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U.S. DEPARTMENT OF THE NAVY  
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NAVAL SURFACE WARFARE CENTER

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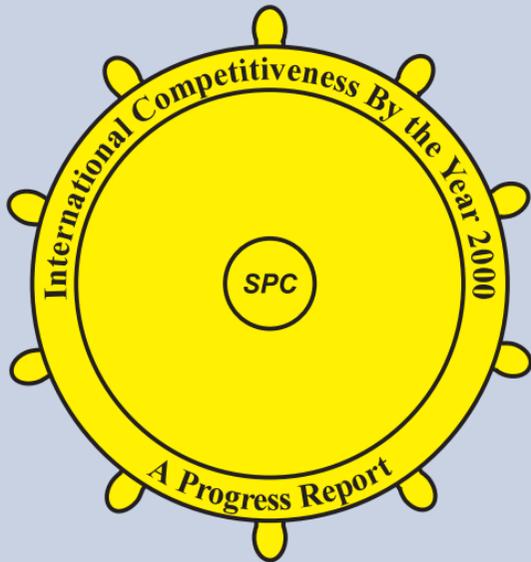
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**THE SOCIETY OF NAVAL ARCHITECTS AND MARINE ENGINEERS**  
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# Environmentally Acceptable Corrosion Resistant Coating For Aluminum Alloys

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## ABSTRACT

*A coating system is described that is based on passivation of aluminum alloys by application of Lithium salts as pigments. The resulting composition and morphology of coating films are discussed. Pigment selection applying Greco-Latin Squares statistical method to evaluate corrosion as a function of current flow on 6061-T6 test surfaces was performed. The test device is a potentiostat made by Princeton Applied Research. The pigment is an Aluminum-Lithium powder which has been surface enriched with Lithium by heating under an argon blanket and subsequently treated with the selected anions. The author calls this process "nanostructural inhibitors." The vehicle in this case is a lithium silicate inorganic water soluble matrix which becomes water insoluble upon drying. The vehicle is commercially available. Testing by an independent laboratory to ASTM B117 for 168 hours of scribed panels showed no corrosion on various alloy substrates with and without topcoats.*

*KEYWORDS: Coating system, passivation, aluminum alloys, potentiostatic selection, lithium salts, nanostructural inhibitors, lithium silicate.*

## INTRODUCTION

In the 1980's an alloy of aluminum which contained lithium was being considered as an alternate to the 2219 alloy used in aerospace since it offered about a 10% weight savings for the weight conscious designers. The product was available from France, Russia, and Australia. No American companies had pilot plant production at the time. The English were producing some small scale aluminum/lithium alloys. They could be riveted, but welding was limited by the volatility of the lithium. Some applications required welding, such as hydrogen gas tanks, where riveting was not sufficient to contain the gas molecules. This was not considered a limitation but rather a challenge to the engineers.

Another potential problem was the reactivity of lithium. As the lightest of the alkali metals, it was assumed that the alloy would exhibit some of the reactivity characteristics of sodium metal. This was especially a concern by the corrosion engineers.

However, to their surprise, when similar alloys with and without 3% by weight lithium were tested, the one with lithium proved to be more corrosion resistant.

Chromium compounds provide outstanding corrosion protection for 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 replacement 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.

Ships require primers for aluminum which can be applied by shipboard 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.

Buchheit [1] reported that lithium carbonate in solution protects certain metals, particularly aluminum, from corrosion by reacting at the surface. Analysis by a Secondary Ion Mass Spectrometer (SIMS) confirms this phenomena. Sodium carbonate and potassium carbonate reactions produced a soluble product and no alkali was 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.

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 by briefly heating the alloy 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. 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.

### TEST PROCEDURE

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

The instrument was installed and qualification tests per ASTM G-3 and G-5 [2] were performed to ensure the proper function.

A series of chemicals was selected and purchased for the passivation tests. Substrate aluminum panels were selected. Some aluminum-lithium was ordered in both powder and plate form. Some vendors are reluctant to send certain aluminum-lithium products since they are considered confidential.

The American Conference of Governmental Industrial Hygienists in their 1994-1995 "Threshold Limit Values for Chemical Substances and Physical Agents and Biological Exposure Indices" [3] does not list lithium compounds as particular problems, 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 Threshold Limit Values (TLV) list.

Generally, the lithium compounds are not considered toxic, depending on the anion. Lithium hydride, lithium hydroxide, lithium fluoride, lithium 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 the salts such as acetate, benzoate, borate, carbonate, lactate, nitrate, and sulfate are commercially available and regarded as environmentally acceptable. The overall toxicity is determined when the final formula is selected. The paint vehicles were chosen from those which are environmentally most acceptable.

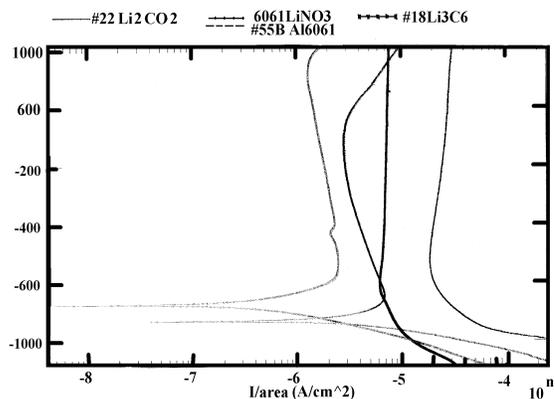
Aluminum-lithium powder is a fundamental material studied in this project. It is available from several sources but most require orders of substantial quantities. One source confirmed that patents being sought by manufacturers create some limits. The material is commercially available, but quantities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

### INHIBITORS

A variety of lithium salts were selected and ordered as potential pigments which would not present a pollution problem. The objective was to suppress corrosion of aluminum and possibly steel with a satisfactory substitute for chromium to avoid environmental problems.

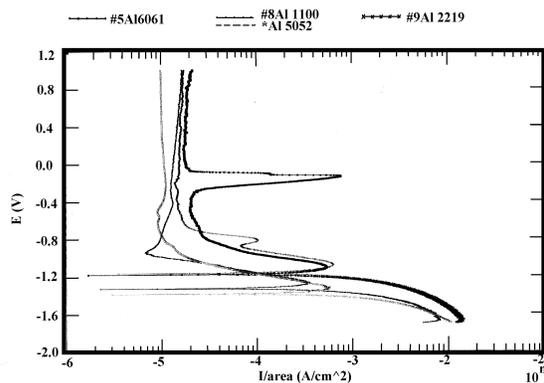
Such materials as lithium molybdate, lithium nitrate, lithium carbonate, lithium formate, lithium acetate, lithium sulfate, lithium citrate, and lithium hydroxide were included. All of these salts of lithium passivated to some extent. Combinations were sometimes more effective than the individual components. To optimize the combination of these salts for corrosion suppression, "Greco-Latin Squares" statistical methods were used. Figure 1 shows a curve comparing the individual passivators versus the

blend. Generally, the less current that flows the less is the

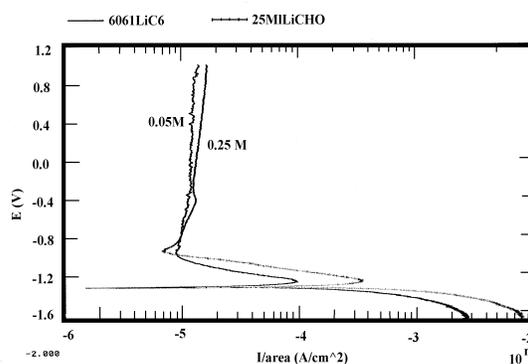


**Figure 1.** Anodic polarization curves (from left to right) for aluminum alloy AL6061 in 0.05 M/l blend solution,  $\text{Li}_2\text{CO}_3$ ,  $\text{LiNO}_3$  and  $\text{Li}_3\text{C}_6\text{H}_5\text{O}_7$  (lithium citrate) individually.

corrosion. Notice the abscissa is exponential and the curve to the left has considerably less current, hence less corrosion.



**Figure 2.** Anodic polarization curves (from left to right) for different aluminum alloy Al 5052, Al 6061, Al 1100 and Al 2219 in lithium citrate 0.05 Moles.



**Figure 3.** Anodic polarization curves (from left to right) for Al 6061 in 0.05 Moles lithium citrate and 0.25 Moles lithium citrate.

Most of the tests were run on 6061-T6 aluminum. Other alloys were tested to determine if they could also be passivated. The high copper content of the 2000 series aluminum alloys makes

them susceptible to pitting corrosion and are, therefore, difficult to passivate. Figure 2 shows some results.

Concentrations of the salts within limits do not exhibit a large influence on short term passivation as indicated in Figure 3.

### NANOSTRUCTURAL INHIBITORS

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 ten-thousand interior atoms, the amount of passivating chemical can be much less. A patent application is also being prepared on this concept, called "nanostructural inhibitors."

Two phenomena occur which can be adapted to pigments. First, the lithium near the surface provides galvanic protection. Secondly, the lithium on the surface is very reactive and it can be a source for passivating salts of lithium.

The heated surface of the aluminum alloy is up to 90% lithium. For each surface atom there are 5,000 or so inside the paint pigment particle.

### SURFACE MICROSCOPE

Surface inspection of the aluminum lithium alloy panel and treated aluminum lithium alloy panels provides evidence of reaction products and film quality. The nature of the oxides and hydrates and salts becomes apparent. Figure 4 shows the bland surface of the aluminum lithium alloy. Figure 5 shows the formation progress on these analyses.



Figure 4. Scanning electron micrograph of the bland surface of the aluminum lithium alloy.

### PAINT VEHICLES

The next phase of this work was to incorporate the pigments into paint vehicles. The scope of such a project was very broad and it was necessary to try a few vehicles and select one which satisfied the overall goal: which was to formulate a paint which was essentially non-polluting and which would protect aluminum from ocean water. Latex, epoxy, solvent cast, and

inorganic vehicles were considered. The selected was the inorganic

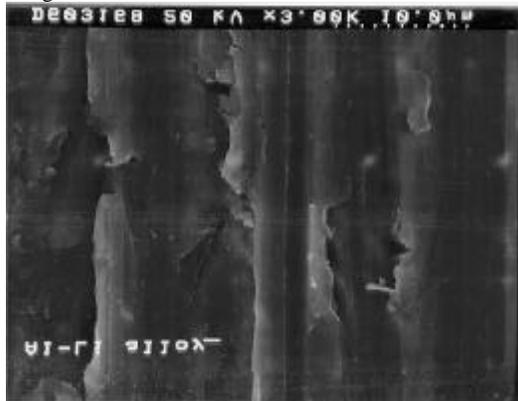


Figure 5. Scanning electron micrograph of the oxidized

lithium silicate "Lithsil-6" of FMC Corporation. It is water based and commercially available. It becomes water insoluble and it has good adhesion to metal after cure and drying. It resists heat and ultraviolet and is relatively inexpensive.

The solutions are relatively non-toxic, but they are alkaline.

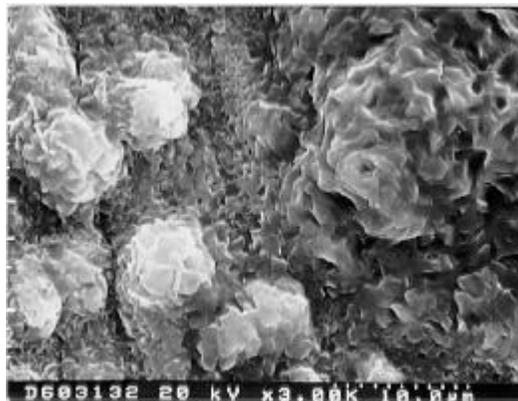


Figure 6. Scanning electron micrograph of the oxide formation following the 350C

When aluminum lithium powder is used as a pigment, the coating is light in weight. Zinc filled coatings such as Carboline's<sup>4</sup> inorganic zinc primer are recommended for steel and under some circumstances other metals. The success of these coatings is predicated on galvanic protection, but the zinc is less electronegative than most aluminum alloys. Lithium is the most electronegative metal and can protect aluminum, but the reactivity limits the use of the pure metal.

The aluminum lithium alloy is heated to drive the lithium to or near the surface. The surface lithium, which is heated under an argon blanket, is metallic but the oxides, hydroxides, and salts form rapidly on the surface. The heated powder reacts rapidly if it is immersed in water.

However, the lithium which has migrated toward the surface but not on the surface is available for galvanic protection. The surface lithium is available for salt formation and passivation. The lithium silicate generates the glass vehicle and alkaline lithium oxides or salts, much of which can be washed from the surface.

The Carboline base material with zinc and aluminum pigments was compared to the lithium silicate base.

The constituent range for the lithium silicate paint varied, but generally had the following formula:

Lithsil-6	1.0	parts
MICA	0.1	parts
Al-Lithium Powder	0.9	parts
Lithium Molybdate	0.005	parts

To provide a comparison, the Carboline product CarboZinc<sup>®</sup> 11 represented the standard.

The latex, epoxy and solvent based vehicles were compatible, but the inorganic material seemed to offer the "cleanest" system. Since the scope of this project was to demonstrate the feasibility of a minimum polluting system and a corrosion resisting pigment to replace chromium, it was decided that the inorganic was readily formulated into an acceptable product.

Three types of aluminum Q-panels and one kind of steel panel were used for pigment tests. They were Al 6061, Al 5052, Al 3003, and cold roll steel panels. Seven groups of samples were tested that involved different formulated pigments and various treating conditions. "Lithsil-6" was used as the main vehicle of pigment. The other additives included aluminum-lithium powder, MICA, lithium molybdate, sodium borate, and zinc powder.

## RESULTS

The treated panels were sent to the independent testing laboratory KTA Tater per ASTM-B117 salt spray for 168 hours. After 168 hours of salt fog exposure, the panels were evaluated, and the results are in the following paragraph. The panels were evaluated for face rust in accordance with ASTM D-610, blistering in accordance with ASTM D-714, and undercutting in accordance with ASTM D-1654. Face rust ranges from a rating of 10, corresponding to no rust, to a rating of 0, corresponding to 50% or more rust (Figure 7).

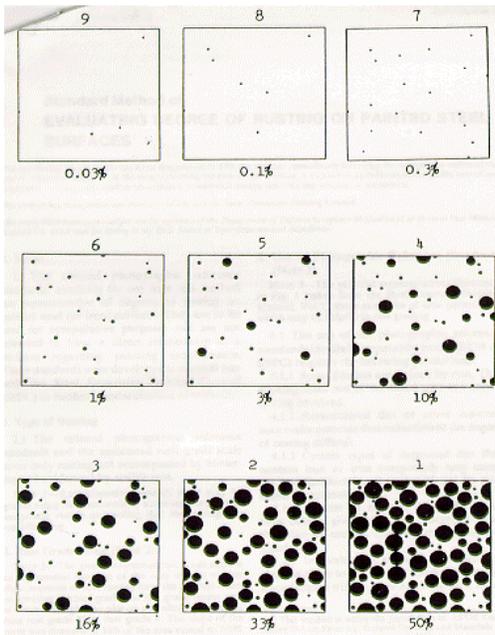


Figure 7. Examples of Area Percentages (ASTM D-610)

The results of the tests at KTA Tater confirmed the effective corrosion protection. Although the steel panels corroded seriously, the aluminum panels only had a few pits in the panels as evidenced by the white powder on the surface. The scribes which exposed bare aluminum did not corrode or undercut. No blisters on the coating were discovered. Closer inspection showed the pits were caused by lumps of pigment. The pigment which was preheated and screened had no corrosion. The top coated primer had no corrosion. The large unfiltered particles caused a circumstance of pitting corrosion which was reduced by the lithium molybdate passivator, but could be eliminated entirely by screening the lumps out prior to painting.

The mechanism of corrosion protection appears to be a combination of galvanic action by the lithium and passivation by the reaction products. The inhibitor was a complete success on aluminum. In the case of the four steel panels, the galvanic action probably inhibited corrosion but the reaction products promoted corrosion on the cold rolled steel. The technique of corrosion protection by nanostructural inhibitors is still possible, but the sacrificing pigment must not generate a compound which promotes corrosion. Lithium does not function on steel as it does on aluminum.

## SUMMARY

The lithium salts passivate aluminum. They can be some viable substitutes 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.

These corrosion inhibitors can be used in other vehicles and may be used as latexes, epoxies, or solvent based coatings. This work remains to be done.

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