ENCLOSURE (B) 15

STUDIES ON THE PREVENTION OF CORROSION OF METALLIC MAGNESIUM AND MAGNESIUM ALLOY BY METHANOL

by

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LIST OF TABLES AND ILLUSTRATIONS

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SUMMARY

Studying the action of pure methanol on metallic magnesium ribbon from Kahlbaum, the following conclusions were reached:

1. The corrosive action of pure methanol is prevented by addition of water, especially when potassium chromate is added.

2. A precipitate is formed by the reaction of potassium chromate and methanol which can be removed by addition of very small quantity of alkali.

3. Methanol of 99.0% purity and of sp.gr.0.769-0.799, when 5% of 0.1% potassium chromate solution and 5% of 0.1% caustic potash solution are added may be kept for 50 days in a magnesium vessel without any precipitation or corrosive action.

4. The anti-corrosive action of an alkaline solution of potassium chromate is also effective for 40% methanol solutions.

I. INTRODUCTION

A. History of Project

The purpose for which this research was made was to examine a method of preventing the corrosion of magnesium by methanol and to find whether or not methanol could be used for aviation fuel. There are several methods for rendering magnesium alloys anti-corrosive, such as the fluoridation method, Sutton method, and Bengaugh method. These methods are effective against air and sea water, but are not effective in the presence of methanol. Therefore, the present experiment was undertaken with metallic magnesium ribbon and a magnesium alloy.

B. Key Research Personnel

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II. DETAILED DESCRIPTION

A. Materials

Materials which were used in this experiment are:

Mg - metallic ribbon from Kahlbaum.
Mg-alloy - contains Mn 0.1 - 0.5%, Al 5 - 7%, Zn 1.5%
CH_3OH - CH_3OH from market, d. 0.796, purity 99.0% by wt.

Methanol was purified by removing acetone by Bate's* method, aldehyde by Dumlop** & Lenz's*** method, and acids and esters by distillation with

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*Bates, J. Chem. Soc. 123, 401 (1933)
**Dunlop, J. Am. Chem. Soc., 28, 395 (1906)
***Lenz, A. Anlyt. Chem., 52, 96 (1933)

caustic potash, dehydrating with magnesium according to Bjerrum's method and finally rectifying with a rectifier of 100cm length and 6mm diameter. At 64.5°C., 99.5% was distilled. From the density of 0.7865, the purity was estimated to be 99.99% by the method of Bjerrum.

B. Method of Experiment

In this experiment, the metal was dipped into the liquid to be examined and kept at room temperature for a definite time. Observations were made and recorded.

III. EXPERIMENTAL RESULTS

A. Experiments with Mg-ribbon

Pure methanol reacts violently on Mg-ribbon with the evolution of hydrogen. The corrosive action of commercial methanol on magnesium and its alloys was therefore attributed to the chemical property of the methanol and not to impurities. Influences of water and other substances on the corrosive action of methanol were studied.

1. Influence of water. The results of the experiment are shown in Table I(B)15. The corrosive action of CH_3OH on Mg-ribbon decreases as the water concentration is increased. With less than 2% water present, this corrosive action is excessive.

2. Influences of Inorganic Substances. When 2% of 0.1 molar aqueous solutions of various inorganic compounds were added, some comparatively effective inhibitors were found, and the results are recorded in Table II(B)15.

3. Influences of Organic Substances. Aniline, pyridine, quinoline, hydroxylamine, ether, acetone, acetaldehyde, ethyl, propyl and butyl alcohols, lecitine, and soap were tried as inhibitors. The corrosive action of methanol on metallic magnesium was prevented by the presence of soap.

B. Experiments with magnesium alloy

The alloy was polished with emery-paper, washed with petroleum ether, and then immersed in methanol.

1. Pure methanol acts on the alloy and the original shape of the alloy is lost after 5-6 hrs.

2. The corrosive action of the methanol is diminished by the addition of water. With methanol containing 4% water, apparent corrosion does not take place for 2-3 days.

3. Potassium Bichromate. The anti-corrosive action of the addition of potassium bichromate solution to methanol is stronger than that of water. The results of experiments using potassium bichromate solution are shown in Table III(B)15.

4. Potassium Chromate. The results using potassium chromate as an inhibitor are shown in Tables IV & V(B)15. It was found that a precipitate appeared when K_2CrO_4 was used as an inhibitor. The formation of this precipitate could be delayed by adding a small concentration of alkali as shown in Table VI(B)15.

IV. CONCLUSIONS

When Mg-ribbon is immersed at room temperature in pure methanol, hydrogen and magnesium methylate are formed. The latter is soluble in methanol, and thus the corrosive action of methanol on the metal and alloy will proceed. However the corrosive action is prevented by the addition of water, since the methylate is decomposed by the action of water and is converted to magnesium hydroxide, which is deposited on the metallic surface. Thus, the water serves to inhibit the corrosive action of the methanol. Potassium chromate was also found to be a useful corrosion inhibitor.

Table I(B)15
INFLUENCE OF WATER UPON THE CORROSION OF Mg BY CH_3OH

Time (hr)	Amount of H_2O (%)						
	0.1	0.5	1.0	2.0	5.0	10.0	30.0
1	1 b	1 b	2 c	3 c	4 f	5 f	5 f
2	a	b	2 b	3 b	4 f	4 f	5 f
4			b	3 b	cf	df	df
24					cf	cf	df
120					ce	cf	cf
240					b	be	cf
1200					b	b	ce

Key to the Meaning of Symbols

1. Violent evolution of H_2
2. Rapid evolution of H_2
3. Moderate evolution of H_2
4. Slow evolution of H_2
5. Very slow evolution of H_2

a. Original form destroyed.
b. Entire surface corroded.
c. Some surface corrosion.
d. Little surface corrosion.
e. Original gloss destroyed.
f. Original gloss maintained.

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Table II(B)15
INFLUENCES OF INORGANIC SUBSTANCES UPON THE CORROSION OF MG BY CH_3OH

Inorganic Substances	Appearance of Mg & CH_3OH	Degree of Corrosion
Potassium ferrocyanate	The surface of Mg loses its gloss	slight
$K_2Cr_2O_7$	Brownish precipitate formed	very slight
Borax	The surface of Mg blackened	slight
NH_3	The gloss is lost	slight
$(NH_4)_2CO_3$	The surface of Mg blackened	slight
Sodium acid phosphate	The gloss is maintained	slight
$NaHCO_3$	The gloss is maintained	slight
$KClO_3$	The gloss is maintained	slight
$NH_4\ CH_3COO$	The precipitate is formed	slight

Table III(B)15
INFLUENCE OF $K_2Cr_2O_7$ UPON THE CORROSION OF Mg BY CH_3OH

Exp. No.	$K_2Cr_2O_7$ Amount of Aqueous Solution Used	$K_2Cr_2O_7$ Concentration of Aqueous Solution Used	Time of Exposure (days) 1	3	5	10	20	30	50	70	Precipitant Remarks
K_1	(Vol % of CH_2OH) 1	(%) 0.1	-	-	-	-	-	#	###	###	slight
K_2	5	0.1	-	-	-	-	-	-	#	##	slight
K_3	1	1.0	-	-	-	-	-	-	--	#	slight
K_4	1	2.5	-	-	-	-	-	-	--	#	slight
K_5	5	1.0	-	-	-	-	-	-	-	-	Excessive
K_6	5	2.5	-	-	-	-	-	-	-	-	Excessive

Key

The degree of corrosion is shown as follows:

(-) no corrosion of Mg.
(#) less than 3 corroded spots.
(##) Mg slightly corroded.
(###) Mg excessively corroded.

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Table IV(B)15

INFLUENCE OF K_2CrO_4 UPON THE CORROSION OF Mg ALLOY BY CH_3OH

	K_2CrO_4		Time of Exposure (Days)							
Exp. No.	Amount of Aqueous Solution Used (Vol % of CH_3OH)	Concentration of Aqueous Solution Used (%)	1	3	5	10	15	20	30	40
K_1	2	0.1	-	-	# P	#	#	#	##	##
K_2	5	0.1	-	-	- P	-	-	-	#	#
K_3	10	0.1	-	-	- P	-	-	-	-	-
K_4	15	0.1	-	-	-	-	-	-	-	-
K_5	20	0.1	-	-	- P	-	-	-	-	-
K_6	1	1.0	-	-	- P	-	-	-	#	#
K_7	5	1.0	-	-	- P	-	-	-	-	-
K_8	10	1.0	-- PP.	-	-	-	-	-	-	-
K_9	1	2.5	-- PP.	-	-	-	-	-	-	-
K_{10}	5	2.5	-- PP.	-	-	-	-	-	-	-
K_{11}	1	5	-- PP.	-	-	-	-	-	-	-

Key

The degree of corrosion is shown as follows:

p. slight precipitate
pp. excessive precipitate
-. no Mg corrosion
#. less than 3 corroded spots
##. Mg slightly corroded

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Table V(B)15
INFLUENCE OF ADDITION OF $K_2Cr\ O_4$ AND H_2O UPON
THE CORROSION OF Mg-ALLOY BY CH_3OH

Exp. No.	Amount of Aqueous Solution Used (Vol % of CH_3OH)	K_2CrO_4 Concentration of Aqueous Solution Used (%)	The Amount of H_2O (Vol %)	Time of Exposure (days)							
				1	3	5	10	15	20	30	40
46	5	0.1	5	-	-	-	-	-	-	-	-
82	10	0.1	10	-	-	-	-	-			-
71	20	0.1	20	-	-	$\bar{P}$	-				#
73	5	0.1	5	-	-	P	-				-
74	10	0.1	10	-	-	P	-				-
51	K_2CrO_4 wt. % CH_3OH 0.01		10	-	-	$\bar{P}$	-				-
52	0.01		20	-	-	$\bar{P}$	-				-
53	0.01		40	-	-	$\bar{P}$	-				-
	$K_2Cr_2O_7$ wt. % CH_3OH										
48	0.06		10	$\bar{P}$.$\bar{E}$-		-	-		--		-
49	0.06		20	$\bar{P}$	-	-	-				-
50	0.06		40	$\bar{P}$	-	-	-				-

Key

The degree of corrosion is shown as follows:

- p. slight precipitate
- pp. excessive precipitate
- -. no Mg corrosion
- #. less than 3 corroded spots
- ##. Mg slightly corroded

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Table VI(B)15
INFLUENCE OF ADDITION OF K_2CrO_4 AND ALKALI
UPON THE CORROSION OF Mg-ALLOY BY CH_3OH

	K_2CrO_4		Alkali		Time of Exposure (days)							
Exp. No.	Amount of Aq. Soln. Used Vol. % of CH_3OH	Concentration of Aq. Soln. Used (%)	Amount of Aq. Soln. Used $NaHCO_3$ Vol % of CH_3OH	Concentration of Aq. Soln. Used (%)	1	3	5	10	15	20	30	40
32	2	0.1	1	0.1	-	-	$\bar{P}$	-	-	#	##	#
23	5	0.1	1	5	-	$\bar{P}$	-	-	-	-	-	-
24	10	0.1	1	2.5	-	$\bar{P}$	-	-	-	-	-	-
25	10	0.1	1	5	-	-	$\bar{P}$	-	-	-	-	-
35	2	0.1	NaOH 1	0.1	-	-	-	#	#	#	#	#
36	2	0.1	5	0.1	-	-	-	-	# PP	#	#	#
38	2	0.1	10	0.1	-	-	-	-	# P	#	#	#
42	5	0.1	1	0.1	-	-	-	-	# P	#	#	#
43	5	0.1	5	0.1	-	-	-	-	$\bar{P}$	-	-	-
37	2	0.1	NH_4OH 5	0.1	-	-	-	$\bar{P}$	-	-	-	-
39	2	0.1	10	0.1	-	-	-	-	$\bar{P}$	-	#	#
44	5	0.1	5	0.1	-	-	-	$\bar{P}$	-	-	-	-
45	5	0.1	10	0.1	-	-	-	$\bar{P}$	-	#		#

Key

The degree of corrosion is shown as follows:

p. slight precipitate
pp. excessive precipitate
-. no Mg corrosion
#. less than 3 corroded spots
##. Mg slightly corroded