varied slightly (see Table 1).

Another test (Table II) was conducted whereby two series of AZ31B alloy panels were spray treated by phosphating solutions conforming to Military Specification TT-C-490, type II.

A number of cursory laboratory tests were also performed whereby magnesium panels were treated by solutions of NaH₂PO₄ under various operating conditions including the application of an external EMF. Tests involving baths containing Na₂P₂O₇ and mixtures of Na₂P₂O₇ with NaH₂PO₄ were also conducted. The results of this effort showed that an anodizing bath containing NaH₂PO₄ H₂O at a concentration of 13.7 gms/liter offered the most promising results. The phosphite anodizing process consisted of connecting the magnesium component to the anode of a D. C. source and using one or two steel plates immersed in the bath as the cathode. A current density of 16 amps/sq.ft. was applied for a period of ten minutes during which time the potential remained rather steedy around 20 volts, dropping possibly a maximum of two volts. The bath was maintained at room temperature and the pH rose during the operation from about 5.0 to 5.5 where it reached a plateau. Studies were made to determine the operating limits by varying the bath concentration between 0.5 to 1.0 moles NaH₂PO₄/liter cf water, the pH from 4.3 to 6.9, the current desnity from 8 amps/sq.ft. to 60 amps/sq.ft. and operating times from 8 to 25 minutes (see Table 111).

This phosphate anodizing treatment was compared with three other proprietary magnesium treatments used quite extensively in industry, namely a chemical pretreatment conforming to Specification MIL-M-3171, Type III; an anodic pretreatment conforming to Specification MIL-M-45202 (Ord), type I, clars C; and a chemical treatment consisting of a five minute immersion at room temperature in a bath containing chromic acid (CrO_3) and calcium sulfate ($CaSO_4$) (see Table IV). The phosphate anonizing treatment was also evaluated on magnesium-stee: couples. Test specimens were prepared by placing a steel bolt through a magnesium panel and creating the specimen after assembly (see Table V).

III. DISCUSSION

The TT-C-490, type I zinc phosphate immersion produced a loose, powdery coating bluish-gray in appearance. Upon removal of the powder, a dark, adherent coating was noticed on the immediate surface. The spray zinc phosphate freatment produced a coating that was free from the powdery deposit and similar in appearance to the dark undercoating of the immersion treated panels. The salt spray results shown in Table I indicate that the immersion treatment offers only slight corrosion resistance whereas the spray method offers none.

The TT-C-490, type ii treatment produced only slight discoloration on the panel surfaces. The results in Table II show that the four minute spray method afforded considerably more protection than the two minute spray.

The phosphate anodizing treatment produces a surface film which is dark a grainy in appearance. Unfortunately, the bath becomes readily depleted and in doing so, a white, powdery precipitate forms on the edges of the test panels giving the appearance of corrosion product. This precipitate is easily washed off upon subsequent rinsing and seems to have no detrimental effects upon the performance of the coating, nevertheless, it produces a rough, uneven surface. This same observation was made when the bath was operated at a high pH around 6.8, even though exc. lient corrosion resistance was noted (see Table 111). This effect became worse upon subsequent treatments in the same bath. In fact, it was found that operating conditions varying slightly from a pH of 4.3 to 5.5, a current density of 16 amps/sq.ft., and an operating time of 10 to 15 minutes made the treatment considerably less effective.

When strict control over the operating variables is exercised, however, this phosphate anodizing treatment seems to offer considerable protection to magnesium alone. As can be seen in Table IV, when compared with three proprietary treatments, it offered the best corrosion resistance, being somewhat better than MIL-M-45202 and considerably better than MIL-M-3171 and the chromic acid/calcium sulfate immersion treatment.

Unfortunately, the phosphate enodizing treatment is not applicable to magnesium-steel couples. The results in Table V demonstrate the ineffectiveness of the treatment for such applications.

IV- SUMMARY

Although the phosphate anodizing treatment has been demonstrated to be nonapplicable to magnesium-steel couples, further testing and development should be conducted before it can be accepted as an effective procedure for magnesium alone. Such efforts should be concentrated in(a) determining more closely the operating limits of the bath, (b) evaluating more extensively the effectiveness of the treatment by comparing it with many proprietary treatments, (c) aliminating the deposit of white precipitate on the edges of the test panels and increasing the life of the phosphate bath. Of course the greatest efforts in future studies should be directed to develop a method of preventing galvanic corrosion. The ideal treatment would be one that contains a self-healing ingredient which, when the film is scored, would leach out of the coating and treat the newly exposed metal. Without this particular feature, it would be thermodynamically impossible for a scored bimetallic assembly to resist corrosion.

Because of the difficulty encountered in attempting to develop an aqueous treatment for magnesium-steel couples, a study should be initiated into the use of organic media for treating bimetallic assemblies. Such a study would involve much basic research since limited information can be found in this field.

V. REFERENCES

- Military Specification MIL-P-15930 Primer, Vinyl-Zinc Chromate Type (Formula 120).
- 2. Federal Test Method Standard No. 141 Paint, Varnish, Lacquer and Related Materials, Methods of Inspection, Sampling and Testing.
- 3. Hilitary Specification TT-C-490 Cleaning Methods and Pretreatment of Ferrous Surfaces for Organic Coatings.
- 4. MIL-M-3171 Magnesium Alloy, Processes for Corrosion Protection of.
- 5. MIL-M-45202 (Ord) Magnesium Alloys, Anodic Treatment of.

「あるのない」を見ているとなっている。

ŝ

.

. .

APPENDIX

5

TABLE I

PHOSPHATE PRETREATMENT TT-C-490, TYPE I ON MAGNESIUM			
<u>No Pretreatment</u>	Onc minute @ 180°F Immersion process	Five minutes @ 180°F Immersion process	One minute (# 150*F Spray process
24 24	72 ² 722 962 722 24	96 ² 722 722 722 722 24	24 24

SALT SPRAY RESULTS (HOURS TO FAILURE)

After pretreatment test panels were coated with the mil dry film of primer conforming to Specification MIL-P-15930, Primer, Vinyl Zinc Chromate Type, Formula No. 120.

²The loose powdery crystals formed on the surface by the immersion process were removed prior to application of primer.

TABLE II

SALT SPRAY RESULTS (HOURS TO FAILURE)

Pretreatment	Two minutes @ 150°F Spray process	Four minutes @ 150°F Spray process
24	96	120
24	72	144
	96	216
	96	216
		144

PHOSPHATE PRETREATHENT TT-C-490, TYPE II ON MAGNESIUN

¹After pretreatment test panels were coated with one mil dry film of primer conforming to Specification MIL-P-15930 Primer, Vinyl Zinc Chromate Type, Formula No. 120.

TABLE III

SALT SPRAY RESULTS

NaH2PO4 Concentration (moles/liter)	pH	Current density (amps/sq.ft.)	Operating time (minutes)	Tomperature °F	Hours Exposure Before Fallure
0.1	5.0	8.0	15	74	600
0.1	4.3	16.0	10	73	912
0.1	6.6	16.0	15	72	8001
0.1	6.9	24.0	10	74	912
0.5	4.0	16.0	15	73	792
0.5	4.4	60.0	8	75	600
0.1	4.3	16.0	10	75	792
0.1	5.0	12.0	25	77	600
0.1	5.0	12.0	2 0	78	600
0.1	5.4	12.0	20	80	552
0.1	5.5	16.0	10	82	912
0.1	5.5	16.0	10	82	792

PHOSPHATE ANODIZING ON MAGNESIUM

¹After pretreatment test panels were coated with one mil dry film of primer conforming to Specification MIL-P-15930 Primer, Vinyl Zinc Chromate Type, Formula No. 120.

TABLE IV

PHOSPH	PHOSPHATE ANODIZE VS PROPRIETARY PRETREATMENTS ON MAGNESIUM			
No Pretreatment	Phosphate anodize ²	MIL-M-3171 Type 111	MIL-M-45202(Ord) Type I, Class C	Cr03+CaSU4
72	648	168	360	168
72	744	216	672	216
72	720	168	672	168
72	648	240	408	240
72	648	240	408	240
72	648	216	672	216

SALT SPRAY RESULTS (HOURS TO FAILURE)

After pretreatment test panels were coated with one mil dry film of primer conforming to Specification MIL-P-15930 Primer, Vinyl Zinc Chromate Type, Formula No. 120.

²Operating conditions: 0.1 mole/liter; pH = 5.0 to 5.5; current density 16 amps/sq/ft/; operating time 10 min. at room temperature.

³Five minute immersion in the bath at room temperature.

7

TABLE V

SALT SPRAY RESULTS (HOURS TO FAILURE)

PHOSPHATE ANODIZE ON MAGNESIUN-STEEL COUPLE

No Pretreatment	Phosphate Anodiza ²
24	24
24	24
* 24	24
2/+	24
24	24
24	24

Specimens were assembled prior to treating. After pretreatment they were coated with one mill dry film of primer conforming to Specification NIL-P-15930 Primer, Vinyl Zinc Chromate Type, Formula 120.

²Operating conditions: 0.1 mole/liter; pN 5.0 to 5.5, current density 16 amps/sq.ft. Operating time ~ 10 minutes at room temperature.

DISTRIBUTION LIST FOR AMENS CODE 5026-11.842

Department of Defense	No. of Course
Arme Services Technical Information Agency Arlington Hall Station Arlington 12, Virginia	10
Department of the Army - Technical Service	
Commanding General	
U.S. Army Materiel Command	
ATTN: AMCORTB	1
Washington 25. D. C.	
Continental Army Command	
Department of the Army	3
Fort Monroe, Virginia	
Commanding General	
U.S. Army Mobility Command	
U.S. Army Tank-Automotive Center	
ATTN: Mr. J. P. Jones	1
Mr. V. Pogano	1
Center Line, Michigan	
Commanding Officer	
J.S. Army Munitions Command	
ATTN: SMUFA 1320	1
Library)
Philadelphia 37, Pa.	
Commanding Officer	
J.S. Army Materials Research Agency	
Watertown Arsenal	
ATTN: Technical Information Center	2
datertown 72, Mass.	
Commanding Officer	
larry Diamond Laboratory	
ATTN: Library	1
Vashington 25, D. C.	
Commanding Officer	
J.S. Army Test Activity	
luma Test Activity	1
fuma, Arlzona	
Commanding Officer	
J.S. Army Munitions Command	
Picatinny Arsenal	
ATTN: Mr. J. J. Begley	1
)over, New Jersey	

DISTRIBUTION LIST CONTINUED

	No. of Capies
Commandin_ `fficer	
U.S. Army Ballistic Research Laboratories	
ATTN: Mr. W. C. Pless	8
Mr. R. Elchelberger	1
Mr. J. Sporrazza	1
Aberdeen Proving Ground, Maryland	
Technical Library	
Aberdeen Proving Ground, Maryland	2
Department of the Navy	
Department of the Navy	
c/o Navy Liaison	1
Aberdeen Proving Ground, Maryland	
Commander	
U.S. Naval Weapons Laboratory	1
Dahlgren, Virginiø	
Department of the Navy	
Chief, Burcau of Naval Weapons	1
Washington 25, D. C.	
Other Government Agencies	
Scientific and Technical Information Facility	
ATTN: NASA Representative (S-AK/DL)	
P. 0. Box 5700	3
Bethesda, Maryland	-
Office of Technical Services	
Acquisitions Section	100
Department of Commurce	
Washington 25, D. (
Foreign Address	
Ministry of Supply Staff	
British Joint Services Mission	
1800 K Street, N. W.	2
Washington 6, D. C.	
Canadian Army Staff	
ATTN: GSO-1 ASR Section	
2450 Massachusetts Avenue, N. W.	2
Washington 8, D. C.	

AD NO Comparing & Chemical Laborator, Aberdeen Proving Ground, Md., CCL # 135 - EXPLOR- ATION OF NEW NETWEDN FOR PREVENTING GAL- VANIC CORROSION BETWEEN MAGNESIUM AND STEEL - Lt. Dunmaid K. Stelling, Rpt No. 136, 8 January 1963, 13 pgs, AMCMS Code 5026.11.84205, DA Proj No 593-32-007	An investigation was conducted to explore new methods of treating magnesium- steel couples after the two metals had been assembled and placed in electrical contact with each other. A phosphate anodizing treatment, prepared with this objective in mind, proved to be ineffec- tive when applied to such couples. The	AD No Accession No Coating & Chemical Laboratory, Aberdeen Proving Ground, Md., CCL # 136 - EXPLON- ATION OF NEW NETHODS FOR PREVENTING GAL- VANIC CORROSION BETWEEN AVGNESIUM AND STEEL - Lt. Donald K. Stelling, Ppt No. 136, 8 January 1963, 13 pgs, AMCNS Code 5026.11.84205, DA Proj No 593-32-007	An investigation was conducted to explore new methods of treating magnesium steel couples after the two metals had been assembled and placed in electrical contact with each other. A phosphate anodizing treatment, prepared with this objective in mind, proved to be ineffec- tive when applied to such couples. The
Unclassified		Unclass i fied	•
Un classifi ed		Unclass i fied	
AD NO AD NO Accession No Conting & Chemical Laboratory, Aberdeen Proving Ground, Md., CCL # 136 - EXPLOR-ATION OF NEW NETHODS FOR PREVENTING CAL-VANIC COMMONSION BETWEEN NAGHESIUM AND STEEL - Lt. Donald K. Stalling, Rpt No. 136, 8 January 1963, 13 pgs, AMCMS Code 5526.11.84205, DA Proj No 593-32-007	An investigation was conducted to explore now methods of treating magnesium- steel couples after the two metals had been assembled and placed in electrical contact with each other. A phosphate anodizing treatment, prepared with this objective in mind, proved to be ineffec- tive when applied to such couples. The	AD NO ACCESSION NO Conting & Chemical Laboratory, Aberdeen Proving Ground, Md., CCL # 136 - EXPLON- ATION OF NEW METHOOS FOR PREVENTING GAL- VANIC CORNOSION BETWEEN MAGKESIUM AND TFEL - Lt. Donald K. Stelling, Rpt No. 156, 8 January 1963, 13 pgs, ANCHS Code 5026-11.84205, DA Proj No 593-32-007	An investigntion was conducted to explore new methods of treating magnesium steel couples after the two metals had been assembled and placed in electrical contact with each other. A phosphate anodizing treatment, prepared with this objective in mind, proved to be ineffec- tive when applied to such couples. The

1

.

.

•

н Е – •

-

ACCR.

1		
•	Unclassified treatment seemed to offer considerable corrosion resistance to magnesium alone when the operat g conditions of the treatment were controlled within close limits.	Unclassified treatment seemed to offer considerable corrosion resistance to magnesium alone when the operating conditions of the treatment were controlled within close limits.
	Unclassified treatment seemed to offer considerable corrosion resistance to magnesium alone when the operating conditions of the treatment were controlled within close limits.	Unclassified treatment seemed to offer considerable corrosion resistance to magnesium alone when the operating conditions of the treatment were controlled within close limits.