REPLACEMENT OF CHROMATES IN PAINTS AND CORROSION PROTECTION SYSTEMS

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### Title and Subtitle
Replacement of Chromates in Paints and Corrosion Protection Systems

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### Abstract
This technical report presents the first stage results of a multi-year project to develop chromate-free paints and corrosion protection systems. Chromate coatings and chromate-containing paints are very effective in providing corrosion resistance and are widely used in the manufacturing, transportation and defense industries; however, there is a need to find an environmentally- and occupationally-friendly replacement to chromate (chromium VI is considered a carcinogen with an extremely low personal exposure limit). The tasks of this first stage consisted of the scale-up and corrosion testing of an alternate-to-chromate coating, initiation of biocorrosion tests, and development and corrosion testing of a wash primer. The alternate-to-chromate coating involves substituting titanium for chromium (titanium is much safer than chromium and it is used for hip replacement in humans). The new formulation protects in the same manner as chromate and has been able to match the test data for chromated surfaces. Microbially-influenced corrosion (biocorrosion) studies were initiated by establishing marine bacteria cultures and conducting preliminary electrochemical impedance spectroscopy measurements. A wash primer containing polyaniline (an electroactive polymer) instead of chromate was also developed and corrosion tested. The report ends with a summary of future tasks to further develop chromate-free paints and anti-corrosion systems.

### Key Words
Chromate alternatives, microbially-influenced corrosion, wash primer.
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INTRODUCTION

Chromate coatings are very effective in providing corrosion resistance and are widely used in the manufacturing, transportation and defense industries: equipment and car manufacturers as well as auto-body shops use chromate in paints to prevent corrosion; chromate-containing paints are also used in bridges, rail stock and ships. However, chromium (Cr VI) is considered a carcinogen with an extremely low (1 mg/m$^3$) personal exposure limit (PEL) (1); therefore, it is necessary to find an environmentally and occupationally friendly replacement.

The National Center for Manufacturing Sciences conducted an extensive analysis of twenty-five alternatives, which included performance tests (2); the results of this analysis were that none of the alternatives passed the testing for corrosion. The US Army has considered using a chromate-free conversion that forms a thin aluminum oxyhydroxide, which is then sealed with solutions of metallic salts and organic compounds (3). The Air Force Research Laboratory (AFRL) at Wright Patterson Air Force Base initiated the investigation on the non-chromate conversion coating of 7075 and 2024 aluminum (4). Potential material and technology candidates for chromate replacement are: acid aqueous solutions containing potassium permanganate and cerous chloride (5), silane-based materials (6), sol-gel technologies, vapor deposition processes, thermal spray technologies including high velocity oxygen and flame spray technologies, and anodizing using sulfuric acid/boric acid processes (7).

The University of Rhode Island (URI) Corrosion Laboratory has undertaken a novel and different approach by developing a new chemical formulation for a non-chromate alternative; it involves substituting titanium for chromium (titanium is much safer than chromium and it is used for hip replacement in humans). The new formulation protects in the same manner as chromate and has been able to match the test data for chromated surfaces. Chromated surfaces decrease the oxygen reduction limiting current density for the cathodic reaction to 7 µA/cm$^2$ as compared to 20 µA/cm$^2$ for uncoated surfaces. The URI alternate to chromate decreased the oxygen reduction reaction down to between 3 and 9 µA/cm$^2$. An examination of the NIOSH (National Institute of Occupational Safety and Health) index does not mention a PEL for the new formulation. Therefore, before any further development of the new formulation and transfer of the technology to local and national industry, it is necessary to conduct a study of the effects of the new coating system on marine life.

The various surface treatments produced by this research will revolutionize the conversion coating of aluminum and steel and allow paint manufacturers to move away from chromates. URI is uniquely positioned as the leader of alternates to chromates due to the existing patents in the area and the quality of the personnel. Licensing of patents will permit Rhode Island businesses to develop into this major market. Conversion coatings, wash primers, and electrophoretic coatings can all be developed at URI and licensed to major international paint companies. They would be the result of this research.

This technical report presents the first stage results of this research, consisting of five tasks: scale-up and corrosion testing of alternate-to-chromate coating, initiation of biocorrosion tests, and development and corrosion testing of a wash primer.
METHODS AND RESULTS

This section describes the methods used to approach the five tasks mentioned above and the results obtained.

Scale-up and Corrosion Testing of Alternate to Chromates:

One of the tasks in this first stage of the project was to scale-up the coating process of alternates to chromates from 1x4-inch samples to 10x3-inch panels of Al 2024 T3 and to test their performance in a salt spray chamber (ASTM B-117). Details follow:

Substrate Materials

Aluminum alloy 2024 T3 panels (3x10x0.063-inch) from Q-Panel Lab Products were used throughout the study. The alloy composition is: Cu 4.4%, Mn 0.6%, Mg 1.5%, Al 93.5%.

Coating Process

After the 10x3-in Al 2024 T3 panels were cleaned with a solvent, alkaline-degreased and deoxidized, a proprietary titanium-based conversion treatment was applied to the panels by an immersion process. The whole treatment procedure was:

(Solvent cleaning, alkaline degreasing) (Deoxidizing) (Film Formation)

After drying, the sample was placed in a salt spray chamber for 15 days (ASTM B-117), figure 1.

FIGURE 1. Salt spray chamber.
Testing in the salt spray chamber usually includes an uncoated sample as a control, to characterize the performance of the salt spray unit. The results of the testing are shown in figures 2 and 3. Figure 2 shows from left to right, a bare panel followed by a panel coated with titanate (URI coating) and a panel chromate-coated. Figure 3 shows a panel with URI coating.

**FIGURE 2.** Panels of Al 2024 T3, bare and coated, after 15 days in a salt spray chamber.

**FIGURE 3.** 10x3-inch panel of Al 2024 T3 with URI coating after 15 days in a salt spray chamber.
The surface condition of the sample did not change after 15 days of testing. No localized brown colored areas, typical of breakdown of a coating on Al 2024 T3 when copper is dissolved and redeposited on the surface, were found. This indicates that the alternate conversion coating can be successfully scaled up.

**Electrochemical Testing**

In task 2 corrosion testing was to be conducted to determine the effectiveness of the coating process. Cyclic polarization tests were carried out in an aerated 0.5N NaCl solution using an EG&G Model 273 potentiostat and Model 342C corrosion test software. The Al 2024 T3 panel served as the working electrode in an EG&G Model K0235 three-electrode cell. A 1-cm² area of the panel was exposed to the electrolyte. A platinum-wire mesh and a saturated calomel electrode (SCE) served as the counter electrode and reference electrode, respectively. The threshold current was 200 µA/cm² and the initial delay was 6 minutes. From a potential 150 mV below the open circuit potential, a scan rate of 0.1 mV/sec was used. The test set-up is shown in figure 4.

Data from this testing technique are shown in figure 5. The open circuit potential is the potential when the current is at its lowest value, tending towards zero in this figure. For this initial cycle of polarization the open circuit potentials are similar and independent of surface conditions. This would indicate that for both coating types, the coating is imperfect and allows the aluminum substrate to be exposed to the environment. For both the alternate-to-chromate and chromate conversion coatings, there is a tendency to form a passive layer indicated by the near independence of the current density to potential after open circuit. The alternate to chromate is stable over a wider potential range than the chromate is, as evidenced by the higher breakdown potential at the end of the passive region.

![Figure 4. Test cell for electrochemical studies.](image-url)
The cyclic polarization test was then repeated and the open circuit potential after testing measured again. This was repeated for eleven cyclic polarization tests on the same coated area. The data are shown in figure 5.

**FIGURE 5** Cyclic polarization data for Al 2024 T3 with different surface coatings.

**FIGURE 6.** Open circuit potential after cyclic polarization tests in 0.5 N NaCl for Al 2024 T3 with an alternate-to-chromate conversion coating.
The aim of a second series of polarization testing was to investigate the mechanism of protection of the alternate-to-chromate. After the initial cyclic polarization to test the ability of the coating to resist localized corrosion, cyclic polarization was then repeated and the open circuit potential measured. An interesting phenomenon was the change in open circuit potential to more positive values. The potentials reached during the testing were far removed from that of unprotected Al 2024 T3, which is around – 0.675 V relative to SCE. The open circuit potential changed very rapidly in the first three tests, suggesting the surface being tested was significantly modified during exposure. One possible surface modification is the healing of imperfections on the initial conversion-coating layer to form a surface layer on the sample that is highly protective; if the layer were not protective, the final open circuit potential would be the same as the unprotected aluminum alloy, i.e. – 0.675 V (SCE). A second possible surface modification is the formation of a new layer of different composition from the initial layer. This testing therefore suggests that the mechanism of protection for the alternate-to-chromate involves either a healing process or the establishment of a new protective layer incorporating components of the conversion coating. This further suggests that the conversion-coating layer is electrochemically reactive in nature. Similar testing on chromate conversion-coating on the same material and under the same conditions indicated that chromate conversion-coatings behave the same way.

A good correlation between the cyclic polarization data and salt spray testing was found. Cyclic polarization was used to prequalify potential titanate coating formulations. Poor performance in cyclic polarization on a coated Al 2024 substrate indicated poor performance in salt spray (8).

Initiation of Biocorrosion Tests

It was initially proposed that the effects (or lack thereof) of the alternate-to-chromate coating on marine life would be assessed by measuring the motility of marine microorganisms using the stopped-flow diffusion chamber (9). This technique is very useful for studies where either a chemical gradient or microbial population gradient can be sustained over a period of few hours. However, because the long-term use of coated metals in the manufacturing, transportation and defense industries we concluded that a more relevant assessment would be provided by studying the formation of bacterial biofilms on the metal samples.

It has been observed that in aqueous environments, organisms (bacteria, protozoa, algae, etc.) attach to and colonize surfaces to form biofilms (10). This is facilitated by extracellular, polymeric substances (EPS) secreted by microorganisms present in the biofilm (11). If the colonized surface is a metal, it has been suggested that the presence of the microbial cells (and their metabolic activities) modifies conditions at the metal-liquid interface resulting in the formation of local anodes and cathodes; this is known as microbiologically-influenced corrosion (MIC) or biocorrosion (12–17). Therefore, we chose to study the formation of bacterial biofilms on uncoated samples of Al 2024 T3, with the intent of later on conducting biocorrosion experiments on samples coated with the alternate-to-chromate.

Bacterial cultures

Cultures of a marine bacterium, *Pseudomonas fluorescences* (ATTC 43666), were established and later used in (MIC) experiments. Although the initial biofilm formation experiments were carried
out under sterile conditions, the bacterial cultures got contaminated and died. A new batch of *Pseudoalteromonas atlantica* was ordered and cultures were established. At present, we have successfully established cultures of *P. atlantica* and determined their growth curves in Zobell 2166 medium and sterile Narragansett Bay seawater.

Briefly, *P. atlantica* is streaked from a \(-75^\circ\text{C}\) glycerol stock onto an agar plate. A single colony is then picked and used to inoculate 5 mL of sterile Zobell 2166 medium (5 g/L peptone, 1 g/L yeast extract, filtered seawater) without shaking at 19°C. After two days the inoculum is transferred into larger Erlenmeyer flasks. Once the bacterial suspension reaches a cell density of at least \(10^6\) cells/mL, it is used for MIC experiments. Figure 7 shows the growth curves of a set of duplicates kept for 28 days at 19°C. It can be seen that bacteria reach the stationary growth phase at about 12 days.

*Biocorrosion Experiments*

Biocorrosion experiments on uncoated aluminum alloy Al 2024 T3 samples were initiated. Steps involved are as follows:

**Metal Sample Preparation:** Bare, unpolished aluminum 2024 T3 square samples (7.6x7.6-cm) were degreased and cleaned with DI water, acetone and alcohol, air-dried in a laminar-flood hood and sterilized by UV light overnight before each experiment.

**Experimental Set-up:** The experimental set-up (figure 8) consists of a 4-cm diameter, open-ends glass tube clamped to an aluminum alloy sample; this results in a 12.6-cm² exposed metal surface area to the bacterial suspension. An ethylene propylene O-ring is used to create a watertight seal. After assembly, the set-up is sterilized by autoclaving at 121°C for 20 minutes before initiating the experiments.

**Experiments and Assessment of Biocorrosion:** Biocorrosion experiments were conducted in duplicate set-ups containing 200 mL of medium with or without bacteria (control) at 19°C for one month. Electrochemical impedance spectroscopy (EIS) was used to assess the biofilm’s contribution to corrosion. EIS is a relatively new (16), nondestructive electrochemical technique, which has recently been used in MIC studies (18–21). We have adapted the technique as to allow us to conduct measurements throughout the duration of a particular experiment, e.g. one month, without having to take the set-ups apart.

Briefly, the technique consists of using a three-electrode electrochemical cell connected to a potentiostat and a frequency response analyzer (Gamry EIS300), figure 9. The aluminum alloy sample is one of the three electrodes, the working electrode, and two platinum wires separately placed in the bacterial suspension are used as the counter and reference electrodes, respectively. A sinusoidal voltage signal of 10 mV and a frequency range of 0.05–100 Hz are used, and the impedance (resistance) of the system is obtained. Typical raw data obtained from the experiment are shown in figure 10.

Table 1 shows preliminary impedance results; the impedance values are generated by the equipment. Three duplicate set-ups were used for a month; one set of duplicates for the control (plain, sterile seawater). Notice that after 18 days, one of the control set-ups showed signs of contamination. The results obtained seem to suggest that the presence of bacteria on the alloy samples provide a resistance to corrosion as the impedance values increased with exposure time;
these observations could be in line with corrosion inhibition results recently reported by Nagiub and Mansfeld (22). However, subsequent modeling of the raw data by equivalent electrical circuits will allow us to ascertain whether or not that is the case; of relevance to this experiment will be the determination of the charge transfer resistance, which directly relates to the aluminum alloy corrosion resistance.

![Figure 7](image1)

**Figure 7.** *Pseudoalteromonas fluorescencens*’ growth curves: sterile seawater enriched with Zobell 2166 medium at 19°C (set of duplicates).

![Figure 8](image2)

**Figure 8.** Biocorrosion experimental set-up.
FIGURE 9. Electrochemical impedance spectroscopy (EIS) equipment.

FIGURE 10. EIS raw data.
TABLE 1. Impedance as a Function of Cell Density of *P. atlantica* in Suspension

<table>
<thead>
<tr>
<th>Time (days)</th>
<th>Plain Seawater</th>
<th>Seawater with <em>P. atlantica</em></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Duplicate 1</td>
<td>Duplicate 2</td>
</tr>
<tr>
<td></td>
<td>Impedance (ohm)</td>
<td>Impedance (ohm)</td>
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<td>4419</td>
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<td>7864</td>
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<tr>
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</tr>
</tbody>
</table>

**Development and Corrosion Testing of Wash Primer**

As mentioned in the project description, current coating technology (for lightweight high-strength aluminum alloys) involves the use of toxic chromates. Chromates are currently used in both the pretreatment of aluminum surface and in the primer layer of the coating. In this project we studied the replacement of chromates by electroactive polymers. We have employed two approaches.

The first approach is to use an electroactive polymer, polyaniline, as an additive to the water-borne epoxy used for electro-coat (e-coat). In a formulation patented by URI, the double-strand polyaniline was used as an additive at 1% weight to a commercial e-coat. The coating was tested by salt-fog spray (ASTM B-117) and electrochemical impedance spectroscopy (EIS). The results show that the electroactive primer protects the aluminum alloy without the use of chromate in the surface pretreatment and without the use of zinc chromate in the epoxy primer. The filiform corrosion tests show that the electroactive polymer is effective for preventing filiform corrosion (figure 11). Samples were sent to ALCOA for evaluation. The results indicate that the electroactive primer perform well in comparison with the lead-containing commercial electro-coat.

In a second approach, we replaced the chromate component of the wash primers by the electroactive polyaniline. Six different formulations of polyaniline wash primer were tested for adhesion with epoxy primer. Two best formulations were selected for tests. Results indicated that this new chromate-free wash pretreatment is promising as a chromate replacement coating.
CONCLUSIONS

1. The alternate-to-chromate coating was successfully scaled up from 1x4-inch to 10x3-inch panels of Al 2024 T3. The scaled-up samples provided protection comparable to chromate-coated samples.

2. Growth curves of *P. atlantica*’s suspensions exposed to bare Al 2024 T3 samples were determined.

3. Impedance results of Al 2024 T3 samples exposed to bacterial suspensions for a month showed an apparent increase in corrosion resistance. However, future equivalent-circuit modeling of the experiment will determine whether or not the presence of the bacterial biofilm on the metal surface contributes to corrosion inhibition.

4. A polyaniline-containing wash primer was developed and corrosion tested.

FUTURE WORK

The present work represents the initial phase of a multi-year project. The principal tasks for the coming years are:

1. To develop wash primers containing phosphates, titanates and conductive polymers.
2. To test the wash primer with color coat on top for adhesion of paints to metal and for corrosion resistance.
3. To measure biofilm formation on metal samples.
4. To model biocorrosion experiments with equivalent circuits.
ACKNOWLEDGEMENTS

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REFERENCES


APPENDIX

This appendix contains information on publications, including Ph.D. dissertation titles of students who contributed to the project, and other “success” stories.

Publications


“Success Stories” e.g., Patents, Awards, etc.

1. Patent: A patent entitled “Functionalized Double-Strand Conducting Polymer Composition” was filed by URI with co-inventors Wenguang Li and Sze C. Yang.

2. Student internship award ($20,000 for six months): Wenguang Li was awarded a 6-month internship at the Los Alamos National Laboratory in 2001.

3. Award: Wenguang Li and Sze C. Yang were co-recipients of a URI Foundation Intellectual Property Development Award in March 2001.