INEXPENSIVE NON-TOXIC PIGMENT SUBSTITUTE FOR CHROMIUM IN PRIMER FOR ALUMINUM SUBSTRATE

19961205 009

INTERIM REPORT

DTIC QUALITY INSPECTED 4

١

GULF COAST REGION MARITIME TECHNOLOGY CENTER

DISTRIBUTION STATEMENT A

Approved for public release; Distribution Unlimited

INEXPENSIVE NON-TOXIC PIGMENT SUBSTITUTE FOR CHROMIUM IN PRIMER FOR ALUMINUM SUBSTRATE

INTERIM REPORT

by

Alfred F. Daech, B.S. CHE. Department of Civil and Environmental Engineering University of New Orleans New Orleans, LA 70148

Kenneth L. McManis, Ph.D. Department of Civil and Environmental Engineering University of New Orleans New Orleans, LA 70148

Nikhil K. Sarkar, Ph.D. Department of Biomaterials - LSU Medical Center New Orleans, LA 70124

Li Li, M.S. Physics,& C.E. Department of Civil & Environmental Engineering University of New Orleans New Orleans, LA 70148

GCRMTC RESEARCH PROJECT NO. 1 "ONR Cooperative Agreement No. N00014-94-2-0011"

CONDUCTED FOR UNIVERSITY OF NEW ORLEANS GULF COAST REGION MARITIME TECHNOLOGY CENTER

The contents of this report reflects the views of the authors(s) who is(are) responsible for the facts and the accuracy of the data presented herein. The contents do not necessarily reflect the official views or policies of the GCRMTC or its Sites, the State of Louisiana or Texas, the U.S. Navy, or appropriate funding agency. This report does not constitute a standard, specification, or regulation. The GCRMTC does not endorse products, equipment or manufacturers. Trademarks or manufacturer's names appear herein only because they are considered essential to the object of this report.

MARCH 7, 1996 "APPROVED FOR PUBLIC RELEASE; DISTRIBUTION IS UNLIMITED"

ACKNOWLEDGMENTS

We wish to acknowledge our appreciation to EuroNavy, USA for technical formulation and testing of paint products that we have been developing over the past year of our research.

ABSTRACT

One objective of the project is to identify non-polluting Li-based inhibitors for suppressing the corrosion of aluminum alloys to a degree that they will represent satisfactory substitutes for environmentally hazardous chromium coatings that are widely used.

Since all corrosion involves oxidation and reduction it can be measured by observing the flow of electrons in a system. A device which does this is a "Potentiostat." If no current flows, corrosion is stopped.

A series of non-carcinogenic and low toxicity lithium salts passivate aluminum and hence interrupt corrosion. A statistical series was set up to optimize the salts. A patent application is being prepared. A literature search has indicated that this is a new approach.

Another concept which shows promise is to heat aluminum-lithium alloys (about 3% lithium) to 350°C for 30 minutes in argon gas. This relocates the lithium onto the surface of small (200 to 320 mesh) pigment particles. In this way the passivating lithium salts can be concentrated on the surface. In many instances only the pigment surface produces passivating influences on the substrate. Since molecules on the surface are a very small percentage on the order of one atom to then-thousand interior atoms the amount of passivating chemical can be much less. A patent application is also being prepared on this concept. This concept is called "nanostructural inhibitors".

The second objective is to incorporate these inhibitors into a paint vehicle as primers. An arrangement has been made with "EuroNavy USA" for this phase which has not yet begun. They will test and manufacture the paints.

The final objective is to accommodate the products to Navy requirements for various paint specifications where possible. We have already tested some of the proposed passivators on 1000, 2000, 5000 and 6000 series alloys successfully.

TABLE OF CONTENTS

(

6

Page No.

Acknowledgments	iii
Abstract	iv
Introduction	1
Objective	2
Scope	3
Method of Procedure	4
Discussion of Results	9
Table I - Matrix Ratings by Current Flow	11
Table II - Statistical Matrix	14
Conclusions	15
Recommendations	16
Time Line	16A
References	17
Appendix A Tables A0-A5 Matrix for Blending Inhibitors Experiment Made by Greco Latin Squares Method	19
Appendix B Figures B1-B55 Anodic Polarization Curves	26

INTRODUCTION

Lithium Carbonate in solution has been shown to protect certain metals, particularly aluminum, from corrosion by reacting at the surface. SIMS (Secondary Ion Mass Spectrometer) confirms this phenomena. Sodium carbonate and potassium carbonate reactions produce a soluble product and no alkali is detected on the surface by SIMS. Because of their high solubility and reactivity most "alkaline metal" compounds are not suitable for corrosion protection. Metallic aluminum normally provides its own corrosion protection due to its tendency to form an aluminum oxide insulator on the surface, but the matrix of hydrated aluminum oxide is penetrated by chemicals such as NaCl, acid and bases.

Engineers and scientists observed that certain aluminum-lithium alloys demonstrated some diffusion of lithium to the surface of the alloy. The lithium ion is so small that it penetrates the large interstitial spaces of the aluminum oxide layer. The aluminum - lithium alloys are stable in chemical composition at ordinary temperatures but a lithium-rich surface can be easily produced in the alloy by briefly heating to facilitate the migration. It appears that certain lithium alloys or compounds can be incorporated into a paint vehicle or otherwise deposited on the surface of aluminum alloys to provide corrosion protection when exposed to salt water, humidity and other corrosive environments.

The corrosion propensity of the various alloys of aluminum may be measured by electrochemical techniques. Electrochemical techniques of corrosion testing have continued to be attractive to investigators interested in corrosion. The imposition of a controlled potential via a potentiostat is a very attractive concept from a reaction kinetics point of view. Furthermore, electrical currents are simple to measure and can be directly related to electrochemical reaction rates through Faraday's Law. AC techniques can be used to determine film resistivity and thickness values. A variety of electrochemical tests have been proposed and developed. Scanning electron microscopy (SEM) and simple magnification of target metals illustrates the surface modification caused by the lithium salts. The problem is to select inhibitors, optimize them and to make them available to protect the aluminum substrates by a coating process.

The United States Navy has established an operations requirement for primers for aluminum which can be applied by personnel while on patrol. The desired product must be a fire retardant, general purpose primer which will be both protective for the exterior as well as the interior surfaces of aluminum. Material selection and usage are rigidly governed by codes; for example, those contained in proposed contaminant restrictions.

Chromium compounds provide outstanding corrosion protection of certain metals. Chromates are used in the chemical conversion coating of Aluminum, (MIL-C-5541). Chromates have reportedly been determined to be carcinogenic and therefore a replacement for them is currently being sought. Environmental Agencies limit the amount of chromium ion tolerated in waste water to less than one part per million. Thus an environmentally benign substitute is desired. Since most available corrosion inhibitors are based on heavy metals or reactive amides, the available alternates appear to fall short of the desired performance in corrosion inhibition and/or environmental suitability.

Various lithium compounds appear to offer a viable alternative to chromium using a new concept of corrosion inhibition.

OBJECTIVE

The objective of the first phase of this project is to identify or create new primer inhibitors based on aluminum-lithium to a degree where they will represent satisfactory substitutes for the chromium paints for aluminum.

The second phase objective is to incorporate the pigments into paint vehicles which can be used as primers and which are essentially non-polluting.

The final objective will be to accommodate the products to Navy requirements for various paint specifications where possible and to arrange a manufacturing facility.

SCOPE

The scope of this project as described is very broad. Obviously one cannot develop a new concept in coatings and follow through to a broad set of specifications and uses in one or two years for a few hundred thousand dollars. However, we will demonstrate that the product can fulfill all of the requirements from the pigment concept to the final use. The pigment will be investigated in detail. The coating will utilize existing vehicles i.e. latexes, etc. used by the Navy under military specifications with chromate pigments. We will then assess the suitability of the developed product to meet existing specifications and propose modifications, inserts, or deletions.

METHOD OF PROCEDURE

The fundamental piece of equipment used in this part of the program is the Model 352/252 Soft Corr™II Corrosion Measurement & Analysis Software manufactured by EG&G Instrument Division of Princeton Applied Research.

The instrument is installed and running. Qualification tests per ASTM G-3 and G-5 were run to ensure proper functioning of the equipment. The first machine was out of calibration and was replaced by the vendor. The recent flood in New Orleans, in May 1995, also led to some delays since the airport was closed, the motels and hotels were filled with flood victims and those rental cars which were not flooded were rented out to victims. This delayed the technician coming from the factory for thirty days.

The technician determined that the defect was not correctable without major repair. The machine was replaced by the vendor. In the interim, we purchased training films, programs and books and began test runs and procedure trials.

A series of chemicals were selected and purchased for the compounds tests. Substrate aluminum panels were selected and purchased. Some aluminum-lithium compounds have been ordered and others will be chosen as time allows. Some vendors are reluctant to send certain aluminum-lithium products because they are considered proprietary.

The American Conference of Governmental Industrial Hygienists in their 1994-1995 "Threshold Limit Values for Chemical Substances and Physical Agents and Biological Exposure Indices" does not list lithium compounds as a particular problem although the subject has been studied in connection with batteries, ceramics and as an absorber of atomic particles in nuclear reactors. Only Lithium Hydride is listed on the TLV list. The Material Safety Data Sheet reports that Lithium Citrate is stable, has no hazardous reactivity, and is not carcinogenic, but is considered toxic by ingestion, injection and inhalation.

Generally, the lithium compounds are not considered poisonous, depending on the anion. Lithium Hydride, Lithium Hydroxide, Lithium Fluoride, Chloride and Lithium Selenite, to name a few are toxic, largely due to the toxicity of the anions. Lithium is a common element and many of its salts, i.e., acetate, benzoate, borate, carbonate, lactate, nitrate and sulfate are commercially available and regarded as moderately toxic. The overall toxicity will be determined when the final formula is selected. The paint vehicles will be selected from those which are environmentally acceptable.

We are now members of the SP-3 committee of the Steel Structures Painting Council (SSPC). This group is involved in surface preparation and painting of ships. As the name suggest the prime problem is Steel, however all members contacted have aluminum corrosion as well as steel. The members include military and commercial builders. The large commercial ships are concerned primarily with steel hulls and structures.

Aluminum-Lithium powder is the fundamental material studied in this project. It is available from many other sources but most require orders of substantial quantities. One source confirmed that patents being sought by manufacturers create some limits. The material is commercially available but quantities limit the variety, since a minimum purchase can be \$5,000 to \$10,000 worth of material. However, enough is available to complete the study.

The first year's schedule has slipped in some task areas due to the flood and the defective equipment, which could not be corrected until the factory representative arrived to verify the problem.

(1) Contact Suppliers by Phone

We have contacted Doctor Alex Chou of Reynolds who has agreed to send us the version of Aluminum-Lithium proposed for use on the Space Shuttle. Comalco (Australia) has supplied a sample of high lithium content alloy. Alcoa has provided sheets of alloy 2090.

The Aluminum Powder Company Limited in England unofficially suggested a price of \$8/lb in large quantity, but for 150/lb. minimum the price is about \$40/lb. We are negotiating to get smaller quantities at a better price. International Nickel, Pichonet, Kaiser, Alcan and International Light Metals have not yet agreed to participate.

(2) Perform Survey of Similar Studies

The only studies found in references was the study by R.G. Buchheit of Sandia and Jing Gui and M.T. Douine (University of California, Berkley). It appears that they are working on the "Anodize" or "Irridite" approach. Buchheit has sent his papers to us and the literature study has given us published work to date by the University of California. The formation of "talc" if it occurs, is probably not the source of our corrosion resistance since no carbonate was used in many of the experiments and passivation occurred with inert gas and ASTM pure water. The literature search is complete. Although many references to lithium were found only Buchheit and Associates propose a lithium corrosion inhibitor.

(3) Study Literature

The pertinent papers from the literature survey have been received and all but two or three of sixty are on file and have been studied. This will be periodically updated but is essentially complete.

(4) Order Any Other Promising Inhibitors

Many of these chemicals are on hand and will be disclosed as they are tested.

(5) Prepare Screening Tests

The first screening tests have been performed on pure aluminum panels. We looked at passivation by combinations of inhibitors. 5,000 and 2,000 series were checked to look at alloying effects on the aluminum corrosion properties as related to the passivity produced by the lithium and its salts. Alloys 1100, 2219,5052 and 6061 were passivated. Tempers of the metals did not seem to substantially change the results.

(6) <u>Perform Rating by Electrochemistry</u>

A statistical series was started to determine the type and quantity of passivators to be used. The layout of the series is four lithium salts at four levels. The series has sixteen combinations each representing combinations of passivators. This enables us to get data equivalent to four to the fourth power or 256 experiments. (See Appendix A). The pH for the first set was maintained at 10.5. Another set was run at Ph 9.0. Other passivators will also be run. The passivators are compared on the curves by the degree of passivation and the quality of the exposed panels (i.e. deposition of protective coating and lack of corrosion.)

The two month delay due to floods and defective equipment has shifted this work from 4th. Quarter 1995 thru 1st. Quarter 1996 to 1st. Quarter 96 thru 2nd. Quarter 96. Once the optimum combination of inhibitors has been established the Aluminum-Lithium pigment will be treated so as to provide the desired ratio to the substrate when coated and thus passivate the painted substrate.

The statistical series is now underway and as the sets of curves indicate the wide range of curves promises a good result. Page 9 of this report provides an explanation of the Greco-Latin Squares. One set of curves represents each passivator at a fixed concentration in combinations with every level of other passivators. The result optimizes the passivator combinations based on the ratings of the individual results. The curves should stabilize at zero ampheres of current. If there is no current there is no corrosion. There are some circumstances where the current when stable at some value (indicated by a horizontal line on the curve) can represent passivation. A detailed evaluation will be presented in the first or second quarter of 1996.

(7) Treat Pigments

We cannot treat pigments until an argon oven is functional so that we can check the results. This also will be reported in the next quarter. Appendix A discusses the pigment base which will ultimately be used.

(8) Scanning Electron Microscope

A surplus Scanning Electron Microscope has been made available to UNO from LSU. Having this device at the center will facilitate metal inspection for quality of the passivating film.

(9) Analyze Lithium Salts & Metals

A study was made and promising materials are now on hand. Corrosion inhibitors were selected. The results are encouraging. Lithium Nitrate looks particularly good. Since no carbonate is available in the test, the formation of "talc" does not occur. The solution is ultra pure water with nitrogen purge. The passivity appears superior to lithium carbonate but the exact compound formed at the surface has not been determined. Several analyses remain to be performed.

(10) Select and Order Inhibitors

Forty inhibitor possibilities were selected from the literature, from the bender catalogs and from our own analyses of chemicals. Most were lithium compounds with a few possible modifiers of zinc and other metals. These were screened electrolytically and by surface analysis.

(11) Select and Order Metals for Test Panels

A set of panels was ordered from the "Q-Panel" Company. Some "buttons" of various aluminum alloys certified as Al1100, Al2090, Al2219, Al5005, Al5052, Al5456, Al7075 and Al6061. Tests were run on passivity and Al6061T6 was selected as the alloy for general testing although all were passivated by the Lithium salts.

(12) Test Panels & Proposed Mechanisms

This study is ongoing. SEM photos and surface studies are under way.

(13) Verify Theory and Relate To Military Specifications

This task was not completed due to lack of time. This task will be proposed for year 1997.

(14) General

Four significant developments resulted from the first year investigations. First, several inhibitors in the form of lithium salts seem to show promise. "Lithium Nitrate" looks particularly good possibly from the lithium atom in the molecule and possibly because of the nitrate. Lithium Sulfate also looks good. Since all carbon dioxide was flushed out of the water and certified ultra pure water, with no carbonate, was used, the formation of "Talcite" coating described in U.S. Patent 5,266,356 does not seem probable with these inhibitors. It appears more likely that Lithium Alumnate (inert ceramic) or some other reactant or structure is probable. Investigations will continue into 1996. Combinations of passivators looked better without the lithium citrate.

In any event, the passivation was verified on aluminum alloys 1100, 2024, 2219, 5052, and 6061. The 2219 showed a unique second peak which also passivated. This may be pitting corrosion.

The second innovation is called "Nanostructural Inhibitors." The ratio of atoms on the surface to the body of a typical tiny pigment particle is about 1:10,000. If we heat Aluminum Lithium to 300° C, the Lithium migrates to the surface. This is done under Argon and although the Lithium is only 2 or 3% by weight, the surface collects about 90% Lithium. This should improve the corrosion resistance of the alloy and provide surface sites for reacting citrate, etc.

Typical structures painted 20 or more years ago with chrome or lead pigments retain their color if cut, indicating that surface inhibitors may be effective and that much of the inhibitor is not consumed, and usually not necessary.

Thirdly, since heating in argon, the Lithium tends to migrate to the surface of the Aluminum-Lithium alloy, properties such as fracture toughness, and weld ability should be improved. This will be a separate investigation. The lightweight of the Aluminum Lithium alloy is desirable but the fracture properties and welding present problems. The relocation of lithium to the surface should enhance corrosion resistance, improve fracture properties and simplify welding.

The fourth thrust is a statistical study of the inhibitors. It seems that there are advantages in blending inhibitors. These salts are particularly adaptable to statistical analyses since they are compatible with one another. Greco Latin Squares are presently being used. Taguchi methods may be used later. Typical results are in the attached Appendix A.

Dr. Nikhil Sarkar has been used as a consultant as planned in the first year. He has twentyfive years experience in electro-chemistry work and is enthusiastic about the results.

DISCUSSION OF RESULTS

Research efforts the past year were directed at accomplishing the first objective. Significant progress made to date is reported here. Electrochemical corrosion tests were performs on alloy 6061T6 in electrolytes containing a combination of four soluble Li-salts at pH 9 and 10.5, respectively. The inhibiting effect of Li-salts has been found to be pH dependent in the past.

The four Li-salts that have been used are listed below along with information on their molecular weight and solubility characteristics in water.

(1) List of Lithium salts:

SOLUBILITY	FORMULA WEIGHT	CHEMICAL COMPOUND	
0.2M	73.89	A=Li ₂ CO ₃	Lithium Carbonate
0.26M	281.99	B=Li3CO6H5O7.4H ₂ O	Lithium Citrate
1.3M	68.95	C=LiN0 ₃	Lithium Nitrate
Very Sol.	173.82	D=Li ₂ MoO ₄	Lithium Molybdate

(2) The various subscripts indicate variations in molar concentrations: (Moles/liter)

$A_{1=}0$	$\mathbf{B}_1 = 0$	$C_1 = 0$	$D_{1} = 0$
A ₂₌ 0.018	$B_2 = 0.09$	$C_2 = 0.09$	$D_{2} = 0.01$
$A_{3} = 0.03$	$B_3 = 0.15$	$C_3 = 0.15$	$D_{3} = 0.02$
$A_{4} = 0.05$	$B_4 = 0.25$	$C_4 = 0.25$	$D_{4} = 0.03$

⁽³⁾ Sixteen solutions were prepared blending the above:

$\mathbf{A}_1 \mathbf{B}_1 \mathbf{C}_1 \mathbf{D}_1$	$\mathbf{A}_2 \mathbf{B}_1 \mathbf{C}_2 \mathbf{D}_2$	$\mathbf{A}_3 \mathbf{B}_1 \mathbf{C}_3 \mathbf{D}_3$	$\mathbf{A}_4 \mathbf{B}_1 \mathbf{C}_4 \mathbf{D}_4$
$\mathbf{A}_1 \mathbf{B}_2 \mathbf{C}_4 \mathbf{D}_2$	$\mathbf{A}_2 \mathbf{B}_2 \mathbf{C}_1 \mathbf{D}_3$	$\mathbf{A}_3 \mathbf{B}_2 \mathbf{C}_2 \mathbf{D}_4$	$\mathbf{A}_4 \mathbf{B}_2 \mathbf{C}_3 \mathbf{D}_1$
$\mathbf{A}_1 \mathbf{B}_3 \mathbf{C}_3 \mathbf{D}_3$	$\mathbf{A}_{2}\mathbf{B}_{3}\mathbf{C}_{4}\mathbf{D}_{4}$	$\mathbf{A}_{3} \mathbf{B}_{3} \mathbf{C}_{1} \mathbf{D}_{1}$	$\mathbf{A}_4 \mathbf{B}_3 \mathbf{C}_2 \mathbf{D}_2$
$\mathbf{A}_1 \mathbf{B}_4 \mathbf{C}_2 \mathbf{D}_4$	$\mathbf{A}_{2} \mathbf{B}_{4} \mathbf{C}_{3} \mathbf{D}_{1}$	$\mathbf{A}_3 \mathbf{B}_4 \mathbf{C}_4 \mathbf{D}_2$	$\mathbf{A}_4 \mathbf{B}_4 \mathbf{C}_1 \mathbf{D}_3$

(4) The table is laid out so that if one rates the solutions as to their ability to passivate, to form a film and to prevent corrosion by pitting or surface corrosion, each solution will have a numerical value representing the desirability and function of the solution as a passivator.

- (5) The aluminum used in the test was 6061T6 and the pH was adjusted with LiOH or HNO₃.
- If one adds up the values in the vertical columns all A_1 's are in column #1; all A_2 's are in (6) column #2; all A_3 's are in column #3; all A_4 's are in column #4. A₁----A₂----A3----A₄----A,----A₂----A₃----A₁----A_----A₂----A₃----A₁----A₃----A₂----A₁---
- (7) Furthermore each column pairs the particular concentration of A, i.e. 1,2,3,4 with every value of B, C, and D once and only once.
- (8) By adding the values assigned to each solution we can determine which value of A provides the best passivation.
- (9) By adding horizontal rows, values of B may be evaluated in the same way.
- (10) By adding diagonally upper left to lower right, C may be evaluated.*
- (11) By adding diagonally upper right to lower left, D may be evaluated.*
 - * In order to complete diagonals an identical matrix is imposed to the left or right of the original matrix.

The following charts are the results of evaluating the first set of passivators. From these charts a rating is determined and for each panel exposed of alloy 6061 Aluminum, a Scanning Electron Microscopic evaluation a surface chemical analysis is made. These evaluations are being made and will be reported in the next quarter and optimum ratings will be assigned to each solution.

One final note there must be no chemical reaction between A, B, C, or D for this procedure to be valid.

The final electrolytes using a combination of different salts in various concentrations were used. The pH of the electrolytes was adjusted by using LiOH or HNO_3 . The electrolytes are degassed by bubbling high purity N_2 .

The following values are from Appendix A. A few extra values are on the tables.

TABLE IMATRIX RATINGS - BY CURRENT FLOW

MA RANGE	SCORE	RATIONALE	
1.0 - 2.0	10	Virtually no current	
2.0 - 3.0	8	Still pretty good	
3.0 - 4.0	7	Accepted	
4.0 - 6.0	6	Some passivation indicated	
6.0 - 10.0	5	Some promise	
10.0 - 50.0	1	Little or no passivation	
50.0 -	0	Metal Corrodes	

MATRICES @ pH 10.5 & 9

10.5	A ₁ 9	10.5A ₂	9	10.5A ₃	9	10.5A ₄	9	
0	1	6	10	5	8	6	7	
0	10	0	1	0	0	6	6	pH 9 much better than
1	5	8	5	0	0	1	6	10.5 $\text{Li}_2 \text{CO}_3$ good
1	0	0	6	1	6	0	0	at A_2, A_3, A_4
2	16	14	22	6	14	13	19	
10.5	RQ	10 5 B	0	10 5B	0	10 5 B	0	
10.5	$\begin{bmatrix} \mathbf{D}_1 & \mathbf{y} \\ 1 \end{bmatrix}$	$10.3D_2$	10	$10.5D_3$	5	$10.3D_4$	9	1
6	10	0	10	1 8	5	1	0	I ithium Citrate P or
5	8	0	1	0		1	1	R low level or none
6	7	6	6	1	6	1	5	B ₂ low level of hone
17	26	6	17	10	16	2	6	
1 1/	, <u>~</u> ~							
	· · · · · · · · · · · · · · · · · · ·				- <u>-</u> <u>-</u>			.
10.5	C ₁ 9	10.5C ₂	9	10.5C ₃	9	 10.5C₄	9	• · · · · · · · · · · · · · · · · · · ·
10.5	C ₁ 9	10.5C ₂	9	10.5C ₃	9	10.5C₄ . 0	9 10]
10.5 0 0	C ₁ 9 1 1	10.5C ₂ 1 6	9 0 10	10.5C ₃	9 5 5	10.5C ₄	9 10 5	Lithium Nitrate
10.5 0 0 0	C ₁ 9 1 1 0	10.5C ₂ 1 6 0	9 0 10 0	$10.5C_3$ 1 0 5	9 5 5 8	10.5C ₄ . 0 . 8 . 1	9 10 5 6	Lithium Nitrate C_2 , C3, C4, Best
10.5 0 0 0 0	C ₁ 9 1 1 0 0	$10.5C_2$ 1 6 0 8	9 0 10 0 6	$10.5C_3$ 1 0 5 0	9 5 5 8 6	10.5C ₄ . 0 . 8 . 1 . 5	9 10 5 6 7	Lithium Nitrate C_2 , C3, C4, Best
10.5 0 0 0 0 0	$ \begin{array}{ccc} C_1 & 9 \\ \hline 1 \\ \hline 0 \\ \hline 0 \\ \hline 2 \\ \end{array} $	$10.5C_2$ 1 6 0 8 14	9 0 10 0 6 16	10.5C ₃ 1 0 5 0 6	9 5 5 8 6 24	$ \begin{array}{r} 10.5C_4 \\ 0 \\ 8 \\ 1 \\ 5 \\ 14 \end{array} $	9 10 5 6 7 28	Lithium Nitrate C_2 , C3, C4, Best
10.5 0 0 0 0 0	$ \begin{array}{ccc} C_1 & 9 \\ 1 \\ 1 \\ 0 \\ 2 \\ D_1 & 9 \end{array} $	$ \begin{array}{r} 10.5C_2 \\ 1 \\ 6 \\ 0 \\ 8 \\ 14 \\ 10.5D_2 \end{array} $	9 0 10 0 6 16 9	10.5C ₃ 1 0 5 0 6 10.5D ₃	9 5 5 8 6 24 9	$ \begin{array}{r} 10.5C_4 \\ 0 \\ 8 \\ 1 \\ 5 \\ 14 \\ 10.5D_4 \end{array} $	9 10 5 6 7 28 9	Lithium Nitrate C ₂ , C3, C4, Best
10.5 0 0 0 0 0 10.5	$ \begin{array}{ccc} C_1 & 9 \\ \hline 1 \\ \hline 0 \\ \hline 0 \\ \hline 2 \\ \hline D_1 & 9 \\ \hline 1 \\ \hline \end{array} $	$ \begin{array}{r} 10.5C_2 \\ 1 \\ 6 \\ 0 \\ 8 \\ 14 \\ 10.5D_2 \\ 6 \end{array} $	9 0 10 0 6 16 9 10	$ \begin{array}{c} 10.5C_{3} \\ 1 \\ 0 \\ 5 \\ 0 \\ 6 \\ 10.5D_{3} \\ 1 \end{array} $	9 5 5 8 6 24 9 5	$ \begin{array}{r} 10.5C_4 \\ 0 \\ 8 \\ 1 \\ 5 \\ 14 \\ 10.5D_4 \\ 1 \end{array} $	9 10 5 6 7 28 9	Lithium Nitrate C_2 , C3, C4, Best Molybdate D
10.5 0 0 0 0 0 0 10.5 0 0	$ \begin{array}{ccc} C_1 & 9 \\ \hline 1 \\ \hline 0 \\ \hline 0 \\ \hline 2 \\ \hline D_1 & 9 \\ \hline 1 \\ \hline 5 \\ \end{array} $	$ \begin{array}{r} 10.5C_2 \\ 1 \\ 6 \\ 0 \\ 8 \\ 14 \\ 10.5D_2 \\ 6 \\ 1 \end{array} $	9 0 10 0 6 16 9 10 6	$ \begin{array}{r} 10.5C_{3} \\ 1 \\ 0 \\ 5 \\ 0 \\ 6 \\ 10.5D_{3} \\ 1 \\ 0 \\ \end{array} $	9 5 5 8 6 24 9 5 1	$ \begin{array}{r} 10.5C_4 \\ 0 \\ 8 \\ 1 \\ 5 \\ 14 \\ 10.5D_4 \\ 1 \\ 0 \\ \end{array} $	9 10 5 6 7 28 9 1 0	Lithium Nitrate C_2 , C3, C4, Best Molybdate D_a
10.5 0 0 0 0 0 10.5 0 0 0	$ \begin{array}{ccc} C_1 & 9 \\ 1 \\ 1 \\ 0 \\ 2 \\ D_1 & 9 \\ 1 \\ 5 \\ 0 \\ \end{array} $	$ \begin{array}{r} 10.5C_2 \\ 1 \\ 6 \\ 0 \\ 8 \\ 14 \\ 10.5D_2 \\ 6 \\ 1 \\ 1 \\ \end{array} $	9 0 10 0 6 16 9 10 6 6	$ \begin{array}{r} 10.5C_{3} \\ 1 \\ 0 \\ 5 \\ 0 \\ 6 \\ 10.5D_{3} \\ 1 \\ 0 \\ 5 \\ \end{array} $	9 5 8 6 24 9 5 1 8	$ \begin{array}{c} 10.5C_{4} \\ 0 \\ 8 \\ 1 \\ 5 \\ 14 \\ 10.5D_{4} \\ 1 \\ 0 \\ 0 \\ 0 \end{array} $	9 10 5 6 7 28 9 1 0 0	Lithium Nitrate C_2 , C3, C4, Best Molybdate D_a Result pH = 9

The above combinations, (see Table I on previous page) based on a statistical design (Greco Latin Squares), offers the potential to evaluate the inhibiting effectiveness of various Li-salts in a reasonably short time. With 16 electrolytes, it in effect enables us to collect data on 256 (4⁴) experiments that would have been necessary using each electrolyte singly.

The following electrochemical tests have been performed: (a) open circuit potential (ocp) versus time measurement and (b) potentiodynamic polarization measurement. The first test is the most basic electrochemical corrosion test. It monitors the electrode potential (E-volts) of a metal sample with respect to a reference electrode as it freely corrodes in an electrolyte. The value of the potential when analyzed on the basis of Pourbaix potential -pH (E-pH) diagrams provides valuable information on the electrochemical nature of the metal surface, whether it is active, passive, immune or transpassive in the corroding electrolyte. The potential in the present study was measured until it reached a steady-state value. The time to reach a steady-state potential varied in different electrolytes as this potential is controlled by several anodic and cathodic reactions. The potential was measured with respect to a saturated calomel electrode (SCE).

Following the above measurement, the second test was performed. The procedure for this test was as follows. At the beginning, the potential of the alloy was maintained at 500 MV more negative than the measured steady-state potential (OCP) for 10 minutes. Then polarization was begun at a scanning rate of about 10 mV/sec and stopped at a potential of +500 mV above the OCP. This procedure was chosen to characterize the nature of the metal surface within a range of potentials close to its freely corroding conditions. The resultant polarization curves yield numerical parameters such as corrosion potential, corrosion rate, passive current density, passive potential range, breakdown potential, etc. These parameters can be used to compare the effectiveness of various inhibitor systems used.

Only partial analysis of the voluminous amount of data generated has been accomplished to date. A brief discussion of this analysis is presented here to give an overview of our findings and to highlight the significance of the electrochemical corrosion work.

Referring to the OCP-time plots, Appendix B, in all inhibitor systems, time dependent excursion of potential in the positive direction has been noted. Such excursion is an indication of a reaction layer (passive film) on the alloy surface. However, the rate of passivation as determined by the change in slope of the OCP-time curves is different in different systems. Also different is the relative change in potential with time in different systems suggesting that some systems are more effective than others in passivating the alloy surface. In general, the OCP's of the allowed in different electrolytes stayed within the range of -1.3 to -0.9 V(SCE). Two exceptions were noted in electrolytes #62 and #67 suggesting that these electrolytes are more effective passivators.

Referring to Appendix B, it should be noted that each E vs Log I plot consists of both cathodic and anodic segments. The transition from cathodic (no corrosion) to anodic current occurs at the corrosion potential, E corr. While each segments of the curve will be analyzed carefully in future studies, for the purpose of initial screening, anodic current at +200mv above respective corrosion potentials (ECORR) has been used for comparative evaluation of various inhibitor systems.

The passivity of the alloy in all electrolytes at or close to its respective corrosion potentials has been reflected in anodic polarization curves in Appendix B. Alloys that are passive display current densities that remain more or less steady over a range of potential. This leads to a near vertical current density profile within a range of potentials in the anodic range. As shown in Appendix A, the current density (passive) for various inhibitor systems covered a wide range (from 1.1 to 464.2 μ A/cm²). In passive systems, lower the passive current, more stable and protective is the passive film. Passive films associated with anodic current density larger than 10 μ A/cm² are not considered to be suitable for corrosion protection. Based on this preliminary analysis, several inhibitor systems with passive current sensitizes in the range of 10uA/cm² appear to be promising.

The data is presented in Appendix A and summarized in Table II on the following page.

The Table indicated the concentration of each salt, the passivation current, the pH of the solution and the score regulated to each test solution.

A=Li2CO3 B=Li3C6H5O74H2O C=LiNO3 D=Li2MoO4

۵

All Unit = Mole/L A1=0 B1=0 C1=0 D1=0 A2=0.C B2=0.09 C2=0.0 D2=0.01 A3=0.C B3=0.15 C3=0.1 D3=0.02 A4=0.C B4=0.25 C4=0.2 D4=0.03

Score: $1 \sim 5 = 10$ 30 ~ 50 = (200 ~ 300 = 2 $6 \sim 10 = 9$ 50 ~ 70 = (300 ~ 400 = 1 $10 \sim 20 = \epsilon$ 70 ~ 100 = 400 ~ 600 = 0 $20 \sim 30 = 7$ 100 ~ 200 = 3

			Inhibito	r Syster	m					Corrosion	Potential (Current at	OCP+200	Score
ID#	Ph		A		В		С		D	Time (sec	E (Volt)	E (mV)	l (uA)	
34	10.5	A1	0	B1	0	C1	0	D1	0	1800	-1.199	-1186	58	5
35	10.5	A1	0	B2	0.09	C4	0.25	D2	0.01	1800	-1.319	-1220	176.5	3
36	10.5	A1	0	B3	0.15	СЗ	0.15	D3	0.02	1200	-0.927	-540.8	21.25	7
37	10.5	A1	0	B4	0.25	C2	0.09	D4	0.03	1800	-0.96	-616	22.93	7
38	10.5	A2	0.018	B1	0	C2	0.09	D2	0.01	1800	-1.163	-1039	4.797	10
39	10.5	A3	0.03	B1	0	C3	0.15	D3	0.02	1200	-0.888	-801.1	6.117	9
40	10.5	A4	0.05	B1	0	C4	0.25	D4	0.03	1500	-0.7827	-766.1	5.608	9
41	10.5	A2	0.018	B2	0.09	C1	0	D3	0.02	1800	-1.079	-992.2	503.8	0
42	10.5	A3	0.03	B2	0.09	C2	0.09	D4	0.03	1800	-0.9762	-689.2	56.18	5
43	10.5	A2	0.018	B3	0.15	C4	0.25	D4	0.03	1800	-0.9008	-482.2	2.941	10
44	10.5	A4	0.05	B2	0.09	C3	0.15	D1	0	1800	-0.9094	-628.6	5.008	10
45	10.5	A3	0.03	B3	0.15	C1	0	D1	0	1200	-1.233	-1142	464.2	0
46	10.5	A4	0.05	B3	0.15	C2	0.09	D2	0.01	1800	-0.9329	-630.6	33.55	6
47	10.5	A2	0.018	B4	0.25	C3	0.15	D1	0	1200	-0.9476	-678.2	102	3
48	10.5	A3	0.03	B4	0.25	C4	0.25	D2	0.01	1800	-0.9171	-462.7	18.25	8
49	10.5	A4	0.05	B4	0.25	C1	0	D3	0.02	1800	-1.126	-992.9	249.6	2
51	10.5	A4	0.05	B4	0.25	C3	0.15	D4	0.03			-1136.9	95.13	4
52	10.5	A3	0.03	B2	0.09	C1	0	D4	0.03	1000	-1.289	-1249	237	2
53	10.5	A4	0.05	B2	0.09	C4	0.25	D1	0	1000	-1.27	-824.6	8.714	9
54	10.5	A2	0.018	B3	0.15	C3	0.15	D4	0.03	1000	-1.292	-1288	232.9	2
55	10.5	A3	0.03	B3	0.15	C2	0.09	D1	0	1200	-1.303	-768.9	2.286	10
56	9	A1	0	B1	0	C1	0	D1	0	1000	-1.1	-1049.2	12.54	8
57	9	A1	0	B2	0.09	C4	0.25	D2	0.01	1000	-0.9061	-485.5	1.726	10
58	9	A1	0	B3	0.15	СЗ	0.15	D3	0.02			-433.4	8.531	9
59	9	A1	0	B4	0.25	C2	0.09	D4	0.03	1000	-1.01	-896.2	331.2	1
60	9	A1	0	B4	0.25	C3	0.15	D4	0.03	4100	-0.918	-329.7	15.09	8
61	9	A1	0	B4	0.25	C1	0	D4	0.03	1000	-1.148	-1058	146	3
62	9	A2	0.018	B1	0	C2	0.09	D2	0.01	23850	-0.699	-519	1.111	10
63	9	A2	0.018	B2	0.09	C1	0	D3	0.02	1800	-1.044	-740.3	45.69	6
64	9	A2	0.018	B3	0.15	C4	0.25	D4	0.03	1800	-0.9096	-441	7.053	9
65	9	A2	0.018	B4	0.25	C3	0.15	D1	0	1583	-0.891	-325.7	6.536	9
66	9	A2	0.018	B3	0.15	C1	0	D4	0.03	1800	-1.085	-987.5	134.2	3
67	9	A3	0.03	B1	0	C3	0.15	D3	0.02	1800	-0.6559	-293.2	2.941	10
68	9	A3	0.03	B2	0.09	C2	0.09	D4	0.03	1800	-0.9611	-744.5	111.4	3
69	9	A3	0.03	B3	0.15	C1	0	D1	0	1800	-1.06	-984.4	198.5	3
70	9	A3	0.03	B4	0.25	C4	0.25	D2	0.01	1800	-0.9232	-319.1	4.822	10
71	9	A4	0.05	B1	0	C4	0.25	D4	0.03	1800	-0.773	-268.8	3.055	10
72	9	A4	0.05	B2	0.09	СЗ	0.15	D1	0	1800	-0.897	-312.6	4.441	10
73	9	A4	0.05	B3	0.15	C2	0.09	D2	0.01	1800	-0.967	-407	4.141	10
74	9	A4	0.05	B4	0.25	C1	0	D3	0.02	1800	-1.095	-1001	321.6	1

CONCLUSIONS

The lithium salts passivate aluminum. They can be a viable substitute for chromium in corrosion preventive systems. They can be used in small quantities as a pigment substitute. The aluminum-lithium provides a base for minimal amounts of corrosion inhibitors as nanostructural cores or bases of other systems.

Two patent applications are being prepared and two more are planned and will be pursued if data supports the theory.

Delays due to flooding in the city and equipment problems have caused the schedule to slip about three months, however, when the work proceeded as planned, the results continued to be positive.

Since the scope of this project is limited to demonstration of a suitable system, the goal is still achievable.

RECOMMENDATIONS

(1) <u>Continuing Pigments</u>

The fundamental goal is to find the optimum pigments. Many possibilities exist. Experimental data will be continuously gathered.

Proposed:

- 1. Electrochemical Tests of Promising Systems
 - (a) Determination of corrosion rates by polarization resistance and Tafel-slope measurements;
 - (b) Cyclic polarization tests to determine pitting and protection potentials.
- 2. Optical and Scanning Electron Microscopy for characterization of the morphology and adherence of passive film.
- 3. Energy Dispersive X-ray Analysis for characterizing the chemical nature of the passive film.

(2) <u>Argon Oven</u>

An argon oven will be used to generate Lithium-rich surfaces.

(3) Surface Analysis

Surfaces will be analyzed to verify the results. Various reactants will be added to the lithium at the surface.

(4) Formulate Simple Paint

Pigments will be produced in the Argon Oven with subsequent reactions on the surface. A simple latex paint will be made and extensive tests at EuroNavy USA will be planned with Navy coordination.

(5) <u>Reports</u>

Reports will be prepared as indicated on the schedule.

												_			_			+				+	+	T
		+		+	╋	+							-			-						_	+	T
				E DESI	1 TS	+-		-					_					+		+		+	+	T
						-							+		+		+					+	-	1
TOTAL DECIENTION	NEVDENEN	NON-T		MENT S	TITSAUS	UTE FOR	CHRON	ALUM				_	-					YEAR			+	╉	+	T
AL DAECH FROJECT NO. 1	IN PRIME	R FOR A	TUMINU	M SUB	STRATE			┝╌┥					-+-	-+-	-+-	+	+	+-				+	-	
				_			-						+	+-	+								_	
								8	DDELAY				+	+	+-		+							
				-				>	>			- Ajrif		Nugust	S S	tembe	-	October	2	Vovembe	<u>,</u>	December	5	tatus
Schedule	January	Febr	ary C	Marc	¢		6	A III	5	4 1 2	8	1 2	3 4	1 2	3 4	1	4	7	3	7	3	1 2	4 10	
WEEK	1 2 3	4	2	4	2 7	┛	0 4) 1					 										
				-+	-	+				-			+											T
ATP				-	+		+		-	-										-	-	-		
		+	-	+														-+					+	
CONTACT SUPPLIERS BY PHONE		-						-							+	+	+	+		+			+	Τ
DEDECOMULATED AT DE SUBVEY OF SMILAR STUDIES									+	+	+		+		+			1						
									-		+													
STUDY LITERATURE			+						+-	+												-		
		+	+		-														-				+	
ORDER ANY OTHER PROMISING INHIBITORS					_													+		+				T
TTTTC															+	+	Ŧ	1	T	-				
PREPARE SUREENING 15313													-			1			-	-				
PERFORM RATING BY ELECTROCHEMISTRY												-	-		-									
	-	+		-	T	T	+	+												-			-	
		+		1	T																+			T
TREAT PIGMENTS				1	T											_			-			+		Ι
															+				-					Ι
ANALYZE LITHIUM SALIS & MEIALS										_	-	_	_	+	+			-				-		
SELECT & ORDER INHIBITORS										-					-			-	-					
					-				-		-	-	_			-	-						-	
SELECT & ORDER METALS FOR TEST PANELS				+					-															T
			-	-																		+		
TEST PANELS & PROPOSED MECHANISMS										_				-	+		-			-			-	
VERIEY THEORY & RELATE TO MILL SPECS							-			+														
				T				+	-														-	
PREPARATION & SUBMIT PHASE II TEST PLAN															+									
COOPDINATE TEST DI AN										-	+	+	+											
										+			+-											
INTERIM REPORTS				-											-									
NOTE: MONTHLY PROGRESS REPTS DUE.							$\frac{1}{1}$					-	-					_	_	_				
				+														-						
PREPARE FINAL REPORT				+	+													$\frac{1}{1}$	-	-				
						ŀ																		
											-	-	-											

					Finish	3/96		5/96		11/96		7/96		11/96		3/96		10/96		3/96		3/96	96/6						
		t	T	atus	art	φ		l g		g		g		l g	t†	ģ	T	8		99		é	y c		Π				Ħ
		_		5	お	ų,		lõ	 	ž		ø	-	ž		7/5	 	3/6		1/6		2	200	i	Ĺ				Ц
	ļ	-			4			╢-	╢	╢											<u> </u>		_					4	
				be	3		4	μ.	╢_														_	1.			ē	e	
		1		Ee m	~			∥_	1	[[Ĕ	2	
				ది	-			11	╢																		ě	-	
					4																							4	Π
				ē	m										1												Þ	m	
				emb	2															Π	Ι			Π			Ē	2	Π
				§	÷	Π		Π	Π															П			Ž	7	Π
					4	Π											Π				T			Π				4	П
Π		Π			m			t –	11-								Π						+	Ħ				~	П
				Ā	2			fi-	#					Ī			Π	Π					\uparrow	H			þ	~	Η
				8	Ţ	Н	1	11-	11-								Η				t		+	[]			5	_	Η
				Ŭ	4	Η	+	╢╌	╢								\square	\square		+	\mathbf{T}	+	+	\mathbb{H}		Ť		4	H
Η		$\left \right $		7	6	H	+	╟─	\parallel			$\left - \right $	\vdash				$\left \cdot \right $	+	Η	+	+	+	+	╞┼	-		2	1	Н
Н		$\left \cdot \right $	\vdash	đ		H	+	╟─	#-		$\left \right $	\mathbb{H}	+		\parallel	$\left - \right $	$\left \cdot \right $	+	+	+	\vdash	$\left \right $	-	┢┼	\neg		å	~	Н
\vdash		H	$\left \right $	epte	E	$\left \cdot \right $	-	╟─	╢		\parallel	$\left\ \cdot \right\ $	+		₩	H	H	H	+	+	$\left \right $	$\left \cdot \right $		⊢∤	\dashv	\neg	epte	+	Н
Η	-	$\left \right $	\parallel	Ō	Ŀ	$\left \cdot \right $	╀	╂	╫		+	+	╀			$\left \right $	H	+	+	+	+		-	\vdash	-	-	<u>v</u>	-	H
\square		H	Н	-		\mathbb{H}	+	╟			$\left\ \cdot \right\ $	\parallel	-				$\left \cdot \right $	$\left \cdot \right $	\square	+	\mathbb{H}			┞┤	-		-	4	Н
\vdash		\parallel	Ц		5	$\left \cdot \right $	+	₩			$\left - \right $	$\left \right $	+		μ		$\left \right $	+	$\left \right $	$\left \right $		-		⊢∤	_		-	۳ ۳	Ц
Ц	_		Ц	snBi	~		-	₽		\parallel	\parallel		\vdash					$\left - \right $	$\left \right $				+-	\square	_		Snb	2	\square
Ц	<u> </u>	Ц	Ц	¥	Ē	\square	+	╢					-						\square		 		-	\square			₹	7	Ц
_			_		4	$\left \right $		μ.	 .						-		$\left - \right $				\vdash		+	⊢∔	\neg		-	4	
					e	H	-						-		-	-					-		_				-	6	
				٢	2				μ									$\left \right $	\square		.						1	~	
				١u	-		-		∥	4_											ļ		_				3	-	
_					4												\square											4	
			_		3				1									\square										ო	
					2																							~	
				Jun	-																						ĥ	←.	
					4																							4	
					З												Π	Π										3	
					7	Π	Γ						Π			Π	Π						Т	Π				2	\square
	Å			May	*	Π																		Π			May	-	Π
	Y				4					Π				T				Π					T	Π				4	П
	NO				ო						Π		\square					\mathbf{T}						Ħ				3	Н
	Ň				2	Ħ											Ħ	Ħ			Π		╈	H	-			~	Н
	•/			April	-								-		-			+			Η		+				5	+	Н
	SE			-	4												\uparrow	\uparrow			Н							4	Η
	¥			-	m	\uparrow	\mathbf{H}	t			$\left \right $	\uparrow					\uparrow				Η				-	+	+		Н
	<u>a</u>			£	3						$\left \right $					╟╢	†		+					H	\neg	+	╞	7	Н
	监		-	Aano	-						┼┥	+	+		+		$\left \cdot \right $		+	+	Н	+		\vdash	+	-	larci	╞	Н
-	8	\vdash		2	4		+-				$\left \cdot \right $	╞┤	\square		\parallel	$\ $	H		┼┤	+	H			H	+	ł	4	╡	Н
-	Σ	Η	-	-			\vdash		\parallel		+	┼┤	H		$\left \right $	+	┟┤	┼┤	+	$\left \cdot \right $	H		+	\mathbb{H}	+	+	+	_	Н
-	51#	$\left \right $		<u>P</u>	~		H		$\ - \ $	$\left \cdot \right $		$\left \cdot \right $	H	Η	$\left - \right $		\vdash	╀┦	+	+	+		+	⊢┤	+	+	ž	+	Н
┥	Ř	\mathbb{H}	-	enc			$\left \cdot \right $		\parallel	$\left \cdot \right $	$\left \cdot \right $	H	H	\vdash	$\left - \right $	$\left - \right $	┝┤	╞┤	$\left \cdot \right $	┝┤	H		╋	┝┤	+	-	립		Н
+	Å	$\left \right $	-	ш			H	╟─	\parallel	$\left - \right $	$\left \cdot \right $	$\left \cdot \right $	$\left \cdot \right $	$\left \right $	$\left \right $	$\left \cdot \right $	$\left \cdot \right $	┝┤	┿┥		$\left \cdot \right $		+-	H	-	-	щ	+	Н
-	입	\vdash	-		4		H	\parallel	\parallel	$\left - \right $	+	$\left \cdot \right $	Η	$\left - \right $		$\left - \right $	┝┥	┝┤	+		Н		+	\vdash	+	\rightarrow	4	4	Н
	CRN	μ	-	2	() ()		\mathbb{H}	ş			+	╀┦	\mathbb{H}			+	\square	$\left \cdot \right $	$\left - \right $		H			$\left - \right $	-	+	ᅱ	"	Н
_	ŏ			nLa	~		-	E			$\left \right $	$\left \right $			$\left \right $						$\left \right $	_	-	_↓	_		a l	~	Н
_	-		-	ц,	÷		-	1 E		E	$\left \cdot \right $	$\left \cdot \right $		\square	$\left \right $	$\left \cdot \right $	$\left \cdot \right $	\square	+		$\left - \right $	+		╟╌┤	\downarrow		Ja	7	\vdash
					Nee			18		D PA		Ę				8													Ĺ
1								MEN		l 🗒		F PA		╞		Ĕ				NTS			s						
				Ing		ន		SPIG		SEL		13 O		PAIL		N Q				OME			YSE.			Ĕ			
				췽						SOF		TES		L E		Ē		The second secon		₽ P		<u>S</u>	AM			EPC			
						NN		B		TEST		No.		E)FAC		RM		Z		Ó X	ACE		RTS	L R			
			1			OBTA		TEST		8		1×		핕		MAN		Ē		S		ARGC	SURF		Ĕ	LIN'			1
		_			_					1.77											. 1	~1			-1				

•

						EVDENS	VE NON.	TOXOT	CMENT	SUBST1	ITUTE FL	OR CHR	MUMO				_	_							T
		+	+	+			IN PR	MERFOI	R ALUMI	NON SU	BSTRA	ų				_				-				+	Т
															-		+								T
			Ļ						-					_									-		Г
						SEC	OND YEA	IR TIMEL	JNE RES	2012		FAR 19	8					+							Τ
		1	1								-								$\frac{1}{1}$					-	1
		-		-		BCRM	LC PROJ	ECT #1	DAECH	PHASE		AMEN	DED								-		+		1
		+	-										-+						Ŧ						Т
							-	-		+		+	+									-			
			-	-					+			╞			1	a a	amhar	č	toher	Noven	ber ber	Decembe	 	Status	
Schedule	January		ebruary		March		5		Na l					₹ °	Ven V		3 4	-	3 4	1	4	1 2	8 4 Stal	rt Finish	c
WEEK	1 2 3	4	2 3	4	2 3	4	2		2						<u>}</u>								395	6	1
						+			_	+		+					-								
OBTAIN VEHICLES					+		╪	+	╞	+	+-														
	-						+			+														-	
TEST VEHICLES/PIGMENT COMBINATIONS								+			+														
						-																			
LAB TESTS OF SELECTED PANTS														-							_		-		
	-				+	+																			
PHYSICAL TESTS OF PAINT						+			+	╞		+		-		-									1
			+	+		+					÷													-	
FIELD TEST OF PAINT							+		╞	+	+									-	-				1
								+	1		╞												-	-	
MANUFACTURING METHODS		+	+			+	+	+	+	-												-			
		-				+	+-			\downarrow		╞			H							+			
REFORMULATE		T				t		╞		-							-					+		+	
					+		╞	+-							-	-		_		-	-	-		+	
	-	T			+														_				+	+	1
CONTINUE PIGMENT TESTS											-											+	-	-	ł
							+										_			_	_			+	ł
REPORTS					+		┼										_			-	-	-			
			T				╞	+		-	-								-		+				
						+	+-						-					+				10000			
PREPARE FINAL REPORT			Coheren		March	F	And		Mav		June		- Anr	▼	uquist	\$	20 mper			BV04	BOU				
					5 6	T-	6	+	2 3	4	2 3	4 1	2 3	4	2 3	4	2	-	2		2		7	+	L
	0	*	4	1	7	•	,						-		-		_	-			-		-		
					-																				

REFERENCES:

A NERAC search (NERAC, Inc. - One Technology Drive, Tolland, Connecticut, 06084) was run in 1992. A more current search has been performed as a part of this program. Additionally a mail-out was made to about one-hundred and twenty five manufacturers of corrosion resistant coatings and treatments. At the time no products to substitute for chromium were found in the mailout. The literature search produced the following documents which I have on hand.

- (1) "The measurement of lithium depletion in aluminum-lithium alloys using X-ray diffraction"; P. Holdway, A. W. Bowan (1989).
- (2) "On the Mechanical Properties and Stress Corrosion Resistance on Ternary Al-Cu-Li and Quaternary Al-Li-Cu-org Alloys," R.C. Dorlard, 1986.
- "Influence of Aging at 200° C on the Corrosion Resistance of Al-Li and Al-Li-Cu Alloys,"
 C. Kuwal et al 1989.
- (4) "Stress Corrosion Cracking Behavior of an Al-Li-Cu-org Alloy," R.C., Dorward and K.R. Hasse, 1987.
- (5) "Alcoa Alloy 2090," by Ray M. Hart, 1988.
- (6) "Influence of Lithium on the Corrosion of Aluminum," Jing Gui and T.M. Devine, 1987.
- (7) "Tougher Aluminum-Lithium Alloys," Donald Webster and Clive G. Bennett, 1989.
- (8) "An Insight Into the Corrosion Behavior of Aluminum," H.P. Goddard, 1981.
- (9) "Corrosion Testing of Materials with Metallic and Inorganic Coatings," Sheldon Dean, 1986.
- (10) "Protective Finishes for Aluminum and Steel Alloys Subject to Sea Water Exposure on the SRB, Excluding the SRM," F. Key & C.B. Harrison Dwg 10AG05118.
- (11) "Considerations in Accelerated Testing of Anticorrosive Coating," Clive H. Hare, 1982.
- (12) "Applications for the Versatile Molybdate Inhibitor," Mark Vukasavich, 1990.
- (13) "Inhibition of Corrosion Fatigue in High Strength Aluminum Alloys," M. Khobail et al 1981.
- (14) "Soluble Silicate Corrosion Inhibitors in Water Systems," E.P. Katsanis et. al., 1986.
- (15) "Cationic-Film-Forming Inhibitors for the Protection of the AA7075 Aluminum Alloy Against Corrosion in Aqueous Chloride Solution," D.R. Arnott et.al. 1989.

- (16) "Stress Corrosion of Aluminum Alloys A Review" #1364/7608-64-0272 no further identification.
- (17) "Corrosion Inhibitors 22(1) Influence of pH, oxygen, added ions, type and concentrations of acids on the corrosion," Von L. Homer and K. Meisel (1978).
- (18) "Laboratory Studies of Galvanic Corrosion of Aluminum Alloys", Florian Mansfield and J.V. Kenkel (1976).
- (19) "Cathodic Protection of 6351 Aluminum Alloy in Sea Water: Protection Potential and Surface pH Effects," K.G. Watkins and D. E. Davies (1987).
- (20) "Cathodic Protection of Aluminum in Sea Water," R. Gundersen and K. Nisancioglu (1990).
- (21) "The Use of Soluble Corrosion Inhibitors for Aluminum Alloys," T.M. Salem, J. Horvath and P.S. Sidky.
- (22) "Corrosion of Aluminum in NaCl Solutions II Cathodic Protection," R. Narayen and K.P. Sheriff, Dept. of Chemistry, II+ Madras, India (1990)
- (23) "Corrosion Control", R. Heidersbach and J. Smart (1988)
- (24) "Navy Corrosion Overview", A.G.S. Morton, David Taylor Navy Center (not dated).

Some 60 papers have been ordered and received and studied. It will take some time to digest all of the data. Two investigators have been contacted by phone. All of the documents have been read once or twice and valuable information has been received. Briefly the most significant appear to be:

- 1. "Non-Chromate Talc Conversion Coatings for Aluminum". Paper No. 542 NACE Corrosion 94; R. G. Buchheit, C. A. Drewien, J.L. Finch; Sandia
- "Simple Source of Li Metal for Evaporators in Ultrahigh Vacuum.", J. Vac. Sci Technology A 12(6) No. 0/Dec 1994; F.J. Esposito, K. Griffiths, and P.R. Norton; Vor Guntario
- 3. "Surface Segregation of Lithium in Aluminum-lithium Alloys." Physics and Chemistry of Materials Treatment; G.G. Bondarenko and S.I. Kucheryaugi; Translation from Russian.
- 4. "Electrochemical Investigation of the Diffusion of Lithium in Beta-Lithium Aluminum Alloy at Room Temperature." N. Kumagai; Y. Kikuchi, K. Tanno; Iwate University, Japan.

APPENDIX A

6

0

6

0

•

This data rates the passivators from one to ten

MATRIX FOR BLENDING INHIBITORS EXPERIMENT MADE BY GRECO LATIN SQUARES METHOD **TABEL A-0**

Score 00000 20 2 ⋈ <u>ی</u> ۵ ø 00000400 σ 200 ~ 300 = 2 300 ~ 400 = 1 400 ~ 600 = 0 Current at OCP+200 mV(SCE)
 Interfer
 1765

 58
 58

 58
 58

 58
 58

 58
 56

 59
 56

 50
 56

 56
 56

 56
 56

 56
 56

 56
 56

 56
 56

 56
 56

 57
 56

 56
 56

 57
 56

 57
 56

 57
 56

 57
 56

 57
 56

 57
 57

 57
 57

 57
 56

 57
 57

 57
 57

 57
 57

 57
 57

 57
 57

 57
 57

 57
 57

 57
 57

 57
 57

 57
 57

 57
 57

 57
 111.4 198.5 4.822 3.055 4.441 4.141 4.141 321.6 **F (mv)** -1186 -1220 -2220 -2200 -2200 -2200 -2200 -2200 -2200 -2200 -2200 -2200 -2200 -2200 -22 30 ~ 50 = 6 50 ~ 70 = 5 70 ~ 100 = 4 100 ~ 200 = 3
 Corrosion Potential (Long term)
 Corrosion Fotential (Long term)

 Time (sec.)
 E (Volt)

 1800
 -1.199

 1800
 -1.319

 1800
 -1.319

 1800
 -1.319

 1800
 -0.927

 1800
 -0.927

 1800
 -0.926

 1800
 -0.926

 1800
 -0.968

 1200
 -0.926

 1800
 -0.9068

 1200
 -0.9068

 1800
 -0.90762

 1800
 -0.9762

 1800
 -0.9762

 1800
 -0.9762

 1800
 -0.9762

 1800
 -0.9762

 1800
 -0.9762

 1800
 -0.9762

 1800
 -0.9776

 1800
 -0.9329

 1200
 -0.9329

 1200
 -0.9171

 1800
 -0.9376
 -1.01 -0.918 -1.148 -1.148 -0.609 -0.609 -0.609 -1.085 -0.6559 -0.961 -0.9232 -0.9232 -0.9237 -0.9273 -0.967 -0.967 -1.065 -1.289 -1.27 -1.292 -1.303 -1.1 10 ~ 20 = 8 20 ~ 30 = 7 Score: 1 ~ 5 = 10 6 ~ 10 = 9 1000 110000 110000 110000 11000 11000 11000 11000 11000 11000 <u>8888888</u> D1=0 D2=0.01 D3=0.02 D4=0.03 C1=0 C2=0.09 C3=0.15 C4=0.25 B1=0 B2=0.09 B3=0.15 B4=0.25 ο υ A1=0 A2=0.018 A3=0.03 A4=0.05 0 0.15 0.15 0.25 0.25 0.25 0.15 0.15 0.15 0.15 0.15 0.25 0.25 0.25 0.25 0.09 0.25 0.25 All Unit = Mole/L Inhibitor System B B=Li3C6H5074H20 000 o o o തെ ۲ D=Li2MoO4 A=Li2CO3 C=LiNO3

õ

TABEL A-1 EXPERIMENTAL MATRIX SORTED BY COMPOUND A(Li2CO3)

Score vo66ww6wwwvo6666-6wwa4 00000 6 6 % 200 ~ 300 = 2 300 ~ 400 = 1 400 ~ 600 = 0 Current at OCP+200 mV(SCE)
 Final
 11.726

 1.726
 1.726

 1.726
 1.726

 1.726
 1.726

 1.726
 1.726

 1.726
 1.726

 1.726
 1.726

 1.726
 1.1264

 1.726
 1.1264

 1.726
 1.111

 1.726
 1.111

 1.7665
 1.111

 1.7665
 1.111

 1.7665
 1.111

 1.7665
 1.111

 1.7665
 1.111

 1.7665
 1.111

 1.7665
 1.111

 1.111
 1.111

 1.111
 1.111

 1.111
 1.111

 1.111
 1.111

 1.111
 1.111

 1.111
 1.114

 1.111
 1.114

 1.111
 1.114

 1.111
 1.114

 1.111
 1.114

 1.111
 1.114

 1.111
 1.114

 1.114
 1.114

 <t 30 ~ 50 = 6 50 ~ 70 = 5 70 ~ 100 = 4 100 ~ 200 = 3 **F (mV)** 485.5 485.5 485.5 485.5 485.5 485.5 485.5 485.5 485.5 485.5 485.6 41186 411 Corrosion Potential (Long term) Time (sec.) E (Volt) 1000 -0.9061 -1.1-1.148-1.148-1.148-1.148-1.148-1.148-1.1319-0.967-0.9061-0.90762-0.90762-0.90762-0.90762-0.90762-0.90773-0.70773-0.70773-1.126 1~5=10 6~10=9 10~20=8 20~30=7 80 D1=0 D2=0.01 D3=0.02 D4=0.03 C1=0 C2=0.09 C3=0.15 C4=0.25 B1=0 B2=0.09 B3=0.15 B4=0.25 A1=0 A2=0.018 A3=0.03 A4=0.05 All Unit = Mole/L $\begin{smallmatrix} 0 & 0 \\ 0.25 & 0.25 \\ 0.15 & 0.25 \\ 0.00 & 0.00 \\ 0.15 & 0.00 \\ 0.15 & 0.00 \\ 0.00$ Inhibitor System 0.09 £ 000 0000 00 B=Li3C6H5074H20 ៰៰៰៰៰៰<u>៰</u>666660 ៰៰៰៰៰<u>66666</u> ៰៰៰៰<u>៰</u>666666 0 ο ο ο ο Чd D=Li2MoO4 A=Li2CO3 C=LiNO3 #0

ຊ

TABEL A-2 EXPERIMENTAL MATRIX SORTED BY COMPOUND B(Li3C6H5O7*4H2O)

Score <u>666∞6</u>∞∞000066∞∞600∞∞066 200 ~ 300 = 2 300 ~ 400 = 1 400 ~ 600 = 0 Current at OCP+200 mV(SCE 11111 2.941 2.941 5.608 5.6117 5.6117 5.6117 5.618 5.614 5.614 5.614 5.614 5.614 5.614 5.614 5.608 5.608 5.608 5.608 5.608 5.608 5.608 5.614 5.608 5.6 (M) 30 ~ 50 = 6 50 ~ 70 = 5 70 ~ 100 = 4 100 ~ 200 = 3 -1039 -1039 -1186 -1186 -1186 -1245 -1246 -1249 -1248 -1249 -12488 -1248 -1248 -1248 -1248 -1248 -1248 -1248 -1248 -1248 -1248 -1248 E (mV) -519 -519 -268.8 -1049.2
 Corrosion Potential (Long term)

 Time (sec.)
 E (Volt)

 23850
 -0.689

 1800
 -0.689

 1800
 -0.689

 1800
 -0.656

 1800
 -0.773

 1800
 -0.773

 1800
 -0.773

 1800
 -0.788

 1500
 -0.786

 1800
 -0.986

 1800
 -0.906

 1800
 -0.906

 1800
 -0.906

 1800
 -0.906

 1800
 -0.906

 1800
 -0.906

 1800
 -0.906

 1800
 -0.906

 1800
 -1.27

 1800
 -1.27

 1800
 -1.27

 1800
 -1.27

 1800
 -1.27

 1800
 -1.27

 1800
 -1.27

 1800
 -1.27

 1800
 -1.27

 1800
 -1.27

 1800
 -1.27

 1800</ -0.9476 -1.126 0.9096 0.9096 0.9096 0.9096 0.9096 0.9096 0.9008 0.9008 0.9008 0.9027 0.9227 0.9222 0.9222 0.92232 0.92329 0.92329 0.92329 0.92329 0.926 0.9171 0.05 10 ~ 20 = 8 20 ~ 30 = 7 1 ~ 5 = 10 6 ~ 10 = 9 88 D1=0 D2=0.01 D3=0.02 D4=0.03 Þ c1=0 c2=0.09 c3=0.15 c4=0.25 B1=0 B2=0.09 B3=0.15 B4=0.25 0 0.25 0.15 0.15 A1=0 A2=0.018 A3=0.03 A4=0.05 C 0 All Unit = Mole/L Inhibitor System B=Li3C6H5074H20 P D=Li2MoO4 A=Li2C03 C=LiNO3

TABEL A-3 EXPERIMENTAL MATRIX SORTED BY COMPOUND C(LINO3)

Score ~ <u>6 6 6 0 6 0 0 0 0 0</u> 0 55 - 0055 - 0050о e 0 0 0 0
 Current at OCP+200 mV(SCE)

 E (mV)
 I (uA)

 -1049.2
 12.54

 -740.3
 45.69

 -987.5
 134.2

 -987.5
 134.2

 -987.5
 134.2

 -987.5
 134.2

 -987.5
 134.2

 -987.5
 134.2

 -984.4
 321.6

 -1001
 321.6

 -1148
 53

 -922.9
 503.8

 -1249
 237

 -922.9
 249.6

 -922.9
 503.8

 -1142
 4141

 -744.5
 1111.4

 -922.9
 503.8

 -1142
 1111.4

 -923.6
 503.8

 -1142
 1111.4

 -923.1
 1111.4

 -923.6
 503.8

 -1142
 1111.4

 -243.4
 8.531

 -325.7
 650.6

 -312.6
 53.6

 -325.7
 55.00

 -325.6
 50.08

 200 ~ 300 = 2 300 ~ 400 = 1 400 ~ 600 = 0 30 ~ 50 = 6 50 ~ 70 = 5 70 ~ 100 = 4 100 ~ 200 = 3 Corrosion Potential (Long term) Time (sec.) E (Volt) 1000 -1.1 1 ~ 5 = 10 6 ~ 10 = 9 10 ~ 20 = 8 20 ~ 30 = 7 $\begin{array}{c} -1.044\\ -1.148\\ -1.085\\ -1.085\\ -1.085\\ -1.085\\ -1.085\\ -1.085\\ -1.085\\ -1.085\\ -1.085\\ -1.086\\ -1.138\\ -1.01\\ -1.01\\ -1.01\\ -1.03\\ -0.957\\ -0.957\\ -0.9972\\ -0.897\\ -0$ 0.9476 -1.292 0.9061 -0.9232 -0.773 -0.773 -0.773 -0.773 -0.7827 -1.27 -0.9171 -0.891 -0.918 -0.9094 -0.888 -0.927 Score: 200 1000 1 1583 1200 1200 1200 D1=0 D2=0.01 D3=0.02 D4=0.03 C1=0 C2=0.09 C3=0.15 C4=0.25 B1=0 B2=0.09 B3=0.15 B4=0.25 00000 o 000 A1=0 A2=0.018 A3=0.03 A4=0.05 $\begin{array}{c} 0 \\ 0.15 \\ 0.025 \\ 0.025 \\ 0.015 \\ 0.02$ 0.2500 All Unit = Mole/L Inhibitor System m 0.00 B=Li3C6H5074H20 C=LiN03 ደ D=Li2MoO4 A=Li2C03 # <u>0</u>

EXPERIMENTAL MATRIX SORTED BY COMPOUND D(LI2MoO4) **TABEL A-4**

Score σ 200 ~ 300 = 2 300 ~ 400 = 1 400 ~ 600 = 0 Current at OCP+200 mV(SCE) E (mV) I (uA) 30 ~ 50 = 6 50 ~ 70 = 5 70 ~ 100 = 4 100 ~ 200 = 3 **F (mv)** -312.6 -325.7 -325.7 -312.6 -984.4 -984.4 -1049.2 -884.4 -1049.2 -884.4 -1049.2 -883.9 -1142 -1142 -1142 -1142 -1142 -1142 -1142 -1142 -1142 -1142 -1142 -1142 -1142 -1142 -1142 -1142 -1142 -1142 -1145
 Corrosion Potential (Long term)

 Time (sec.)
 E (Volt)

 1800
 -0.897

 1583
 -0.897

 1583
 -0.897

 1583
 -0.897

 1583
 -0.897

 1583
 -0.897

 1583
 -0.891

 1700
 -1.16

 1800
 -1.303

 1800
 -1.303

 1200
 -0.9476

 1200
 -0.9476

 1200
 -0.9476

 1200
 -0.9476

 1200
 -0.9476

 1200
 -0.9476

 1200
 -0.9061

 23850
 -0.69061

 1200
 -1.233

 1800
 -0.9061

 1800
 -0.90732

 1800
 -0.9171

 1800
 -0.9329

 1800
 -0.9329

 1800
 -0.9329

 1800
 -0.9329

 1800
 -0.9329

 1800
 -0.9171

 1800
 -0.9329
 </t -1.292 6 ~ 10 = 9 10 ~ 20 = 8 20 ~ 30 = 7 1~5=10 Score: 88 D1=0 D2=0.01 D3=0.02 D4=0.03 о C1=0 C2=0.09 C3=0.15 C4=0.25 B1=0 B2=0.09 B3=0.15 B4=0.25 0.15 0.15 0.09 0.15 0.25 0.25 A1=0 A2=0.018 A3=0.03 A4=0.05 0.15 0.25 0.25 0.15 0.25 0.25 0.25 0.25 0.25 0.15 0.15 0.09 0.15 0.15 0.15 0.09 0.09 0 All Unit = Mole/L Inhibitor System œ B=Li3C6H5074H20 C=LiNO3 Чd D=Li2MoO4 A=Li2C03 <u>に88884848446666884486888484454886468884466464688</u> # O

0

EXPERIMENTAL MATRIX SORTED BY SCORE TABEL A-5

Score:

Score თ S 0 mV(SCE) 1.111 1.111 1.111 1.126 2.2941 2.2941 2.2941 2.2941 2.2941 2.2941 4.444 4.444 4.797 6.513 8.536 6.536 6.536 6.536 6.536 6.536 6.536 6.536 6.536 6.536 7.053 8.708 8.717 18.25 21.25 21.25 21.25 21.25 23.33 18.25 21.25 21.25 21.25 21.25 21.25 21.25 23.33 16.63 17.63 8.714 17.63 8.714 18.25 21.25 22.93 23.56 23.56 11.11 12.64 12.64 12.64 12.64 12.65 12.64 12.64 12.65 12.65 12.65 12.65 12.65 12.65 12.65 12.65 12.65 23.05 25.05 25.05 25.05 25.05 25.05 25.05 200 ~ 300 = 2 300 ~ 400 = 1 400 ~ 600 = 0 Current at OCP+200 30 ~ 50 = 6 50 ~ 70 = 5 70 ~ 100 = 4 100 ~ 200 = 3 **F (mV)** -519 -519 -519 -519 -519 -519 -519 -283.2 -485.5 -485.5 -485.5 -482.2 -283.8 -482.7 -1039.2 -312.6 -1039.2 -312.6 -1039.2 -462.7 -462.6 -462.7 -462.7 -462.6 -462.7 -462.7 -462.6 -462.7 -462.7 -462.7 -462.6 -462.6 -462.6 -462.6 -462.6 -462.6 -462.6 -462.6 -462.6 -462.6 -462.6 -462.6 -462.6 -462.7 -462.6 -472.6 **Corrosion Potential (Long term)** E. Voit) -0.689 -0.689 -0.689 -0.689 -0.655 -0.967 -0.782 -0.989 -0.887 -0.7827 -0.7827 -0.888 -0.888 -0.888 -0.888 -1.27 -1.1 -1.1 -0.918 -0.9171 -0.927 -0.96 -0.9329 -1.044 -1.044 -0.9476 -0.9611 -1.148 -1.148 -1.148 -1.148 -1.148 -1.148 -1.126 1 ~ 5 = 10 6 ~ 10 = 9 10 ~ 20 = 8 20 ~ 30 = 7 Time (sec. D1=0 D2=0.01 D3=0.02 D4=0.03 C1=0 C2=0.09 C3=0.15 C4=0.25 899888999998989898898898898899989998989988 B1=0 B2=0.09 B3=0.15 B4=0.25 A1=0 A2=0.018 A3=0.03 A4=0.05 All Unit = Mole/L Inhibitor System m 0.01 0.02 0.03 B=Li3C6H5074H20 Ч D=Li2MoO4 C=LiNO3 # 0

24

A=Li2CO3

APPENDIX B

This set of curves established the open circuit potential (OCP) and indicates the passivation current level. Very low current flow is desired. A log scale is used for greater accuracy of current flow.



FIGURE B-1



FIGURE B-2




FIGURE B-4

0



.







.





















6



UKE D-19

















FIGURE B-27













_



ullet





•



FIGURE B-37






•







_



FIGURE B-44





•



-











Note: The original is of poor quality. The curves show comparisons of sets of mixtures of passivators. These curves have been included to show contrast on one page.



Note: The original is of poor quality. The curves show comparisons of sets of mixtures of passivators. These curves have been included to show contrast on one page.



Note: The original is of poor quality. The curves show comparisons of sets of mixtures of passivators. These curves have been included to show contrast on one page.



Note: The original is of poor quality. The curves show comparisons of sets of mixtures of passivators. These curves have been included to show contrast on one page.