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TECHNICAL REPORT ECOM-2517

A STUDY OF FACTORS AFFECTING THE CORROSION RATE OF MAGNESIUM IN VARIOUS ELECTROLYTES UNDER STATIC CONDITIONS

By

CARL A. NORDELL

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U. S. ARMY ELECTRONICS LABORATORIES
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Carl A. Nordell

Power Sources Division
Electronic Components Department

DA Task No. 1A0 13001 A 039-19

Abstract

The corrosion rates of magnesium and magnesium alloys in magnesium salt solutions of chloride, bromide, and perchlorate were studied by measuring the gaseous reaction product as a function of time. Reliable apparatus was developed to accurately determine the volumes of gas generated. Protective films were applied to the surface of the magnesium metal to suppress excessive chemical reactivity at the metal-electrolyte interface, thereby reducing static corrosion rates. Cramolin, one of the films tested, reduced the gas evolution of an AZ21 Mg-2N $MgBr_2$ system from 400 cc/800 hrs to 0.1 cc/800 hrs.

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INTRODUCTION

In a magnesium-manganese dioxide primary cell, water in the electrolyte reacts with the magnesium in accordance with the reaction

$$Mg + 2H_2O \longrightarrow Mg(OH)_2 + H_2$$

to form a protective film of magnesium hydroxide at the anode. Although this hydroxide film enhances the storage life of magnesium dry cells, it induces undesireable transient polarization (delayed-action) when an anodic current is applied to the magnesium anode.

This study is based on the postulation that the application of micro-thin ionic conductive films to the magnesium anode will produce an overall advantageous effect on the shelf life and delayed action of the magnesium dry cell. It was assumed that the protective films would provide the effective separation of active materials so essential to prolonged shelf life, and would inhibit the formation of magnesium hydroxide on the anode, thereby, reducing initial transient polarization.

The objective of this program was to study the chemical reactivity rate between magnesium and various electrolytes on stand and to investigate means of inhibiting this reaction.

The method of investigation in the study involved static tests in which a magnesium alloy of known composition was placed in an environment of electrolyte. The gas generated by the resulting chemical reaction was collected and measured as a function of time. The reaction

$$Mg + 2H_2O \longrightarrow Mg(OH)_2 + H_2$$

indicates that for every mole of $Mg(OH)_2$ that is formed one mole of H_2 is evolved. It then follows that if the gaseous reaction product is collected and measured for a specific period of time, the amount of $Mg(OH)_2$ formed during that period can readily be calculated.

EXPERIMENTAL PROCEDURE

a. Test Equipment

Large volumes of gas were collected in accordance with the displacement of liquid under glass technique. A 50 milliliter burette was inverted in a 100 milliliter beaker of electrolyte. The burette was then filled with electrolyte by the evacuation of air through the stop cock. To prevent a change in electrolyte concentration due to evaporation, paraffin oil was used to cover the surface of the electrolyte remaining in the beaker (Figure 1).

To accurately measure very small volumes of gas, a special glass cell was constructed. This apparatus consisted of a 14/35 tapered ground glass joint that had been fitted at one end with a 1.0 cubic centimeter pipette and sealed at the other end to form a reaction chamber having a volume of approximately 10.0 cubic centimeters. The pipette was extended into the reaction chamber well below the joint so that the capillary of the pipette would always be below the level of the electrolyte. In operation, the gas generated displaces an equal volume of electrolyte from the reaction chamber. The electrolyte is forced into the calibrated pipette allowing measurement of the gas volume. A detailed sketch of this apparatus is shown in Figure 2.

b. Preparation of Sample

All magnesium samples used in this investigation had a surface area of approximately one square inch and were cleaned in trichloroethylene before testing.

c. Accuracy

All of the graduated glassware used was in accordance with specifications of the National Bureau of Standards. The burettes used were graduated from 0 to 50 milliliters in divisions of 0.1 milliliters. The 1.0 cubic centimeter pipettes were graduated in subdivisions of 0.01 cubic centimeters making it possible to read accurately to ± 0.002 of a cubic centimeter. However, when using gas measuring devices certain relative factors must be considered, especially when small volume changes are being determined. For instance, changes in temperature and atmospheric pressure will result in a substantial deviation from true test measurements. Accordingly, these experiments were conducted in a room where the temperature was maintained at 21°C ± 0.5°C. By placing the reaction chambers of the test cells in an ambient temperature water bath, the 0.5°C temperature deviation was reduced to approximately ± 0.25°C. Since atmospheric pressure is somewhat more difficult to control, a method of numerical compensation was devised. An additional microvolumetric gassing cell, containing only the type and concentration of electrolyte being studied, was positioned in the water bath. Any change noted in the electrolyte level in this calibrated pipette was attributed to a change in atmospheric pressure and all other pipette readings were compensated accordingly.

DISCUSSION

The objective of this program was to study the effect of electrolyte and anode composition on the open circuit corrosion rate of magnesium electrodes and to investigate fatty acid and silicon films as corrosion inhibitors. The results of an experiment designed to evaluate the corrosion rate of magnesium and magnesium alloys in aqueous salt solutions of various concentration are shown in Table I. Increasing the concentration of the electrolyte solutions resulted in increased reactivity. Data in Table I also shows that the alloy ingredients have a marked effect on the static corrosion characteristics at all normality levels of the electrolyte solutions tested. Generally, as the aluminum content of the magnesium alloy increases the reactivity decreases.

Magnesium Alloy	% Al	% Zn
AZ-10	1	0.5
AZ-21	2	1
AZ-31	3	1

Aluminum is added to magnesium to reduce local action caused by the presence of iron, the major impurity in magnesium. The addition of zinc to the alloy mixture results in a more uniform surface dissolution of the magnesium alloy.

To determine the relationship between the pH of the test electrolytes and the corrosion rate, pH values were plotted as a function of both electrolyte concentration and gas evolution, (Figures 3 & 4). As the electrolyte concentration increases all solutions become more acidic. It can also be seen that the pH range of magnesium perchlorate is much greater than the other electrolytes; consequently, it is the most acidic at high concentrations and the most basic at low concentrations. Of interest in Figure 4 is the fact that the gassing rates tend to equalize as the electrolytes approach neutrality (pH 7). Figure 5 illustrates that the chemical reactivity of magnesium perchlorate with magnesium is lower than that of magnesium bromide and magnesium chloride, and that gas evolution decreases as the electrolyte concentration decreases. The data also emphasized the advantage of magnesium alloys over pure magnesium.

Under an investigation of anode coatings the following materials were tested:

- Cramolin
- Lanolin
- Ricilan "C"
- Silicone SF-96
- Silicone R-101
- Silicone Varnish #997
- Siliclad
- Oleic Acid
- Polyco

Unless otherwise stated all tests were conducted using a 4 N solution of magnesium bromide as the electrolyte and AZ-21 magnesium alloy. It can be seen from Figure 6 that all of the coatings did retard reactivity as evidenced by the decrease in gas evolution. Cramolin, a commercial electric contact cleaner containing fatty acids, proved to be the most effective. The effectiveness of Cramolin in reducing the corrosion rate of magnesium and magnesium alloys in various electrolytes is further demonstrated in Figure 7.

Experiments were conducted on methods and techniques of applying Cramolin films to magnesium. Benzene, a solvent for Cramolin, was used as a diluent to control film thickness. Cramolin solutions were applied to the magnesium test sample by brushing, dipping, or soaking the anode material for varied periods of time. Magnesium samples that had been immersed in solution for at least two weeks gave the best results. Further experimentation resolved that the soaking process could be accelerated by using an ultrasonic vibration bath. When a sample was removed from the Cramolin solution, it was either air dried at room temperature or oven dried at temperatures ranging from 40 to 60°C. Both drying techniques were investigated through a time range of 1 to 18 hours. Oven drying at 55 to 60°C for periods between 8 and 18 hours proved to be the most favorable. To optimize the ratio of benzene to Cramolin required to form the most effective film, microvolumetric gassing tests were conducted on magnesium test samples in accordance with the following schedule:

Benzene		Cramolin
0	to	1
5	to	1
7	to	1
9	to	1
11	to	1

The results of this experiment are shown in Figure 8. Maximum film protection was attained using a solution of 7 parts of benzene to 1 part of Cramolin.

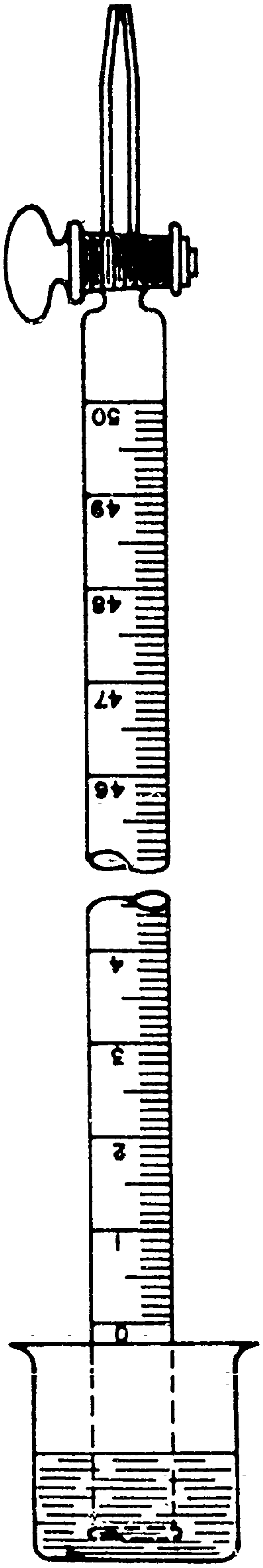
CONCLUSIONS

The magnitude of the corrosion reaction between magnesium and aqueous salt solutions is a function of the following:

Electrolyte concentration
Electrolyte composition
Alloy ingredients
Inhibitors

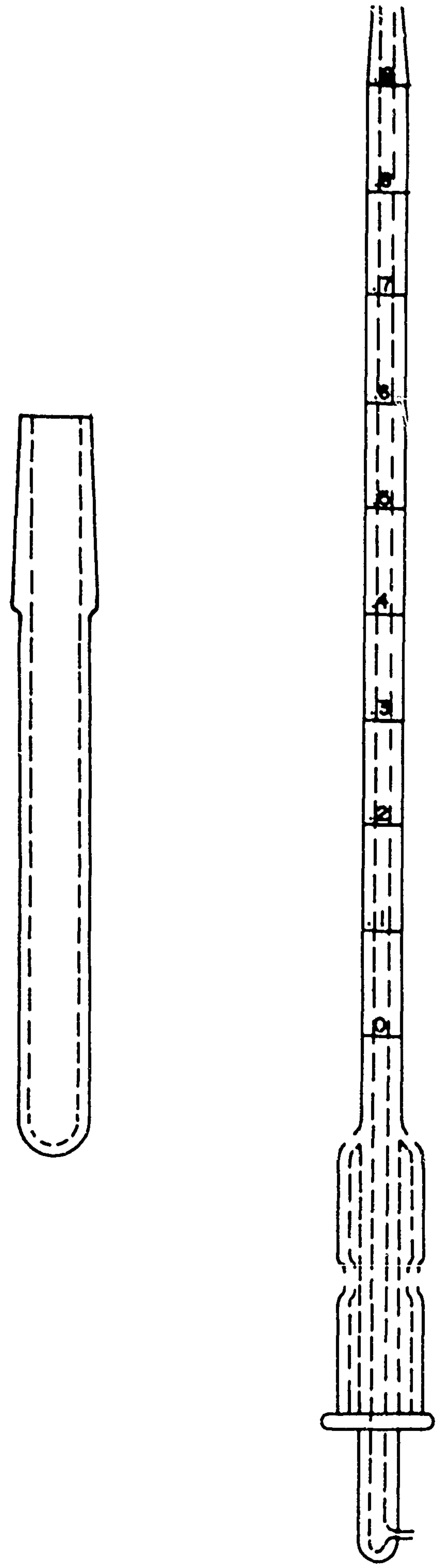
Of all the inhibitor materials tested, Cramolin, when properly applied, most effectively reduces the corrosion of magnesium during stand in aqueous salt solutions.

Cramolin films applied to the magnesium anode limit reactivity at the magnesium-electrolyte interface under static test conditions by hindering the accessibility of the electrolyte to the metal surface. Additional study will be required to determine the effect of this passivity on initial transient polarization when an anodic current is applied to the magnesium anode.



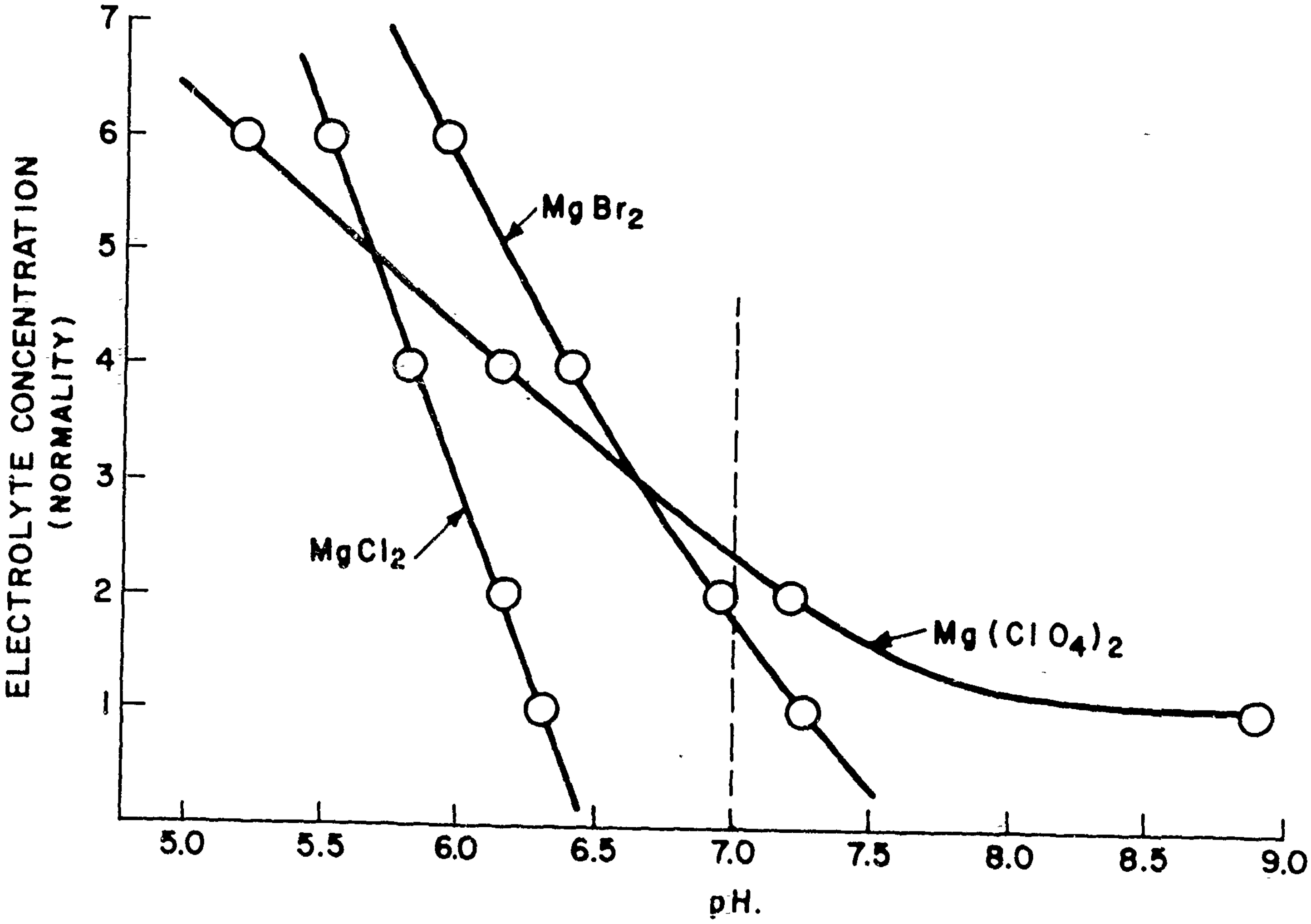
GAS COLLECTING APPARATUS

FIG. 1



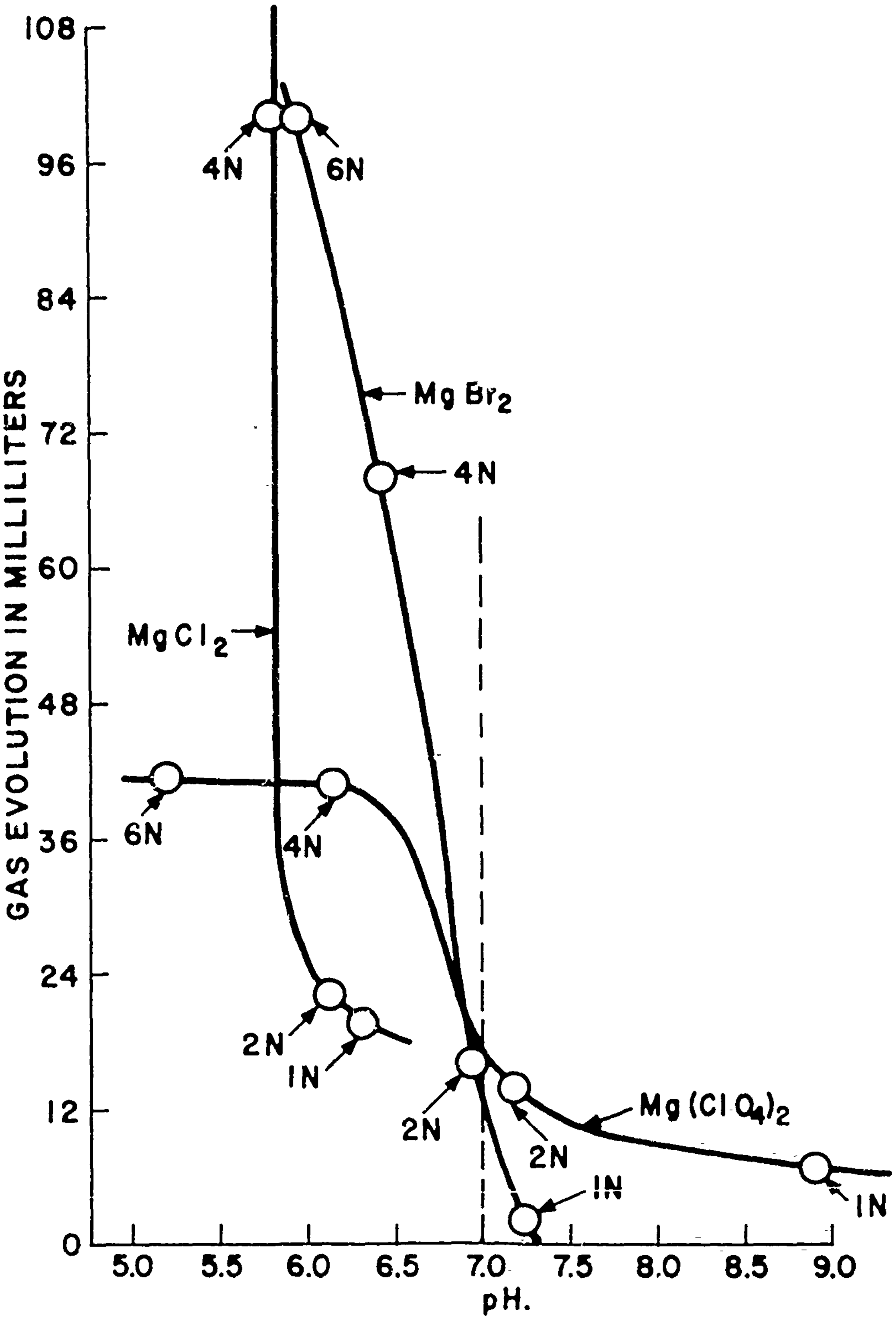
MICROVOLUMETRIC GAS COLLECTING APPARATUS

FIG. 2



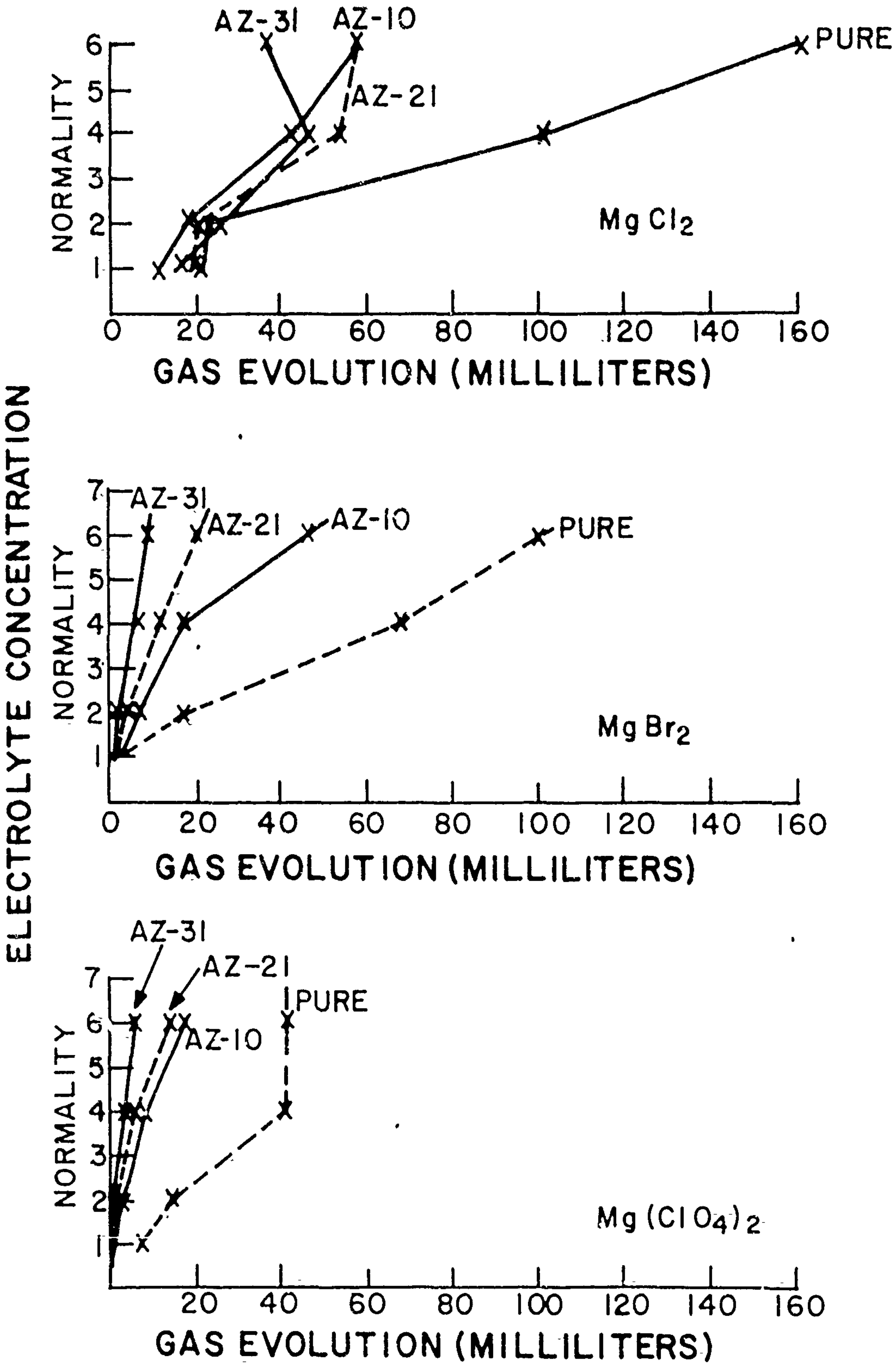
ELECTROLYTE CONCENTRATION VS. pH

FIG. 3



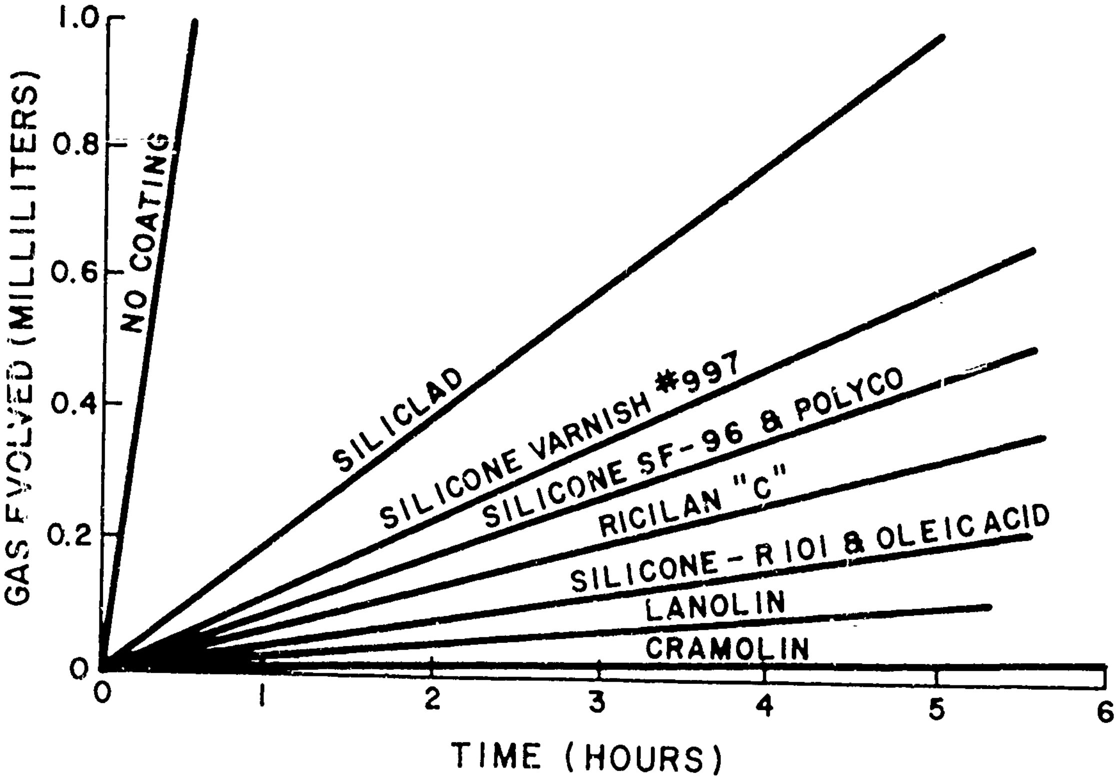
GAS EVOLUTION IN MILLILITERS/IN^2 OF PURE MAGNESIUM DURING 100 MINUTES IMMERSION VS. pH OF SEVERAL ELECTROLYTES

FIG. 4



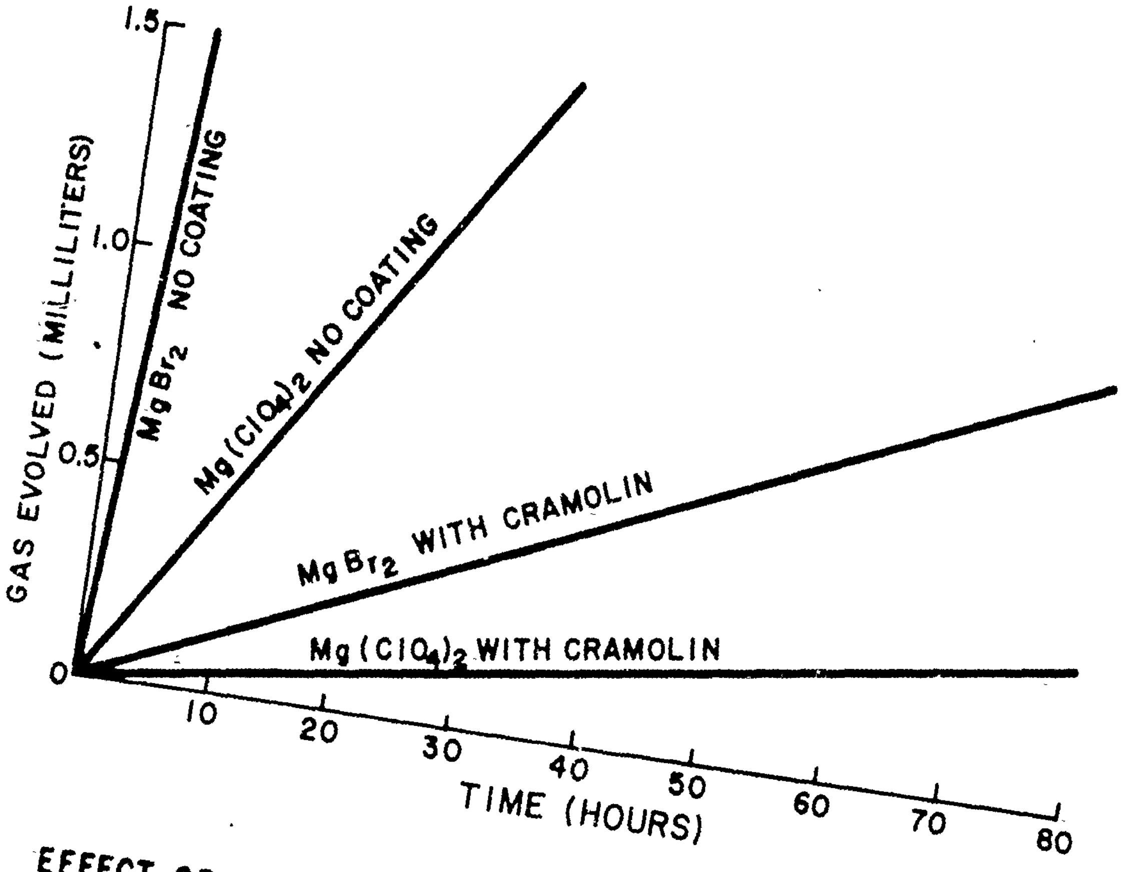
GAS EVOLUTION DURING 400 MINUTE TEST VS. ELECTROLYTE CONCENTRATION

FIG. 5



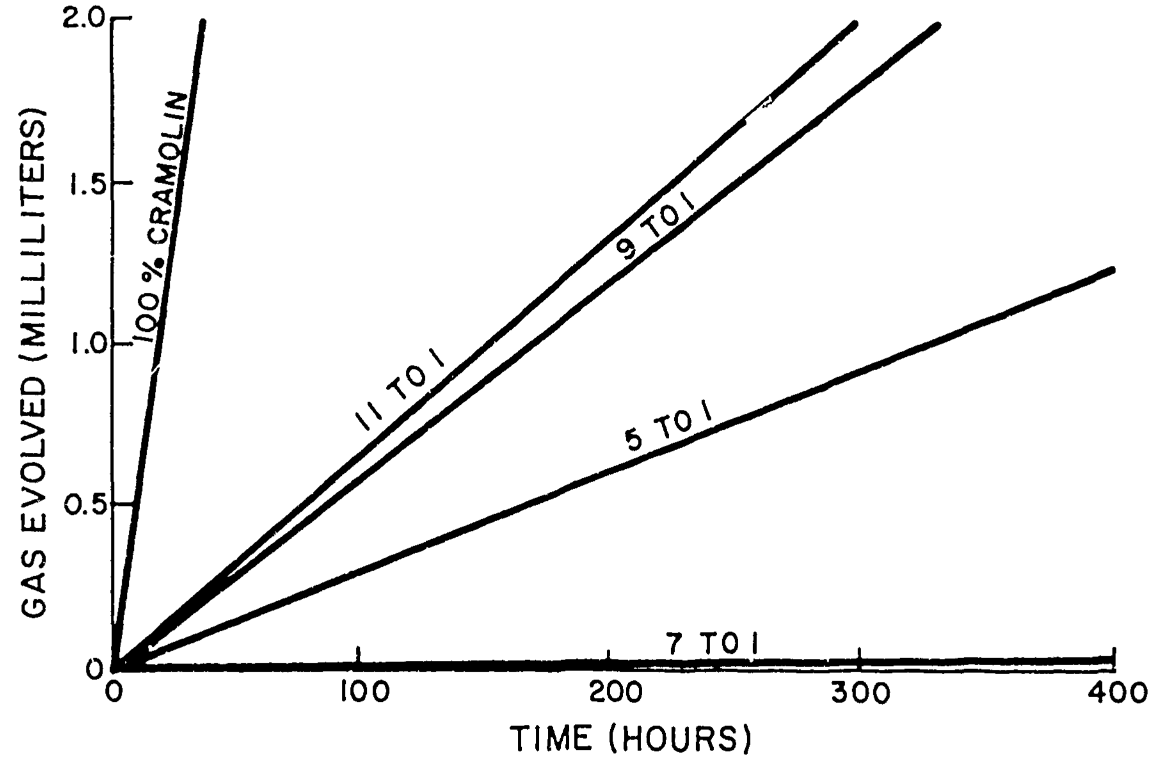
GASSING RATES OF AZ-21 MAGNESIUM IN FOUR NORMAL MAGNESIUM BROMIDE WITH PROTECTIVE COATINGS

FIG. 6



EFFECT OF DILUTE CRAMOLIN ON THE GAS EVOLUTION FOR AZ-21 MAGNESIUM IN MgBr$_2$ & Mg(ClO$_4$)$_2$ ELECTROLYTES

FIG. 7



ALL MAGNESIUM SAMPLES SOAKED IN CRAMOLIN SOLUTIONS FOR FOUR WEEKS AND THEN OVEN DRIED @ 60°C FOR 18 HRS.

EFFECT OF BENZENE TO CRAMOLIN RATIO ON REACTION RATE OF AZ-21 ALLOY WITH $MgBr_2$ ELECTROLYTE

FIG. 8

TABLE I. GAS EVOLUTION IN MILLILITERS PER SQUARE INCH OF MAGNESIUM DURING 400 MINUTE STAND IN VARIOUS ELECTROLYTES

ELECTROLYTE	NORMALITY	PURE	AZ-10	AZ-21	AZ-31
	1	20.0	10.0	16.0	15.0
Mg Cl_2	2	22.0	18.0	20.5	25.0
	4	100.0	41.0	52.0	44.0
* MW = 96	6	160.0	57.0	57.0	35.0
	1	2.0	0.6	0.2	0.2
$MgBr_2$	2	16.0	6.5	2.5	1.5
	4	68.0	17.0	10.5	5.5
MW = 185	6	100.0	47.0	20.0	9.0
	1	7.2	0.9	0.2	0.3
$Mg(ClO_4)_2$	2	14.0	2.0	0.3	0.7
	4	40.5	8.0	4.0	2.8
MW = 224	6	41.0	17.0	13.0	6.0

* MW = MOLECULAR WEIGHT

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Unclassified Report

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2. Primary Batteries

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