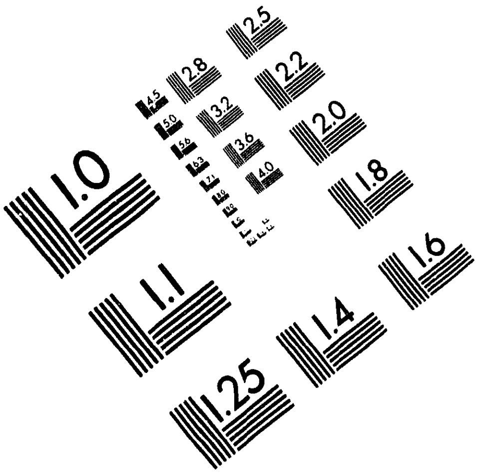

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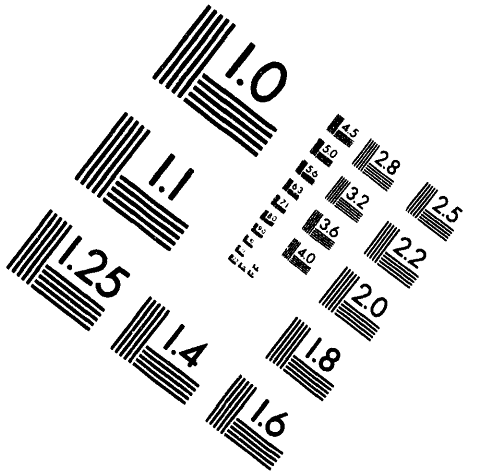

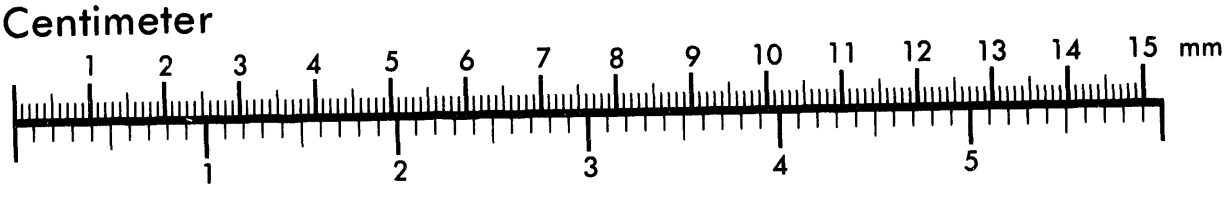

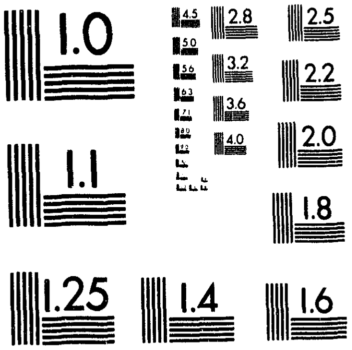

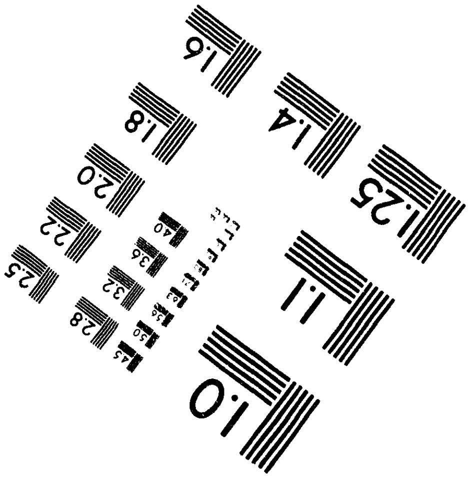

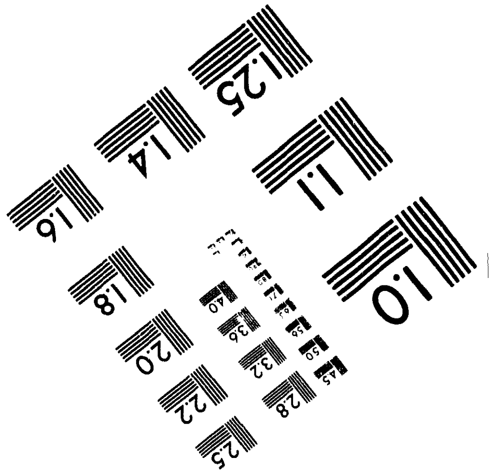

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1 of 3

Minutes of the Third Annual Workshop on Chromate Replacements in Light Metal Finishing

September 15-16, 1993
Holiday Inn Journal Center
Albuquerque, New Mexico

T. R. Guilinger[1], R. G. Buchheit[1], M. J. Kelly[1],
K. R. Zavadil[1], J. Bibber[2], L. Carlson[3],
P. Chalmer[4], M. Kendig[5], F. Mansfield[6],
G. Murphree[7], and R. Taylor[8]

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[3]Parker+Amchem, Inc.
[4]National Center for Manufacturing Sciences
[5]Rockwell International Science Center
[6]University of Southern California
[7]United Technologies, Inc.
[8]University of Virginia

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Minutes of the Third Annual Workshop on Chromate Replacements in Light Metal Finishing

T. R. Guilinger, R. G. Buchheit, M. J. Kelly, K. R. Zavadil,
J. Bibber, L. Carlson, P. Chalmer, M. Kendig,
F. Mansfeld, G. Murphree, and R. Taylor

Purpose:

The purpose of publishing the minutes of this workshop is to document the content of the presentations and the direction of the discussions at the workshop as a means of fostering collaborative research and development on chromate replacements throughout the defense, automotive, aerospace, and packaging industries. The goal of the workshop was to bring together coating researchers, developers, and users from a variety of industries to discuss new coating ideas from the perspective not only of end user, but also from the perspective of coating supplier, developer, and researcher. To this end, we succeeded because of the wide-ranging interests of attendees present in the more than 50 workshop registrants. It is our hope that future workshops, not only this one but others like it throughout government and industry, can benefit from the recorded minutes of our meeting and use them as a starting point for future discussions of the directions for chromate replacments in light metal finishing.

Contents of this document:

The following items related to the workshop are contained in this document:

- Workshop agenda
- List of attendees (50 registered for the workshop)
- Summary of the feedback from workshop attendees
- Workshop notes compiled by the organizers (3 sets of notes)
- Summaries of Sessions II and IV by the session moderators
- Copies of vugraphs and abstracts in the order presented at the workshop

Publication note:

To facilitate the distribution of the results of the workshop, we are making this document available to the general public through the National Technical Information Service (NTIS) via publication of this document as a Sandia Technical Report.

Workshop Agenda

List of Attendees

Workshop Feedback Results

Chromate Replacement Workshop Agenda
September 15, 1993
Morning Session

8:00 a.m.	**Registration**/Continental Breakfast
8:30 a.m.	**Introduction to the Workshop**-Terry Guilinger, Sandia Labs
9:00 a.m.	**Session 1-Commercially Available Products**, Moderators: John Bibber,Sanchem, and Larry Carlson, Parker-Anchem. Ground rules and goals for this session
9:15 a.m.	**Larry Carlson**, "Review and Update on New Non-Chromium Surface Technology for Tomorrow's Environmental Demands"
9:35 a.m.	**John Bibber**, "Sanchem CC-A Chrome Free Aluminum Pretreatment System"
9:55 a.m.	**Don Baudrand**, Allied Kelite-Division of Witco, "Non-Chromium Treatment for Aluminum"
10:05 a.m.	**Dave Halverson**, Birchwood Casey, "Phosphate Polymer"
10:15 a.m.	**Break**
10:30 a.m.	**Florian Mansfeld,** University of Southern California, "Stainless Aluminum Process using Ce and Mo Salts"
10:45 a.m.	**Larry Carlson and John Bibber**-Discussion Agenda/Questions
10:55 a.m.	**Moderated Discussion**
12:00	**Lunch**-Atrium of the Pyramid-Entree: Chicken Marsala

Chromate Replacement Workshop Agenda
September 15, 1993
Afternoon and Evening

1:30 p.m.	**Session 2**-Performance Testing of Coatings, Moderators: Martin Kendig, Rockwell, and Ray Taylor, Univ. of Virginia Ground rules and goals for this session
1:45 p.m.	**Martin Kendig**, "Comparison of Electrochemical Analysis to Salt Fog Behavior of Non-Chromate Sealed Anodized Al and Non-Chromate Conversion Coatings"
2:10 p.m.	**Tony Hughes**, CSIRO-Australia, "Electrochemical Evaluation of Corrosion Performance of Conversion Coatings"
2:35 p.m.	**Peter Walker**, AWRE-United Kingdom, "Testing and Specification of Conducting and Protective Coatings for Al Alloys"
3:00 p.m.	**Break**
3:15 p.m.	**Informal Presentations**-Ray Taylor, Moderator
3:25 p.m.	Ray Taylor-Presentation of Discussion Agenda/Questions
3:35 p.m.	Moderated Discussion
4:30 p.m.	Adjourn
6:15 p.m.	Bus to El Pinto Restaurant
6:30 p.m.	No host cocktail hour on the patio at El Pinto
7:30 p.m.	Informal banquet
9:00 p.m.	Return bus to Pyramid

Chromate Replacement Workshop Agenda
September 16, 1993
Morning Session

8:00 a.m. **Session 3-Preparation for Coating,** Moderators: Florian Mansfeld, University of Southern California, and Gail Murphree, NASA, Ground rules and goals for this session

8:15 a.m. **Luis Vega,** Aluminum Company of America, "Surface Cleaning Methods for Zinc Phosphating of Aluminum Alloys"

8:40 a.m. **Celeste Drewien,** Sandia National Labs, "Surface Pretreatment Aluminum Alloys for Hydrotalcite Deposition"

9:05 a.m. **Florian Mansfeld,** University of Southern California, "Surface Pretreatment of High-Copper Aluminum Alloys-Electrochemical Surface Characterization"

9:30 a.m. **Break**

9:45 a.m. **Informal Presentations from the floor**

10:30 a.m. **Sally Hoier,** Sandia National Labs, "Alternative Cleaning Reagents for Organic Residue Removal from Aluminum Surfaces"

10:50 a.m. **Florian Mansfeld and Gail Murphree,** Presentation of Discussion Agenda/Questions

11:00 a.m. **Moderated Discussion**

11:30 a.m. **Lunch**-Atrium of the Pyramid-Entree: Sandia Broil

Chromate Replacement Workshop Agenda
September 16, 1993
Afternoon Session

1:00 p.m. **Session 4-Emerging Coatings Technology**, Moderators: Rudy Buchheit, Sandia National Labs, and Paul Chalmer, National Center for Manufacturing Sciences
Ground rules and goals for this session

1:05 p.m. **Toshi Sugama**, Brookhaven National Labs, "Sol-Gel Synthesized Polymetallosiloxane Coatings"

1:30 p.m. **Regan Stinnett**, Dale McIntyre, Rudy Buchheit, B. Turman, E. Neau, Sandia National Labs, J. Greely and M. Thompson, Cornell University, and D. Rej, Los Alamos National Lab, "The Use of Intense, Pulsed Ion Beams for Material Surface Treatment"

1:55 p.m. **Rudy Buchheit**, Celeste Drewien, and Jan Finch, Sandia National Labs, and G. Stoner, University of Virginia, "Chromate-Free Talc Conversion Coatings for Aluminum"

2:15 p.m. **Break**

2:30 p.m. **Paul Chalmer**, "Overview of the NCMS Chromate Alternatives Project"

2:50 p.m. Moderated Discussion

3:30 p.m. Summary of the Workshop by Session Moderators

4:30 p.m. Adjourn

Chromate Workshop Attendees 93

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Sandia National Laboratories
Albuquerque, NM 87185

To: Chromate Replacement Workshop Attendees

Below we have summarized the results from the feedback forms that many of you filled out during the workshop. Note that we have made editorial comments on some areas. Thank you for attending and we hope to see you next year.

Sincerely,

for

The Workshop Organizers

Summary of the Feedback from the Chromate Replacement Workshop

Question 1. Was the workshop valuable to you? 28 responded yes, 0 responded no. The most common comments were that the moderated discussions and the networking time allowed were the most valuable parts of the workshop.

Question 2. Was the format of the workshop useful? 22 responded yes, 0 responded no. Among comments, the most frequently mentioned was that the size of the workshop was about right.

Question 3. The mix of presentations and discussions was: Too much presentation: 0 responses; Too much discussion: 0 responses; About right mix: 28 responses. A frequent comment was that slightly more discussion time could have been allowed.

Question 4. I work for a small company: 2 responses; medium company: 7 responses; large company: 16 responses; university: 2 responses.

Question 5. Would you attend next year's workshop? 28 responded yes, 0 responded no.

Question 6. Was there anything you felt was done particularly well, particularly poorly, or was not done and needed to be done? The comments for each category are collected on the next page.

Things done particularly well

-Participation by industry.
-Excellent cross-section of participants.
-Informal atmosphere and meeting structure.
-Keeping on schedule.
-Wide range of discussion.
-Organization of discussion.
-Banquet was a good idea.
-Good organization of presentations.
-Informal format and discussions.
-Description of chromate mechanisms as best we know them.
-Excellent organization of meeting.
-Good mix of attendees.
-Moderators summarizing the message of each session with notes was an effective means of documenting what was accomplished.

Things done particularly poorly

-Lack of attendance by Mil-Spec custodians and military/defense customers.
-Audio-need to use microphone.
-Connection of surface cleaning effects to coating performance was very weak.
-No refreshments on second morning.
-Some material was too technical for production-oriented interests.
-Supper was too late (Editors note-this will be fixed).
-Some material was not technical enough-too much sales pitch.

Things that weren't done or needed to be done

-Establish collective objectives for group to measure against in succeeding years.
-Need smaller room.
-Broaden from mainly aircraft issues to transportation, construction products, packaging, general industrial (Editors note-if you have someone that should be on our mailing list that fits these categories, please send us their address).
-Consider establishing minicourse on EIS and other analysis techniques (Editors note-The University of Virginia offers this minicourse and we are looking into the feasibility of having them teach it in Albuquerque next year. If the course is offered in Albuquerque next year, we will try to make the course and the workshop concurrent).
-Have workshop adjacent to weekend for tourist activities and less expensive airfares with Saturday stayover (Editors note-Please tell us your preference as soon as possible so we can schedule with you in mind).
-Need more discussion from end users.
-Need good amplification system.
-Need more information on non-chromate primer inhibitors (Editors note-We need to get some organic coaters here next year so send us some names for the mailing list)

Workshop Notes Compiled by the Workshop Organizers
(3 sets)

Notes from the Third Annual Chromate Replacement Workshop - Set 1

Introduction:

Talk #1, Guilinger, "Introduction to the Workshop/Review of the Theory, Use, and Performance of Chromate Conversion Coatings": Background on history of this workshop from 1991-present. Introduction to background, use, and applications of chromate conversion coatings (CCC's).

Talk #2, Murphree: Why do we want to get rid of Cr? Answers are numerous. Cr(VI) is a known carcinogen. OSHA is going to reduce the PEL (permissible exposure limit) to Cr by a factor of 200 (imminent). Cr(VI) is viewed by EPA as a hazardous air pollutant. Permitted space for disposing of Cr, even in Cr(III) form, is rapidly diminishing. It is going to become harder and more expensive to get rid of Cr-containing waste. Some states (e.g., California) have more restrictive regulations than federal agencies such as EPA and OSHA.

Questions, Answers, Comments:

Kendig: Cr(III) is apparently non-hazardous, as evidenced by the fact that it is found in cosmetics.
Chalmer: There apparently is some organism or microorganism that can convert Cr(III) to Cr(VI), so that there would be no way to provide 100% assurance that Cr(III) won't be converted to carcinogenic Cr(VI) after disposal. This appears to be the philosophy behind EPA's limit on total chromium (e.g., non-hazardous Cr(III) plus hazardous Cr(VI) plus Cr metal) discharges.

Session 1, Commercially Available Products:

Talk #1, Carlson, "Review and Update on New Non-Chromium Surface Technology for Tomorrow's Environmental Demands": Parker + Amchem and Boeing are jointly working on a Cr-free Al pretreatment for aerospace applications. Alodine 2000 from Parker + Amchem is based on cobamine chemistry. The recommended procedure is as follows:

Aqueous degreaser
Water rinse
Deoxalume 2100
Water rinse
Deoxalume 2200
Water rinse
Alodine 2000
Water rinse
Parker + Amchem sealant
Water rinse
Oven dry

The cobamine chemistry represented by Alodine 2000 is characterized by the following features:

pH = 6.2
no fluoride ions
little or no Al metal dissolution
25-250 mg/sq.ft. coating weight
color: clear to dark gold, similar to CCC's
no ferricyanide (which is used in CCC's to passivate $CuAl_2$, e.g., in 2024-T3)

Performance features were highlighted by the ability of Alodine 2000 to pass (1) 168 hours of salt fog on Al 2024-T3, when sealed with "Seal B", and (2) 336 hours of salt fog on Al 6061 and Al 7075-T6, when sealed with either the Boeing sealant or "Seal B".

Questions/Answers/Comments:

Martinez: What type of primer was used? Carlson: A chromated primer.
Lewis: Shouldn't the corrosion protection be better if a chromated primer was used?
Carlson: There appears to be a synergestic effect between the primer and conversion coating.
Martinez: There needs to be a distinction between the failure of the conversion coating, versus a failure of the paint layer (when it comes to deciding why a sample fails salt fog).
Carlson: When sealed, Alodine 2000 has a resistivity of 7500-8500 microohm-cm, which passes specification.

Talk #3, Baudrand, "Non-Chromium Treatment for Aluminum": Chemidize 727A is a coating process whose primary purpose is to provide a good surface for adhesive bonding. It uses an organic oxidizer. It is supplied in paste or liquid form. It works well on stainless steels and chrome-plated parts. It passes lap shear bonding strength tests (2000-3600 psi required, average value obtained > 4000 psi).

Talk #4, Halverson, "A New Paint Prep Technology - Phosphate Polymer": Described a water-based polymer emulsion process containing both zinc phosphate and zinc chromate. In the resultant film, Cr(VI) is reduced to Cr(III), cross-linking takes place, the coating becomes hard and acts as a barrier (see his extended abstract).

Talk #5, Mansfeld, "Stainless Aluminum": Described this process as corrosion protection by surface modification. Weak spots in the oxide are deposited with cerium and molybdenum which afford corrosion protection. The process for Al 6061-T6 is as follows:

Degrease (Alconox)
Deoxidize (Diversey 560)
Bake (100 C)

Ce Treatment I: 10 mM $Ce(NO_3)_3$ at 100 C, 2 hours
Ce Treatment II: 5 mM $CeCl_3$ at 100 C, 2 hours
Mo Treatment: Polarize in 0.1 M Na_2MoO_4, +500 mV vs. SCE for 2 hours.

The processes for Al 7075-T6 are the same, except for a change in sequence (Ce Treatment I, Mo Treatment, Ce Treatment II).

Questions/Answers/Comments

Kendig: A process identical to the one outlined above, minus the Ce and Mo salts, gives almost the same amount of corrosion protection.
Mansfeld: Experimental design studies showed that that is not the case: Ce and Mo salts are necessary, as evidenced by results for samples treated with boiling water.
Kendig: Boiling in water is an inadequate control in Mansfeld's experimental design studies, says Mansfeld should use something like $NaNO_3$ in his control samples.

Session 1, Moderated Discussion:

Buchheit: Are we just buying time in using materials such as Ce, Co, and Mn in place of Cr? Will these materials also be regulated someday? A great deal of discussion followed, with the general consensus of the workshop being that these other materials will only be short-term substitutes.
Jenkins: Is there presently a strong driving force (e.g., federal regulation) behind Cr replacement?
Carlson: Sludge disposal sites for Cr-containing sludge will soon be gone.
Jenkins: In that case, sludge recycling would probably be a more fruitful research and development area, as opposed to Cr-free metal finishing research.
Buchheit: There is usually a trade-off between performance and cost. In the nuclear weapon complex, one way DOE forces this issue is in the penalty it administers for indiscriminate call-out of CCC's (e.g., Alodine) by design engineers.
Murphree: EPA is not banning Cr(VI) or Cr; however, it will be making it more and more expensive and burdensome to use. This will be a strong driving force for Cr replacement in the future.
Mansfeld: Suggests using Cr-free processes for easy alloys (e.g., 6xxx), while continuing the use of CCC's in more corrosion-susceptible alloys (e.g., 2xxx, 7xxx).
Murphree: One example of a law governing the use of Cr is Federal Regulation FO19, "Wastewater Sludge Treatment for Conversion Coating of Aluminum".
Jenkins: FO19 says any sludge coming from Al conversion coating process is classified as FO19 waste and is, by definition, hazardous.
Fournier: The sequence one should go through in determining if a certain material is regulated is as follows: First, check the Code of Federal Regulations (CFR), e.g., CFR 40 Sec. 261, CFR 433, etc. Second, check general federal regulations. Finally, check applicable state, local, and

municipal regulations. In the case of Ce and Mo, there are no specific federal regulations governing its use.

Session 2, Performance Testing of Coatings:

Goals for this Session, Kendig: Martin outlined the key questions to hopefully be addressed, during this session:

1. What methods are used for rapid life prediction?
2. Is American Society for Testing and Materials (ASTM) Test Method B117 salt fog corrosion test) relevant?
3. What do electrochemical impedance spectroscopy (EIS) and other rapid electrochemical methods predict? If they are predictive, what are the details of the experiment and analysis? What is the correlation, if any, to salt fog testing? What are the statistical implications?
4. Can electrochemical methods be as efficient as salt fog for screening?
5. Do formulators of conversion coatings use electrochemical methods?
6. Do original equipment manufacturer's (OEM's) use electrochemical methods?

Talk #1, Kendig, "Comparison of Electrochemical Analysis to Salt Fog Behavior of Non-Chromate Sealed Anodized Al and Non-Chromate Conversion Coatings": Kendig first referenced a 1991 article that he authored in the journal "Corrosion", which demonstrated the use of electrochemical methods for predicting corrosion failure in phosphated stainless steel samples. Kendig described the EIS and salt fog characterization of 2024-T3 Al alloy samples treated with in a number of ways. The conversion coating replacement technologies examined included:

NADC's Cr(III) process
Sol Gel Deposited coatings
Sandia National Laboratories Hydrotalcite coatings
Allied Kelite Iridite process
Parker + Amchem's chrome-free process

The anodized seal replacement technologies examined included:

molybdenum-based process
vanadium-based process
tungsten-based process
cerium-based process
water seal
Sanchem process
others

The key parameter examined in the EIS measurements is the polarization resistance, in 0.5 M NaCl, at 24 hrs. This parameter was found to correlate very well with salt fog pass/fail probability. In addition, the pit resistance was found to correlate well with the barrier properties of the coating (high pit resistance = good barrier properties). Kendig explained that the excellent performance afforded by CCC's comes from three main features of these coatings:

1. Barrier properties
2. Hydrophobicity
3. Active species in the film (e.g., Cr(VI)) which protect weak spots or developing corrosion pits. The hydrophobicity of some of the replacement technologies appears to be a keycontributing factor to the fairly good corrosion protection performance observed. However, Kendig found no Cr(VI)-free coating process that performs as well (on 2024-T3 Al) alloy as CCC's.

Questions/Answers/Comments:

Mansfeld: In 0.5 M NaCl, EIS measurements of polarization resistance at 24 hours should not, in his opinion, be a good measurement of corrosion protection. The reason is that after this short of a time period, corrosion has not really started to any significant extent.
Rungta: The EIS test could be accelerated by using acidified 0.5 M NaCl as the electrolyte.

Talk #2, Hughes, "Electrochemical Evaluation of Corrosion Performance of Conversion Coatings": He used a variety of methods to study conversion coatings, including:

X-ray photoelectron spectroscopy (XPS)
Scanning electron microscopy (SEM)
Energy dispersive x-ray spectroscopy (EDX)
EIS
Salt fog
Electrochemical Tafel behavior

Over 1000 samples were evaluated by EIS and by the Tafel technique, in the hope of using the corrosion current (i_{corr}), the corrosion potential (E_{corr}), or the difference between the corrosion potential and the pitting potential (E_{corr}-E_{pit}) as an indicator of coating performance. Hughes seemed to find some correlation between E_{corr}-E_{pit} and the aging time of a sample in either water or in a relative humidity (RH) chamber held at relatively high humidity levels. For an as-prepared coating prepared by a $CeCl_3$ process, SEM shows very evident cracks near regions of high intermetallic concentration (particularly intermetallic species containing copper). These cracks are evident even before salt fog exposure.

Questions/Answers/Comments

Mansfeld: The $CeCl_3/H_2O_2$ process can produce pits via a redox process (H_2O_2 reduction coupled with Al oxidation).
Buchheit: The evidence presented in the talks thus far seems to indicate that we are discovering the "normal" pit resistance for 2024-T3 Al alloy (about 7-10 Mohm/cm^2).
Mansfeld, Carlson: CCC's made under different relative humidity conditions (e.g., a high humidity climate such as Hawaii vs. a low humidity climate such as New Mexico) will have different performance properties.

Talk #3, Walker, "Testing and Specification of Conducting and Protective Coatings for Al Alloys": Presented philosophy related to design engineers calling out specifications, and how these specifications should be related to product performance, the choice of materials used in the coating process, etc. Walker promotes the idea of defining specifications for coating performance based on actual requirements, rather than indiscriminate calling out of CCC's based on their excellent performance (e.g., it may be overkill in many instances).

Questions/Answers/Comments

Baudrand: Has observed "capillary holes", e.g., pits, whenever they attempt to perform nickel electrodeposition onto Al alloys. These look very similar to the pits Walker observes in CCC-treated Al alloys where Fe particles are present at the surface.
Jenkins: Doesn't see a need to call out or generate an all-encompassing specification for coating weight. He strongly believes in having conversion coating users tell the vendor what performance requirements have to be met (and then letting the vendor supply the appropriate materials and processes to meet their needs) rather than the user telling the vendor what type of conversion coating process and coating weight they want.

Talk #4, Taylor, Non-Chromate Inhibitive Pigments": Pore resistance (Rpore) is not a good predictor of visual results (e.g., how many pits can be observed on the surface). In contrast, polarization resistance (Rp) is a good predictor.

Talk #5, Walker, "Silane Adhesion Promoters": These materials, applied either as a pretreatment (i.e., a primer) or as an additive to the paint material, have been shown to improve adhesion of paints to Al alloys. In general, better adhesion is observed when the silane is used as an additive.

Talk #6, Mansfeld, Presented results of a study of the use of EIS to discriminate among coatings over untreated 7075-T6 Al alloy and 7075-T6 Al alloy which has been pretreated to remove Cu from the surface. The EIS results for the untreated sample showed a higher impedance in the d.c. limit, while the pretreated samples show a "transmission line" type impedance in the d.c. limit. His conclusion is that is very difficult to discriminate among coatings with this approach.

Session 2, Moderated Discussion of Topics Introduced at Beginning of Session:

1. What methods are used for rapid life prediction?
    - ASTM B117
    - Polarization curves
    - EIS
    - ASTM G85 (Acidified salt fog)
    - "Prohesion Test"

Electrochemical noise method (for polymeric coatings only)
Various cyclic corrosion tests

5. Do formulators of conversion coatings use electrochemical methods?

Jenkins: Electrochemical methods used for R&D purposes only.
Carlson: Electrochemical methods used as research tools only, for measurement of dielectric constant and impedance.
Bibber: Electrochemical methods used only in the measurement of the dielectric constant as specified by an ASTM method.
Jenkins: It is difficult to correlate the results of any test method with the results of the salt fog test. It is a mistake to compare electrochemical results to salt fog results; rather, the important comparison to make is between electrochemical results and the actual performance of the part in the service environment.
Carlson: Harrison/GM is now so confused about testing that some hydrophobic coatings from Parker + Amchem are being evaluated now based only on their performance in a 3 year service test in a car. Rungta concurs.
Golden: 168 hour salt fog is often too slow to give the needed real time or near real time process control required in a manufacturing environment. There are real needs for faster screening methods.
Mansfeld: How can you expect to test an Al part (that is supposed to last 5 years) in a 24 hour test? The only possible way is be incorporating an accelerating condition in the electrochemical test.

2. Is American Society for Testing and Materials (ASTM) Test Method B117 (salt fog corrosion test) relevant?

Kending: Posed the deeper question, "Did ASTM B117 become what is is because CCC's can pass the test?" Another way of asking the question is "Did CCC performance dictate the actual conditions of the test?"
Horner: an active member of ASTM for over 30 years, has served on committees that developed and reviewed test methods. In his opinion, ASTM B117 should be used as a development too, but not as a process specification.
Carlson: Thinks that in the future, test methods will have to be specific for individual CC processes as well as for their use in different applications. ASTM B117 will be complemented by a number of substitute test methods. Also says that ASTM B117 is a very subjective test, such as in the interpretation of the "pits visual to the naked eye" phrase.
Rungta: There will not be any one test method that is relevant to every application. Harrison Radiator/GM uses a very specific test method that makes sense for their particular application.

3. What do electrochemical impedance spectroscopy (EIS) and other rapid electrochemical methods predict? If they are predictive, what are the details of the experiment and analysis? What is the correlation, if any, to salt fog testing? What are the statistical implications?

Mansfeld: They give good information about the status of your coating, but it is dangerous and even impossible to use them as predictors of service life. For polymeric coatings, EIS is an excellent technique for measuring water uptake (capacitance increase), polymer degradation, etc.
Buchheit: EIS also has some subjectivity, something inherent with any technique which relies on equivalent circuit models for data interpretation.
Vega: A combination of accelerated environment testing, electrochemical testing, and ASTM B117 is the best approach to most every problem.
Rungta: It is crucial to the success of electrochemical methods to continuously monitor field service data and feed this information into the electrochemical data base. Only then can correlations be established.
Carlson: The strategy really should be to find the test that correlates with field service life, i.e., build a test capable of testing known field data.
Walker concurs.
Guilinger: Do CCC's ever fail in the field?
Walker: In U.K. weapon applications, he has not observed a failure that could be attributed to the corrosion of a chromate-conversion-coated part.
Golden: A more appropriate question would center around the failure of a part or system which had a complete corrosion protection package (i.e., CCC + topcoat). He has been in the aerospace industry 7 years and is still puzzled by the common practice of corrosion testing of stand alone, chromate conversion coated parts (i.e., parts that have not received a primer or topcoat). Airplanes, for example, always have 1-2 primer coats and 1 topcoat on top of the CCC. The difference in appearance of certain U.S. commercial airliners (the painted planes of United Airlines vs. "clad skin" planes of American Airlines) represent 2 different approaches to the economic and maintenance requirements of corrosion protection.
Kendig: "Does anyone have a screening method that relates to field service life?"
Rungta: Harrison/GM is in the process of uncovering the correlation between ASTM G85 (acidified salt fog) and field use. Correlation will be in place by Fall 1994.
Vega: Suggests that cyclic corrosion testing (cyclic temperature and/or cyclic humidity levels and/or cyclic salt concentration), which can be designed to simulate the cycling between winter and summer corrosion conditions, should be examined as a more pertinent test than ASTM B117.
Horner: Discussions about the relevancy of ASTM B117 is also going on in the ASTM BO8 Committee on Electroplated Coatings and Conversion Coatings. Horner invites all interested and qualified people to join the subcommittee that is examining the possible revision of ASTM B117.

4. Can electrochemical methods be as efficient as salt fog for screening? See above discussions.

6. Do original equipment manufacturer's (OEM's) use electrochemical methods? Not discussed during this session.

Session 3, Preparation for Coating:

Goals for this Session, Mansfeld: Outlined the key topics to be addressed during this session:

1. Active component (e.g., Cu) removal or passivation during surface pretreatment.
2. Alternative surface cleaning and etching methods
3. Alternatives to chromate deoxidizers
4. Environmental, Safety and Health (ES&H) ramifications of alternative technologies.

Talk #1, Vega, "Surface Cleaning Methods for Zinc Phosphating of Aluminum Alloys": Presented balanced chemical equations describing the mechanism for phosphating of metal surfaces . Described the sequence for phosphating metal surfaces as follows:

oxide growth (boiling water, 7 minutes)
zinc phosphate (Fixodine ZN, 30 seconds, room temperature)

Talk #2, Drewien, "Surface Pretreatment of Aluminum Alloys for Hydrotalcite Deposition": Objectives of surface preparation are to provide uniform activity on the alloy surface by removing grease, removing non-uniform/non-homogeneous native oxide, and growing a new, homogeneous oxide. The surface preparation sequence is as follows:

degrease
inorganic clean (detergents, mild etchers, non-etchers (e.g., those containing silicate inhibitors
deoxidation (basic solution, acid solution, or mechanical removal)
desmut (if basic deoxidizer was used)

A number of factors are influenced by surface pretreatment, including adhesion, corrosion resistance, and coating growth and formation. Some of the environmentally-conscious replacement processes in use are as follows:

degrease - d-limonene
clean - phosphate/carbonate, silicate/carbonate
deoxidize - sulfuric acid containing sulfates and/or clathrates (which are H_2 and O_2 gas adsorbing molecules.

Several references regarding the surface enrichment of certain species in Al alloys were given as follows:

Mg - Sun, et. al, 1979; Gaillard, et. al, 1984
Cu - Pocius, 1983; Sun, et. al, 1978
Si - Tallant, 1980
Zn - Solomon and Hanlin, 1980
Cr - McDevitt, et. al, 1976

The sequence of surface preparation steps chosen for Hydrotalcite coating process is as follows:

vapor degrease
alkaline non-etch (Na_2CO_3, $NaSiO_4$)

immersion rinse
deoxidizer (HNO_3, NH_4HF_2)

Drewien then presented a Pourbaix diagram showing the distribution of Al and Cu species present as a function of potential and pH. She summarized her talk by saying that surface enrichment of Cu occurs on Al during deoxidizing pretreatment.

Talk #3, Mansfeld, "Surface Pretreatment of High-Copper Aluminum Alloys -Electrochemical Surface Characterization": Described Cu removal processes for 2024-T3 Al alloy:

1. Electrochemical polarization at -55 mV vs. SCE for 30 min in 0.5 M $NaNO_3$ + 60 mL/L HNO_3
2. 10 minute chemical treatment in a solution made of 22.8 g/L deoxidizer + 100 mL/L H_3PO_4 (which removes Cu but prevents its deposition. The basis for these methods is that Cu dissolves at a much higher rate than Al. The Cu removal process for 7075-T6 alloy is electrochemical polarization at -248 mV vs. SCE for 30 min in 0.5 M $NaNO_3$, (acidified to pH = 1 using HCl).

CCC's over electrochemically- and chemically-prepared samples show much less pitting than untreated samples when exposed for 30 days to 0.5 M NaCl. This is based both on visual observation of pitting and on EIS measurements of R_{pit} and C_{pit}.

Questions/Answers/Comments

Carlson: What is effect of copper concentration on CCC performance?
Mansfeld: We did not measure that, but it definitely will worsen performance at some concentrations.
Carlson: There is an industry specification that at [Cu] = 400 ppm, the bath should be replaced or the copper should be removed from the bath (e.g., by precipitation).

Talk #4, Hoier, "Alternative Cleaning Reagents for Organic Residue Removal from Aluminum Surfaces": Presented a talk on the effects of cleaners on CCC's. Traditional cleaners include:
freons
trichloroethylene (TCE)
trichloroethane (TCA).

Alternative cleaners include:
non-aqueous: terpenes, alcohols, esters
aqueous: high pH cleaners, amines, phosphates, silicates, proprietary solutions.

Described an amine containing cleaner called Kester 5768. A 10% solution in water attacks Cu at a rate of 3.5 microgram/min/cm2. Described another cleaner called Oakite 3800, which has been used on 2024-T3 Al alloy.

Questions/Answers/Comments

Chalmer: Uninhibited TCA will attack Al. TCA that contains small amounts of 1,4-dioxane as an inhibitor will not attack Al.
Murphree: There are a number of ES&H implications for these types of alternative cleaners. According to EPA SNAP rules (which govern Significant New Alternatives), acceptable alternatives for freons and include:

terpenes
alcohols
esters
ketones
supercritical carbon dioxide
perchloroethylene
trichloroethylene
methylene chloride

Unacceptable alternatives include:
hydrogenated chlorofluorocarbons (HCFC's), which will be outlawed by the year 2020.

Session 3, Moderated Discussion of Topics Introduced at Beginning of Session:

Question: What is in Deoxalume 2200?
Carlson: Was not willing to give the entire formulation, but did say that there are no metals or ferricyanide. It is a non-ionic, organic deoxidizer that leaves Al passive and attacks Cu. Cu dissolves and does not replate.
Mansfeld: Describes Deoxalume 2200 as a "chemical potentiostat".
Bibber: Sanchem's non-chrome deoxidizer contains 10% HNO_3, $NaBrO_3$, and wetting agents.
Kendig: It is important to choose a rack material in metal finishing operations that acts as a better cathode than the metal alloy being treated. This will provide a better site for Cu deposition so that redeposition of Cu does not occur on the alloy.
Zavadil: Providing, for instance, a Pt cathode may, however, not totally solve the problem of localized copper concentration increase in the vicinity of the Al alloy boundary layer.
Mansfeld: Removing Cu during pretreatment also does not guarantee that you won't etch through the Cu-free layer down to the Cu-containing substrate during the conversion coating process (which typically occurs at low pH, e.g., pH = 1.8 for CCC process).

Session 4, Emerging Coating Technologies:

Goals for this session, Buchheit: There are a number of important factors to think about when considering new coating technologies. These include:

1. viability of new coatings

2. matching new coating properties to particular applications
3. determining where gaps exist between the performance of CCC's and the performance offered by the suite of new technologies
4. How are the gaps filled (or how are they going to be filled) both in a technical sense and in a management sense?

Talk #1, Sugama, "Sol-Gel Synthesized Polymetallosiloxane Coatings": Described the use of monomeric organosilanes in the formation of coatings that attach themselves, via a polycondensation reaction, to the aluminum surface through a very stable oxane bond (Al-O-Si). The formulation used in the sol-gel process is:

8-11% organosilane
3-5% metal alkoxide
80% water
6% methanol

Tafel experiments on these coatings have successfully related the corrosion current, icorr (microamps), to the corrosion rate (milliinches/year). In addition, they see no significant corrosion after 2000 hours of salt fog.

The processing sequence is as follows:

alkali soak
rinse in water
dry at 100 C
immersion in precursor solution
heat at 100 C to yield xerogel films
pyrolyze at 200 C to form film

Questions/Answers/Comments

Kendig: The contact angles reported in the presentation indicate that the film is still hydrophilic, and hydrophilicity is bad for barrier-type corrosion protection.
Sugama: They are less hydrophobic than they were prior to aging.

Talk #2, Stinnett and Buchheit, "The Use of Intense, Pulsed Ion Beams for Materials Surface Treatment": Described the use of proton beams in aluminum surface modification. Some features of the treatment are:

0.5-1.0 MeV proton beam energy.
Ion range is 3-7 micron in stainless steel (0.5 MeV gives about 5 micron depth in Al).
Energy density is 2-8 J/cm^2 for the melt.
There is high cooling rate (1x10^{10} K/sec) due to thermal diffusion into substrate.

Stinnett presented a fairly thorough cost and throughput analysis of this process, and said 4000 sq.ft./hour at $0.03/sq.ft. is typical.
Buchheit described the corrosion behavior of ion-beam treated Al alloys, and showed that, for some alloys, the corrosion resistance is significantly

enhanced, due to the fact that impurities (e.g., Cu) remain in solid solution and are not available to initiate corrosion. Ion beam surface treatment protects 2024-T3 and 7075-T6 Al alloys, but does not protect 6061-T6 alloy.

Questions/Answers/Comments

Golden: What about fatigue?
Buchheit: Fatigue is currently being investigated.
Rungta: What is the area treated per ion beam pulse?
Buchheit: 200-300 cm^2.
Martinez: Can you process 3-dimensional parts?
Buchheit: The process currently uses a 3-dimensional planetary rotation fixture. It is a "line of sight" process, so it really depends on the details of the part geometry, but some 3-dimensional parts can be processed.

Talk #3: Buchheit, "Chromate-Free Talc Conversion Coatings for Aluminum"

Questions/Answers/Comments

Carlson, Golden: Your polyurethane paint adhesion can probably be improved by an acid rinse of your coating (since urethane curing is an acid-catalyzed process).

Talk #4: Chalmer, "Overview of the NCMS Chromate Alternatives Project": Provided a background of the National Center for Manufacturing Sciences (NCMS), which was organized under the National Cooperative Research Act of 1984, which rescinded some anti-trust laws and allowed pre-competitive cooperative research among industries.

By January 1994, NCMS will make available a thorough report on the emissions from surface finishing operations, based on an extensive survey of plating shops in North America.

Chalmer described in detail the NCMS assessment program on the usefulness of Cr(VI)-free alternative metal finishing processes. This is a 12 month project which will involve the following companies:

Allied Signal
General Motors
Texas Instruments
United Technologies
Kodak
Sandia National Laboratories
CTC (Johnstown, PA)

This project will look at the effectiveness of the following coating processes on 2024-T3, 6061-T6, 7075-T6, 3005, and 356 Al alloys:

Cerium (Australia)
Cerium (General Motors)
Cerium/Molybdate (Mansfeld)

Alodine (phosphate and organic)
Alodine (cobamine)
Betz Metchem
Sanchem
Turco
Hughes
Lithium (Sandia National Laboratories)
Lithium + Nickel Acetate (Sandia National Laboratories)
Silicon (Northrup)
Molybdenum (Northrup)
Okemcote (Oakite)
Polymer coating (University of Connecticut)
Other possibilities identified by check of QPL (Mil-C-81706)

The primary testing protocols will be:
ASTM B117 (salt fog)
Potentiostatic test (RPI method)
Mil-C-81706 (Conductivity)
Mil-C-81706 (Adhesion)

The secondary testing protocols will be:
Acidified salt fog
Other tests

The target start date is November, 1993. The confidentiality and distribution issues related to the final report are still being decided upon.

Talk #5, Murphree: Presented the threshold limit value (TLV) and permissible exposure limit (PEL) for a variety of materials that have been discussed as alternatives during this workshop:

Material	TLV (mg/m^3)	PEL (mg/m^3)
Cr	0.5	1.0
Cr(VI)	0.05	1.0
V_2O_5	0.05	0.05
Mo	5-10	5-10
Mn	1-5	5
Ce	N/A	N/A
Ni	0.1-1.0	0.1-1.0
LiH	0.5	0.025
F-	2.5	2.5

Session 4, Moderated Discussion of Topics Introduced at Beginning of Session:

<u>Martinez:</u> What are the stress corrosion cracking issues related to the use of alternative coating processes? Specifically, do replacement coating processes need to have the self-healing capability that is a characteristic of CCC's?

Golden: For aircraft applications, a substitute CC coating must have self-healing capabilities.

Workshop Summary:

Each of the individual session chairs provided over a summary/discussion session on the topics covered during their sessions.

Session 1

Question: What stage are the commercial replacement coating processes in?
Carlson: Parker + Amchem is in pilot scale phase, are aiming at aircraft applications in collaborative project with Boeing.
Bibber: Sanchem CC is commercially available.
Jenkins: Allied Kelite's Chemidize product is commercially available.
Halverson: Birchwood Casey's phosphate polymer product is commercially available.
Question: What process steps are used in replacement coating processes?
Carlson: Parker + Amchem's process will be in workshop minutes (viewgraphs).
Bibber: Sanchem process for 1xxx, 3xxx, 5xxx, and 6xxx Al alloys is as follows:

alkaline clean
rinse in mild acid solution, or deoxidize
Sanchem 2000 conversion coating process
final rinse

The Sanchem process for 2xxx and 7xxx Al alloys is as follows:

alkaline clean
rinse
deoxidize
rinse
boiling water or steam treatment
rinse
Sanchem 2000 conversion coating process
rinse
Sanchem 3000 process
rinse
Sanchem 4000 process
rinse

Jenkins: Allied Kelite's Chemidize 727A process involves the use of a paste, that is diluted and then applied by airless spray. The sequence is as follows:

1 step cleaning and coating process (produces a 8 mil thick coating)
dry
water rinse
dry
paint

No deoxidizer is needed. Allied Kelite's customers for this process are predominantly in the aerospace industry.
Halverson: Birchwood Casey's process are contained elsewhere in the workshop minutes.

Session 2

Kendig: Provided an excellent summary and overview of the presentations and discussions. These are contained elsewhere in the minutes.
Drake: Future CC's are, in his opinion, going to be very application specific. There will be a world of applications and a world of CC's to cover them.

Session 3

Zavadil: Active Cu (or any other metal) removal may be a misnomer. The preparation for coating process will probably include some combination of removal, prevention of redeposition, and passivation (either by incorporation of a high valence metal, such as Cr(VI), or by complexation of the active metal).

Session 4

The issue of "self healing", which is one of the key characteristics of CCC's and is something that would also be desirable in non-Cr(VI) CC's, was extensively discussed:

Kendig: Self healing does not happen for macroscopic defects in a CCC (i.e., for a visible scratch mark. Rather, it is something that occurs for microscopic cracks only.
Carlson: Soluble Co(III) is chelated by Parker + Amchem's seal process, and it gives a self healing property to their cobamine-based CC process. He sees evidence for soluble Co(III) at deformed areas on the Al surface. In addition, there is 30 years of Parker + Amchem research that proves that water-soluble Cr(VI) is, in fact, solubilized to deformed areas and/or scratches in Al CCC's. Self healing is a real property of CCC's.
Kendig: Cr(VI) is definitely present in CCC's. Reference: Corrosion Science 1993 article authored by Kendig and his collaborators at Brookhaven National Laboratories on XANES of CCC's.
Rungta: XPS does not indicate the presence of Cr(VI) in CCC's.
Kendig: That is because in the XPS experiment, Cr(VI) is reduced to Cr(III).
Bibber: Cited an article authored by someone from Parker + Amchem that questioned the existence of Cr(VI) in CCC's.
Carlson: Debated the point with Bibber.
Kendig: The ratio of the concentration of Cr(VI) to that of total Cr in the CCC is about 0.15-0.25.
Carlson: Concurs with Kendig on this point.

Notes from the Third Annual Chromate Replacement Workshop - Set 2

Introduction:

G. Murphree's (UTRC) presentation on regulations detailed in the Clean Air Act was followed by a discussion of the hazards of Cr. It was emphasized that waste regulations do not distinguish between Cr(VI) and Cr(III) despite the fact that the former is the carcinogen. Kendig suggested the possibility of detoxifying waste by electrochemical oxidation of Cr(VI) to Cr(III) and pointed out that Cr(III) is heavily used in the cosmetics industry. It was suggested that a mechanism exists in nature to reconvert Cr(III) to Cr(VI) indicating that Cr(III) may not be a safe, stable reservoir.

Session 1: Commercially Available Products

L. Carlson (Parker+Amchem) presented a discussion of Alodine 2000, a modified version of cobamine®, being developed through a joint venture with Boeing. Discussion centered on the characteristics and structure of this coating. The coating has a tubular, porous structure based on cobalt oxides. Carlson emphasized that sealing the film provides the resulting corrosion protection. The sealant is an organic-based reagent that penetrates the porous structure producing a more impermeable structure. Improved corrosion resistance for Al 2024 was reported to result from complexiometric passivation of Cu at the coating/Al interface. The process also benefits from the fact that film growth is not accompanied by metal dissolution, so no Cu is released. Cu enrichment at the surface during deoxidation and desmutting can be eliminated with the use of P-A's Deoxalume® products.

J. Bibber (Sanchem) discussed his company's MnO_x-based CC-A coating. Discussion focused on the mechanism of corrosion protection. Bibber invoked the standard chromate mechanism and claimed that a reduced state of Mn^{n+} is the active agent in the film. The films are predominantly Al_2O_3 with MnO_x at the surface. Questions were asked as to why other transition metals, such as vanadium, did not show similar behavior. Differences were attributed to the solubilities of the oxides. The hazards of Mn were also a topic of discussion. Bibber emphasized that the use of $K_2Mn_2O_7$ in water treatment is standard protocol.

F. Mansfeld's (USC) presentation on stainless aluminum generated questions concerning the respective roles of Ce and Mo in the resulting alumina films. Mansfeld's understanding is that Ce deposits preferentially at defects sites in the film and Mo migrates into the film.

General Discussion: Discussion returned to the question of the relative hazardous nature of Cr and other transition metals. A compilation of permissible exposure levels Mo, Mn, etc. versus Cr is not readily available. Comparison of more available lethal dose 50% values based on oral injection provide some insight but do not represent a diagnostic for alternative to pursue. Discussion returned to the concept of coating selection based on application and cost from a host of technologies as opposed the direct replacement of chromate - the goal is "chromate equivalency". It was suggested that cost might drive selection. An alternate method might be preferred based on the added cost of administering a chromate program. Murphree emphasized that the EPA wants to regulate levels and not necessarily eliminate use. Critical technologies may continue to require a chromate process. It was pointed out that waste handling regulation treats all conversion coating processes as Cr-containing irrespective of composition.

Summary of Session 1:
General theme - conversion coating will be application specific - a world of applications exist.
Process flow charts were generated for the major products discussed.

Session 2: Performance Testing of Coatings

Summary of Session 2:
The relevancy of ASTM B117, salt fog testing was discussed. It was agreed that salt fog testing is easily conducted and controlled. Recent developments in cycled fog tests with the introduction of corrosive atmospheric contaminants or drying periods may more accurately depict variations in environment. However, the test provides only a qualitative response and pass/fail determinations are highly subjective. Accelerated testing can only go so far to predict field failure and is not a replacement for field testing.
A list of the electrochemical methods currently be used by attendees to test coating performance was generated. The question of what does electrochemical impedance spectroscopy predict was asked given that performance was evaluated for a limited time. Although EIS can be used to evaluate the presence of transport paths through organic coatings, disagreement still exists over the interpretation of anodized aluminum data and, to a much greater extent, for conversion coatings. The question of whether it was meaningful to correlate electrochemical test results with salt fog results was asked.
General conclusion - testing must be relevant to the application, multi-level testing is expected in most cases.

Session 3: Preparation for Coating

Moderators Mansfeld and Murphree introduced four topical areas of importance to surface preparation for coating:

Active component removal or passivation
Alternate surface cleaners
Alternates to Cr(VI) deoxidizers
Environmental hazards associated with the above alternates

C. Drewein (SNL) presented research and discussion on the pretreatment of Al alloys for hydrotalcite coating. The need to pretreat in order to achieve a uniform activity for coating growth was emphasized. Post-presentation discussion focused on the need to balance traditional and new, environmentally conscious procedures. A suggestion of using d-limonene as a potential reagent for organic removal was discussed. Questions were raised concerning its volatility from a safety perspective.

F. Mansfeld (USC) presented research and discussion focused on selective removal of Cu from Al alloys using electrochemical control as a pretreatment step prior to coating. The goal for electrochemical control is to favor Cu over Al dissolution. Relative dissolution rates are a function of alloy so electrolyte and potential must be matched with the behavior of a given alloy composition. Discussion focused on the likelihood of significant removal and the consequences of incomplete removal with subsequent conversion coating. The improved performance observed in the salt spray tests for 2024 could have resulted from the absence of galvanically redeposited Cu at the alloy surface and not significant Cu removal. It was pointed out that the polarization times (30 min) might be to long for a commercial process and that potential control would be difficult with parts of complex geometry. Comparison was made of electrochemical versus chemical control of potential. The term "chemical potentiostat" was introduced. J. Bibber (Sanchem) explained the role of BrO_3^- as a chemical potentiostat in the Sanchem deoxidizer; BrO_3^- prevents the redeposition of Cu by keeping it in an oxidized state. Kendig suggested the use of a proximal cathode that would serve as a preferred site for Cu redeposition.

S. Hoier (SNL) presented research and discussion centered on the use of alternate cleaners for organic residue removal on metal surfaces. The non-aqueous alternates (terpenes, alcohols, and esters) are all considered too flammable. The aqueous alternates (amines, phopshates, and silicates) form high pH (>10) solutions. Sally has observed selective dissolution of Cu (3.6 $\mu g/sec \bullet cm^2$) in an commercial amine-based cleaner. Concerns were raised over the use of low volatility cleaners and the potential for carrying over contaminants (the cleaner itself) into the next process step. The extensive use of organic reagents at the reducing surface of a metal raised concerns over the possibility of polymerization and a resulting surface product.

G. Murphree (UT) followed-up with an informal presentation addressing what restrictions were currently placed on which commonly used reagents for "precision" cleaning: Perfluorocarbons will be allowed, fluorocarbons will only be allowed for critical applications, and the restriction on brominated hydrocarbons is still pending.

Summary of Session 3:
Active component removal or passivation:

The strategy for dealing with an active component will be application specific. Limited Cu removal from Cu-bearing precipitate phases is possible through selective chemical and electrochemical dissolution. Galvanic redeposition of Cu on the alloy surface can be eliminated with potential control either electronically or chemically. Cu removal may not be feasible for conversion coating of an alloy because additional etching of the substrate is required to form the coating. Passivation may be required to deactivate Cu released or exposed during the conversion coating process. Little discussion was given to possible passivation schemes with the exception of Parker+ Amchem's proprietary organic reagents to penetrate porous cobamine® films. Alternate deoxidizers are also expected to be highly application specific.

Session 4: Emerging Coating Technologies

R. Buchheit (SNL) presented research on hydrotalcite coatings for Al alloys. Interest was focused on film structure and properties. Testing has shown that 1XXX, 2XXX, 6XXX, and 7XXX series alloys all show the characteristic bi-layer structure, complete with the amorphous, carbonate-free inner layer. The different alloys tend to have varying amount of different impurities in this inner layer. Questions were raised about the poor paint adhesion for these talc coatings. Suggestions were made to produce an acidic surface so as to optimize interaction with the paint.

P. Chalmers (NCMS) presented an overview of the chromate replacement program. Suggestions were made for specific materials additions to the round robin tests proposed in the program. Murphree suggested adding Al 2219 because of its high Cu content and its interest to the space flight community. Vega suggested adding a Li/Al alloy. B. Bonivert (SNL) suggested adding a Zn alloy because of interest in Zn alloy cladding. Chalmers indicated that non-Al alloys had been considered but concern existed with burdening the test program. Concerns were voiced over the time delay between coating and painting and the impact on test results. Chalmers explained that not all members would be conducting paint tests.

General Discussion:
G. Murphree successfully tracked down TLV and PEL values transition metal salts, including Cr. A viewgraph was presented with this data.
E. Martinez (SNL) raised concerns over the fact that stress corrosion cracking (SCC) had not been addressed during the workshop. Martinez was of the opinion that Cr activity specifically inhibited SCC. Comments were made that SCC is initiated at surface flaws and any coating can have an impact on the likelihood of SCC becoming a corrosion issue. Kendig suggested that a SCC test can be incorporated into an overall coating evaluation effort. Questions were raised as to how corrosion fatigue and SCC can be differentiated in an electrochemical test. The frequency dependence is expected to be different for these two processes. Appropriate selection of electrolyte should aid in their respective identification.

Session 4 Summary:
General conclusion - a suite of methodologies exist for producing anti-corrosion coatings - the goal is to achieve chromate equivalence for a given application - this approach is in opposition to seeking a single replacement. Discussion of chromate equivalence brought about discussion of the mechanism of self healing of a coating. The active agent in chromate films is thought to be Cr(VI). Kendig commented on measuring 15% Cr(VI) using X-ray Absorption. Carlson concurred with this observation indicating that they

routinely measure 15 - 20% Cr(VI) in Alodine coatings. Coating dehydration leads to Cr(VI) loss. Leaching studies by Kendig suggest a time constant of 10 - 15 days for Cr(VI) in the film. Carlson claims that self healing properties have been observed with the Alodine 2000 coatings. The active agent is reportedly Co(III) stabilized by complexation with the organic infiltrant.

Notes from the Third Annual Chromate Replacement Workshop - Set 3 Supplements to Attached Vugraphs

Introduction:

Gail Murphree:

--Airborne Cr^{VI} standard will reduce by factor of 200.

--EPA says Cr^{VI} is on list of 190 materials to be restricted.

Session I:

Talk 1. Larry Carlson:

Alodine 2000 joint development with Boeing Alodine 2000 in a no-chrome conversion coating.

Goal--develop coating to pass MIL-C 5541, MIL-81406.

Process:

1. Aqueous degrease
2. Tap H_20 rinse
3. Deoxalume 2100
4. Tap H_20 rinse
5. Deoxalume 2200
6. Tap H_20 rinse
7. Alodine inorganic 2000
8. Tap H_20 rinse
9. Parker-Amchem (organic) Sealant
10. Tap H_20 rinse
11. Oven dry 160°F

Alodine 2000 - known previously as Cobamine

--no metal dissolution

--no fluorides, PH 6-6.2

--coating wt. 25-250 mg/ft^2

--coating clear to dark gold

--clear to about 30 mg/ft^2

--chromates clear to only about 5 mg/ft^2

In Carlson's vugraph on salt spray testing, PASS means >95% passed the fewer than 9 pits for 3"x 9" panel requirement.

Talk 2. John Bibber:

--$KMnO_4$ based deoxidizer/coater pH about 7

--Used and approved for mailboxes. One dip process good for 1xxx, 3xxx, 6xxx Al alloys.

--Comes in many colors

--They feel that similarities between Mn and Cr yield positive properties.

--They get mixed Al/Mn oxides

Talk 3. Don Baudrand:

--Chemidize 727A Aluminum paste cleaner and organic conversion coating

--Primary use is for subsequent bonding by paint

--Cleans SS and chrome

--Cleans surface for up to 12 months storage before painting

--Brush on/spray on application
--Gel formulation

Talk 4. Dave Halverson:
Phosphate Polymers

--Zinc Phosphate/Chromate - Phosphate polymer bath
--Reacts with metal
--Form anchoring points with surface
--In the film, Cr^{VI} reduced to Cr^{III} during curing
--Cross-linking occurs during curing
--Curing makes hard, barrier coat
--Suitable for paint base

Talk 5. Florian Mansfeld:
Cerium/Moly complex Process:
- for Al 6061
  - Degrease
  - Deoxidize
  - Bake to get Al oxide
  - Boil in Ce Nitrate
  - Boil in Ce Chloride
  - Polarize in Sodium molybdate
- for Al 7075 do
  - Nitrate
  - Molybdate
  - Chloride in this order

Session II

Martin Kendig -- Goals

-What methods are used for life prediction?
-Is ASTM B117 relevant
-What do EIS and other electrochemical (echem) methods predict?
  Correlations established?
  Statistical implications?
-Can echem be used for screening/process develop?
-Do formulator or end user use any echem methods for qualifying?

Talk 1. Martin Kendig:
Comparison of Echem and salt fog

Found correlation between salt fog passing and Rp (polarization resistance). R_{po}-pit resistance doesn't correlate too well with salt fog. But they see some correlation of wettability (measured with contact angle) and passing salt fog.

Want hydrophobic surface.

Comparison between echem and fog:

echem is submerged -- fog is thin layer. Increased corrosion and O_2 in thin layer.

Talk 2. Tony Hughes:

Characterization techniques	XPS SEM EIS Salt fog

Data on 1000 samples -- salt fog, Tafel slope.

Aging at different RH's indicate early coating failure at 0% RH. Drying of coating. Cracks occur in dry atmosphere aging. Mild or no correlation between salt fog "time to visual corrosion" and impedance. Some correlation of i_{corr} (corrosion current) with performance.

Talk 3. Peter Walker:

Specifications define conversion coatings.

Do we need 14 day salt fog resistance? Do we need conductivity? Contrast preparation conditions of Hawaii and Albuquerque. Do you get different coatings? Yes, Tony Hughes results suggest. This was Florian's question initially. Identical chromate solutions yield different coating weights in successive trials. Different coating weights yield different salt fog failure times. Pointed out salt fog testing differences between wrought and rolled alloy.

-Conductivity: bulk vs. surface, contact resistance, contact pressure.

-Adhesion: What method are we measuring adhesion or coating elasticity? What humidity measured at?

Informal Presentations:

Peter Walker:

Adhesion promoters other than chromate conversion for paint overlayers. He recommends silane promoters. Showed excellent increases in adhesion compared to bare Al for various paint topcoats. Studied with and without water exposure. Non-toxic.

Ray Taylor:

Replacement for Strontium chromate in Pigment. Examines Rpore and Rp vs. exposure time. Work in progress. Sees 3 time constants in impedance data. Rpore/C and Rp/C and some diffusional RC (solid state). New time constants appear with increased exposure. Point: diagnostic on impedance plot may be at low freq. causing long experiments. Look for diagnostic at high freq. for quicker experiments.

Session III

Talk 1, Luis Vega:
Zinc Phosphating of Aluminum Alloys

-Goal -- Process steel and Al in same system
-First step -- grow oxide in boiling H_2O-oxide thickness grows then slows with time after about 30 sec.
-Increasing oxide thickness begins to yield voids in oxide.
-Zinc phosphate coating on oxide deteriorates when oxide thickens > 50 nm.
-Zinc phosphate coverage on 5030 steel greater than on Al C210 or 7003 extrusions.
Future -- Pretreat to enhance Al coverage.

Talk 2, Celeste Drewien:
Surface pretreatment before coating

ASTM B253-Surface preparation for plating on Al
--Purposes of preteatment -- clean organic/inorganic debris, remove native oxide, grow uniform Al oxides, remove alloy constituents that are undesirable.
--Effects of alloy heat treatment
--Mg enriched by oxidation T>450 C affects adhesion

Talk 3, Florian Mansfeld:
Electrochemical pretreatments for Al

-Cu more active than Al in $NaNO_3$ solutions.

-On exposure tests vugraphs in O.15N NaCl, pitted area (%) measured by impedance.

-AR on Florian's vugraphs means as-received.

Discussion:

Larry Carlson:
Deoxalume 2000 (non-etching desmutter-it removes Cu)
    -no ferricyanides
    -no chromates

John Bibber:
Sanchem Deoxidizer 1000
    sodium Bromate + 10% HNO_3
    Lockheed is using it

James Fournier

Their chromate elimination team found that there was no significant effect of deoxidizer on performance of chromate conversion coatings.

Gail Murphree:

Non-Acceptable cleaners:	perfluoro carbons some HCFC's brominated hydrocarbons

Session IV

Talk 1. Toshi Sugama:

Sol gel coatings

Composition: Si, Zr, O, Cl polymer

Process:	1. Alkali soak		2. Rinse
	3. Bake		4. Sol-gel dip
	5. Cure		6. Pyrolyze

Talk 2. Regan Stinnett:

Metal cleaning using pulsed power

-RHEPP = Repetitive high energy pulsed power

-Treats >100cm^2 at a time. Chamber P=100 mtorr, part must be at partial vacuum (industrial type -- not research type vacuum).

Talk 3. Rudy Buchheit:

Talc-based coatings for Al

-Temp effect -- Talc outgasses @ 115-160°C

-Bilayer structure present on all A1 alloys tested, 1100, 6061, 2024, 7075.

Talk 4. Paul Chalmer:

-Chromate replacement project

-Over 12 months, test emerging technologies in a board range of applications, using different member companies.

-Substrates: 2024, 6061, 7075, 3005 alloys, cast alloy 356

Suggestions: Gail Murphree: 2219 alloy
Luis Vega: Al-Li alloy -He could supply them

-Participants contributing $10-40K in-kind each

-NCMS contributing $60K

-Total Project $250K

-Testing done in-kind

-Funds for environmental impact studies.

-Testing to do:
Primary Salt spray per ASTM B117
Potentiostatic testing by RPI
Conductivity per MIL 81706
Paint adhesion per MIL 81706

-Samples prepared by each supplier using their own pretreatments.

-Final report hopefully will include assessment of every coating and every test result identified by coating.

Fred Drake: suggests watching out for painting on old, prepared substrates. May get different results than if you had painting on freshly prepped surface.

Discussion for Session IV:

Ed Martinez: What about stress corrosion cracking (SCC) and chromate conversion coatings?
Consensus from Rudy Buchheit, Johnny Golden, Celeste Drewein is that SCC is not affected by coating as long as it protects. But Martin Kendig says Cr^{VI} in coating could be aiding in preventing SCC.
Johnny Golden discussed fatigue vs. SCC testing at Boeing.
Mel Jenkins said NADC did extended study on SCC and chromate conversion coatings.

Question to Sugama: What is the MW of organic chain. Does alkoxide MW affect coating?
Sugama: Cross-linking depends on MW

Workshop Discussion and Summary:

Session 1

John Bibber: 7 years of research on Sanchem process. Working with several companies. We can get references for users of all commercial products. Working with Warminister on Naval Air Uses. 2 processes -- one for 1000, 3000, 5000, 6000, one for 2000 and 7000 series. Final seal is a silicate seal producing an aluminosilicate.

Mel Jenkins: Al paste single step process for large structures. For painting on or spraying on. No clean necessary generally. It cleans and coats in one step. Thickness about 8 mil. After drying then ready to paint or adhesive bond.

Session 2

Martin Kendig: Stressed that we should not forget the SCC issue.
Fred Drake: noted that we must link application with particular coating.

Session 3

Gail Murphree: Fit deoxidizer to application. Non-chrome deoxidizers appear to substitute nicely for chrome-based deoxidizers.

Kevin Zavadil: Mix of metals in bath can give you mixed potential and preferential etching.

Session 4

Rudy Buchheit: Final discussion about scratching and healability. Discussion then turned to Cr^{VI} vs. Cr^{III}. Which are present?

Summaries of Sessions II and IV by the Session Moderators

Session II: Performance Testing of Coatings

I. Summary of the Discussion of Papers

"Comparison of Electrochemical Analysis to Salt Fog Behavior of Non-Chromate Sealed Anodized Al and Non-Chromate Conversion Coatings" (Martin Kendig)

What was the thickness of the sol gel tested?

Presenter: They are on the order of several microns

Florian Mansfeld suggested that rather than look at Rpit, it would be of more interest to look at dRpit/dt. He also commented on the differences between salt spray and salt fog. Salt fog is much more severe because of the thin layer of concentrated salt solution.

Can changes in the phase angle be used to predict the quality of the sealing process?

Presenter: Although the phase angle can reflect pore development, it is not predictive of performance.

Luis Vega asked was a CPE used to model the oxide capacitance?

Presenter: It accounts for the chemical heterogeneity of the oxide among others.

Ray Taylor added that the CPE behavior is ubiquitous to EIS measurements and can result from surface roughness, chemical heterogeneity and non-uniform current distribution. Aluminum is particularly susceptible to CPE behavior caused by surface roughness.

Isn't the polarization resistance value a function of the test solution? Should you use acidic solutions?

Presenter: Yes, Rp will be a function of the test solution. The acidity to use would depend on what environment you were trying to simulate.

"Electrochemical Evaluation of Corrosion Performance of Conversion Coatings"(Tony Hughes)

Are there different mechanisms for the different coatings which require different models for interpretation?

Presenter: Possibly.

Martin Kendig pointed out that an Rp of 10-30 Mohm cm2 correlated with passing the 168 h salt fog test - a result that is consistent with Rockwell results but it is not known whether this value applies to all alloys (other than for the observed anodized 2024-T3 materials).

Florian Mansfeld suggested that the performance of conversion coatings may depend on where you age it (e.g. Hawaii vs. Albuquerque).

This met with general agreement.

"Testing and Specification of Conducting and Protective Coatings for Al Alloys" (Peter Walker)

A participant from Allied Kelite pointed out that failures on Ni plated aluminum memory discs occurred at intermetallics, reminding us that the ability of a conversion coating process to protect aluminum may be limited by second phase particles in any given alloy.

II. Chromate Replacement Workshop -Report of the Performance Testing of Coatings Discussion Session

The discussion session focused on the following questions:

- What methods are used for rapid life prediction?
- Do formulators use electrochemical methods?
- Do OEMs use electrochemical methods to control and/or qualify processes?
- Is ASTM B117 relevant?
- What do EIS and other rapid electrochemical methods predict?
- What sort of accelerating environment should be used?

The discussion can be summarized in the following:

- What methods are used for rapid life prediction?

Methods used for predicting corrosion resistance include: B 117 salt fog, potentiodynamic polarization and polarization resistance measurement, EIS, G85 acid salt spray, 'Prohesion', electrochemical noise, cyclic corrosion tests.

- Do formulators use electrochemical methods?

Parker+Amchem, Allied Kelite, and Sanchem representatives all said that they use electrochemical tests including dielectric measurements, ac and dc resistance measurements. These tests are used only for a point of reference and some screening. The formulators pointed out that the customers require salt fog tests which are usually used for screening. It was pointed out that effort replacing the salt fog test with an electrochemical method should not focus on correlating electrochemical methods with salt fog, but rather correlating electrochemical methods with field experience or the 'real world'. Perhaps the best approach is to find a rapid test to correlate with field experience.

- Do OEMs use electrochemical methods to control and/or qualify processes?

Boeing has used electrochemical methods for screening, but would like to use rapid electrochemical methods in the production environments. Here rapid means test completion within 24 h. In production, the concern is not to predict corrosion life, but rather to recognize abnormal process conditions.

Ravi Rungta (GM) said that he uses electrochemical techniques for screening in limited applications, e.g. impedance of coating can be related to bath properties. They also use polarization resistance as determined by DC methods.

- Is ASTM B 117 relevant?

The above test is relatively easy to perform, is well controlled, represents a recognized norm, and detects changes in the process. Instances of the irrelevance of B117 to field conditions can be cited, in particular the order of Zn and Cd behavior in actual atmospheric exposure is reverse that from salt fog testing (Jack Horner). Indeed, there exists a considerable body of experience which suggests that the salt fog test does not correlate with environmental exposure. In general, salt fog testing does not correlate to field data but gives a "norm" by which things can be compared.

Other problems include the actual interpretation of the results since the pass/fail decision is highly subjective. Any rapid exposure test must be relevant to the application.

In general, it was pointed out that field experience should drive the development of a relevant test. Furthermore, acceleration should reproduce the field failure. However, it is not clear as to exactly what is the failure mode of conversion coatings (chromate or other). Cyclic test and accelerating chemistries (acidic) have been suggested. In the automotive industry, neutral salt + SO_2 relates to the service environment for certain parts. Comparable failures would take 3000 h in Bl17 test.

As a related issue, the question regarding the necessity of chromate conversion coatings for inhibiting SCC and CF has not been completely addressed. Do non-chromate films that resist pitting in salt fog have the same level of resistance to SCC or CF? This remains an important question that should not be neglected.

ASTM committee B08 deals with many of the issues brought up during the discussion of this question.

- What do EIS and other rapid electrochemical methods predict?

It is the consensus that EIS will not predict very long into the future, a 10 year life for example. However, EIS accurately and quantitatively describes the state of the coating at open circuit and non-destructively. (The impedance behavior for organic coatings, for example, is well understood.) It provides a useful research tool to characterize the kinetics of the degredation process.

It was suggested that the quantitative parameters from EIS for coatings may be used in statistically designed experiments. There was one word of caution that the interpretation of EIS is not entirely unambiguous in all cases.

A test that provides a continuous output rather than a binary pass/fail (like the salt fog) would be useful.

- What sort of accelerating environment should be used?

Regarding accelerating environments, the following points were made throughout the discussion:

- The acceleration should reproduce field failure,
- Acidified salt fog and cyclic corrosion tests should be considered,
- An accelerating environment in conjunction with electrochemical methods is necessary to develop corrosion life prediction,
- SCC and CF testing should also be considered. This point was not brought up in this session, but was considered important during one of the other discussion sessions,
- A lower chloride environment for organic coated materials should be considered as possibly more aggressive.

- Miscellaneous: During the summary session, the meeting organizer posed the following: Does corrosion testing of bare aluminum make sense, since it will be primed and coated?

In light of the session discussion, the session chairman suggested that it would make more sense for coated material to pass accelerated exposure using an accelerated test environment which simulated the field.

Rudy Buchheit brought up the issue regarding the wisdom that solving the problem for 2024 will then lead to solutions for all alloys by asking "Should we be looking at different coatings for individual materials?" There may be some coatings which will not be applicable for protecting Al 2024-T3, but can protect other alloys. It was pointed out that cast alloys may be as hard to protect as Al 2024.

Summary

The one theme of the discussion seemed to emphasize that there is a clear lack of connection between rapid electrochemical or accelerated exposure test methods and field behavior. Correlation would clearly depend on the particular application. In general, rapid testing, both electrochemical and accelerated exposure, provide for screening and process control. In the case of the B117 salt fog, it is recognized by customers, and easy to perform if not directly correlated to all or maybe any field behavior. Regarding the development of rapid electrochemical methods, effort would be better spent correlating it to field experience rather than the salt fog or other accelerated tests.

Emerging Coatings Technology

This session began with four presentations representing surface treatment technologies that may offer processes capable of replacing chromate-based metal finishing operations. Toshi Sugama of Brookhaven National Laboratories provided an overview of **sol-gel synthesized polymetallosiloxane coating methods** for aluminum alloys with emphasis on processing reactions, routes and resulting coating structure. Regan Stinnett of Sandia National Laboratories outlined a development effort underway at Sandia and Cornell University aimed at exploring the use of **intense pulsed ion beams for generating rapidly solidified surface layers** on aluminum alloys up to tens of microns in thickness for corrosion resistance. Rudy Buchheit, also from Sandia, presented a summary of results from an effort to develop a **chromate-free hydrotalcite (talc) conversion coatings** for aluminum using simple low-cost chemicals and traditional metal finishing processes. Finally, Florian Mansfeld from the University of Southern California presented results from work aimed at **passivating aluminum surfaces in cerium and molybdate solutions** under conditions of electrochemical polarization.

Additionally, Paul Chalmer of the National Center for Manufacturing Sciences (NCMS) provided an overview of the **NCMS Chromate Alternative Project** scheduled to begin in late 1993. This effort will comparatively examine the viability of approximately 20 candidate chromate alternatives. This project will undertaken by a consortium comprised of partners representing the commercial sector, universities and the National Laboratories with project coordination by NCMS.

The moderated discussion for this session was wide ranging with focus on general issues such as **"why replace chromate in the first place ?"**, and specifics like **"what emerging technologies are capable of generating self-healing coatings ?"** (answer: none yet).

There is apparently no lack of motivation for continuing to develop alternative metal finishing operations for chromate-based light metal finishing. For example, Gail Murphree from NASA? pointed out that the Occupational Health and Safety Administration (OSHA) is proposing a **200 fold reduction (100 μg/m to 0.5 μg/m3) in Permitted Exposure Limits (PEL) for airborne chromium in the workplace by 1995**. Several anecdotal reports were made concerning difficulties in finding certified dump sites willing to accept chromium-bearing sludge for disposal. It was also pointed out that **government agencies will regulate based on chemical species and not on oxidation state**. The net effect being that metallic Cr, Cr (III), and Cr (IV) will be considered equally hazardous from a regulatory perspective.

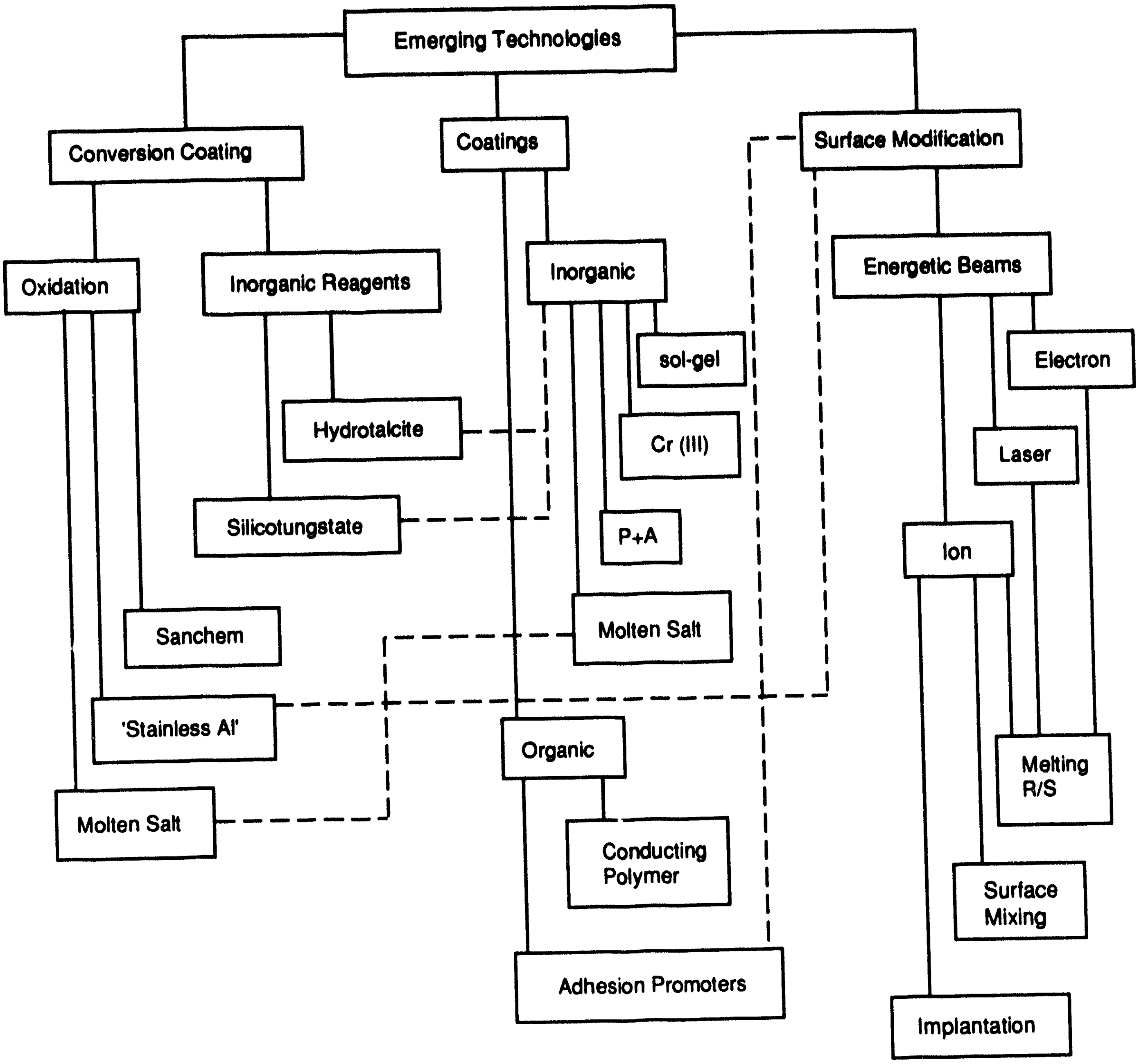
It was clear from the presentations and discussions that the technical arena for chromate alternatives is still wide open. **No single technology has yet emerged that can serve as a "drop in replacement" for chromate conversion coating**. For example coatings that offered outstanding corrosion protection were typically formed through complicated processes that are difficult to implement. Conversely simple coatings methods do not yet offer coatings that can provide corrosion resistance to high-Cu aluminum alloys.

The ability of an emerging coating technologies to gain trust among metal finishers was identified as a crucial component for widespread acceptance. The metal finishing community recognizes chromate conversion as the benchmark for inorganic corrosion resistant coatings for light metals, since chromate-based processes have been used for so long in so many applications with acceptable levels of performance. Recognition and trust is something that few if any of the emerging technologies currently enjoy. It is likely that lack of trust will slow acceptance of new technologies in favor of traditional ones. For the future, however, **the prognosis is that chromate conversion will not be replaced by a single technology, but rather by a suite of**

technologies that are selected based on application-specific performance requirements. It is also likely that chromate conversion will never be fully replaced, but rather a cost premium will be associated with its use for a given product.

What emerging technologies are available for metal finishers to choose from? Based on discussions at the Workshop, Martin Kendig devised Figure 1 which shows individual technologies, how they might be categorized, and relationships among similar technologies. Essentially **emerging technologies discussed fall into three basic groups**: 1.) **Conversion coatings** - where the substrate material is "converted" into the protective oxide coating through chemical or electrochemical action, 2.) **Coatings** - which are, for the most part, compositionally distinct materials applied to the substrate, and 3.) **Surface modification** - where the composition, structure, or chemistry of the surface is altered, without necessarily growing a thickened barrier oxide, to enhance corrosion resistance.

In the end, the group agreed that the metal finishing industry if facing a fundamental technological change driven by regulatory constraint that is being imposed on chromate-based processes. No single technology has yet emerged that offers simple fabrication methods and high corrosion resistance for all Al alloys. However, with continued research and development it appears possible that progress in emerging technologies will be sufficient to offer the metal finishing industry acceptable alternatives that will enable regulatory compliance in the next 5 years.


Emerging Technologies
Conversion Coating
Coatings
Surface Modification
Oxidation
Inorganic Reagents
Inorganic
Energetic Beams
sol-gel
Electron
Hydrotalcite
Cr (III)
Laser
Silicotungstate
P+A
Ion
Sanchem
Molten Salt
'Stainless Al'
Organic
Melting R/S
Molten Salt
Conducting Polymer
Surface Mixing
Adhesion Promoters
Implantation

Introduction to the Workshop

Terry Guilinger

Introduction to the Workshop

- Workshop History
  - Year 1: Mostly Sandia
  - Year 2: Add aerospace companies
  - Year 2.5: Recognized other workshops exist
  - Year 3: Expand to involve other industries
- Other Workshops
  - DoD/Air Force
  - Automotive
  - NCMS
  - Others → NASA Technical Interchange
- Goal of this Workshop
  - Recognize suite of replacements exist
  - Match replacements with existing needs
  - Recognize similar needs from dissimilar industries
- Looking Ahead
  - Improve communication with other workshops
  - Include representatives from all other workshops
  - Expand our attendee list to include other industries

Properties of Chromate Conversion Coatings for Aluminum

Objective

* How chromate conversion coatings are formed

* Common structural features and properties

* How conversion coatings work and why

* Process variables and effects on performance

Chromate Conversion Processes are long-standing, strongly entrenched technologies in the metal fininshing industry.

- * widely used
- * easily implemented
- * processes are optimized
- * field tested

Performance Metrics:

- * Corrosion Resistance
- * Conductivity
- * Adhesion
- * Thermal Stability
- * Lubricity
- * Appearance

Chromate Conversion Coatings

Uses:

- "stand-alone" corrosion protection
- improved paint adhesion
- decorative finish

Applied by :

- immersion
- spraying
- brushing
- dip & squigee
- electrostatic spray
- anodic deposition

Applied to:

- Aluminum
- Zinc
- Steel
- Copper
- Tin
- Silver
- Magnesium
- Cadmium
- others . . .

Technologies have been used for 40+ years:

- mature
- field tested
- optimized
- easily applied

'Generic' Chromate Conversion Process for Aluminum

Procedure	Primary Ingredients	Goal
Degrease	(Vapor Degrease)	Remove oil & grease
Alkaline Cleanse	$Na_2O \cdot xSiO_3/Na_2CO_3$	Remove organics, surface precipitates
Deoxidize/Desmut	HNO_3/HF or NH_4HF_2	Remove oxides/ Activate Surface
Coat	$Cr_2O_7^{2-}/HF/(CN)_6^{6-}$	Develop Coating
Age	water/air	Harden Coating

* Rinse between each step to avoid "drag in"

The Conversion Process

Chromate conversion is a redox process:

$$2Al^0 + Cr_2O_7^{2-} + 2H^+ + 6HF \rightarrow 2AlF_{(aq)} + 2CrOOH_{(s)} + 3\,H_2O$$

$Cr^{6+} + 3e^- \rightarrow Cr^{3+}$ is the reduction reaction

$Al \rightarrow Al^{3+} + 3e^-$ is the oxidation reaction

Normally, Al^{3+} hydrolyzes in solution to form insoluble $Al(OH)_3$:

$$Al^{3+} + 3H_2O \rightarrow Al(OH)_{3(s)} + 3H^+$$

In the presence of HF :

$$Al^{3+} + 3F^- \rightarrow (AlF^{2+}, AlF_2^+, AlF_3)\ (aq)$$

which increases aluminum solubility.

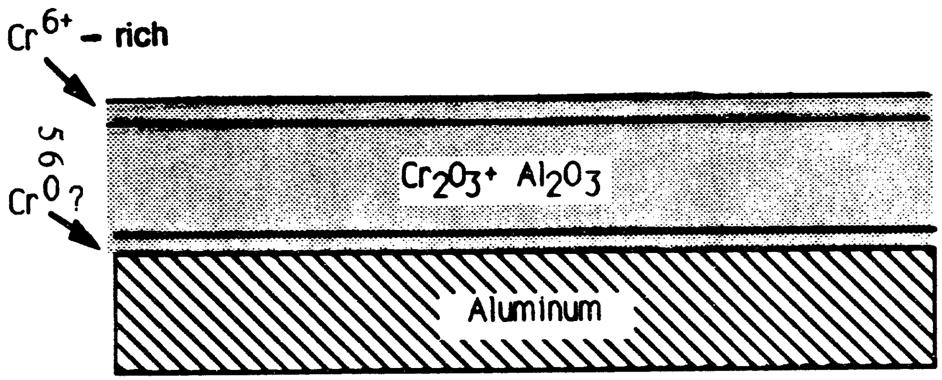
- * Increases the amount of chromium oxides relative to aluminum oxides in the film
- * Prevents premature formation of aluminum oxides that stop the redox process

How Chromate Conversion Works:

$$H_2Cr_2O_7 + 2Al \longrightarrow Cr_2O_3 + Al_2O_3 + H_2O$$

$$Cr^{6+} + 3e^- \longrightarrow Cr^{3+}$$

$$Al^0 \longrightarrow Al^{3+} + 3e^-$$

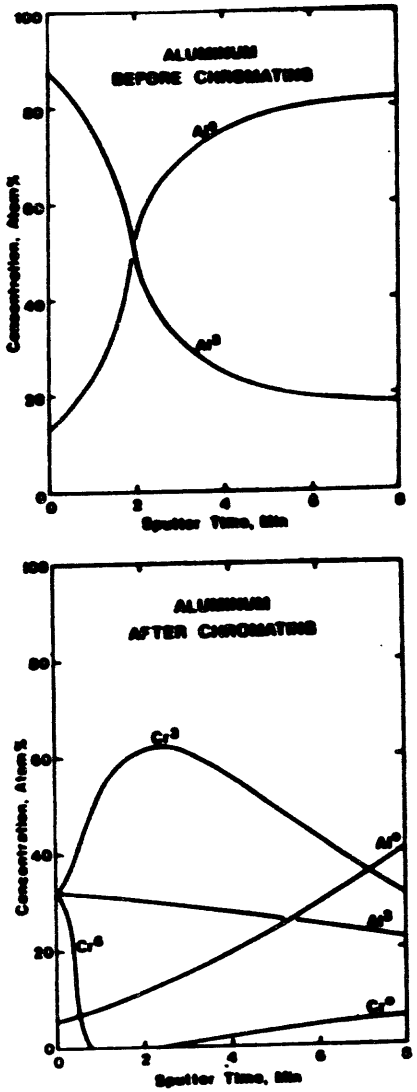


100 to 1000 nm thicknesses are produced

amorphous to crystalline structures are reported

functions as a barrier to the environment

high electronic resistivity inhibits ETR
like H_2 and O_2 reduction



H.E. Townsend, JES, 1984.

Corrosion Failures of Conversion Coatings

- * lack of coverage
- * mechanical damage eg. scratches
- * precipitates, impurity particles or deposits at the metal surface

In the presence of a condensed electrolyte, local galvanic cells are established at coating breaks.

Chromate conversion coatings have the capacity for "self-healing" scratches that are not too large.

Coating Designations

ASTM	Coating Weight (mg/ft^2)	Color	Use
Class 1	30 - 100	yellow to brown	corrosion resistance for painted and unpainted surfaces
Class 2	10 - 35	irridescent to yellow	corrosion resistance paint base
Class 3	not specified	colorless to light yellow	low electrical resistivity decorative finish

9904151	Coating Weight (mg/ft^2)	Color	Use
Grade 1	1 - 15	colorless	low electrical resistivity
Grade 2	20 - 40	colorless to tan	low electrical resistivity
Grade 3	20 - 90	light yellow to brown	corrosion protection paint base

ASTM	9904151
Class 1	Grade 3
Class 2	Grade 2
Class 3	Grade 1

Process Variables

Surface Condition:

Si, Fe bearing impurity particles
Copper
scratches are acceptable
surface roughness commensurate with a mill finish performs well

Alkaline Cleaner:

etch cleaned surfaces do not perform as well as non-etch cleaned surfaces in salt spray testing

Deoxidizer:

contamination limits must be observed:

$$12 \text{ ppm} < Cl^- < 350 \text{ ppm}$$

$$Cu^{2+}, Fe^{2+} < 50 \text{ ppm}$$

$$7{,}000 \text{ ppm} < Al^{3+} < 11{,}000 \text{ ppm}$$

Process Variables (continued)

Coating Bath:

pH 1.8±0.1

$Cl^- < 200$ ppm or $(Cl^- + SO_4^{2-}) < 400$ ppm
$SO_4^{2-} < 800$ ppm

Influence of $[Al^{3+}]$ and $[Cr^{6+}]/[Cr^{3+}]$ is debated

Temperature 70° to 85° F is reported to generate satisfactory coatings

Post-Coating Aging

A minimum of 24 hours is required to age the coating

Aging temperatures in excess of 140° to 150° F are not recommended

Performance Metrics

Corrosion resistance

Conductivity

Adhesion

Lubricity

Appearance

Dimensional stability

Relative importance depends on application.

Corrosion Performance - Salt Spray

(per ASTM B117)

Alloy	Coating Type	Time to Failure (hours)
3003 (Al-1.2Mn-0.12Cu)	class 3	60 - 120
	class 1	250 - 800
7075-T73 (Al-5.6Zn-2.5Mg-1.6Cu)	class 1 (Alodine 1200 S)	< 168
	class 1 (Alodine 600)	<168
7075-T6	class 1 (Alodine 1200 S)	> 168
7175-T73 (same as 7075)	class 1 (Alodine 600)	>/< 168
2024-T3 (Al-4.4Cu-1.5Mg-0.6Mn)	class 1 (Alodine 1200 S)	< 48
6061-T6 (Al-1.0Mg-0.6Si)	class 1 (Alodine 1200 S)	> 168
1100 (Al-0.5(Fe, Cu, Si))	class 1 (Alodine 1200 S)	> 168
Bare Alloys (cleaned)	none	< 24

Rules of Thumb:

Between alloy classes, salt-spray performance follows alloy susceptibility to localized corrosion.

(best) 5xxx, 6xxx > 3xxx, 1xxx > 7xxx > 2xxx (worst)

Between tempers:

Peak aged > Overaged

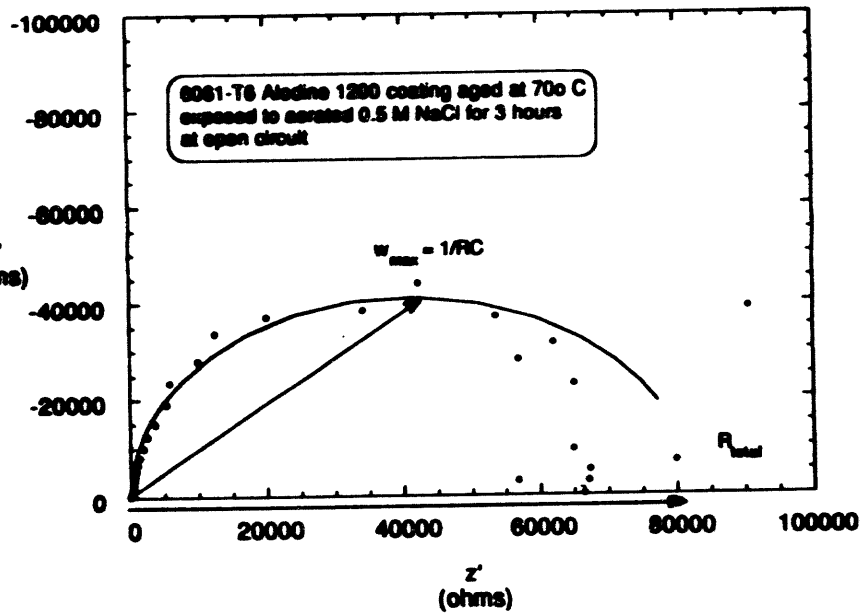
Corrosion Performance - Electrochemical Impedance Spectroscopy

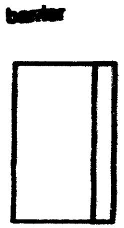
Alloy	Coating Type	Log R_{total} (Ω–cm^2)
1100	class 1 (Alodine 1200 S)	4.4[1]
	bare	3.0[1]
2024-T3	class 1 (Alodine 1200 S)	4.0 - 5.0[1,2]
	bare	3.0 - 4.0[1,2]
6061-T6	class 1 (Alodine 1200 S)	6.9[1]
	bare	- -
7075-T6	class 1 (Alodine 1200 S)	4.7 - 6.5[1,3]
	bare	2.0[1]
7075-T73	class 1 (Alodine 1200 S)	5.5[3]

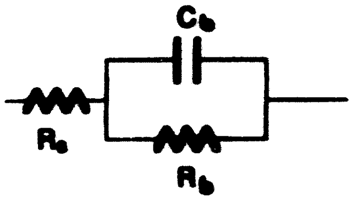
1. Aerated 0.5 M NaCl, pH 5.5 for 3 hours.
2. Aerated 0.5 M NaCl, pH 2.0 for 20 minutes.
3. Aerated 0.5 M NaCl, pH 5.5 for 2 hours.

EIS Advantages:

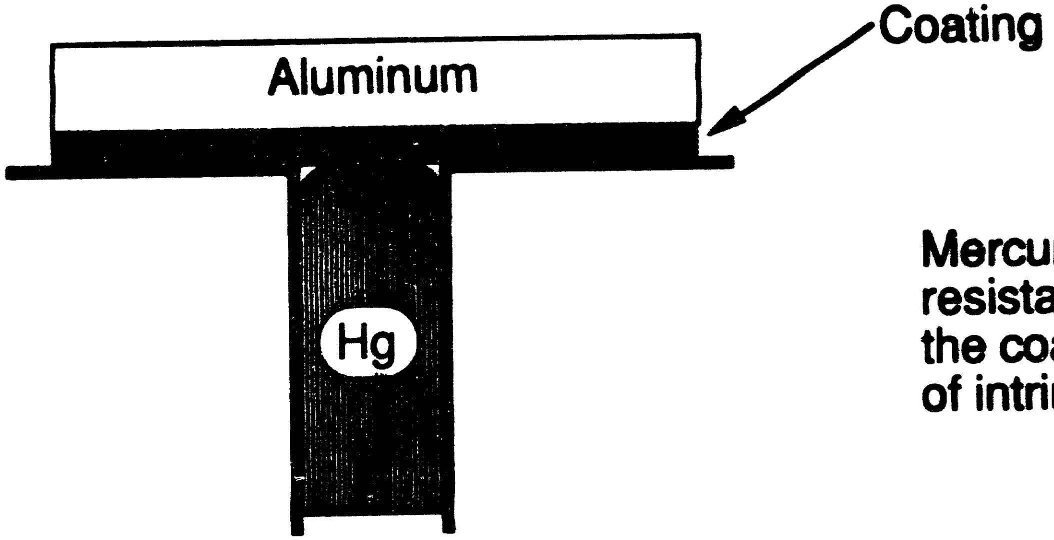
* Quantitative
* Sensitive
* Rapid
* Relevant ?


6061-T6 Alodine 1200 coating aged at 70o C
exposed to aerated 0.5 M NaCl for 3 hours
at open circuit
w max = 1/RC
R total
-100000
-80000
-60000
-40000
-20000
0
Z"
(ohms)
0
20000
40000
60000
80000
100000
Z'
(ohms)

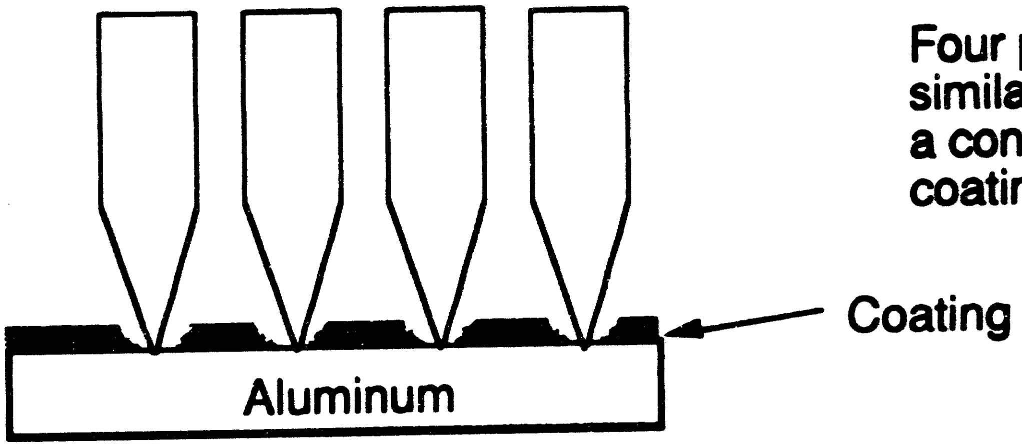

barrier


Cb
Rs
Rb

Resistivity Measurement Techniques



Mercury measures a resistance without breaking the coating -- More representative of intrinsic resistivity



Four point probe (and similar techniques) measure a contact resistance-- coating is probably fractured

Both measurements are useful.

Resistivity

Alloy	four point probe (mΩ)	mercury probe (0 Hz) (Ω)	mercury probe (10^{4}Hz) (Ω)	mercury probe (10^6 Hz) (Ω)
1100 (bare)	0.34[1]	2.7, 3±1	$< 10^4$	$< 10^4$
2024-T3 (bare)	0.32[1]	1.6	$< 10^4$	$< 10^4$
6061-T6 (bare)	0.36			
7075-T6 (bare)	0.33[1]	2.7	$< 10^4$	$< 10^4$
1100 (Alodine)	0.31[1]	10^{10}	3.8×10^7	
2024-T3 (Alodine)	0.29[1], 2.0[2]	2.4	$< 10^4$	$< 10^4$
6061-T6 (Alodine)	0.36			
7075-T73 (Alodine)	17[2]			
7075-T6 (Alodine)	0.29[1], 2.0[2]	33	7.1×10^6	1.5×10^5

All Alodine coatings are class 1

1 - four point probe with no load control
2 - four point probe with 200 psi contact pressure, per MIL-C-81706

5 mΩ is passing
12 to 40 mΩ is a high contact resistance

Paint Adhesion

Paint adhesion is much better on coated surfaces than on bare surfaces

Exposure testing is normally performed on painted coupons that are scribed
exposure per ASTM B117

* results in “filiform” corrosion
* damage is usually cosmetic and not structural

In general, performance depends on:

* composition of the base alloy
* alloy temper
* integrity of the paint layer
* type of primer (conversion coat) used
* surface preparation

Typically there is large scatter in the test data

Difficult to identify root cause of failures

One consistent trend however:

Filiform corrosion increases with increasing copper content

Effect of Elevated Temperature on Chromate Conversion Coatings

Industry consensus is that coating should not be subjected to temperatures higher than 120° to 140° F for air or water exposure.

9904151 specifically indicates:

- * post coating rinse water shall not exceed 150° F and rinse time shall be minimized
- * heating (in air) at temperatures exceeding 160° F for 2 hours can cause significant deterioration of the coating

Coating Dehydration and phase transformations have been proposed to account for coating deterioration:

$$2CrOOH \rightarrow Cr_2O_3 + H_2O$$

amorphous → crystalline

Class 1 coatings are probably crystalline

Salt Spray Results for Alodine Coatings on Alloys 1100, 6061-T6, and 7075-T6 Subjected to Ambient Air Exposure at Various Temperatures

	1100		6061-T6		7075-T6	
Temp. (^{o}C)	A	B	A	B	A	B
25	Pass	Pass	Pass	Pass	Pass	Pass
70	Pass	Fail	Pass	Pass	Pass	Pass
115	Fail	Fail	Pass	Fail	Pass	Pass
160	Fail	Fail	Pass	Fail	Fail	Fail
205	Pass	Fail	Pass	Pass	Fail	Fail
250	Pass	Pass	Pass	Pass	Pass	Pass
300	Pass	Pass	Fail	Fail	Fail	Fail

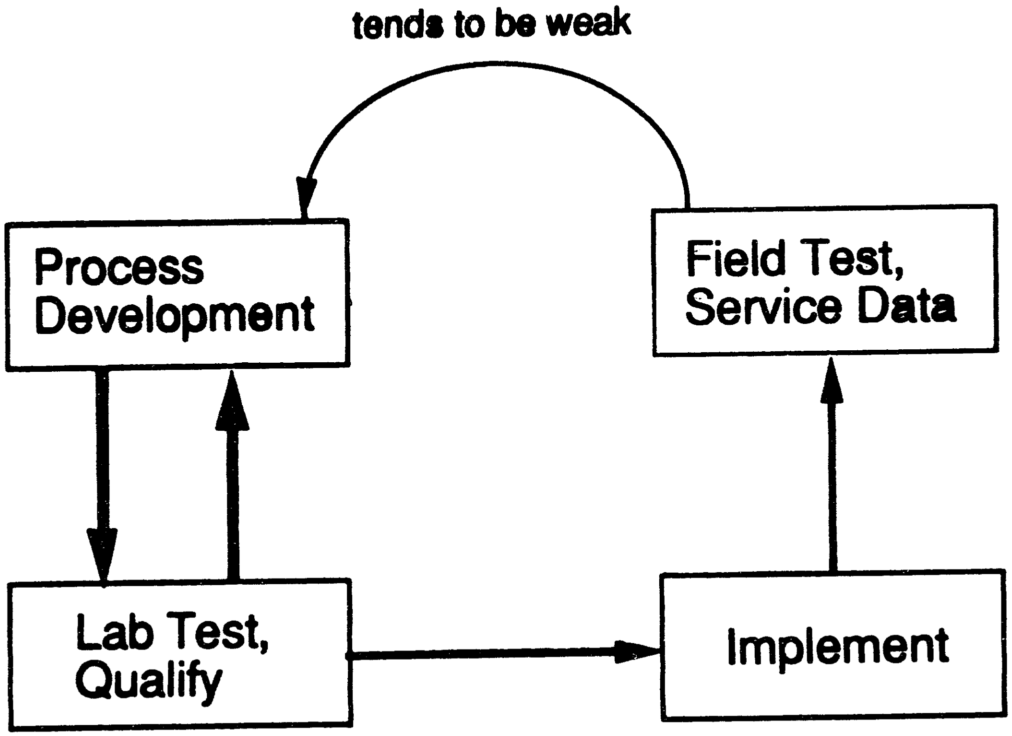
Salt Spray performed per ASTM B117 and MIL-C-5541D

Exposure time: 168 hours.

A, B refer to coupon numbers

4" X 5" coupons were tested

Test Data vs. Service Data



tends to be weak

Process Development

Field Test, Service Data

Lab Test, Qualify

Implement

No failures to report?

Not inspected?

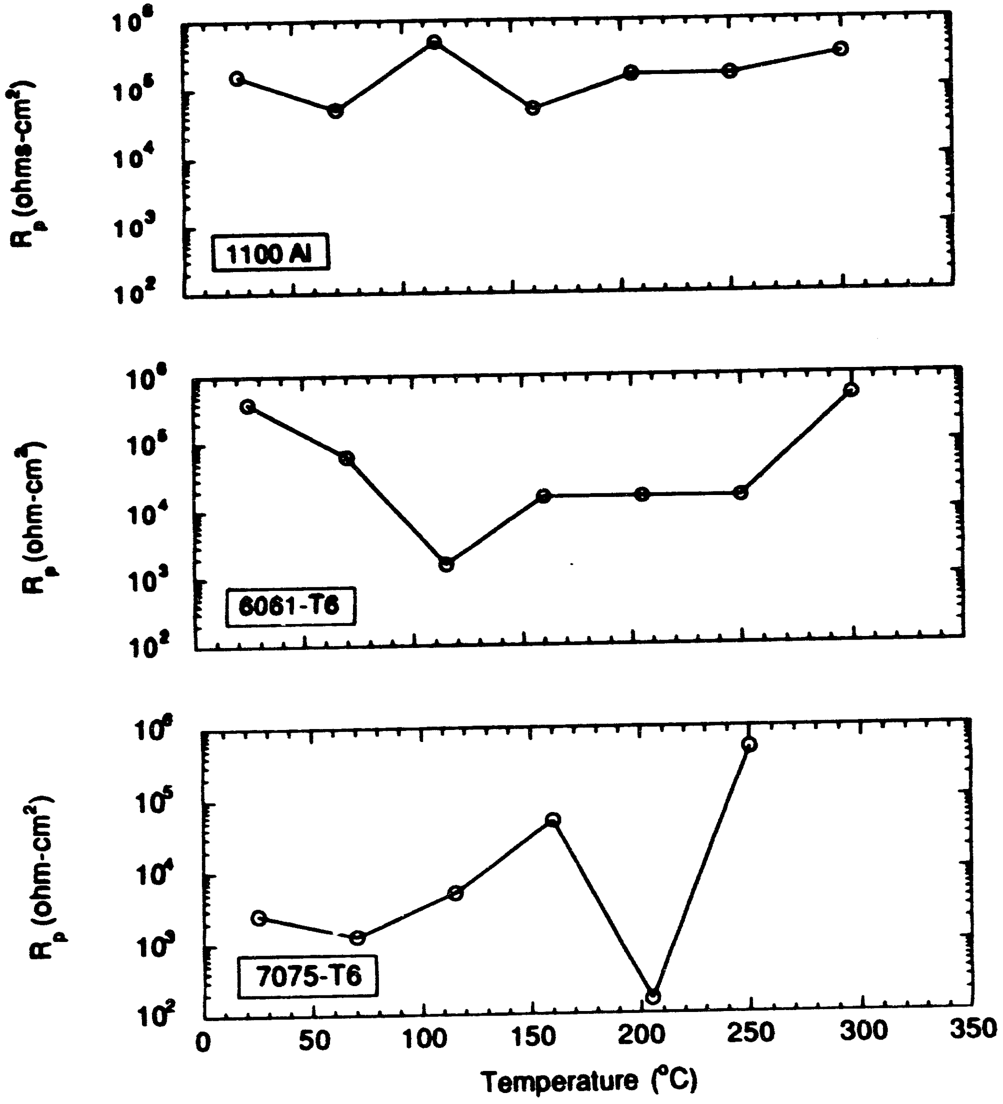
Not accessible?

Not patient?

Conversion coatings are engineered to pass salt spray exposure

Are coatings with lower corrosion performance acceptable?

EIS Results for Alodine Coatings on Alloys 1100 and 6061-T6 Subjected to Ambient Air Exposure At Various Temperatures

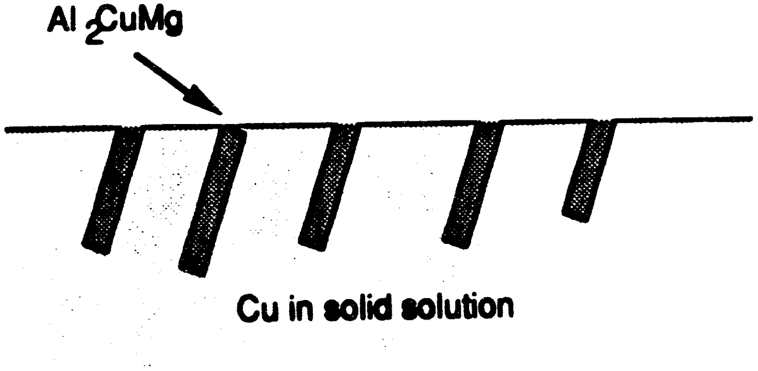


The Effect of Copper

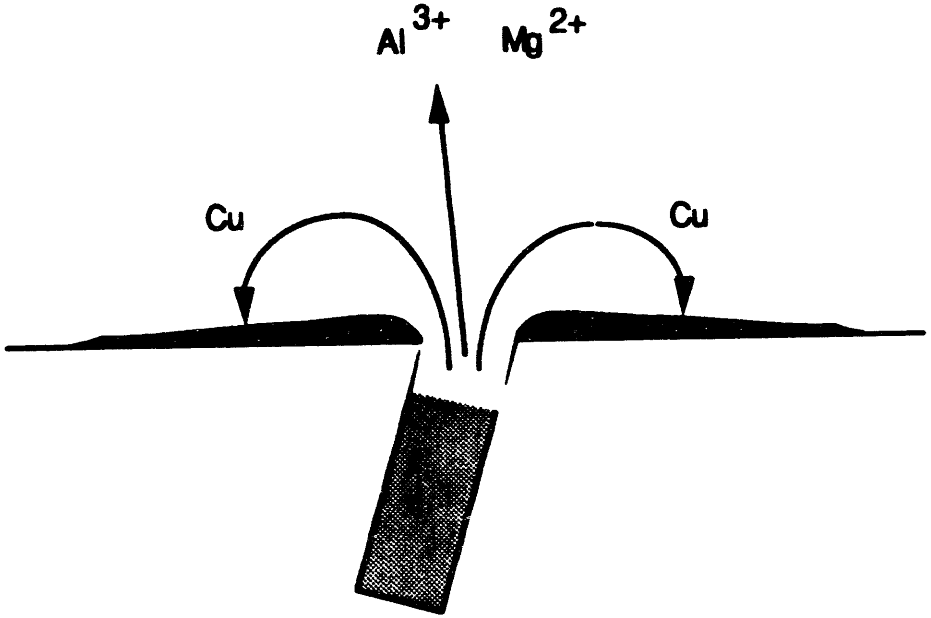
SSSS → GP zones → S'(Al_2CuMg) → S(Al_2CuMg)

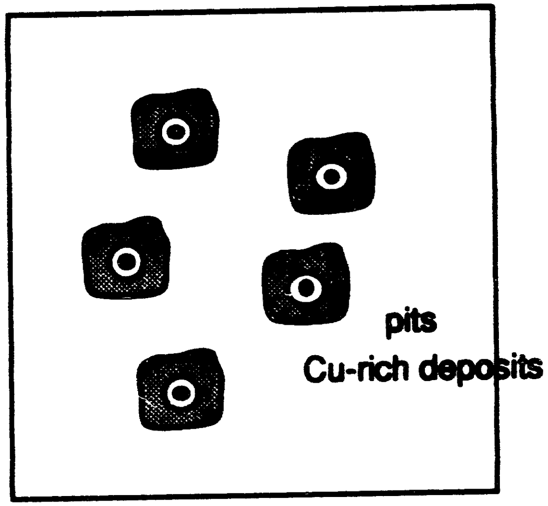
under aged → peak aged → over aged

T3,T4 → T6 → T7



In Cleaning solutions:





Summary

Positives . . .

Chromate conversion coating of aluminum is a trusted technology

Satisfies a range of engineering needs for aluminum surfaces

It is the standard against which low-toxicity substitutes will be judged

Negatives . . .

Wide variety of factors can influence performance

Failures are not always traceable

Some structure-property relationships are not well characterized

* thermal breakdown
* self healing

Chromate conversion is probably used indiscriminantly:
Need for chromate conversion is not always balanced with the demands of the particular application

Session I:
Commercially Available Products

John Bibber and Larry Carlson
Moderators

ALODINE® 2000

A REVIEW AND UPDATE ON
NEW NON-CHROMIUM SURFACE TECHNOLOGY
FOR TOMORROW'S ENVIRONMENTAL DEMANDS

THIRD ANNUAL WORKSHOP ON
CHROMATE REPLACEMENTS IN LIGHT METAL FINISHING

Lawrence R. Carlson, CEF
Technical Research Manager
General Line Aluminum
PARKER+AMCHEM

ALODINE® 2000

INTRODUCTION:

THE BOEING COMPANY AND PARKER+AMCHEM JOINTLY AGREED TO WORK TOGETHER GOVERNED BY A LICENSE AGREEMENT. THE WORK UNDERTAKEN IS TO INVESTIGATE AND EXAMINE RECENTLY DEVELOPED TECHNOLOGY BY THE BOEING COMPANY AND PARKER+AMCHEM. THE SCOPE OF THE STUDY WOULD FOCUS PRIMARILY ON THE APPLICABILITY OF THIS TECHNOLOGY FOR COMMERCIAL AIRCRAFT AND, AS A SECONDARY ENDEAVOR, INVESTIGATE OTHER POSSIBLE MARKET APPLICATIONS. THE STATUS OF THE PROJECT IS HEREIN DESCRIBED AND OUTLINED.

ALODINE® 2000

CHROME-FREE ALUMINUM TREATMENT FOR AEROSPACE

GOAL:

DEVELOP AND COMMERCIALIZE A NON-CHROMIUM CONVERSION COATING PROCESS THAT WILL CONSISTENTLY MEET MIL-C-5541, MIL-C-81706, AND BAC 5719 REQUIREMENTS.

ALODINE® 2000

ALODINE® 2000 PROCESS - AEROSPACE

		TIME	TEMPERATURE
1.	AQUEOUS DEGREASE	5-10 MIN.	100-160°F.
2.	TAP WATER RINSE	5 MIN.	AMBIENT
3.	DEOXALUME™ 2100	4 MIN.	65 ± 85°F.
4.	TAP WATER RINSE	3 MIN.	AMBIENT
5.	DEOXALUME™ 2200	7 MIN.	AMBIENT
6.	TAP WATER RINSE	5 MIN.	AMBIENT
7.	ALODINE® 2000	5-10 MIN.	120 - 140°F.
8.	TAP WATER RINSE	5 MIN.	AMBIENT
9.	PARKER+AMCHEM SEALANT	5 MIN.	160°F
10.	TAP WATER RINSE	5 MIN.	AMBIENT
11.	OVEN DRY	2-5 MIN.	130°F.

ALODINE® 2000

HOW DOES COBAMINE CHEMISTRY WORK?

====> HOW DO WE CONTROL / IMPROVE CHEMISTRY?

- NEAR NEUTRAL pH
- NO FLUORIDES
- DOES NOT "ATTACK" SUBSTRATE - INVOLVES LITTLE TO NO METAL DISSOLUTION AS A CONVENTIONAL CONVERSION COATING REQUIRES.
- COATING WEIGHTS CAN VARY BETWEEN 25 - 250 MG/FT^2 DEPENDING ON TIME, TEMPERATURE, pH, AND CONCENTRATION.
- COATINGS CAN BE CLEAR TO DARK GOLD, VERY SIMILAR IN APPEARANCE TO CHROMATE OXIDE COATINGS.
- NO FERRICYANIDE CONTENT.

ALODINE® 2000

2024 ALLOY ALUMINUM T3 BARE

TREATMENT	DRY ADHESION BMS 8.2.8 PRIMER	DRY ADHESION BMS 8.2.8 PRIM W/TC	7 DAY WATER SOAK BMS 8.2.9 PRIMER	7 DAY WATER SOAK BMS 8.2.9 PRIM W/TC	120 DEG. 30 DAY HUMIDITY PRIMER 8.2.16	120 DEG. 30 DAY HUMIDITY PRIM W/TC	168 HRS. BARE SALT SPRAY	336 HRS. BARE SALT SPRAY
ALODINE® 1200S	PASS	PASS	PASS	PASS	VF9	FM9	PASS	PASS
ALODINE® 2000 BOEING SEAL	PASS	PASS	PASS	PASS	D9	D9	FAIL (100 HRS)	FAIL
ALODINE® 2000 SEAL B	PASS	PASS	PASS	PASS	VF9	VF9	PASS	FAIL (275 HRS)
ALODINE® 2000 NO SEAL	FAIL	FAIL	FAIL	FAIL	D9	D9	FAIL (96 HRS)	FAIL

THIRD ANNUAL WORKSHOP ON
CHROMATE REPLACEMENTS
L. R. Carlson - September 1993

ALODINE® 2000

6061 T6 BARE ALLOY ALUMINUM

TREATMENT	DRY ADHESION BMS 8.2.8 PRIMER	DRY ADHESION BMS 8.2.8 PRIM W/TC	7 DAY WATER SOAK BMS 8.2.9 PRIMER	7 DAY WATER SOAK BMS 8.2.9 PRIM W/TC	120 DEG. 30 DAY HUMIDITY PRIMER 8.2.16	120 DEG. 30 DAY HUMIDITY PRIM W/TC	168 HRS. BARE SALT SPRAY	336 HRS. BARE SALT SPRAY
ALODINE® 1200S	PASS	PASS	PASS	PASS	VF9	VF9	PASS	PASS
ALODINE® 2000 BOEING SEAL	PASS	PASS	PASS	PASS	FM9	D9	PASS	PASS
ALODINE® 2000 SEAL B	PASS	PASS	PASS	PASS	N	VF9	PASS	PASS
ALODINE® 2000 NO SEAL	PASS	PASS	FAIL	FAIL	D9	D9	FAIL (120 HRS)	FAIL

ALODINE® 2000

7075 T6 BARE ALLOY ALUMINUM

TREATMENT	DRY ADHESION BMS 8.2.8 PRIMER	DRY ADHESION BMS 8.2.8 PRIM W/TC	7 DAY WATER SOAK BMS 8.2.9 PRIMER	7 DAY WATER SOAK BMS 8.2.9 PRIM W/TC	120 DEG. 30 DAY HUMIDITY PRIMER 8.2.16	120 DEG. 30 DAY HUMIDITY PRIM W/TC	168 HRS. BARE SALT SPRAY	336 HRS. BARE SALT SPRAY
ALODINE® 1200S	PASS	PASS	PASS	PASS	N	VF9	PASS	PASS
ALODINE® 2000 BOEING SEAL	PASS	PASS	PASS	FAIL	D9	D9	PASS	PASS
ALODINE® 2000 SEAL B	PASS	PASS	PASS	PASS	N	VF9	PASS	PASS
ALODINE® NO SEAL	PASS	PASS	FAIL	FAIL	FM9	D9	FAIL (110 HRS)	FAIL

ALODINE® 2000

CONCLUSIONS:

AS QUALITY AWARENESS, ENVIRONMENTAL RESTRICTIONS, AND DEVELOPMENT OF NEW MATERIALS ESCALATE, THE NECESSITY FOR UNDERSTANDING AND CONTROLLING CURRENT TECHNOLOGIES AS WELL AS IMPLEMENTING NEW, INNOVATIVE ONES WILL ALLOW USERS TO ACTIVELY PARTICIPATE FOR YEARS TO COME IN AN EVER-CHANGING REALM OF HIGH PERFORMANCE MATERIALS FINISHING.

ALODINE® 2000

ACKNOWLEDGMENTS:

I MUST PERSONALLY RECOGNIZE THE FOLLOWING COLLEAGUES FOR THEIR CONTRIBUTION TO CURRENT AND FUTURISTIC TECHNOLOGY:

- DR. PAT HAGANS, CENTRAL NAVAL RESEARCH
- MATT SCHRIEVER - THE BOEING COMPANY
- DONNA GARRIGUES, PARKER + AMCHEM
- PHIL JOHNSON, PARKER + AMCHEM
- DENNIS KENT, PARKER + AMCHEM
- DR. JACK KRAMER, PARKER + AMCHEM
- JAMES MAURER, PARKER + AMCHEM
- DR. JOHN PIERCE, PARKER + AMCHEM

SANCHEM, INC.
1600 SOUTH CANAL STREET • CHICAGO, ILLINOIS 60616-1199 • TELEPHONE 312/733-6111
FAX # 312-733-7432

September 8, 1993

Mr. Mike Kelly
Sandia National Labs
Fax # (505) 844-7910

Dear Mr. Kelly:

The following is the abstract of the paper I plan to present:

"SANCHEM CC - A CHROME FREE
ALUMINUM PRETREATMENT SYSTEM"

The cleaning, deoxidization and conversion coating of aircraft and non-aircraft alloys with a commercial non-toxic and chrome-free pretreatment system is described in detail. The results of paint adhesion and filiform testing with commercial military primers, various epoxies, and urethane paints by a number of companies is presented along with comparison data for various chrome and other non-chrome systems. The results of neutral salt-spray tests is presented. In addition, scanning electron micrographs of deoxidized and conversion coated surfaces are shown along with data on the physical and chemical composition of the surfaces.

If you have any questions, please do not hesitate to call me.

Sincerely,

John W. Bibber

John W. Bibber, Ph.D.
Research Director

JWB/pdl

9-8-93

Post-it™ brand fax transmittal memo 7671 # of pages ▸ 8

To Mike Kelly	From Pat
Co. Sandia	Co. Sanchem
Dept.	Phone # 312-733-6100
Fax # 505 844 7910	Fax # 312-733-7432

"Trust Us For Anti-Rust"

A CHROME FREE
ALUMINUM PRETREATMENT SYSTEM

BY: JOHN W. BIBBER, PH.D.
RESEARCH DIRECTOR

SANCHEM, INC.
1600 S. CANAL STREET
CHICAGO, IL 60616

Current environmental legislation is moving toward the total exclusion of hexavalent chromium from pretreatment finishing systems. A number of alternative systems have been advanced,[1,2] but all fall short of the paint adhesion and corrosion resistance shown by current chrome-chromate conversion coatings. A new conversion coating process[10] meets or exceeds chrome-chromate paint adhesion requirements[3] and meets the corrosion requirements of MIL-C-5541.[4] In addition, studies indicate[5] that under acid conditions, this conversion coating outperforms chrome-chromate conversion coatings. The conversion coating is harder, more scratch and mar resistant, and will not break down under conditions of high temperature or humidity.

CLEANING AND DEOXIDIZATION:

As with all pretreatment systems, the most important aspect is proper cleaning and deoxidization prior to application of the conversion coating. Cleaning removes oil and dirt, which would interfere with the application of the conversion coating. Cleaners should be non-silicated to prevent depositation of silica on the aluminum surface and non-etching to prevent deposits of alloyed elements such as copper.

Deoxidization is the removal of oxides and other inorganics that would interfere with further processing without significant attack on the aluminum surface.[6] To prevent excessive attack, deoxidizers usually contain an oxidizing agent to maintain a thin oxide film on the surface of the metal during processing. Most chrome-free alternatives use iron (III) salts coupled with hydrogen peroxide [7] or ammonia persulfate, ammonia nitrate and sulfuric acid mixtures.[8] The iron deoxidizers generally leave iron deposits, which encourage galvanic corrosion while the nitrogen based deoxidizers are not very effective at removing inorganics, and have a tendency to form toxic nitrosoamines. The deoxidizer used in the new conversion coating system contains no iron salts, chromates, fluorides, sulfates, nitrites, ammonia salts or amines. Product performance equals or exceeds that of chromate deoxidizers. There is no sludge build up, a low concentration of total dissolved solids, little or no disposal problems, and a relatively low hazard level associated with the product. Studies indicate that the surface is cleaner and more highly activated toward acceptance of conversion coatings or an anodic oxide coating.

CONVERSION COATING PROCESS:

The primary step in the conversion coating process is the formation of a hydrated aluminum oxide film by the use of boiling D.I. water or steam. In boiling D.I. water the metal will start to react $(Al+3H_2OAl(OH)_3+1.5H_2)$ within 15 to 30 seconds and completes the formation of a 300 to 500 nanometer unit thick coating in about five minutes. With steam at 290° - 300°F, the process is much faster, being generally completed within one minute. The process gives the metal a blueish-gray appearance, which serves as a quick check of areas not properly cleaned and thus not blue-gray in appearance.

SECOND STAGE

The second stage of the process involves treatment of the metal in a proprietary aluminum salt solution for at least one minute at 205°F or higher. With Dry steam equipment the solution is aspirated into the stream of the dry steam. The process decreases the amount of hydrated water in the oxide film by replacing it with aluminum hydroxide and gives an acid character to the surface of the coating. At this point, the coating is metallic in color.

THIRD STAGE

The third step of the process involves treatment of the metal in a proprietary permanganate solution at 135° - 145°F for at least one minute. With dry steam equipment the solution is aspirated into the stream of the dry steam and the temperature adjusted by lowering the amount of steam in the mixture. This increases the aluminum oxide content of the coating and imparts corrosion resistance by leaving deposits of various manganese oxides trapped in the coating. At this point the coating will be metallic in color or have a light pink color. Dark brown stain will show up if the oxide film was not properly formed in the initial stages of the process.

OPTIONAL FOURTH STAGE

The fourth stage of the process is only used for maximum corrosion resistance on unpainted metal parts of a high copper content such as the wrought alloys of the 2000 series. It involves treatments of the metal in a proprietary potassium silicate solution at 205°F or higher for not more than one and a half minutes. This converts the aluminum oxide film to potassium aluminum silicate and very completely seals the surface of the metal while still providing for excellent paint adhesion.

CONCLUSION

While the precise mechanism by which chromic oxides impart corrosion resistance may never be known, an alternative must involve the use of materials which have similar chemical properties. Manganese oxides are by far the most closely related to chromic oxides in terms of their respective chemistries. Thus, the aluminum oxide film containing various reduced manganese oxides, as produced by the new process, very closely matches the performance of chrome-chromate conversion coatings.

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4. Independent Testing by "The Naval Air Development Center", Warminister, PA
5. Independent Testing by "The Naval Air Development Center, Warminister, PA, and "Rockwell International Science Center", Thousand Oaks, CA
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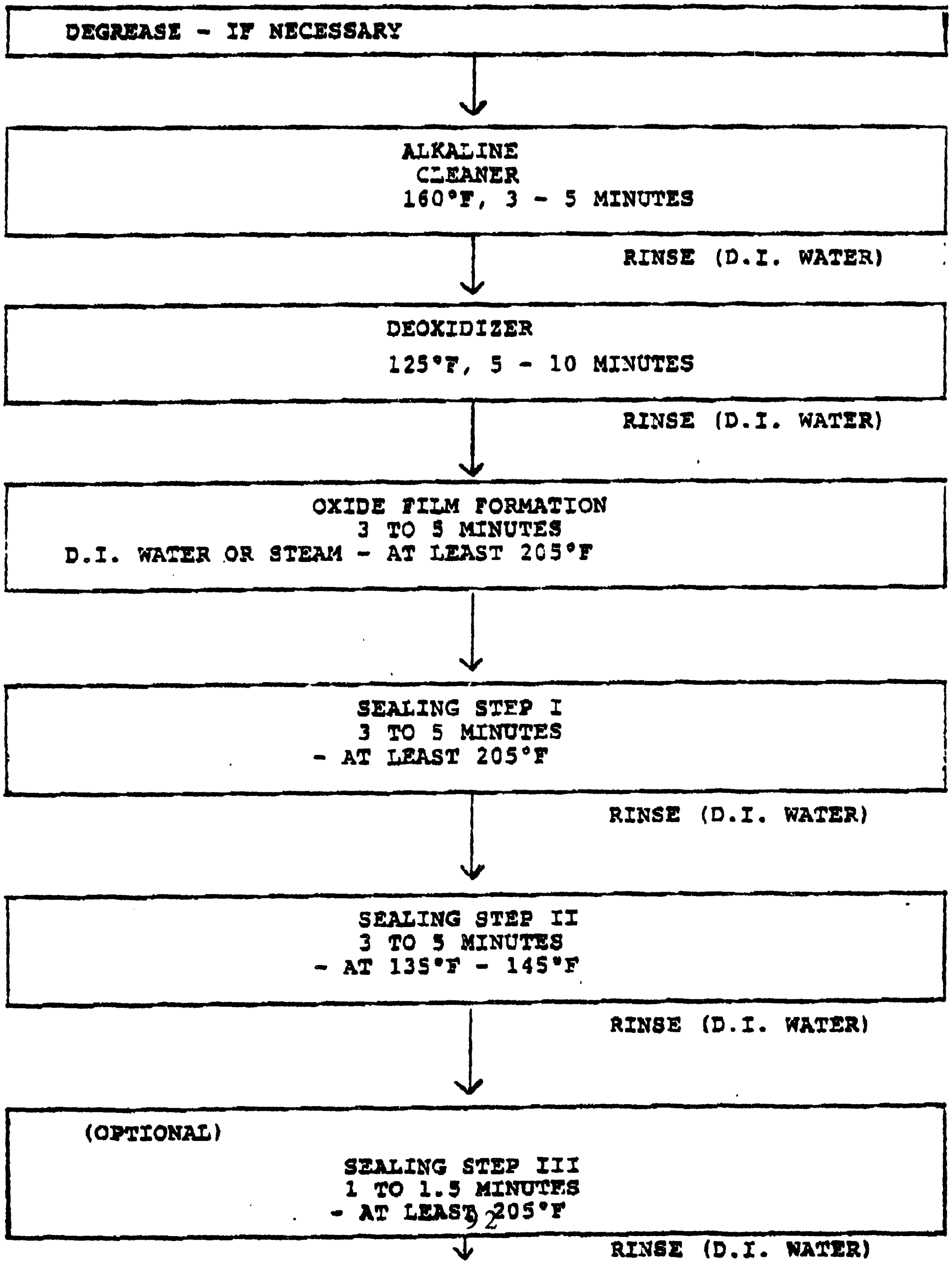
10. Sanchem, Inc., 1600 S. Canal Street, Chicago, IL 60616 (312) 733-6100

PROCESS


DEGREASE - IF NECESSARY
ALKALINE CLEANER
160°F, 3 - 5 MINUTES
RINSE (D.I. WATER)
DEOXIDIZER
125°F, 5 - 10 MINUTES
RINSE (D.I. WATER)
OXIDE FILM FORMATION
3 TO 5 MINUTES
D.I. WATER OR STEAM - AT LEAST 205°F
SEALING STEP I
3 TO 5 MINUTES
- AT LEAST 205°F
RINSE (D.I. WATER)
SEALING STEP II
3 TO 5 MINUTES
- AT 135°F - 145°F
RINSE (D.I. WATER)
(OPTIONAL)
SEALING STEP III
1 TO 1.5 MINUTES
- AT LEAST 205°F
RINSE (D.I. WATER)

ABSTRACT OF PRESENTATION
BY
DONALD W. BAUDRAND
ALLIED-KELITE, A WITCO COMPANY

FOR

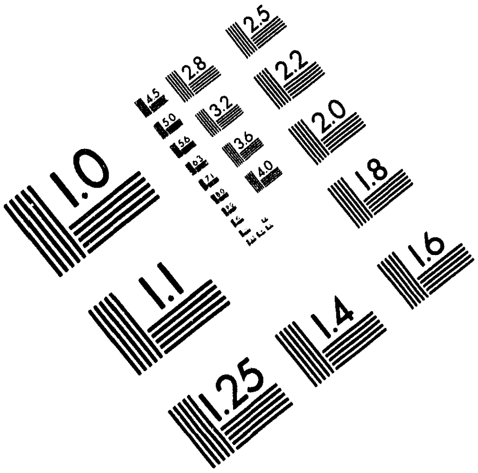
SANDIA NATIONAL LABORATORIES
CHROME REPLACEMENT WORKSHOP
SEPTEMBER, 1993

CHEMIDIZE 727A

Chemidize 727A is a treatment for aluminum, stainless steel and chromium-plated material which produces an oxide coating. It promotes excellent adhesion properties for coating or adhesive bonding. It is in paste form and can be applied by spray, wipe or brush. It contains a cleaner, a "deoxidizer" and film-forming chemicals all in one.

Simply apply, let dry, and rinse. Dry before coating or bonding.

Typical adhesion value as measured by the lap-shear method is 4000 psi. Typical specifications for adhesion range from 2000 to 3600 psi.



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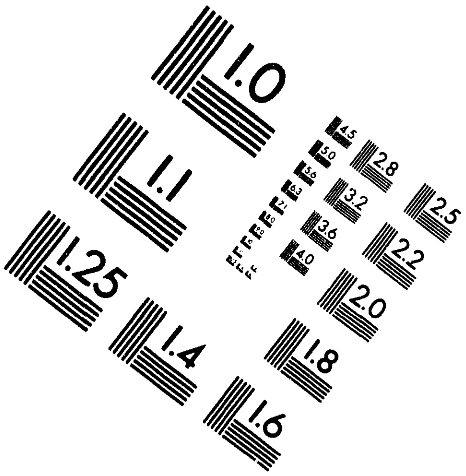

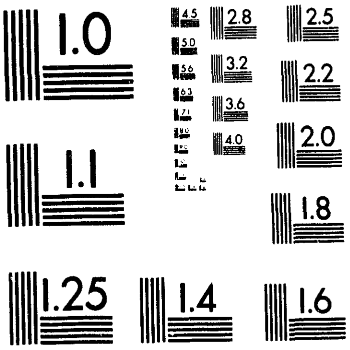

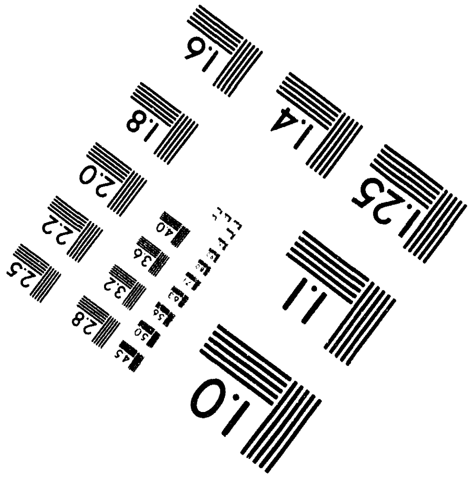

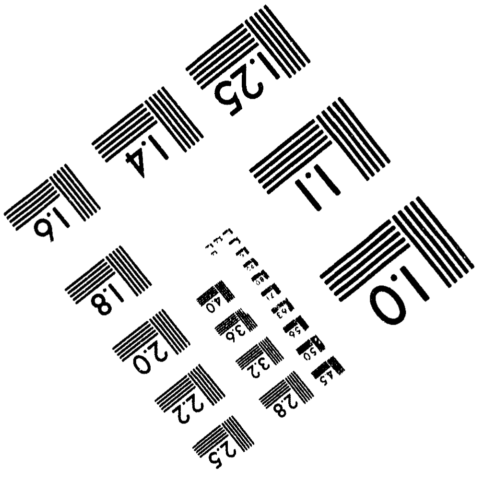

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2 of 3

Chemidize® 727A

Paste cleaner & treatment for aluminum

Allied-Kelite, A Witco Company
2701 Lake Street, Melrose Park, IL 60160, 1-800-323-9784, In IL 1-800-942-9767

Rev.030874

Introduction.

Chemidize 727A is an easy-to-use paste that cleans and treats an aluminum surface in a single operation. It removes soils, inks and lubricants and provides a treated surface with good adhesion properties for coating and bonding. The paste application can be used before other treatment, or for repair or patch-up work. It is an outstanding base treatment for air-dry, polar, organic type topcoats.

Chemidize 727A is applied by airless spray or brush-on methods. It does not require mixing with acids. For most applications a 50% Chemidize 727A paste to 50% water (by volume) mixture is recommended. The paste treatment is non-discoloring and, after rinsing, leaves no residue or heavily etched appearance. It also cleans stainless steel and chrome-plated surfaces.

Chemidize 727A maintains its properties for at least a year in a closed container. One gallon of Chemidize 727A paste with one gallon of water provides an 8 mil thick wet film to treat and clean approximately 400 square feet of surface.

Applications.

1. Treatment of aluminum products too large or awkward to handle by dip tank methods. (Example: Trailer and truck bodies, boats, aircraft sections, etc.)
2. As an aluminum pre-treatment for applications requiring a high level of adhesion with all types of coatings or adhesives.
3. For production applications which do not require or justify the installation of a full-scale multiple tank processing line.
4. Spot treatment of large surfaces requiring lettering or painting on a limited area.
5. Preparation of aluminum before coating with clear acrylic lacquers for best appearance and adhesion.
6. Field repair of damaged aluminum parts or surfaces that must be repaired or rebonded.
7. Cleaning stainless steel surfaces such as railroad equipment, building panels and misc. hardware.
8. Cleaning chrome-plated surfaces.

Operating data.

Operating ranges.

Film thickness — 8 mils

Solution temp. — Room to 135F. (57C)

Contact time — 1.5 hours

Equipment.

Spray — Acid-and solvent-resistant materials, such as stainless steel, glass, and polyethylene

Brush-on — Natural or nylon bristle brushes

Wipe-on — Soft cotton rags, & vinyl, urethane or cellulose sponges

General instructions.

Chemidize 727A is easily applied by spray, brush or wipe-on. Because of impingement, spray application is the most efficient method. Usually a wet film thickness of about 8 mils (0.008 in. or .02 cm) should be applied, although on many aluminum alloys 5 mils is sufficient. In about an hour and a half, the film dries and usually appears crazed and powdery. The powder

Witco

easily rinses off with water. As soon as the rinse water has dried, painting or bonding may proceed.

To treat anodized aluminum, first remove the oxide layer with an acidic oxide stripper. Following this, use the normal Chemidize 727A treatment sequence. Rinse surfaces heavily encrusted with salt or other chemicals with water before applying Chemidize 727A.

Coverage.

Generally, an 8-mil thick coating of Chemidize 727A should be applied. (This is equivalent to covering 200 square feet of surface with a gallon of undiluted Chemidize 727A.) On lightly soiled metal or on aluminum alloys containing substantial quantities of copper (Series 2000), magnesium (Series 5000 and 6000), or zinc (Series 7000), a coating of 5 mils may be adequate. It is important to obtain the proper thickness of coat. Use of a paint film thickness gauge is recommended.

On severely oxidized surfaces, or surfaces such as castings which may have baked-in lubricants, it may be necessary to treat the surface twice. This, however, is done only under extreme conditions and is very rarely necessary.

Spray.

Using acid-resistant, pressure-fed air atomizing, or airless spray equipment, apply a uniform 5 to 10 mil coat to the dirty aluminum surface. For best results use a 50% Chemidize 727A paste to 50% water (by volume) mixture. It is necessary to insure continuous flow of material from the supply tank into the feed line. The equipment may be easily cleaned by flushing with water.

Good ventilation and protection of adjacent surfaces which would be damaged by acid or solvent are necessary.

Brush-on.

Apply a continuous uniform coat of 5 to 10 mils of Chemidize 727A directly over the soils, lubricants, etc., on the aluminum surface. Cross brushing with short, light strokes is recommended to obtain adequate film thickness. A long fiber, natural or nylon bristle brush is suitable. The paste may be applied at full strength or reduced to any desired brushing consistency by diluting with up to one-fifth of its volume with water.

Wipe-on.

Using a cloth, sponge or other convenient applicator, continuously wipe a generous amount of Chemidize 727A over a workable area on the aluminum surface for approximately three to five minutes. Wiping usually deposits a thin film of material; therefore, the continuous mechanical action is necessary for thorough treatment. If a thick film can be laid down, continuous wiping can be eliminated.

Drying.

Allow the Chemidize 727A paste to remain on the aluminum surface until it is dry. This usually takes about an hour and a half at room temperature. The treatment material visibly becomes dry, whitens and may crack or flake. The dried residue may safely be left on the metal indefinitely. Chemical action continues as long as the film is moist but stops when it becomes dry.

The chemical action and the drying rate may both be accelerated by heating. Care must be taken to prevent the temperature of the paste material from exceeding 135F (57C). Fast evaporation is not desirable because solvents and moisture may be driven out of the film before their function is completed. Infra-red drying, because of reduced air circulation, is more satisfactory than forced hot air drying.

A typical cycle is to hold the coated parts at room temperature or warm them in still air to about 100F (38C) for 15 minutes and then heat with circulating air to 125F (52C) until dry.

Removing the dried residue.

The dry residue is easily rinsed away with a gentle stream of fresh tap water. It can be wiped away with a wet sponge or rag, or brushed away with a dry brush, or blown away with an air jet. A final water rinse is usually desirable to remove the fine dusty particles of residue that may cling to the aluminum surface.

The rinsed aluminum surface may be allowed to dry at room temperature or may be heated. Retention of a continuous water film for at least 15 seconds without break or drawback is evidence of an effective treatment.

Coating or bonding treated metal.

Coating with paints, lacquers, or adhesives may proceed at soon as the surface is dry. Coating may be deferred as long as a year without significant loss of adhesion capability, provided contamination is avoided by paper wrapping or otherwise protecting the surface.

Treatment effectiveness.

An aluminum surface cleaned and treated with Chemidize 727A retains a continuous water film for 30 seconds or more. The continuity of the film and the length of time it lasts without breaking indicate the extreme wettability of the treated surface. An untreated or greasy metal surface will de-wet, i.e., water will draw back and form beads, in 5 to 10 seconds. The "water break" test may be run on dried parts by rewetting them with clean water from an atomizer or other convenient source.

After Chemidize 727A treatment, most aluminum alloys take on a slightly white appearance which should be uniform over the entire surface. This appearance, while not a true etch, is the best visual evidence of the efficiency of the treatment. The whitening may not be visible on heavily pitted metals. Observation of the parts for continuity of water film following the final rinse, and uniform color as they dry, is an effective method of process control.

Cleaning of stainless steel and chromium.

The Chemidize 727A application techniques suggested for aluminum should be followed for stainless steel and chromium. Soil, grease, and localized rusting will be removed, and the bright, attractive surface of the metal restored. Retention of the surface finish depends on the suitability of subsequently applied protective coatings.

Warranty.

We warrant our goods to conform to our standard specifications. This Warranty is in lieu of any and all other warranties or guarantees and our obligation hereunder for breach of such warranty is limited to either refund of the purchase price or replacement of said goods as we may elect. We make no other warranties, express or implied, including those of MERCHANTABILITY and FITNESS FOR A PARTICULAR PURPOSE.

We believe that the statements, technical information and recommendations contained herein are reliable, but are given without warranty or guarantee of any kind except as specified above. Beyond that specified above, we assume no responsibility for any loss, damage or expense, direct or consequential, arising out of the use of, or inability to use, our goods. Their quality and suitability for any particular purpose or use should be confirmed by the user's own tests.

Standard packages.

5 gallon pail

Note: All gallon measurements are U.S. Gallons

CAUTION: Chemidize 727A is acid and can cause burns. Exercise caution in its use. Avoid contact with skin, eyes and clothing. Carefully read precautionary and first-aid information on container label.

ALLIED-KELITE

Your single source for tried and proven, brand-name metal treating and finishing products, industrial cleaning products, and support material and equipment.

Surface Preparation Products

- **Isoprep®** Cleaners...and etchants, derusters, deoxidizers, desmutters, descalers, paint strippers and rust-preventive oils
- **Alprep™** Cleaners...cleaners and activators expressly formulated to prepare aluminum surfaces for Niklad™ electroless nickel plating
- **Ferroprep™** Cleaners...soak cleaners and electrocleaners expressly formulated to prepare ferrous alloy surfaces for Niklad electroless nickel plating
- **Multiprep™** Cleaners...picklers, descalers, desmutters and activators expressly formulated for a wide variety of basis metals that are to be plated with Niklad electroless nickel

Plating Products

- **Niklad™** Electroless Nickel Systems...nickel-phosphorus, nickel-boron, and polyalloy processes and companion products for engineering, electronic and printed circuit board applications
- **Barrett SN®** Sulfamate Nickel System...high-purity, low-stress nickel plating for electroforming and plating applications
- **Isobrite®** Brighteners...additives and systems for bright nickel, chromium, zinc, cadmium and copper electroplating
- **ARP®** Specialty Chemicals...includes metal strippers, wetting agents, bath contamination control additives, mist suppressants, foam control additives, chromate coating tester, blackening salts, and immersion tin and zincate processes

Protective/Pre-Paint Coating Products

- **Iridite®** Chromate (Or Chromate-Free) Conversion Coating Systems
- **Keykote®** Zinc, Iron And Manganese Phosphatizing Systems
- **Irilac®** Clear Protective Treatments
- **Iridize™** Zinc Anodize Coatings

Industrial Cleaning Products

- Chemicals for cleaning and maintaining machinery, paint lines, refinery and petrochemical equipment, vehicles and aircraft

Support Material And Equipment

- Everything that's needed to support your operation including basic chemicals, anodes, polishing equipment, tanks, rectifiers, automatic feed systems, heaters, test apparatus and kits.

File Under SURFACE PREPARATION PRODUCTS

Witco

CHEMIDIZE 727 A

ALUMINUM PASTE CLEANER

AND ORGANIC CONVERSION

COATING

Chemidize 727A...

- is especially adapted to on-the-job, plant or field applications.
- provides a treated aluminum surface with exceptionally fine adhesion properties for either coating or bonding.
- is easily applied by spray, wipe or brush.
- is non-discoloring and leaves no unsightly residue or heavily etched appearance.
- provides an excellent surface for air drying lacquers and enamels.
- may be used as is; requires no mixing with acids.
- provides a surface which will retain its bonding properties for 12 months or longer without unusual storage precautions.
- cleans stainless steel and chrome-plated surfaces.

RECOMMENDED USES

- treatment of aluminum products too large or awkward to handle by dip-tank methods (example: trailer and truck bodies, boats, aircraft sections, etc.).
- as an aluminum pre-treatment for applications requiring a high level of adhesion with all types of coatings or adhesives.
- for production applications which do not require or justify the installation of a full-scale multiple tank processing line.
- spot treatment of large surfaces requiring lettering or painting on a limited area.
- for preparation of aluminum before coating with clear acrylic lacquers for best appearance and adhesion.
- for field repair of damaged aluminum parts or surfaces that must be repaired or rebonded.
- for preparation of aluminum prior to anodizing.
- for cleaning stainless steel surfaces such as railroad equipment, building panels and miscellaneous hardware.
- for cleaning chrome-plated surfaces.

BONDING STRENGTH REQUIRED
ON SPECIFICATIONS WRITTEN FOR
CHEMIDIZE 727A

Company	Specification	Lap Shear Required (psi)
Allied-Kelite	(On the average, our QC tests yield 4000 psi. Tests are performed by an independent laboratory)	
Hughson/Lord Corp.	(Original QC spec)	3600
Hercules (Poseidon)	WS12437	2000
Hercules	HS-6-0103	2500
Aerojet Strategic Prop.	SPC-34428	2000
Kaiser Aerotech	SPC-34592	2000
Morton Thiokol	STW4-6244A	(not specified)

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TEL (612) 937-7931 FAX (612) 937-7979

A NEW PAINT PREP TECHNOLOGY - PHOSPHATE POLYMER

by D.J. Halverson

Introduction

In response to rising quality standards and stringent safety and pollution regulations, a new pretreatment was developed for painted metal surfaces - the Phosphate Polymer system. This pretreatment technology combines an inorganic base coat which is chemically anchored to the metal surface, a non-leachable chromate corrosion inhibitor and a cross-linking acrylic polymer into a single operation. Applied to the surface of any metal by dip or spray, the phosphate polymer is warm dried without rinsing, then painted as usual. The treatment provides a highly effective barrier against filiform corrosion and an aid to adhesion of the paint film, resulting in significant improvement in the corrosion resistance of the final paint finish. The phosphate polymer system utilizes a solution which is used as a permanent bath in the line without periodic dumping.

Phosphate Polymer Bath

The Phosphate Polymer solution is made up from a two-part concentrated product. The "A" concentrate is a mildly acidic water-based acrylic polymer emulsion. The "B" concentrate is a blend of zinc phosphate and chromate corrosion inhibitors. The "A" and "B" concentrations are mixed together with deionized water to make a stable operating bath.

Mechanism

Though the phosphate polymer bath does not form a true crystalline phosphate or chromate film in the conventional sense, the solution does contain phosphoric and chromic acids which carry out a "micro-etching" of the metal surface to form chemical anchoring points. The acrylic polymers and metal complexes can chemically and physically attach to these anchoring points to achieve adhesion to the substrate.

Since the solution is applied at room temperature with a short contact time, the chemical reactions take place in the heated drying stage. While curing, the hexavalent chromium reacts with the organic polymer and is partially reduced to a trivalent state. Concurrently, the polymer is oxidized and cross-links to form a stable metallo-organic structure which is a suitable base for subsequent paint films. Once fully cross-linked, the polymer structure prevents any leaching of chrome.

Processing Options

The phosphate polymer concept can be incorporated into any conventional phosphating or chromating line, according to the following guidelines;

A) In a 5-stage phosphating line, the phosphate polymer application can take place

- in stage 5, to replace the chrome seal, or
- in stage 3, to replace the phosphate stage, leaving stages 4 and 5 empty, or
- in stage 4, using stage 3 as an empty drain stage (allowing a good separation from the rinse in stage 2). In like manner, stage 5 becomes an empty drain stage prior to drying.

Note: The preferred method is to use the phosphate polymer in stage 5 over a conventional zinc or iron phosphate. This technique results in best overall adhesion and corrosion resistance because the film thickness of the phosphate polymer coating will be the most uniform across the metal surface.

B) In a 3-stage line, the phosphate polymer application takes place in stage 3, replacing the chrome seal or phosphate. Ideally, a cleaner/phosphate should be used in stage 1.

C) In an aluminum chromate line, the phosphate polymer can be used as a direct replacement of the chromate bath. No rinsing is necessary after application; the parts would proceed directly to drying.

In many cases, the conventional iron phosphate coating is insufficient to meet rinsing quality standards. This is commonly observed in lines which have been converted to a non-chrome seal. One option which has proven to be less than ideal is to convert the iron phosphate to a zinc phosphate. Despite better adhesion and salt spray performance, the zinc phosphate is not workable in many lines because of higher heating requirements, heavier sludging and mandatory zinc effluent treatment.

There are also painting options which can be considered in order to improve performance. These options, however, generally are more costly to operate or require significant capital expenditures.

The phosphate polymer concept offers the paint finisher an attractive new option because it allows him to take advantage of the proven corrosion resistance of chrome without the normal pollution problems associated with the conventional chrome seal. In addition, the phosphate polymer structure acts as an excellent paint base, and is more compatible with the paint than a crystalline phosphate surface. The resultant finish often flows and levels better over the phosphate polymer surface than over a conventional phosphate.

Operationally, the phosphate polymer requires only wetting of the surface with the solution - no extended dwell times. Consequently, the tanks and spray vestibules can be designed smaller, according to component dimensions. A drip pan and air knives may be necessary, but no rinse tanks or tank heaters. In most cases, an existing wash line can be converted to the phosphate polymer system for very little capital expense.

After drying at 175-230°F, the surface of the phosphate polymer is still reactive enough to permit a strong interbonding with the paint film. Complete cross-linking occurs only after curing together with the paint.

PHOSPHATE POLYMER BATH MAINTENANCE

The phosphate polymer solution is operated as a permanent bath in the line without periodic dumping. Regular additions of fresh concentrate are made to keep the bath at proper concentration.

Routine bath maintenance includes monitoring of pH and solids content by specific gravity checks or by other solids determinations.

It is recommended that the bath be checked occasionally for hexavalent chrome and total chrome content.

PHOSPHATE POLYMER CHARACTERISTICS

Dry Film Thickness	.05 - .10 mil
Cure Temperature	175-230°F
Cure Time	5-10 minutes
Coverage (depending on application) (sq. ft. / gallon of concentrate)	8,000 - 15,000
Solvent	Deionized water
pH	1-2
Suitable substrate	Steel, Aluminum, Zinc, Alloys
Method of Application	Immersion, flow coat, electrostatic atomized spray

BENEFITS OF THE PHOSPHATE POLYMER SYSTEM

* The Phosphate Polymer can be used in a 3-stage line to improve coating performance. In a 5-stage line, the Phosphate Polymer offers possibilities for improving corrosion resistance and/or for shortening the process.

* Room temperature application - energy cost savings.

* Water-based solution - no solvent emission.

- No rinse required after application - no waste treatment under normal conditions.

  Low-Viscosity liquid penetrates recessed areas - coats blind areas without excessive build up.

- Short processing time - requires only wetting of the surface, no extended reaction or dwell times.

- Excellent adhesion to metal substrates.

- No sludge formation - easy bath maintenance.

- Compatible with almost any kind of paint.

- Easy equipment conversion - low capital expense required.

Surface Modification of Aluminum Alloys with a Chromate-Free Process

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Corrosion and Environmental Effects Laboratory (CEEL)
Department of Materials Science & Engineering
University of Southern California
Los Angeles, CA 90089-0241

Abstract

The patented Ce-Mo process for the production of "stainless aluminum" has been applied successfully to Al 6061. No indication of corrosion was observed after 60 days immersion in 0.5 N NaCl (open to air). Electrochemical tests suggest that the incorporation of Ce and Mo has transformed the Al surface into an insulator on which electrochemical reactions occur at very slow rates. Ce and Mo apparently produce a synergistic effect leading to the exceptional corrosion resistance of Al 6061. Evidence from surface analytical evaluations suggests that weak spots in the natural oxide which would have become initiation sites for pits dissolve in the boiling Ce salt solutions and are replaced by Ce oxides. Mo reinforces the modified surface by an yet unknown mechanism.

Samples of Al 6013-T6 treated with the Ce-Mo process have passed the salt spray test according to ASTM B117. In immersion tests significant pitting corrosion was observed for untreated Al 6013, while only a few pits occurred on the treated sample.

For Al 7075-T6 it has been found that the $CeCl_3$ immersion step needs to be carried out after the Mo-step. For samples treated in this manner the passive current density in 0.5 N NaCl was reduced significantly and the pitting potential was increased by about 200 mV. During anodic polarization sudden jumps in the current were observed which correspond to the formation of new, single pits. EIS data recorded during immersion in NaCl show capacitive behavior for treated samples and the typical transmission line impedance at low frequencies for untreated samples. For the treated samples R_p was about 500 kohm.cm^2 during a 30 day test period. The capacitance C_p increased slowly from 7.5 µF/cm^2 to 9.5 µF/cm^2 which is typical for a thin hydrated oxide.

Present efforts concentrate on modifications of the basic Ce-Mo process for Al 2024. It seems necessary to use a pretreatment step for removal of Cu from the outer surface layers for this alloy.

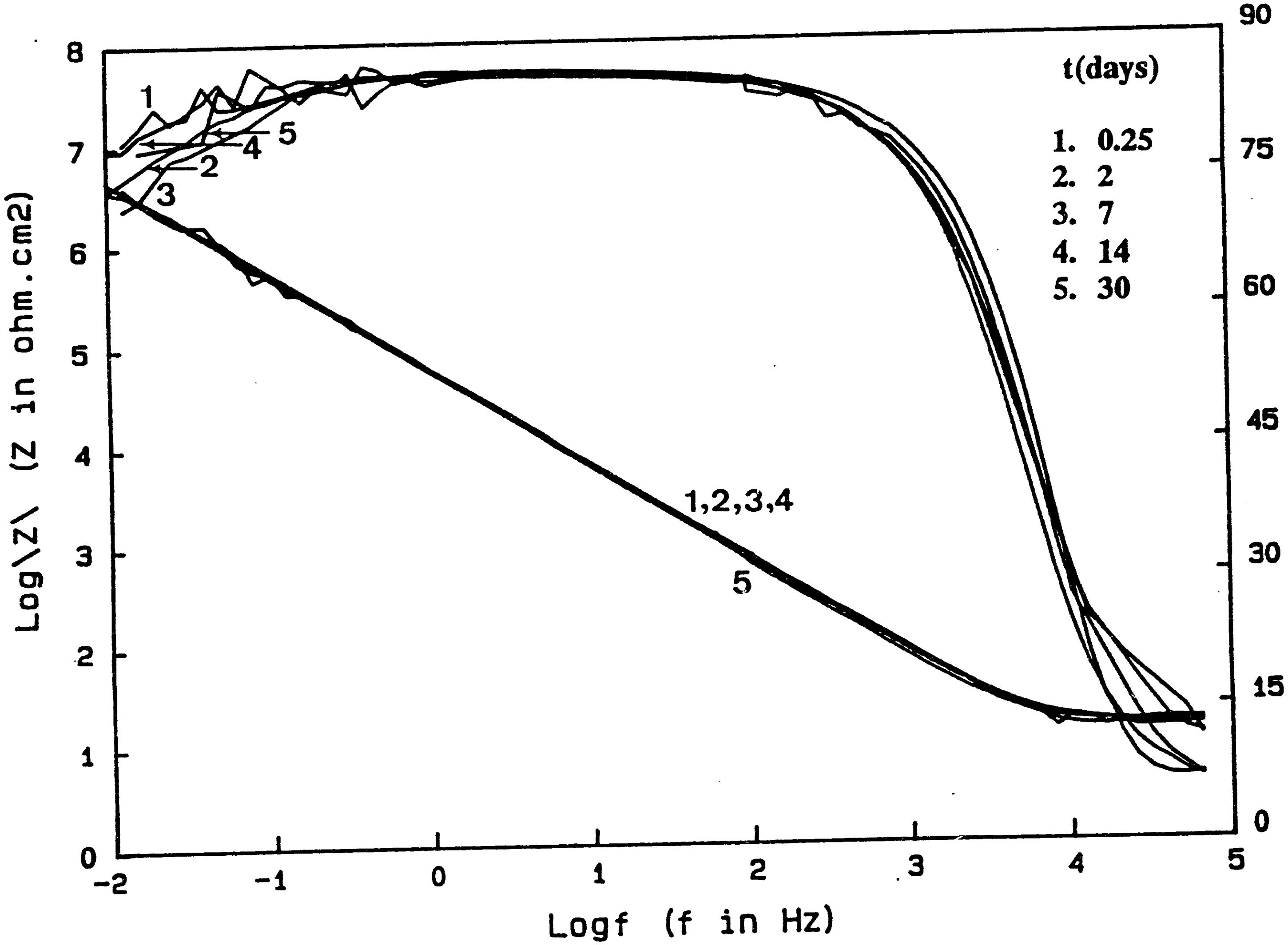
(This work is being funded by the Office of Naval Research (Dr. J. Sedrik.) under Contract No. N00014-91-J-1041).

Ce-Mo Process for Al 6061-T6

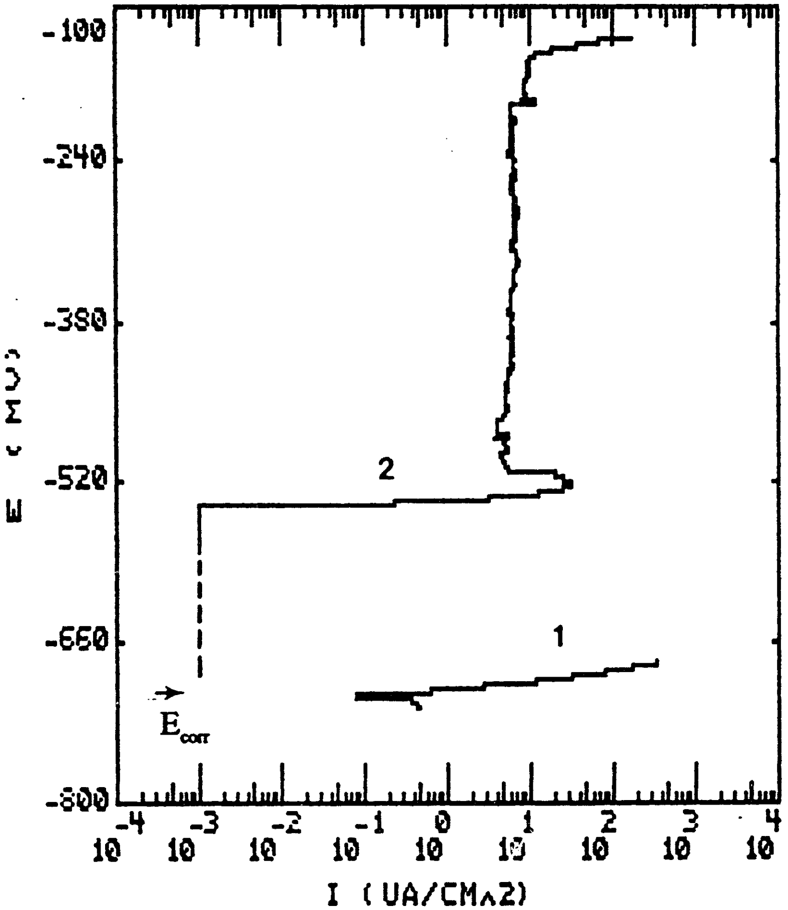
Steps	Treatments
1. Degreasing	Brushing with Alconox
2. Deoxidizing	Diversey 560 at room temperature for 10-15 min, then rinsing
3. Baking	In Oven at 100°C for 48 hours
4. Ce-treating I	Immersing in 10 mM $Ce(NO_3)_3$ at 100°C for 2 hours, then rinsing
5. Ce-treating II	Immersing in 5 mM $CeCl_3$ at 100°C for 2 hours, then rinsing
6. Mo-treating	Polarizing in 0.1 M Na_2MoO_4 at +500 mV vs SCE for 2 hours

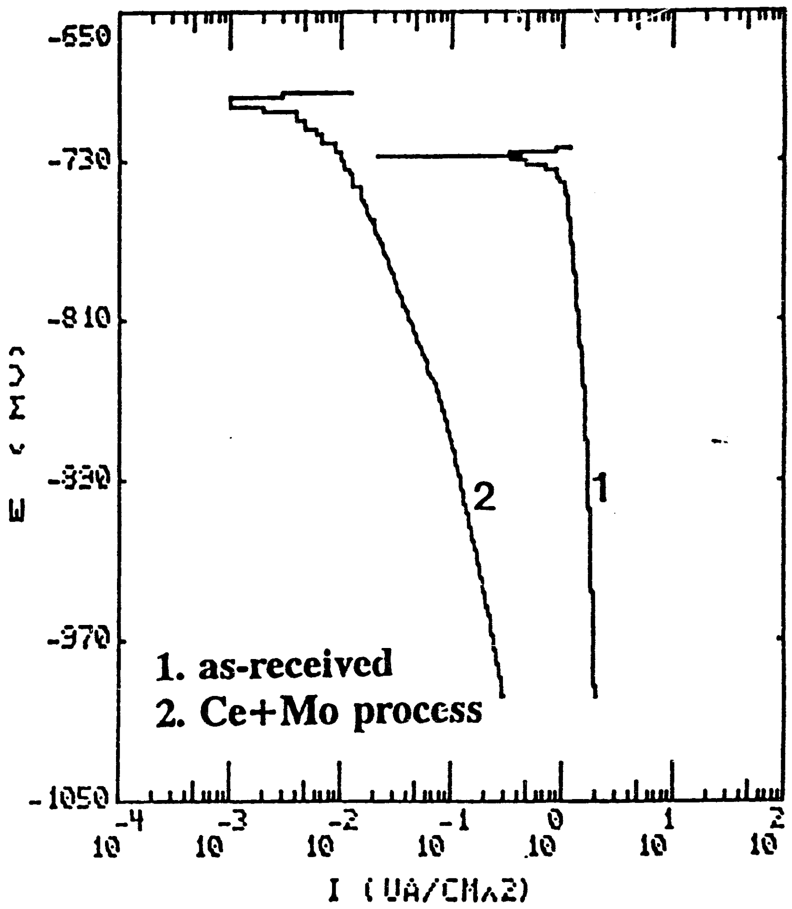
Ce-Mo Process for Al 7075-T6

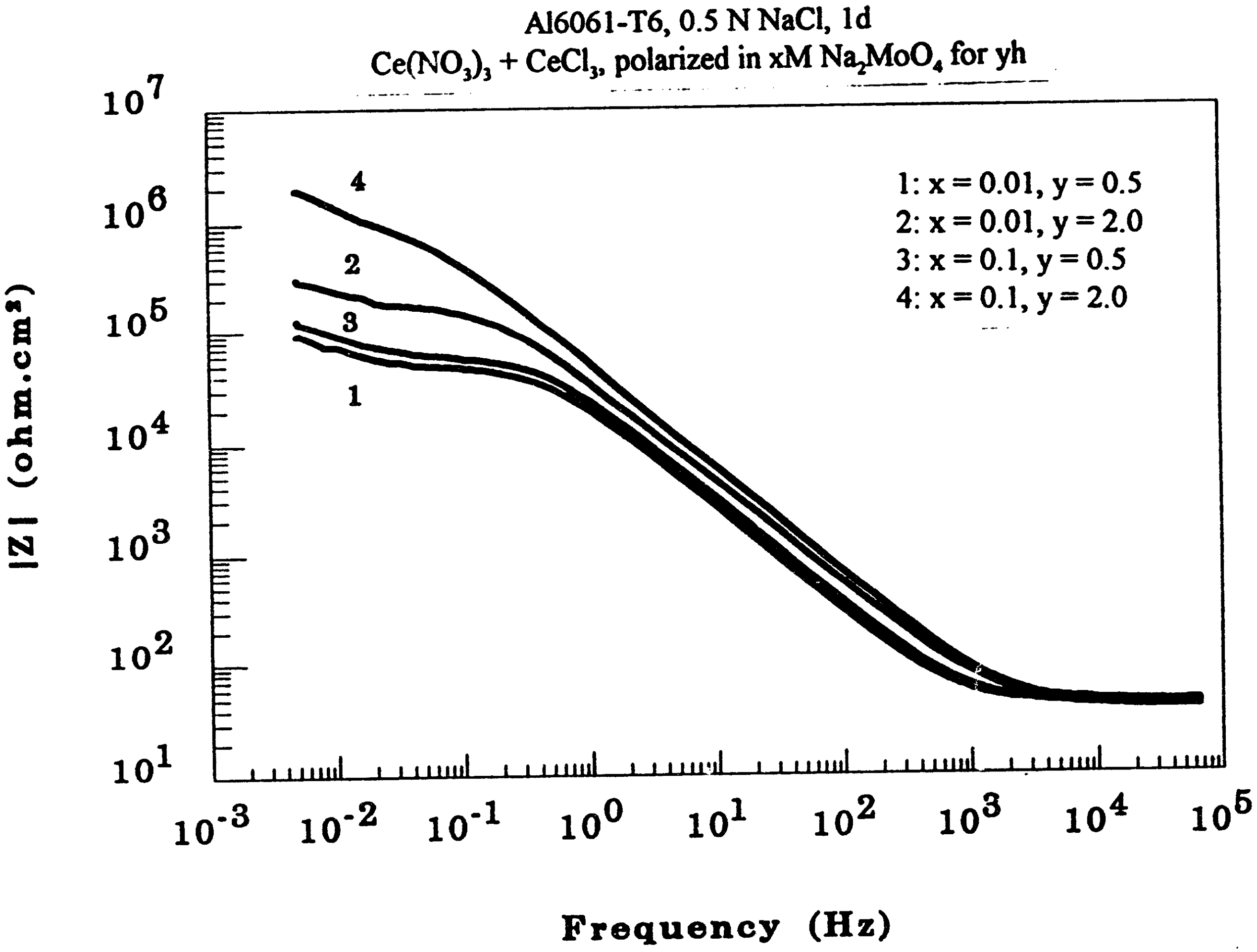
Steps	Treatments
1. Degreasing	Brushing with Alconox
2. Ce-treating I	Immersing in 10 mM $Ce(NO_3)_3$ at 100°C for 2 hours, then rinsing
3. Mo-treating	Polarizing in 0.1 M Na_2MoO_4 at +500 mV vs SCE for 2 hours
4. Ce-treating II	Immersing in 5 mM $CeCl_3$ at 100°C for 2 hours, then rinsing

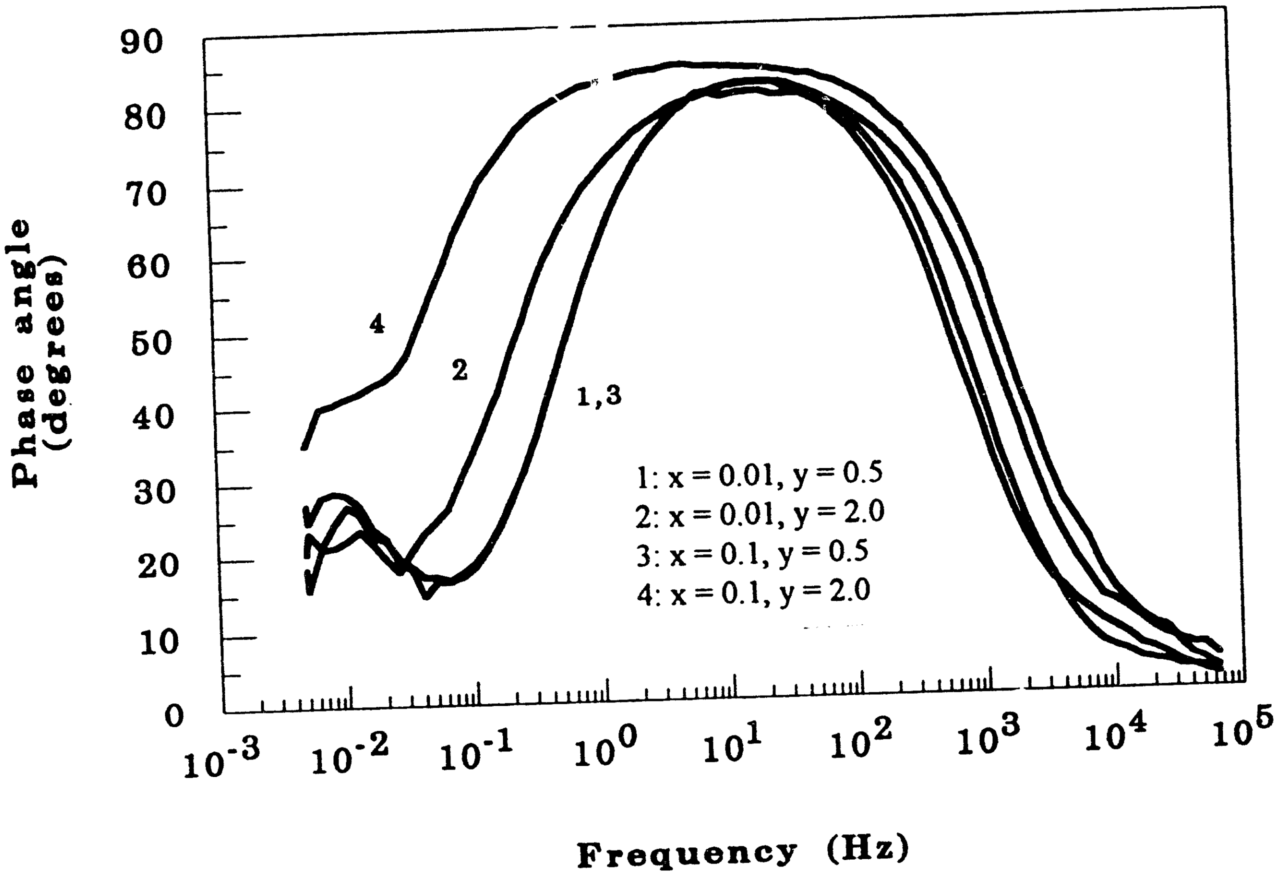


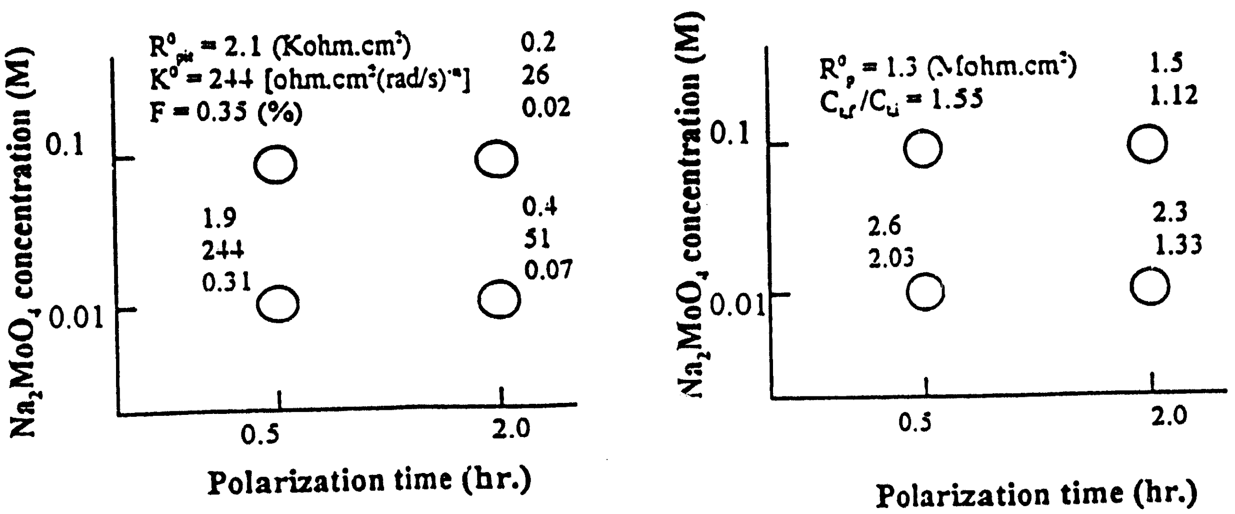
Bode-plots for Al 6061-T6 treated with the Ce + Mo Process; exposure to 0.5 N NaCl for a total of 30 days


-100
-240
-380
-520
-660
-800
E (MV)
2
1
E_{corr}
10^{-4} 10^{-3} 10^{-2} 10^{-1} 10^{0} 10^{1} 10^{2} 10^{3} 10^{4}
I (UA/CM^2)


-650
-730
-810
-890
-970
-1050
E (MV)
2
1
1. as-received
2. Ce+Mo process
10^{-4} 10^{-3} 10^{-2} 10^{-1} 10^{0} 10^{1} 10^{2}
I (UA/CM^2)

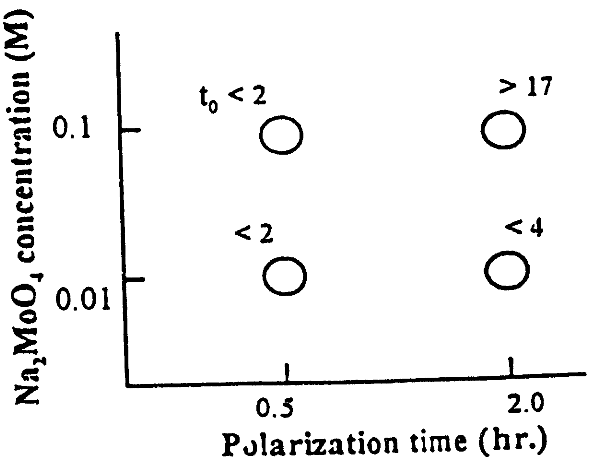

Al6061-T6, 0.5 N NaCl, 1d
Ce(NO$_3$)$_3$ + CeCl$_3$, polarized in xM Na$_2$MoO$_4$ for yh
1: x = 0.01, y = 0.5
2: x = 0.01, y = 2.0
3: x = 0.1, y = 0.5
4: x = 0.1, y = 2.0
4
2
3
1
|Z| (ohm.cm²)
10^7
10^6
10^5
10^4
10^3
10^2
10^1
10^-3
10^-2
10^-1
10^0
10^1
10^2
10^3
10^4
10^5
Frequency (Hz)


Phase angle (degrees)
0
10
20
30
40
50
60
70
80
90
Frequency (Hz)
10^{-3}
10^{-2}
10^{-1}
10^{0}
10^{1}
10^{2}
10^{3}
10^{4}
10^{5}
4
2
1,3
1: x = 0.01, y = 0.5
2: x = 0.01, y = 2.0
3: x = 0.1, y = 0.5
4: x = 0.1, y = 2.0



R^0_{pit} (10^3 ohm.cm^2) = 2.36 - 0.97t + 4.17c - 2.92ct
K^0 [ohm.cm^2(rad/s)$^{-n}$] = 307 -127t + 93c - 185ct
F (%) = 0.38 - 0.15t + 0.78c - 0.67ct

R^0_p (10^6 ohm.cm^2) = 2.86 - 0.24t - 16.3c + 3.70ct
$C_{t,f}/C_{t,i}$ = 2.33 - 0.49t - 6.3c + 2.00ct

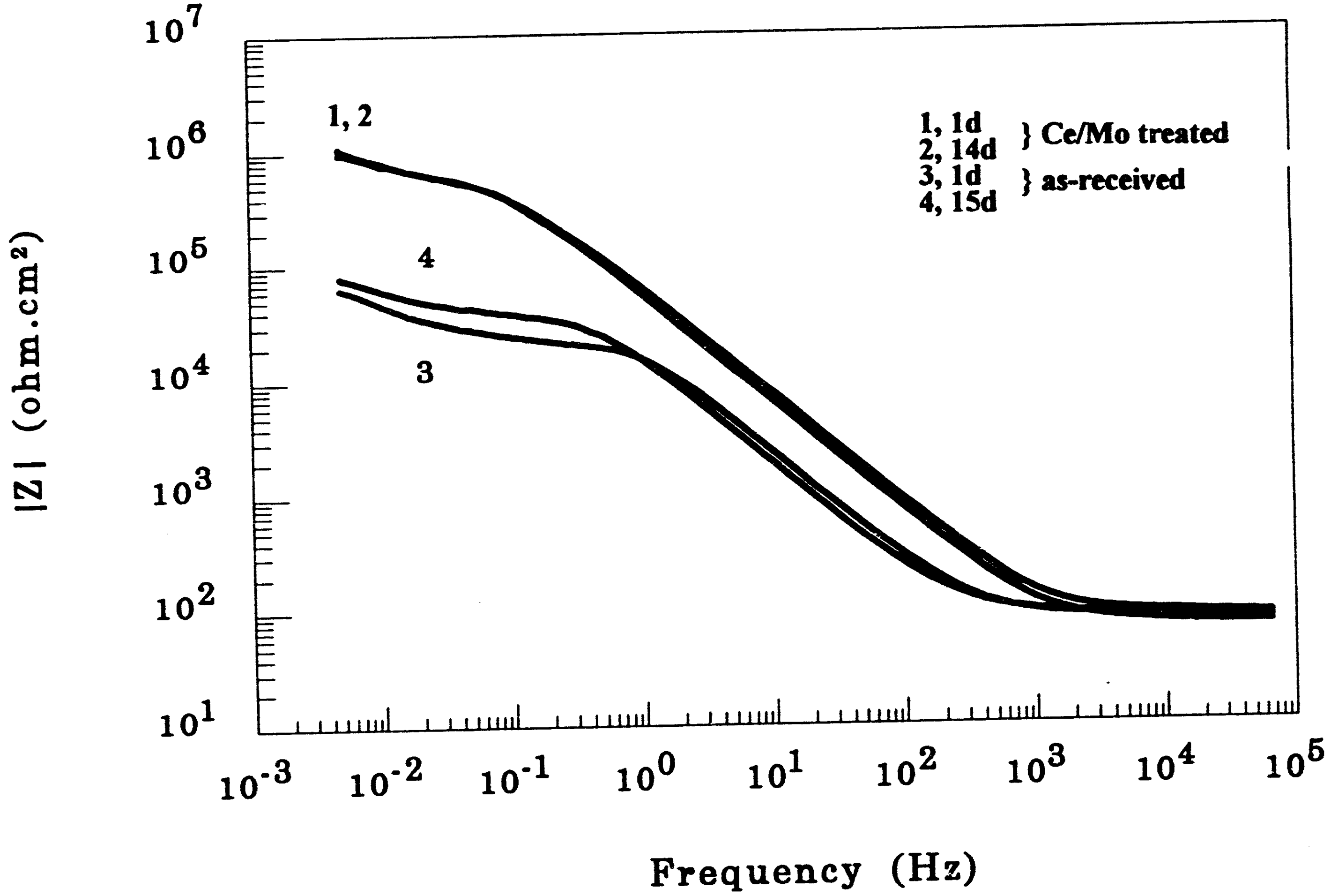


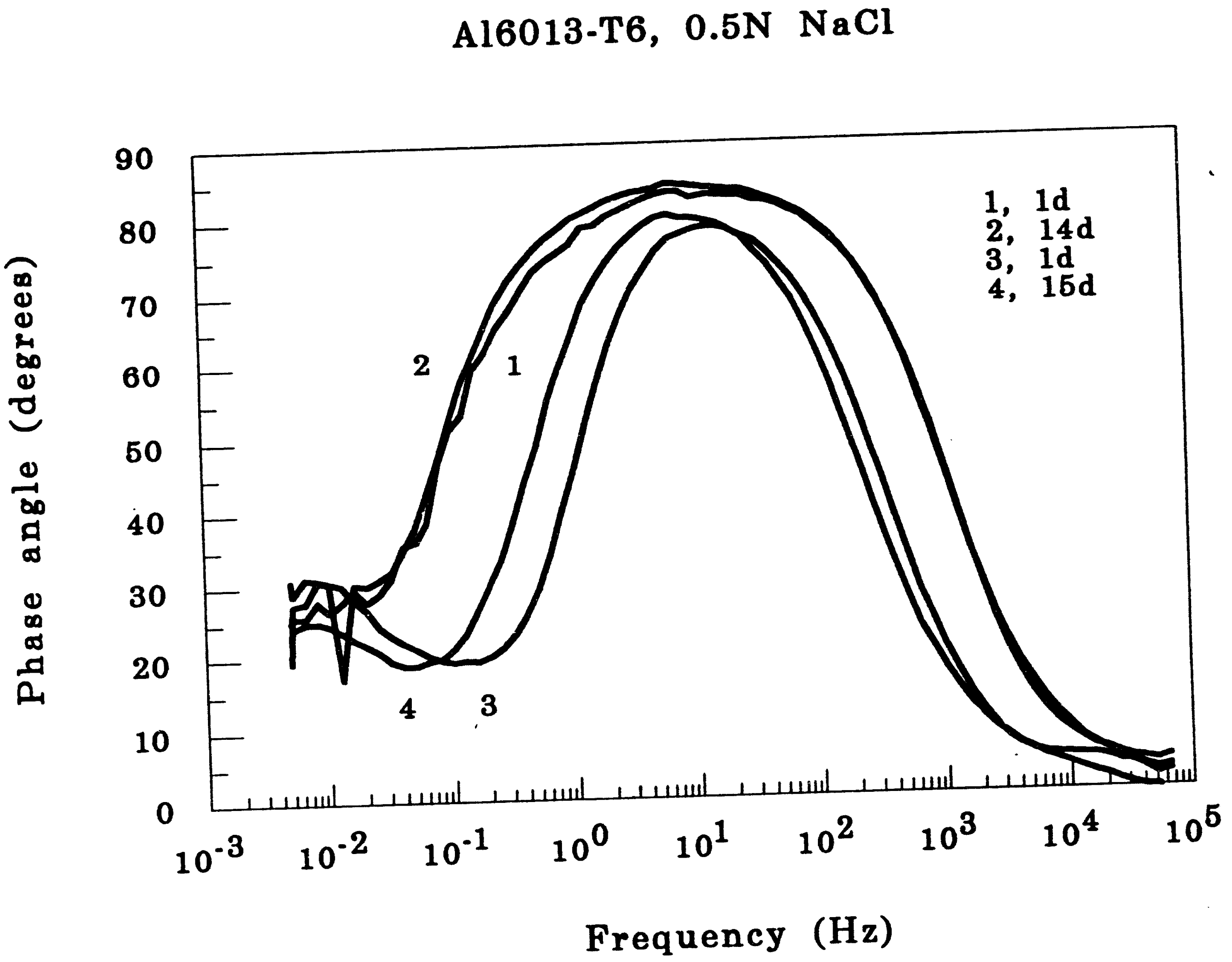
t_0 (d) = 1.8 + 0.4t - 48.2 + 96.3ct

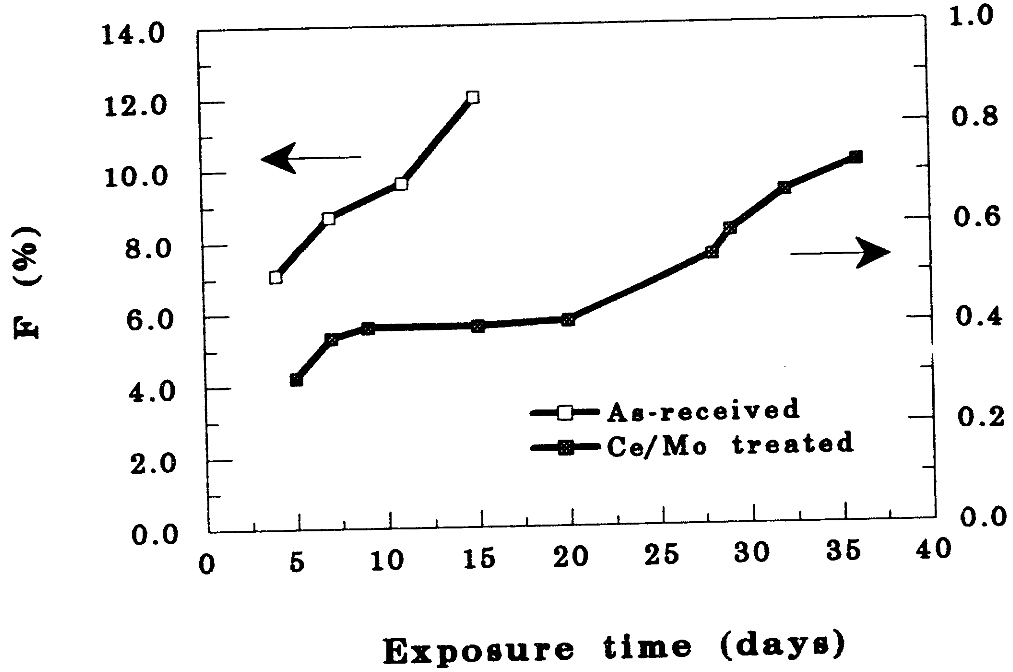
F: the pitted area fraction (30 days)
t_0 : the time when pits were first observed
$C_{t,i}$: total capacitance calculated from the first EIS measurement (1 day)
$C_{t,f}$: total capacitance calculated from the last EIS measurement (30 day)
R^0_p and K^0 were determined at the time t_0
R^0_{pit} was determined at t-t_0 = 1 (day)
R^0_{pit} and K^0 are normalized to the pit area

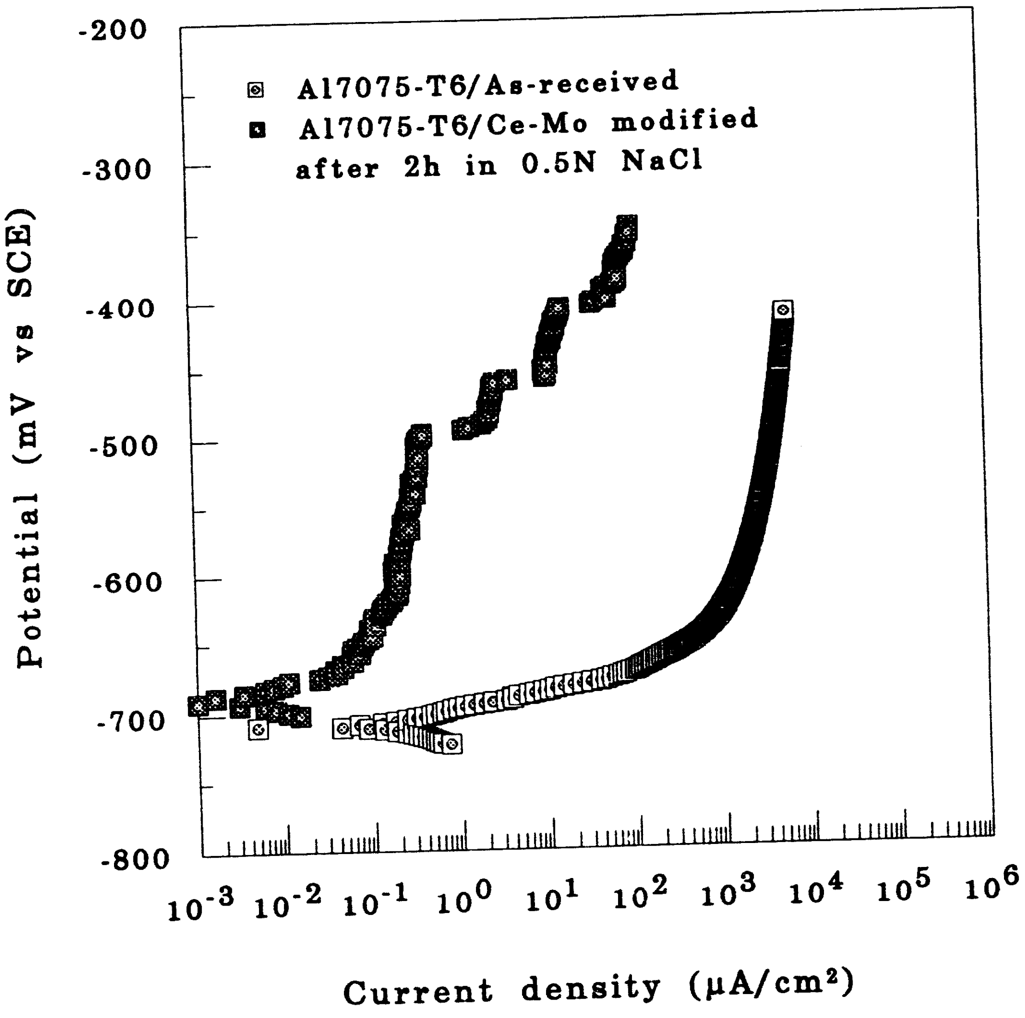
Fig. 5. Estimated effects of polarization time t and Na$_2$MoO$_4$ concentration c on characteristic parameters for the pitting behavior for Al 6061-T6 in 0.5 N NaCl.

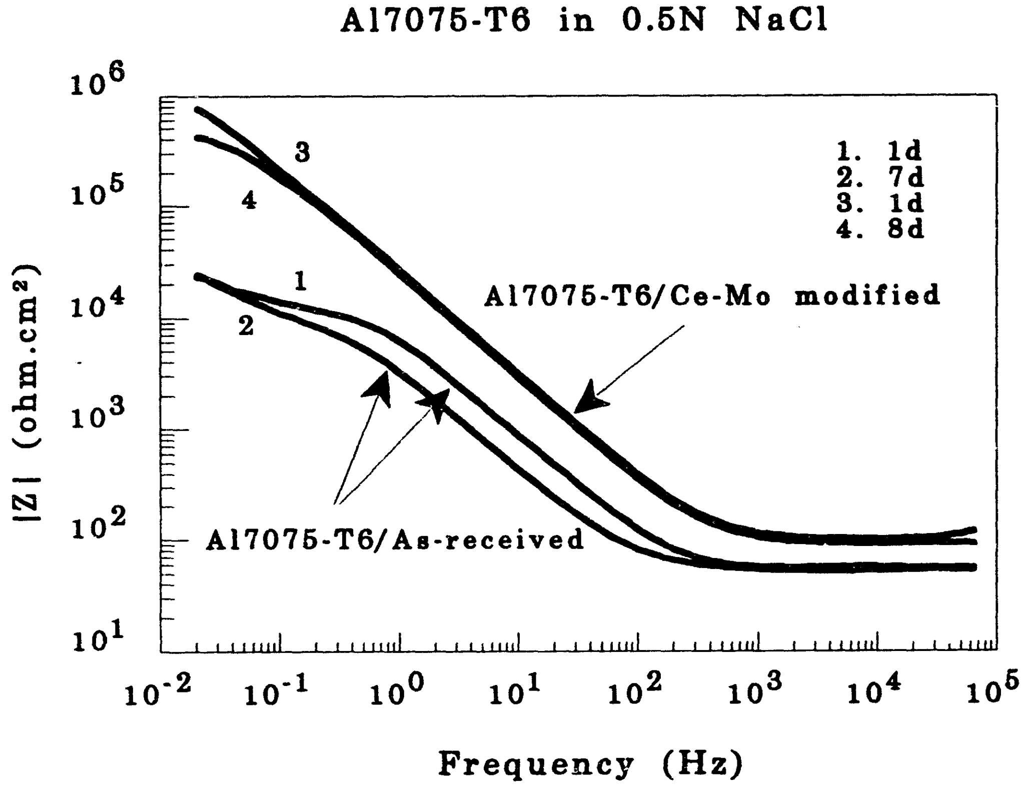
Al6013-T6, 0.5N NaCl

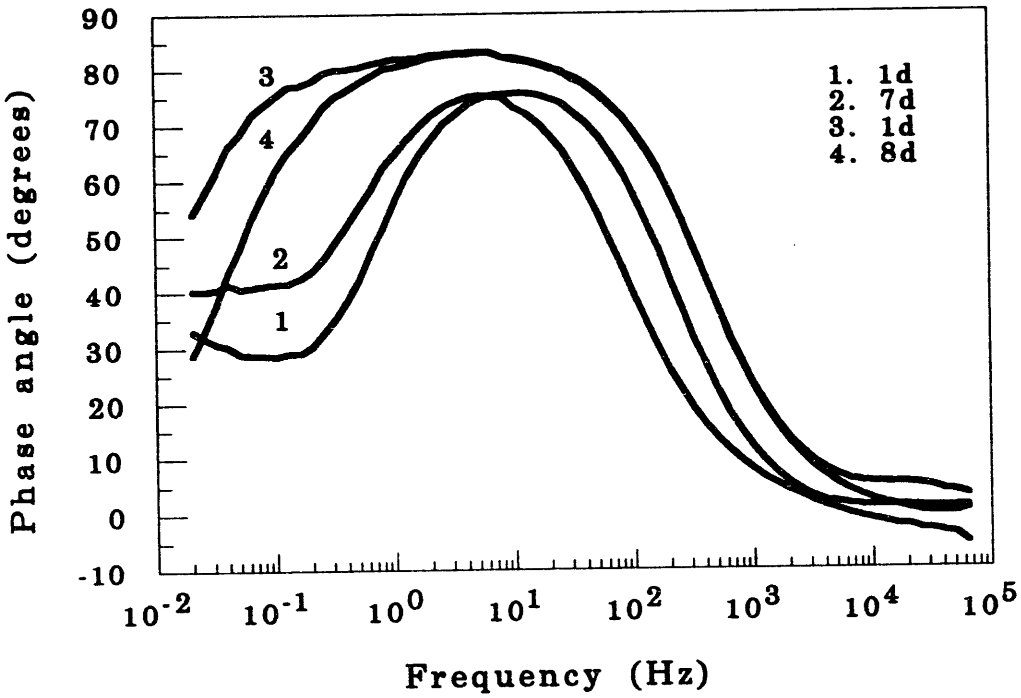



Al6013-T6, 0.5N NaCl
Phase angle (degrees)
90
80
70
60
50
40
30
20
10
0
Frequency (Hz)
10^{-3}
10^{-2}
10^{-1}
10^{0}
10^{1}
10^{2}
10^{3}
10^{4}
10^{5}
1, 1d
2, 14d
3, 1d
4, 15d
2
1
4
3

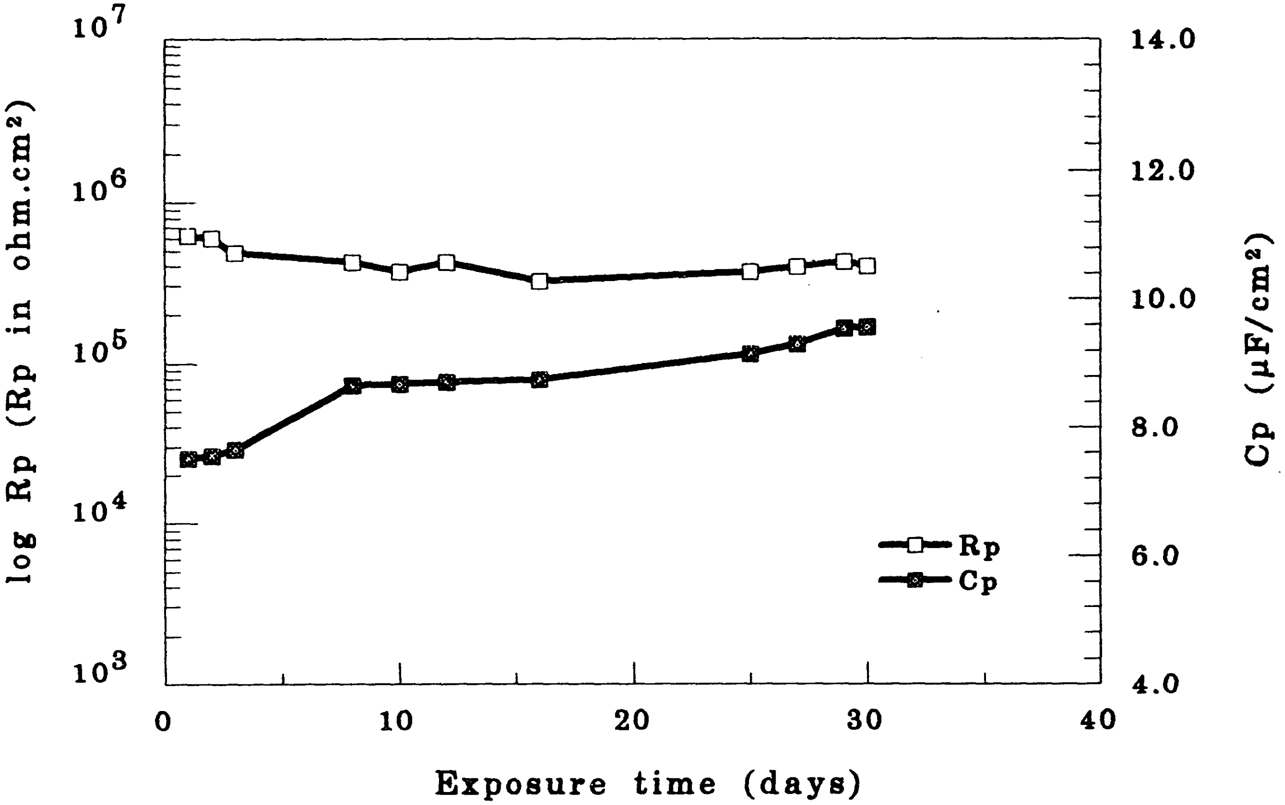

F (%)
14.0
12.0
10.0
8.0
6.0
4.0
2.0
0.0
1.0
0.8
0.6
0.4
0.2
0.0
0
5
10
15
20
25
30
35
40
As-received
Ce/Mo treated
Exposure time (days)


▨ Al7075-T6/As-received
■ Al7075-T6/Ce-Mo modified
after 2h in 0.5N NaCl
Potential (mV vs SCE)
-200
-300
-400
-500
-600
-700
-800
10^{-3}
10^{-2}
10^{-1}
10^{0}
10^{1}
10^{2}
10^{3}
10^{4}
10^{5}
10^{6}
Current density (μA/cm²)


Al7075-T6 in 0.5N NaCl
|Z| (ohm.cm²)
10^6
10^5
10^4
10^3
10^2
10^1
Frequency (Hz)
10^-2
10^-1
10^0
10^1
10^2
10^3
10^4
10^5
1. 1d
2. 7d
3. 1d
4. 8d
1
2
3
4
Al7075-T6/Ce-Mo modified
Al7075-T6/As-received



Al7075-T6 in 0.5N NaCl


10^7
10^6
10^5
10^4
10^3
log Rp (Rp in ohm.cm²)
14.0
12.0
10.0
8.0
6.0
4.0
Cp (µF/cm²)
0
10
20
30
40
Exposure time (days)
Rp
Cp

Session II:
Performance Testing of Coatings

Martin Kendig and Ray Taylor
Moderators

Correlation of Electrochemical Analysis tc Salt Fog Testing of Non-Chromate Conversion Coatings and Anodic Seals

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Introduction

A number of commercial and experimental non-chromate conversion coatings and anodic seals for boric sulfuric acid anodization (BSAA) were evaluated by both salt fog testing (B117) and electrochemical impedance spectroscopy. The coatings were applied to Al 2024-T3, considered to be a bell weather for the efficacy of a given coating owing to the difficulty in protecting this particular material which is rich with Cu intermetallics.

Experimental

Samples that were prepared at the Science Center were degreased in hot xylene and deoxidized using a non-chromate Sanchem 1000 treatment and then subjected to either the BSAA or the coating with the chromate conversion coating alternatives. Baseline BSAA samples were sealed with either a 5% dichromate or a dilute dichromate. Other BSAA samples were sealed with a variety of commercial and experimental non-chromate seals. The baseline conversion coating was an Alodine 1200 sample processed by Rockwell International Space Systems Division. In addition a number of commercial or experimental samples were received from other sources. The resulting samples were subjected to a B117 salt fog test for 168 h in the case of the conversion coating replacements or for 336 h for the anodized samples. Duplicate samples were subjected to electrochemical impedance measurements after 1 and 24 h immersion in 0.5 M NaCl.

Results

Figure 1a-b show a typical impedance spectrum for an anodized sample, and the calculated spectrum using the model in Figure 1c. There is relatively good agreement between the observed and calculated spectra. The 1 and 24 h parameters obtained from such spectra were evaluated and compared to the salt fog test results.

A comparison of the salt fog results to the 24 h corrosion resistance, Rp @24h , for the anodized samples demonstrates that the early, 24 h impedance measurement predicts the longer term (336 h) salt fog behavior. No apparent correlation to longer-term salt fog test appeared for the other impedance parameters. The salt spray data were first plotted in terms of (1=pass, 0.5 = marginal, 0= fail) as a function of the log of the polarization or corrosion resistance R_p. This plot was then smoothed by performing a sliding or running average on the data. Figure 2 shows a plot of this resulting average salt spray behavior as a function of R_p. The data indicate a threshold of 30 M ohm-cm^2 below which samples will not pass the salt fog test. Above this corrosion resistance the probability is good regarding passage of the salt fog test. This represents an important result since it allows rapid screening of anodization sealing processes without the necessity of a long term (336 h) salt fog test.

The correlation of the number of pits observed on the samples and salt fog behavior shows a threshold of about 5 M ohm-cm^2 for the 24 h measurement of R_p below which a high rate of pitting occurs as observed after 336 h of salt fog (Figure 3). Above this threshold the rate of pitting appears to decrease approximately linearly with Log(R_p) as measured at 24 h. The marked contrast between samples above and those below the 5 Mohm cm^2 value means that there is a qualitative similarity of the samples which exhibit impedances above 5 M-ohm cm^2 but do not pass the salt fog test and those that do pass this test. In other words, the samples above 5 M ohm cm^2, but which do not pass the salt fog test should be considered marginal in that slight modification of their processing may enable their passing. The materials that fall into this category include the single sol-gel layer (AN4S), the Novomax 1000 (AA5) and the Novomax non-nickel (AN5).

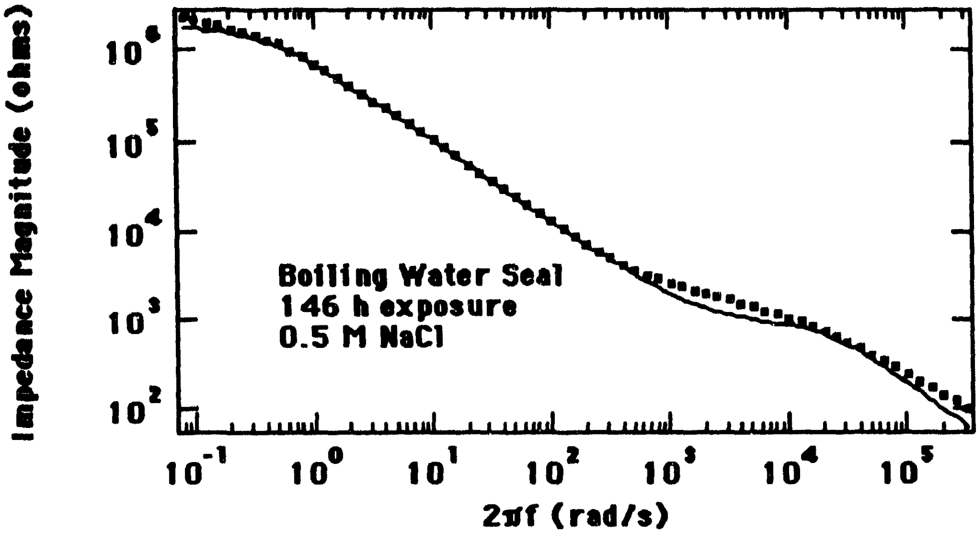
No good correlation existed between early impedance data and the 168 h salt fog test for replacement conversion coatings. Contact angle data suggest that surface energy (hydrophobicity/hydrophilicity) may contribute the salt fog resistance of conversion coatings in addition to the barrier properties of films observed when they are subjected to forced wetting by immersion.

Summary and Conclusions

One of the more important results of this work is that a correlation has been established between the 336 h salt fog test and the corrosion resistance for anodized and sealed Al 2024-T3, R_p, as determined from EIS after only 24 h. A threshold of 30 M ohm cm^2 defines the boundary above which the sealed anodized film probably will pass the 336 h salt fog test. Sealed BSA anodized Al 2024-T3 that exhibit R_p determined at 24 h that fall above 7.5 M ohm cm^2 show low levels of pitting but may not pass the 336 h test unless R_p is above the 30 M ohm cm^2. This is to say the 245 h R_p threshold for inhibition of gross pitting equals 17.5 M ohm cm^2. This rapid evaluation methodology can be used to rapidly screen anodic seals for BSA anodized Al 2024-T3.

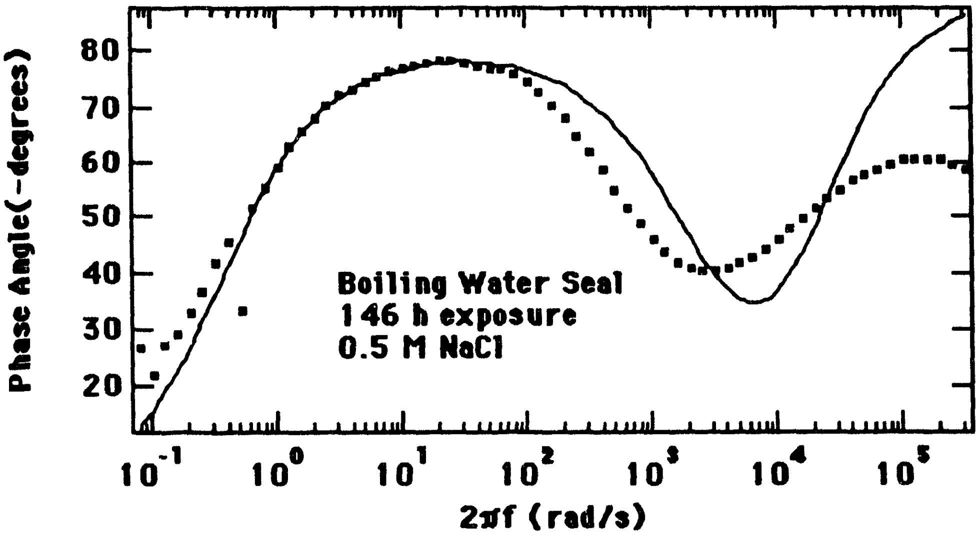
Acknowledgment

This work was supported by the Rockwell International Science Center Independent Research and Development Program and the South Coast Air Quality Management District



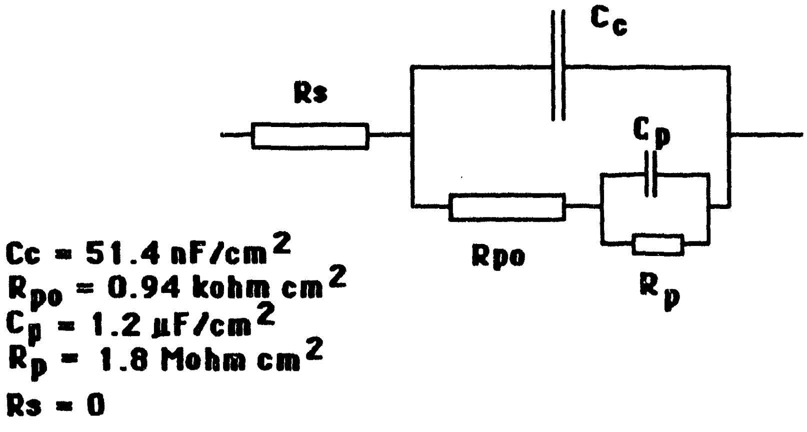
Impedance Magnitude (ohms)
10^6
10^5
10^4
10^3
10^2
Boiling Water Seal
146 h exposure
0.5 M NaCl
10^-1
10^0
10^1
10^2
10^3
10^4
10^5
2πf (rad/s)

(a)



Phase Angle(-degrees)
80
70
60
50
40
30
20
Boiling Water Seal
146 h exposure
0.5 M NaCl
10^-1
10^0
10^1
10^2
10^3
10^4
10^5
2πf (rad/s)

(b)



(c)

Figure 1 Typical impedance spectrum, (a) magnitude and (b) phase, for a boiling water sealed anodized aluminum 2024-T3 sample after 146 h exposure to 0.5 M NaCl. Solid line represents simulated spectrum using the best fit parameters for the model (c).

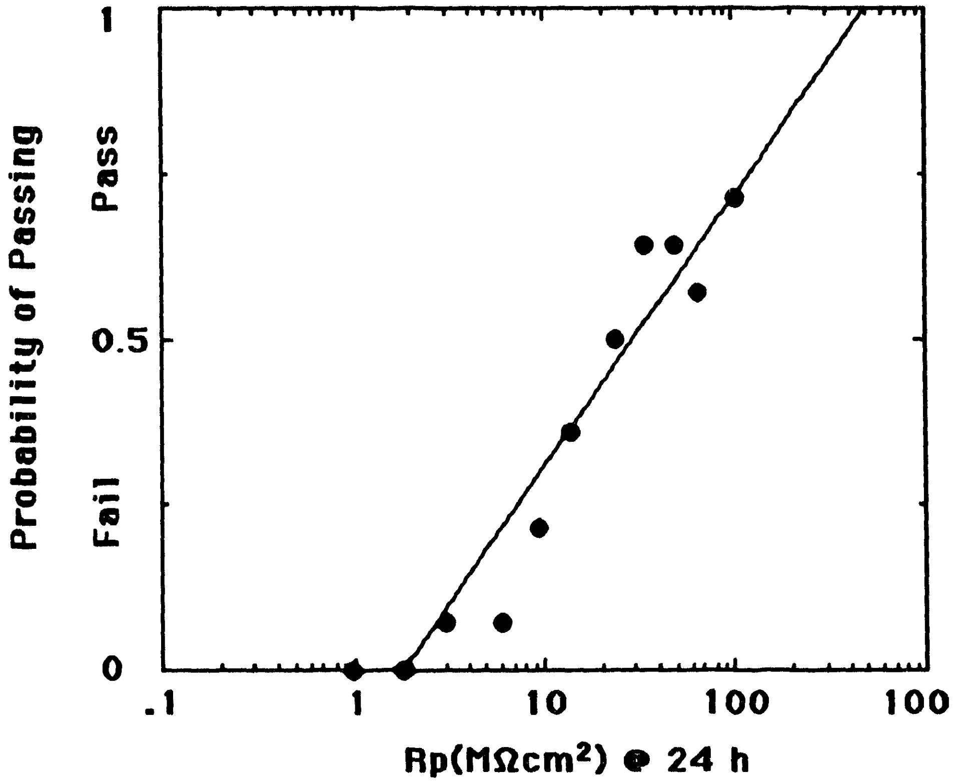


Figure 2. Estimated probability for passing the salt spray test as a function of Rp measured after 24 h immersion in 0.5 M NaCl

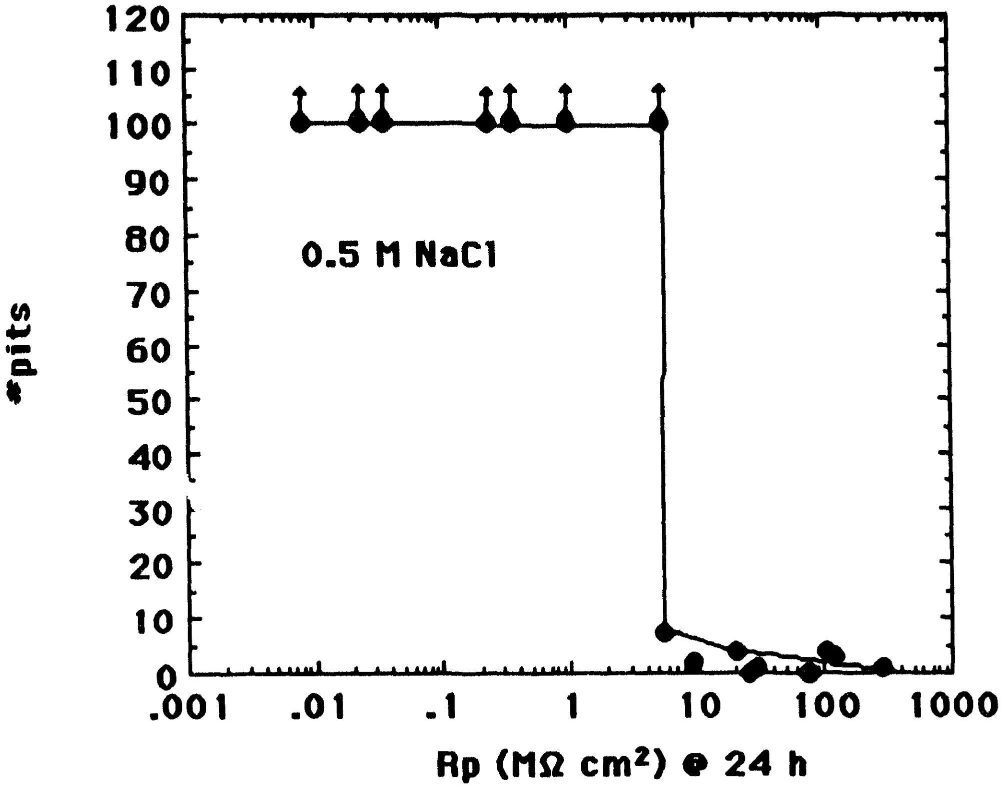


Figure 3 Relationship of Rp for sealed anodized Al 2024-T3 to the number of pits observed after the 336 h salt spray test.

Correlation of Electrochemical Analysis to Salt Fog Testing of Non-Chromate Conversion Coating and Anodic Seals

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Acknowledgement

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Rockwell International IR&D
South Coast Air Quality Monitoring District

Objective

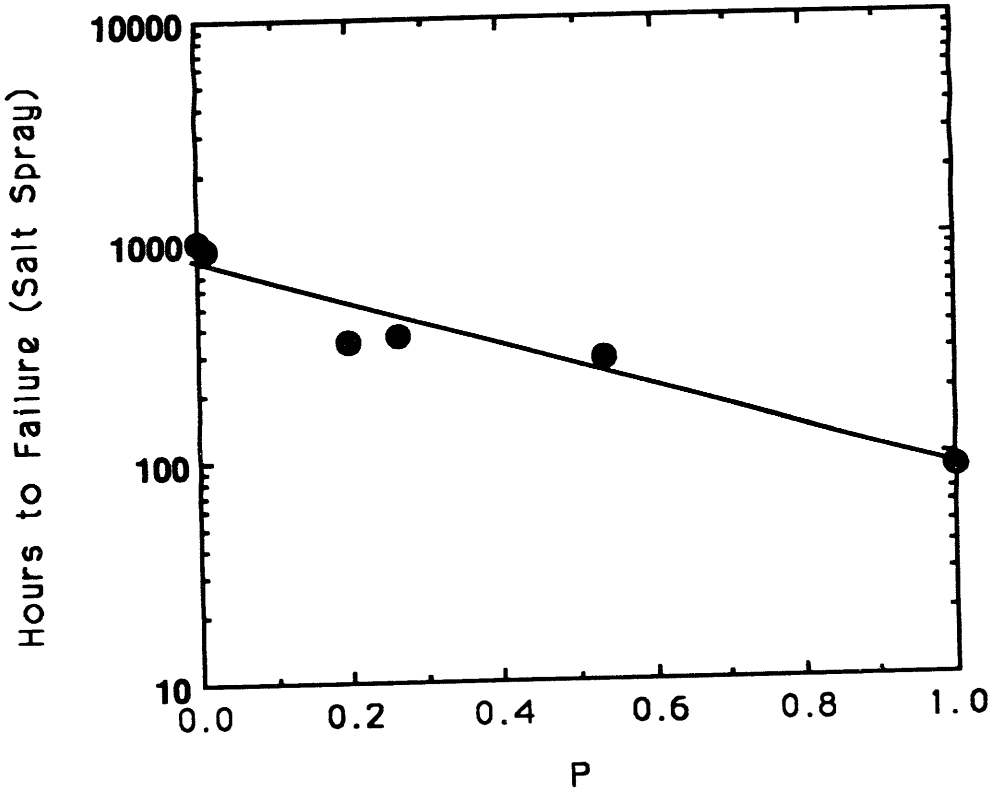
- Select non-chromate processes to replace chromate conversion coatings.
- Select non-chromate processes to replace seals for thin-film anodic coatings.

Background - EIS Predicts Long Term Behavior for Organic Coatings

A-B Phosphated+Coated Steel

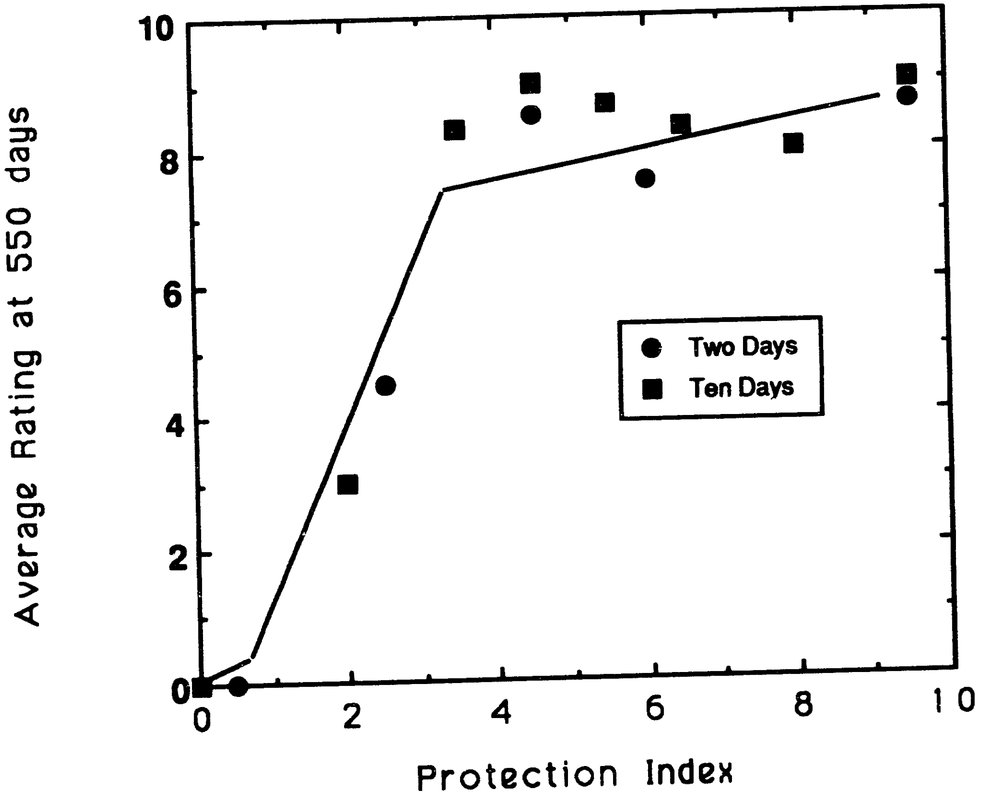
P-Corrosion = P(diff)*P(disb) + P(defects)

P= [v(24h)*Ad(72h) +2*(1Mohm/Rpo)]/Pmax



- Published in <u>Corrosion</u> 1991
- Work performed 1987
- v = volume of water taken up from capacitance measurement
- Ad = area disbonded by cathodic polarized scribe
- Rpo = coating resistance

Long Term Sea-Water Exposure



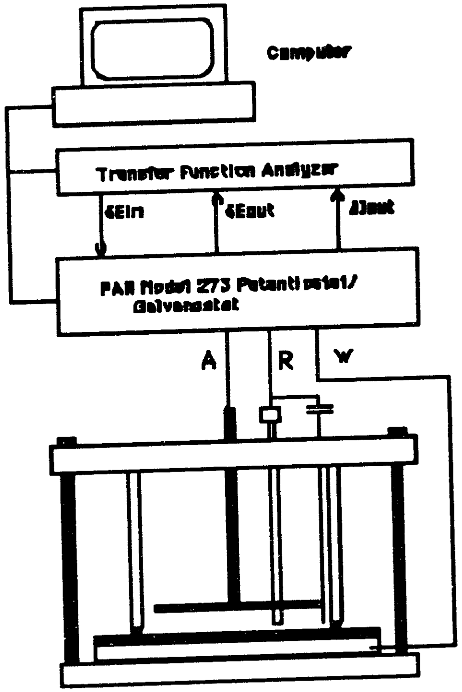
- Protection Index - Function of EIS Parameters
- Rating - ASTM D610 after 550 days exposure to artificial sea water
- EIS - measured at 2 and 10 days
- Rating made after 550 days

- Data reformulated from paper by J. Scully, J. Electrochem. Soc., 136(4), 1989.

Approach

- Anodic Films
  - Sanchem 1000 Deoxidation
  - Al 2024-T3
  - BSAA
  - Inorganic and sol-gel coatings
  - Commercial non-chromate seals
- Chromate Conversion coating replacements
  - Sanchem 1000 Deoxidation
  - Al 2024-T3
  - Sol-gel
  - Inorganic oxy anions
  - Other commercial and experimental
- Rapid Assessment - EIS
- Salt Fog (B117, 336 h)

Apparatus for EIS



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Replacements for Conversion Coatings

Sample Code	Process
ACF1*	Standard Chromate Conversion Coating (Alodine 1200)
ACR3E	NADC Trivalent Cr
ASG3L1	3 sol-gel layer
ASG3L2	3 sol-gel layer
ASG6L1	6 sol-gel layer
ASG6L14	6 sol-gel layer
ASG6L2	6 sol-gel layer
ASG6L24	6 sol-gel layer
HT ***	Hydrotalcite
HTS1	Hydrotalcite/Sol-Gel
HTS3***	Hydrotalcite/Sol-Gel
IRA **	Iridite
IRB **	Iridite
PA ****	Parker Amchem Non-Chrome Experimental
SC Sanchem 1000	Sanchem
SCS Sanchem 1000	Sanchem/Silicate Post Treatment
SG1 Sanchem 1000	Sol-gel 1 layer
SG3 Sanchem 1000	Sol-gel 2 layer

Anodized Seal Replacements

Code	Description
AFA	Alumitec
A5D5	5% Sodium Dichromate
AA5	Anoseal1000
ABW6	Boiling water
ACN6	Ce(NO3)3
ACP3	Ce(NO3)3 + H2O2 unreacted
ACP9	Ce(NO3)3 + H2O2
ADC8	Dilute chromate
AN4S	1 sol-gel layer
AN7S3	3 sol-gel layer
ANN5	Novomax Non Ni
APM3	Phosphomolybdate
APW2	Phospho tungstate
AS35	Sanchem 3000
ASM2	Silico Molybdate
ASW2	SilicoTungstate
AV2	Sodium Vanadate
AW4	Water Seal

Sol-Gel Chemistry

Materials

ALSBC - Aluminum di(sec-butoxide)acetoacetic ester chelate ($\mathrm{Al(OC4H9)2(C6H9O3)}$)

PDMS - Polydimethylsiloxane $\mathrm{[SiO(CH3)2]22}$

ALSBC/PDMS = 5.8:1 (mole ratio) or (1:1) weight ratio

Procedure

React isopropanol solutions of ALBC and PDMS at 80°C

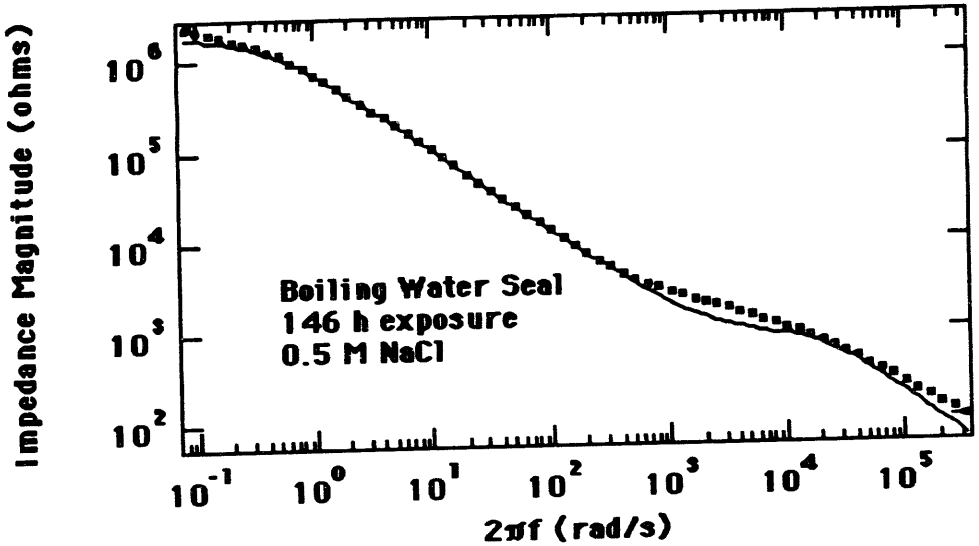
Cool

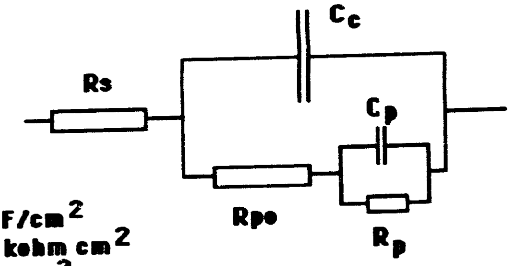
Dilute with isopropanol

Dip coat the sample

Dry at typically 100 C overnight

Typical Impedance Spectra





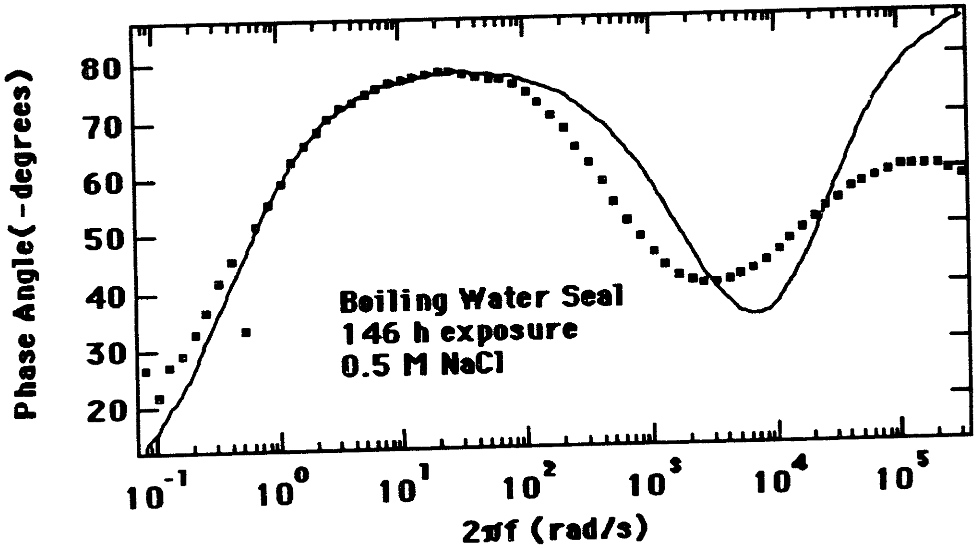
$C_c = 51.4\ nF/cm^2$

$R_{po} = 0.94\ kohm\ cm^2$

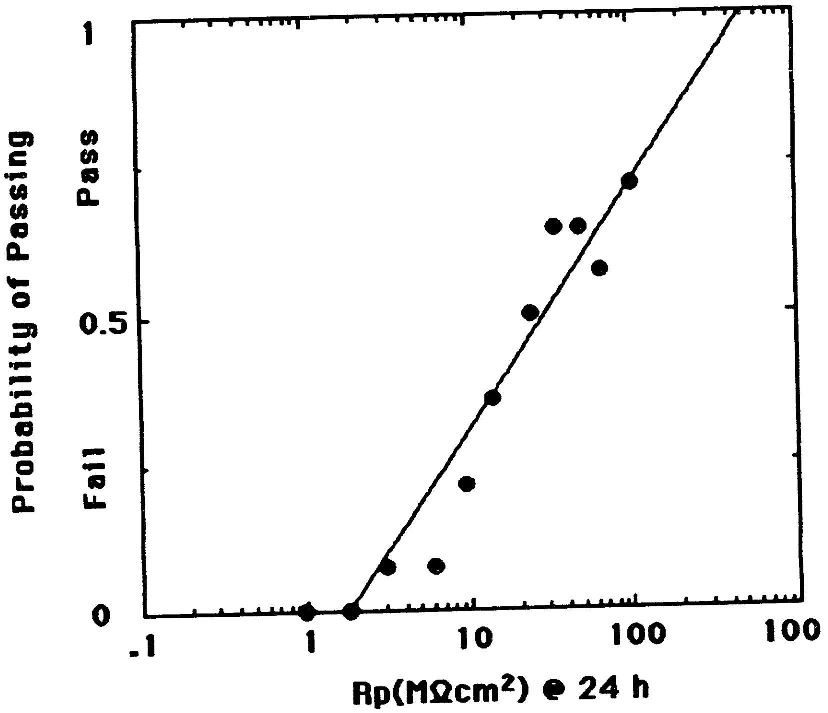
$C_p = 1.2\ \mu F/cm^2$

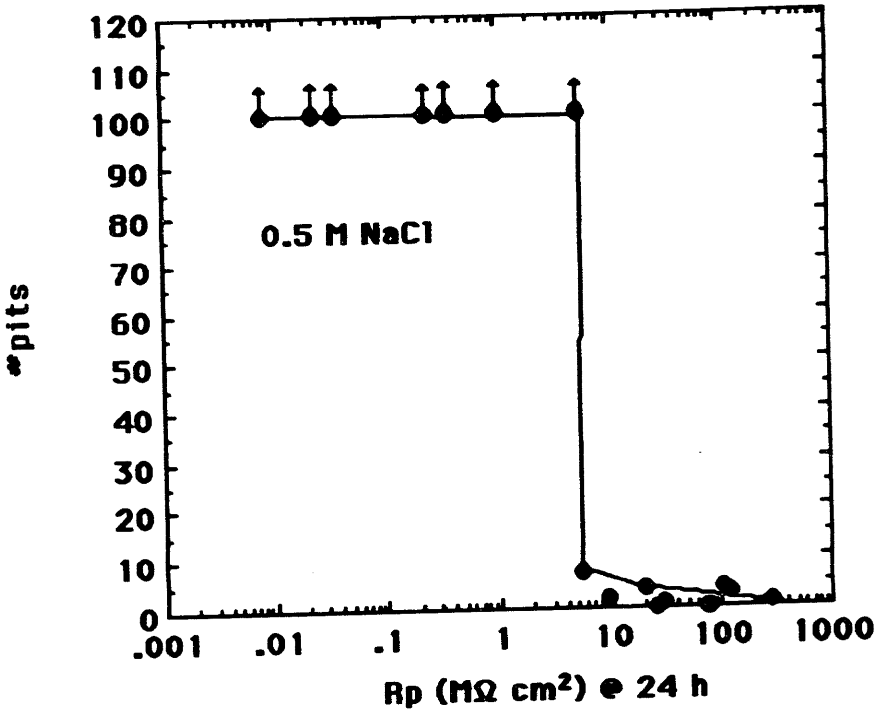
$R_p = 1.8\ Mohm\ cm^2$

$R_s = 0$



Results - Anodized Aluminum





- 2024-T3
- Space Division
- 24 h Impedance Data -------> 336 h ASTM B117 Salt Fog

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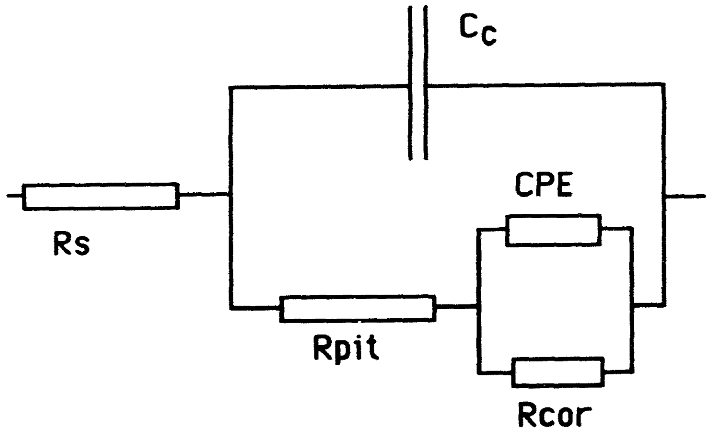
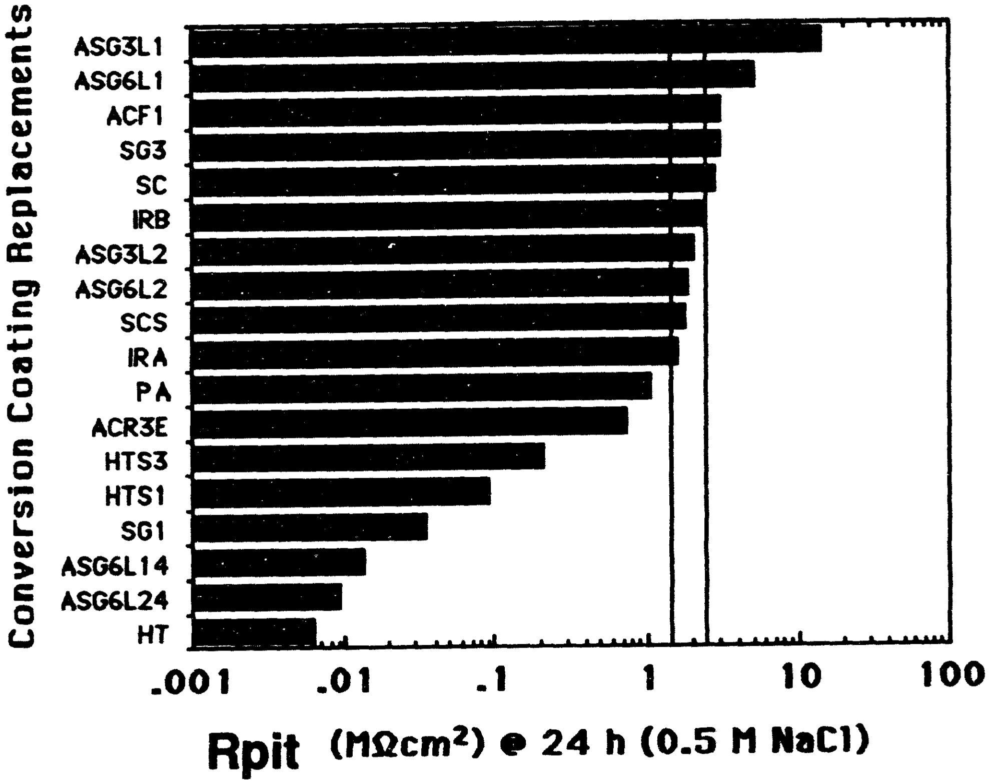
Conversion Coating Schematic



- Simplified version of more general model
- High frequency time constant establishes Rpit, Cc and Rs

Results for Conversion Coating Replacements



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Selected Rpit (24h) and Wetting Data

Code	Material	Contact Angle	Rpit @ 24 h M ohm cm2	Salt Fog 336 h
ASG6L14	Sol-Gel 6 layer	99.5	5.00	n.d.
ACF	Alodine 1200	106	3.05	pass
SC	Sanchem 3000	58	2.75	fail
SCS	Sanchem 3000/Full	20	1.80	fail
ACR3	NAWC Cr(III)	68	0.74	fail

Conclusions

- Chromate Protection
  - Barrier
  - Hydrophobic
  - Active Species

- No Suitable Non-chromate replacement found for Al 2024-T3

- BSAA Seals
  - Rp> 30 Mohm cm2 @ 24 h predicts 336 h passage for Al 2024-T3
  - Rp> 7.5 Mohm cm2 @24 h predicts low levels of pitting/marginal salt fog resistance at 336 h
  - Sanchem 3000, 3 Layer Sol-gel, Hot Cerous Nitrate - Adequate
  - Novomax NN and Anoseal 1000 may pass salt fog with suitable process modification

Testing and Specification of Conducting and Protective Coatings for Aluminum

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The types of specifications possible to describe the composition and properties of conducting and protective coatings will be described together with the degree of detail required to adequately define requirements and ensure reproducibility. The potential problems arising from the many factors governing such general properties as corrosion resistance, conductivity, and resistance will be described with reference to the experience arising from the use of chromate conversion coatings. In particular, it will be argued that:

(a) Current specifications define current materials, i.e. chromate conversion coatings and the properties required are those of this type of coating;
(b) Because of this, they do not necessarily define what is needed;
(c) Because of this, specification is driving development (this aspect is particularly damaging to commercial firms who may be striving for coating properties we do not need);
(d) Because there is a large data base on the use of chromate coatings backed up by years of practical experience, an equally large or larger data base will be required for replacements;
(e) Why make things difficult by claiming that all development work is for <u>replacements</u> for chromate coatings? Why not call them New Technology?;
(f) Why insist on inorganic conversion coatings? Why not organics?;
(g) Ideally, the cycle for development of replacements should be: develop, test, <u>then</u> specify.

TESTING AND SPECIFICATION OF CONDUCTING AND PROTECTIVE COATINGS FOR ALUMINIUM ALLOYS

P Walker

OR ALTERNATIVES FOR SOME ASPECTS OF CHROMATE CONVERSION COATING TECHNOLOGY

AWE plc

Chromate Elimination Workshop
Albuquergu
New Mexic
September 199

TYPES OF SPECIFICATION

(1) A Specific Product Spec - for a proprietory material

(2) Performance Spec - for any material

(3) Material Spec - for a specific formulation

(4) Material and Performance Spec - the ideal

(5) No Spec (or so loose as to be useless) - easiest and worst approach

SPECIFICATION REQUIREMENTS

Corrosion Protection Required

Electrical Resistance
Adhesion
Colour

Processing speed, etc, etc, etc

CORRORSION PROTECTION

(1) On what? - alloy type

(2) To what? - salt spray, humidity, accelerated weathering or external weathering

(3) For how long?

(4) At what coating weight?

(5) What process to achieve (4)

(6) What cleaning methods to achieve (1), (2) and (4)

FACTORS KNOWN TO AFFECT PERFORMANCE

(1) Type of alloy - commercially pure - high performance (Cu, Si, Mn, Zn, etc)

(2) Type of chromate coating - accelerated, non-accelerated, prop.

(3) Efficiency of cleaning

(4) Coating weight

(5) Coating quality

(5) Encompasses (1) to (4)

ALLOYS

A
BS3L70: 3.9 - 5% Cu, 0.2 - 0.8% Mg, 0.5 - 0.9% Si,
0.4 - 1.2% Mn - Solution heat treated

B
BSL104: As above but solution heat treated and precipitation
heat treated

C
NS8: 0.1% Cu, 0.5 - 1.0% Mg, 0.4% Si, 4.4 - 9.0% Mn,
0.2% Ti, 0.25% Cr, 0.4% Fe

D
BS1470: Commercially pure aluminium (99%)
SIC 8H

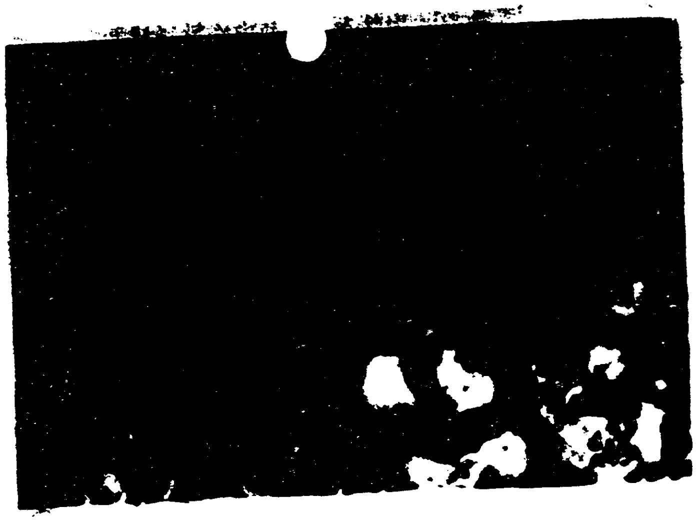
COATING WEIGHT APPLIED AT SAME PROCESSING TIME

TREATMENT	ALLOY g/m²			
	A	B	C	D
Aloclene 302	1.06	0.68	0.49	0.54
Alocrom 1200	0.52	0.41	0.56	0.24
Alocrom 407	2.00	5.32	4.82	4.40
Bonderite 705	2.96	2.35	2.4	1.56
Bonderite 711	0.33	0.37	0.31	0.37
Non-prop.	0.26	0.24	0.56	0.52

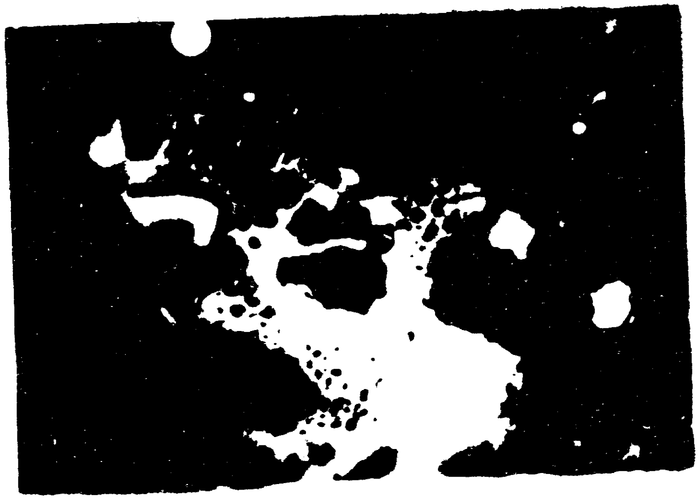
EFFECT OF COATING WEIGHT ON INITIAL CORROSION IN SALT SPRAY

PROCESS	ALLOY							
	A		B		C*		D*	
	wt g/m²	hours	wt g/m²	hours	wt g/m²	hours	wt g/m²	hours
Aloclene 302	0.35	60	0.28	90	0.26	860	0.26	460
	0.66	90	0.54	140	0.43	1270	0.45	590
	0.80	220	1.15	180	0.78	1270	0.63	1700
	1.33	220	1.40	200	1.08	2180	0.80	1700
	1.60	220	1.70	200	1.30	2180	1.02	1700
	1.76	220	1.85	200	-	-	1.23	1700
	1.94	220	1.95	200	-	-	-	-
Alocrom 1200	0.25	96	0.29	80	0.26	72	0.13	600
	0.50	150	0.51	90	0.45	96	0.32	600
	0.62	180	0.60	180	0.68	332	0.58	600
	0.72	180	0.71	180	1.10	2180	0.84	600
	0.79	180	0.96	180	1.35	2180	1.08	600
	-	-	-	-	1.71	2180	1.16	700

* Points of breakdown did not increase with increasing exposure time



Alloy BS3L70
Degreased Only, x2000
Showing iron inclusions



Alloy BS3L70
Sodium hydroxide etched
Showing iron inclusions

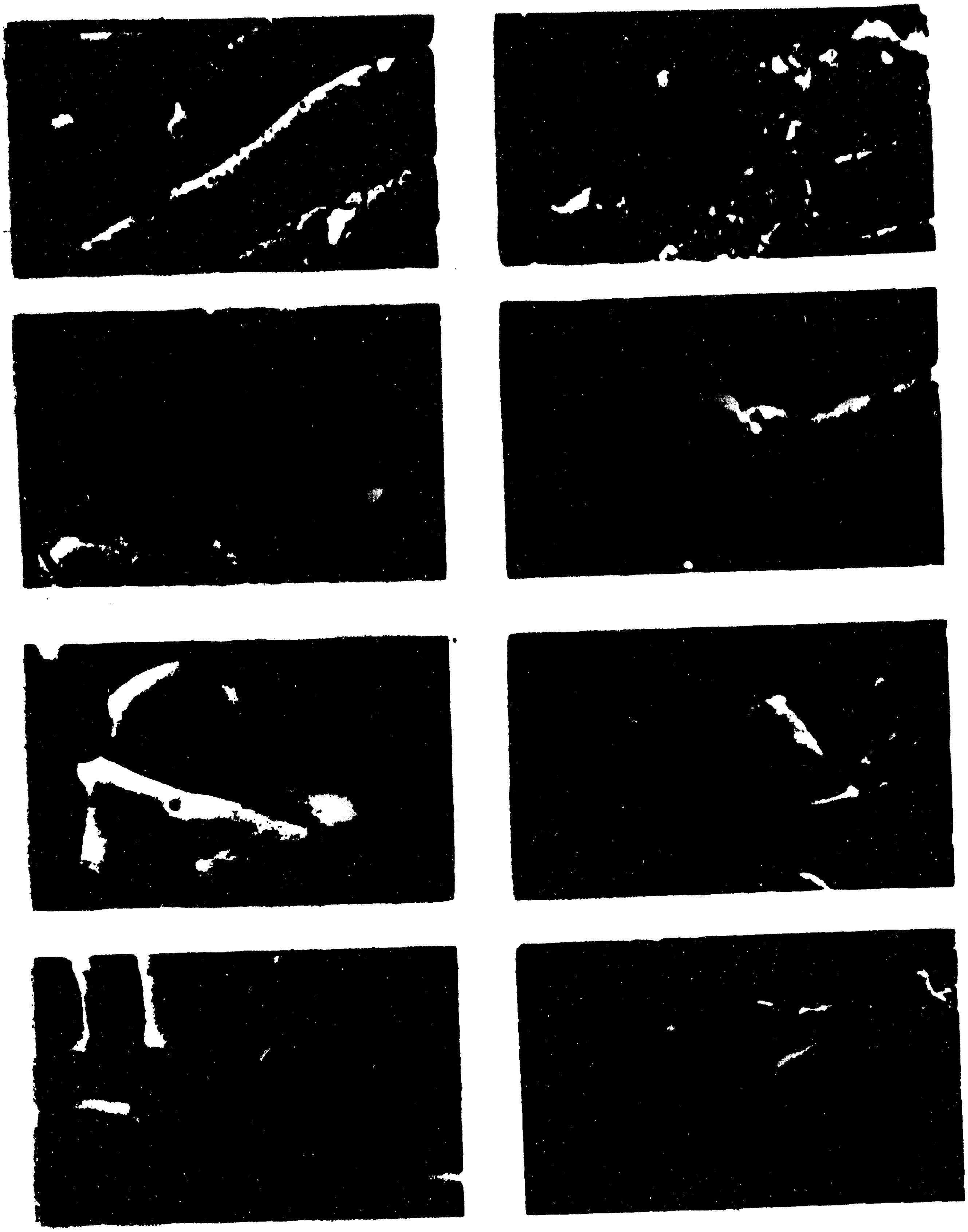
Alloy BS3L70
Degreased Only, x2000
Showing a large iron inclusion

Alloy BS3L70
Sodium hydroxide etched, x 2000
Showing iron inclusions

Plate 2

Alloy BSL104 After 400 Hours
Exposure to Salt Spray X210
Bonderite 705

Alloy BSL104 After 400 Hours
Exposure to Salt Spray X700
Showing iron inclusions at
points of failure.
Bonderite 705



Chromate Coatings on Alloy BS1470-SIC 8H X3750

Aloclene 302	Bonderite 711
Alocrom 1200	Non-Proprietary
Alocrom 407	Bonderite 705 Commercial
Bonderite 705	Bonderite 711 Commercial

Plate 1

CONDUCTIVITY

(1) Surface

or

(2) Bulk

(3) What method - contact resistance,
contact pressure

(4) What coating thickness/weight

(5) What value

(6) reproducibility

ADHESION

(1) To what

(2) What method - Pull-off
Torque Shear
Arco Knife
Cross Hatch & Tape

(3) Under what conditions

(4) What failure value

(5) reproducibility

Adhesion of Silicone Alkyd Paint to Aluminium to BS 1470-SIC-8H

(Conversion Coatings - Torque Shear)

Treatment	Controls			After Humidity Test			After Accelerated Weathering		
	MPa	psi	Failure	MPa	psi	Failure	MPa	psi	Failure
Degrease only	29.3	4250	90% AM	13.5	1960	100% AM	18.1	2620	20% AM
Unaccelerated A	32.9	4770	90% AC	21.5	3110	80% AC	29.7	4300	6% AC
Unaccelerated B	39.3	5700	50% AC	33.1	4800	50% AC	31.7	4600	10% AC
Accelerated A	41.4	6000	50% AC	25.9	3750	80% AC	31.2	4520	CP
Accelerated B	37.2	5400	90% AC	25.9	3750	80% AC	35.2	5100	2% AC

AM - adhesion to metal

AC - adhesion to chromate film

CP - cohesive failure in paint

Adhesion of Two Pack Polyurethane Paint to Aluminium to BS 1470-SIC-8H

(Conversion Coatings - Torque Shear)

Treatment	Controls			After Humidity Test			After Accelerated Weathering		
	MPa	psi	Failure	MPa	psi	Failure	MPa	psi	Failure
Degrease only	29.8	4320	40% AM	9.7	1410	90% AM	15.2	2200	10% AM
Unaccelerated A	43.0	6240	NF	28.3	4100	60% AM	36.9	5350	10% AC
Unaccelerated B	44.7	6480	NF	14.6	2120	100% AC	30.3	4400	5% AC
Accelerated A	37.8	5480	NF	44.1	6400	5% AC	40.3	5850	NF
Accelerated B	41.9	6080	NF	28.6	4150	100% AC	41.4	6000	0.50% AM*

NF - No failure

*Conversion coating failed from metal

SILANES UNDER TEST

Trade Name*	Chemical Name	[illegible]
A 151	Vinyl Trimethoxysilane	[illegible]
A 172	Vinyl tris (2-methoxyethoxysilane)	[illegible]
A 174	γ – methacryloxy propyltrimethoxysilane	MPS
A 186	β – (3, 4-epoxycyclohexyl) ethyltrimethoxysilane	[illegible]
A 187	γ – glycidoxy propyltrimethoxysilane	[illegible]
A [illegible]	γ – mercaptopropyl trimethoxysilane	[illegible]
A 1120	η – beta aminoethyl aminopropyltrimethoxysilane	[illegible]

*Union Carbide

EFFECT OF WATER IMMERSION EPOXIDE PAINT ON ALUMINIUM

(torque shear, 1500 hours, silane in paint, % on solids)

Silane/Surface Preparation	Initial MPa/Area detached	Wet MPa/Area detached	Recovered MPa/Area detached
None/degreased	27.6/100	6.7/100	16.8/100
0.1 MPS/degreased	32.1/80	32.6/0–20	44.1/20–60
0.2 MPS/degreased	45.9/0–5	33.1/0–20	43.1/0–60
0.1 AAMS/degreased	45.8/0	41.4/0	46.9/0
0.2 AAMS/degreased	47.2/0	41.4/0	42.8/20
None/gritblasted	32.7/40	24.0/20–100	29.2/20–60
0.2 MPS/gritblasted	45.1/0	38.6/0	49.7/0
0.2 AAMS/gritblasted	44.4/0	41.4/0	48.3/0

EFFECT OF WATER IMMERSION EPOXIDE PAINT ON ALUMINIUM (direct pull-off, 1500 hours, silane on surface 2% solution)

Silane/Surface Preparation	Initial MPa/Area detached	Wet MPa/Area detached	Recovered MPa/Area detached
None/degreased	21.4/90	5.7/100	11.2/100
MAMS/degreased	30.2/0	12.0/30	19.7/60
AAMS/degreased	31.2/0	11.5/30	20.5/40
None/gritblasted	28.5/30	8.5/100	13.7/80
MAMS/gritblasted	31.8/10	13.3/40	21.6/50
AAMS/gritblasted	32.5/0	13.0/40	25.0/30

EFFECT OF WATER IMMERSION POLYURETHANE PAINT ON ALUMINIUM

(torque shear, 1500 hours, silane in paint, % on solids)

Silane/Surface Preparation	Initial MPa/Area detached	Wet MPa/Area detached	Recovered MPa/Area detached
None/degreased	29.1/90	9.3/100	6.2/100
0.4 MPS/degreased	33.8/90	12.6/100	31.7/100
0.1 AAMS/degreased	36.3/100	10.1/100	14.6/100
0.2 AAMS/degreased	37.7/30	20.0/100	31.1/100
None/gritblasted	33.1/100	21.2/5−10	36.6/20−60
0.1 AAMS/gritblasted	44.3/0	39.7/0	48.3/0
0.2 AAMS/gritblasted	45.7/0	39.2/0	46.9/0

EFFECT OF WATER IMMERSION POLYURETHANE PAINT ON ALUMINIUM (direct pull-off, 1500 hours, silane on surface, 2% solution)

Silane/Surface Preparation	Initial MPa/Area detached	Wet MPa/Area detached	Recovered MPa/Area detached
None/degreased	12.6/100	3.8/100	9.9/100
MAMS/degreased	32.3/30	10.1/30	21.8/30
AAMS	26.3/40	11.1/30	22.8/30
None/gritblasted	28.6/10	8.5/100	13.6/80
MAMS/gritblasted	33.7/0	13.0/20	22.4/40
AAMS/gritblasted	34.0/0	14.9/20	22.0/30

SILANES–ZINC–TORQUE SHEAR ON THE SURFACE, 2% SOLUTION IN ALCOHOL/WATER
1500 HOURS ACCELERATED WEATHERING

Silane/Paint	Initial MPa/Area detached	Wet MPa/Area detached	Recovered MPa/Area detached
Polyurethane			
None	47.8/0–20	27.1/100	26.2/100
MPS	48.2/0	38.6/10–60	44.3/0
AAMS	43.7/0–80	37.2/0–100	46.5/0
Epoxide			
None	37.6/40–100	20.0/100	21.5/100
MPS	49.6/0	37.9/80	44.5/0
AAMS	41.7/0–50	44.8/0–30	47.2/0

TABLE 3

ELECTRICAL RESISTANCE OF EPOXIDE RESIN PAINTS - SILVER FLAKE FS6

Ref	Percentage Silver by Weight in Cured Film	Resistance Ω/cm
CP/1	44	1.5×10^8
CP/2	48	800.0
CP/3	51	950.0
CP/4	54	750.0
CP/5	57	550.0
CP/9	61	5.930
CP/10	65	6.200
CP/11	68	3.600
CP/14	72	0.210
CP/15	78	0.251
CP/16	80	0.035
CP/17	82	0.032
CP/18	85	0.038

TABLE 4

EFFECT OF LOADING AND SILVER CONTENT ON RESISTANCE OF EPOXIDE RESIN PAINTS - BALLOTINI

Ref	Percentage Ballotini by Weight on Cured Film	Resistance Ω/cm
8% Silver		
CP/40	77	0.34
CP/41	80	0.26
CP/42	82	0.18
CP/43	84	0.14
CP/44	86	0.11
12% Silver		
CP/45	77	0.18
CP/46	80	0.12
CP/47	82	0.14
CP/48	84	0.18
CP/49	86	0.22

TABLE 5

EFFECT OF LOADING ON THE RESISTANCE OF THE POLYURETHANE RESIN - SILVER FLAKE

Ref	Percentage Silver by Weight on Cured Film	Resistance Ω/cm
CP/19	76	0.48
CP/20	78	0.25
CP/21	80	0.24
CP/22	82	0.22
CP/23	84	0.36

TABLE 6

EFFECT OF LOADING AND SILVER CONTENT ON THE RESISTANCE OF THE POLYURETHANE RESIN - BALLOTINI

Ref	Percentage by Weight Ballotini on Cured Film	Resistance Ω/cm
8% Silver		
CP/34	61	15,000
CP/35	68	24.33
CP/36	72	4.46
CP/24	76	0.38
CP/25	78	0.30
CP/26	80	0.21
CP/27	82	0.19
CP/28	84	0.16
12% Silver		
CP/37	61	218
CP/38	68	30.75
CP/39	72	0.90
CP/29	76	0.17
CP/30	78	0.19
CP/31	80	0.25
CP/32	82	0.16
CP/33	84	0.12

TABLE 7

PHYSICAL PROPERTIES OF TYPICAL ELECTRICALLY CONDUCTING PAINTS

	CP/16 Epoxide/80% Silver	CP/41 Epoxide/80% Ballotini	CP/21 Polyurethane/80% Silver	CP/26 Polyurethane/80% Ballotini
Scratch Resistance	Passed 1000 gm	Passed 1100 gm	Passed 1200 gm	Passed 1200 gm
Bend Resistance	Passed $\frac{1}{8}$ in.	Passed $\frac{1}{4}$ in.	Passed $\frac{1}{8}$ in.	Passed $\frac{1}{4}$ in.
Adhesion to Epoxide	1500 psi	2000 psi	3500 psi	3600 psi
Impact Test	0.4 in.	0.2 in.	0.4 in.	0.2 in.
Touch Dry Time	3 hours	3 hours	4 hours	4 hours
Hard Dry Time	6 hours	6 hours	8 hours	8 hours
Solvent Resistance	Excellent	Excellent	Excellent	Excellent

TABLE 8

T OF AGEING ON THE SURFACE RESISTANCE OF CONDUCTING PAINTS - HR1627 TYPE 1 (EPOXIDE/SILVE

(CHANGE IN RESISTANCE)

Exposure Time	50°C Ohms/Square	100°C Ohms/Square	150°C Ohms/Square	200°C Ohms/Square	Weatherometer Ohms/Square
0	0.241-0.272	0.188-0.248	0.361-0.502	0.460-0.622	0.578-0.705
10	-0.047	-0.220	-0.330	-0.418	-0.182
100	-0.094	-0.184	-0.427	-0.598	-0.436
500	-0.069	-0.222	-0.335	-0.451	-0.406
750	-0.142	-0.170	-0.435	-0.601	-0.466
1000	-0.136	-0.199	-0.470	-0.612	-0.440

TABLE 10

CT OF AGEING ON THE SURFACE RESISTANCE OF CONDUCTING PAINTS - BR1627 TYPE 2 (URETHANE/BALLOTIN

(CHANGE IN RESISTANCE)

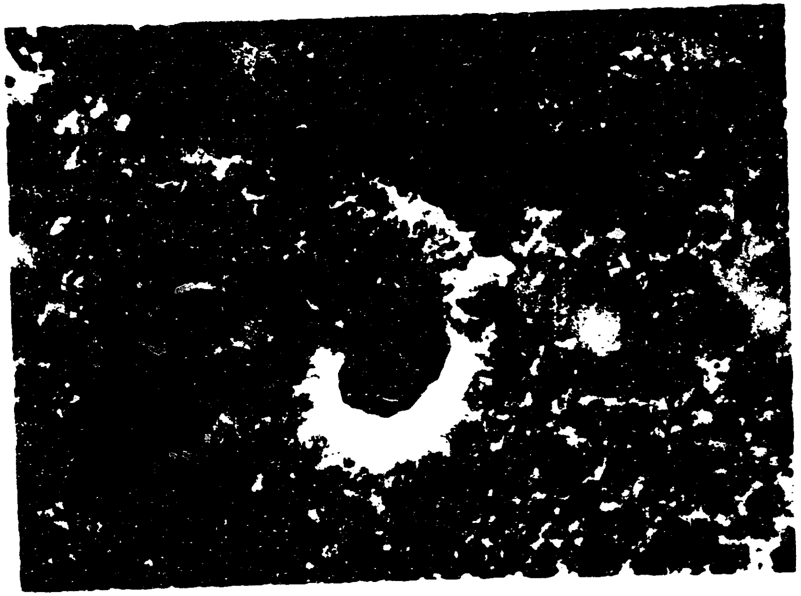
Exposure Time	50°C Ohms/Square	100°C Ohms/Square	150°C Ohms/Square	200°C Ohms/Square	Weatherometer Ohms/Square
0	0.372-0.452	0.449-0.478	0.345-0.431	0.378-0.464	0.367-0.463
10	-0.016	0	+0.051	+3200*	+10.600
100	-0.032	-0.100	+1.782	+0.163	+33.800
500	-0.032	-0.081	+4.752	Failed	+ 0.594
750	-0.060	-0.104	+7.845	Failed	+3.665
1000	-0.082	-0.129	+5.123	Failed	+1.420

* Micro-cracks in the film

Alloy BS1470
Degreased Only, x2100
Showing iron inclusions

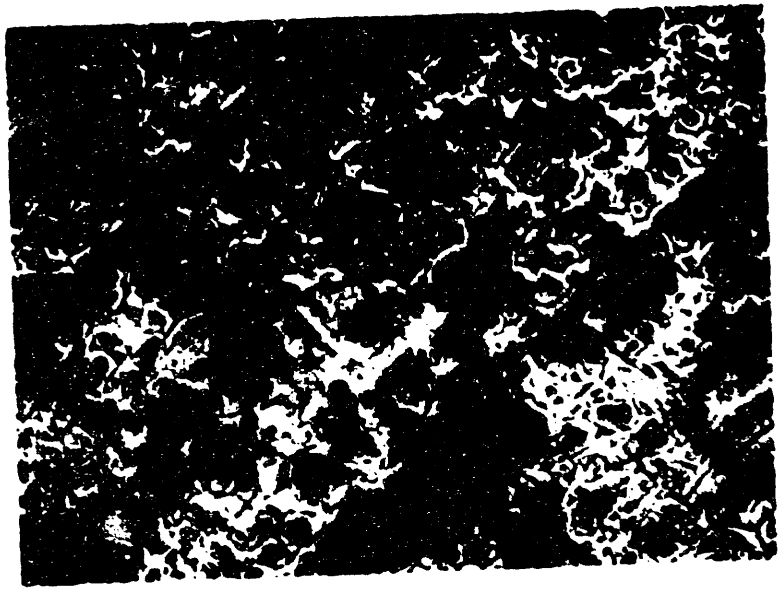
Alloy BS1470
Sodium hydroxide etched x7000
Showing iron inclusions

Plate 4



Alloy BSL104
Degreased Only, x2100
Showing an iron inclusion

Alloy BSL104
Sodium hydroxide etched x2100
Showing iron inclusions



Alloy BS1470 After 400 Hours
Exposure to Salt Spray X210
Bonderite 705

Alloy BS1470 After 400 Hours
Exposure to Salt Spray X500
Showing typical points of
failure. Bonderite 705

Session III:
Preparation for Coating

Florian Mansfeld and Gail Murphree
Moderators

Surface Pretreatment of Aluminum Alloys

C. A. Drewien

Materials and Process Sciences Center
Sandia National Laboratories

This work was performed at Sandia National Laboratories, which is operated for the U. S. Department of Energy under contract number DE-AC04-76DP00789.

Objective of Surface Preparation

- provide uniform activity on the alloy surface
  - remove oil, grease, buffing compound, or other foreign matter
  - remove inhomogeneous native oxide and grow homogeneous oxide
    - » remove thick heat-treated films from unpolished, heat-treated castings
  - remove undesirable microconstituents that interfere with uniformity of surface

Factors Influenced by Surface Pretreatment

- **Adhesion**
  - environment-induced failures occur at or near the adhesive/adherend interface
  - bond durability depends upon surface preparation
- **Corrosion Resistance**
  - pitting corrosionsensitive to surface treatment
  - inhibition influenced by elements on coating surface
- **Coating Growth and Formation**
  - elements enriched on surface or in surface layers become incorporated in coating influencing growth

Surface Preparation Sequence

- de-grease to remove organic debris
  - vapor degrease
  - solvent washing
  - solvent emulsion cleaning
- clean to remove inorganic debris
  - formulated detergents
  - mild etching solutions
  - non-etching solutions
    - » using silicate inhibitors
- de-oxidize to remove original oxide and microconstituents causing inhomogeneities
  - basic solutions requiring subsequent desmutting
  - acid solutions
  - machine or buff followed by cleaning

Tradition/Environmentally Conscious

	Traditional Practice	Environmental Concern	Environmentally Conscious
De-grease	trichloroethylene vapor degrease freon cleaners carbon tetrachloride rinse acetone rinse or wipe	carcinogenic nature ozone depletion residue	d-limonene
Clean	buffered carbonate-phosphate carbonate-silicate mixture	none	same
De-oxidize	chromic-sulfuric acid sodium hydroxide sulfuric acid-hydrogen peroxide nitric acid-ammonium bifluoride	toxicity/carcinogenic nature of Cr N, P, F (in Japan)	sulfuric acid with metal sulfates and/or clathrates

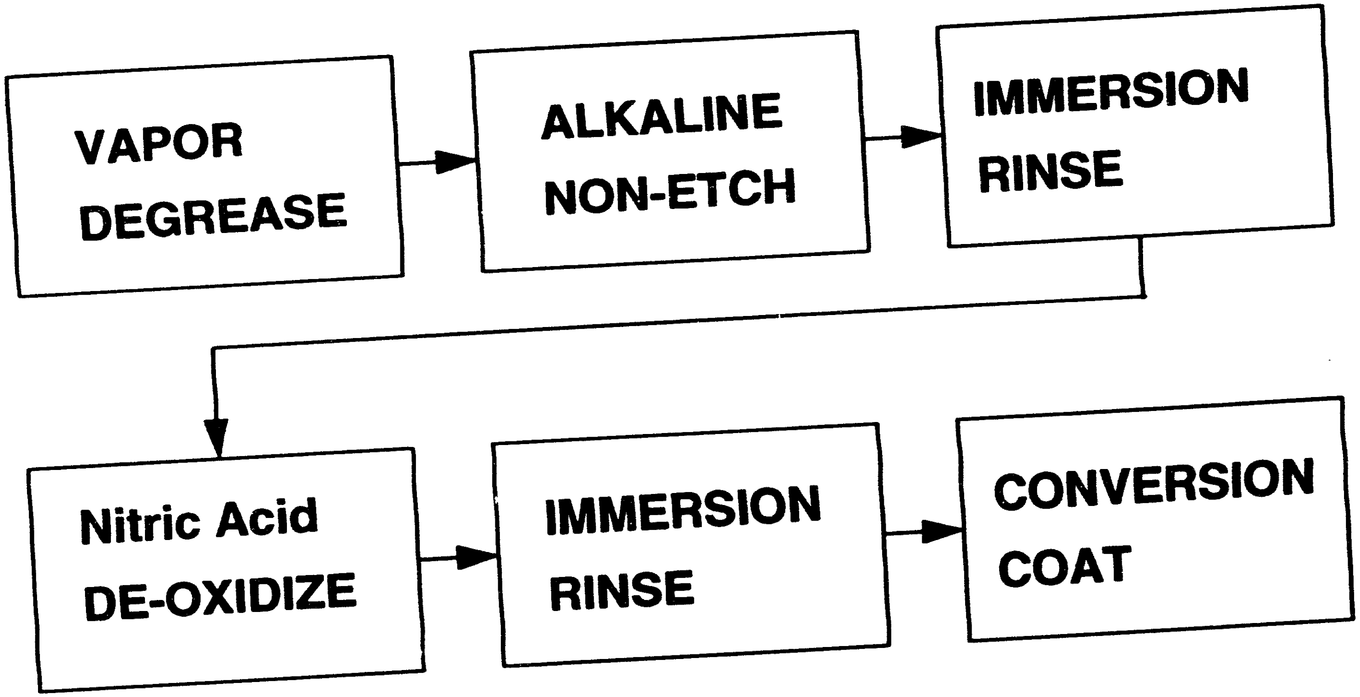
Surface Enrichment

- **Silicon**
  - dissolution of aluminum in NaOH slower than Al leads to Si particles on surface (Tallant, 1980)
- **Zinc**
  - no enrichment in oxide of 7075 during de-oxidizing (Solomon and Hanlin, 1980)
- **Chromium**
  - found (using SIMS) incorporated into anodized film in trace levels (McDevitt et al, 1976)

Surface Enrichment

- **Magnesium**
  - selective thermal oxidation at temperatures > 450 °C (Sun et al, 1979)
  - poor adhesion properties (Gaillard et al, 1984)
- **Copper**
  - enrichment in acid de-oxidizing baths by metallic deposition of Cu in solution (Pocius, 1983)
  - enrichment at metal/interface surface due to preferential oxidation of Al in de-oxidizing or anodizing bath (Sun et al, 1978)
  - poor adhesion properties
  - poor coating formation

Surface Pretreatment



VAPOR DEGREASE

ALKALINE NON-ETCH

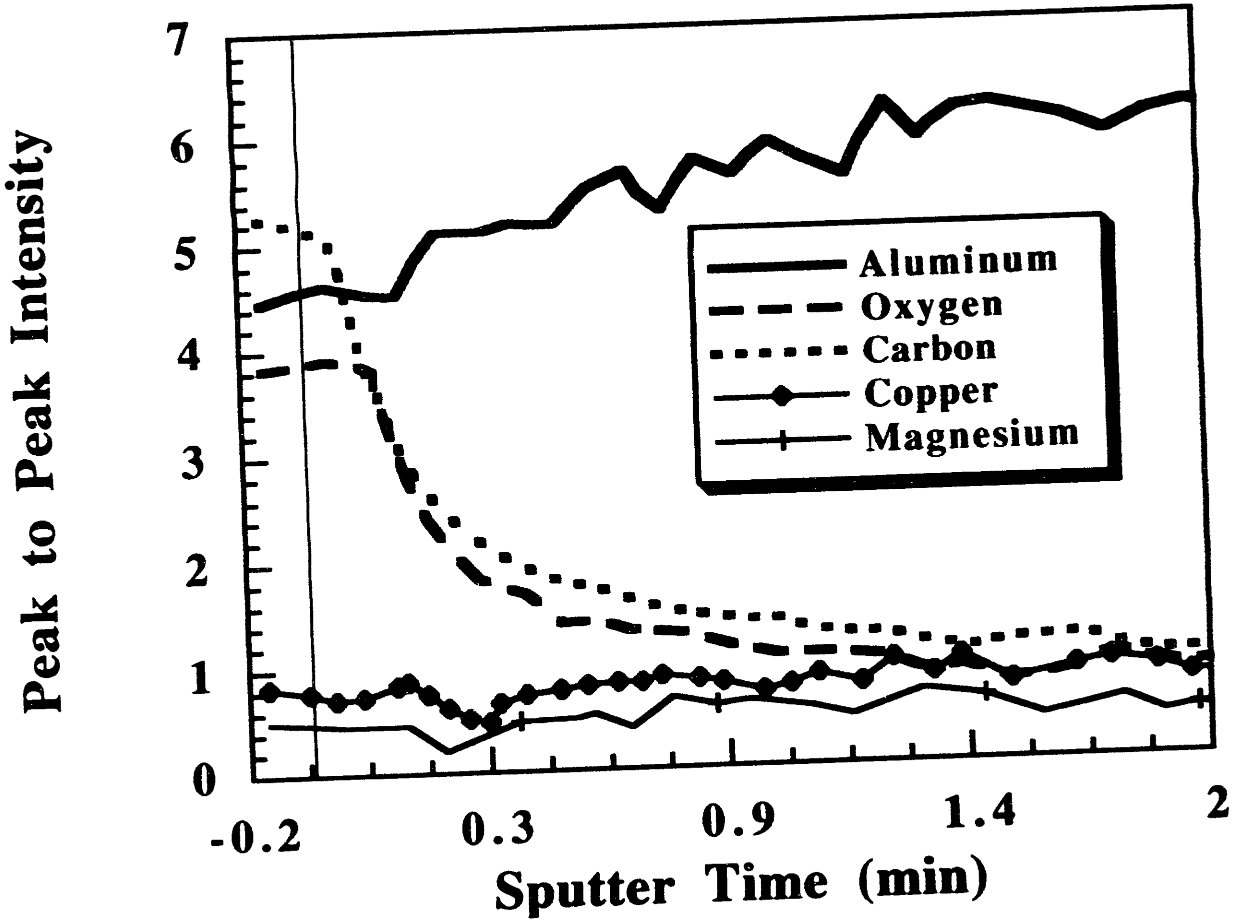
IMMERSION RINSE

Nitric Acid DE-OXIDIZE

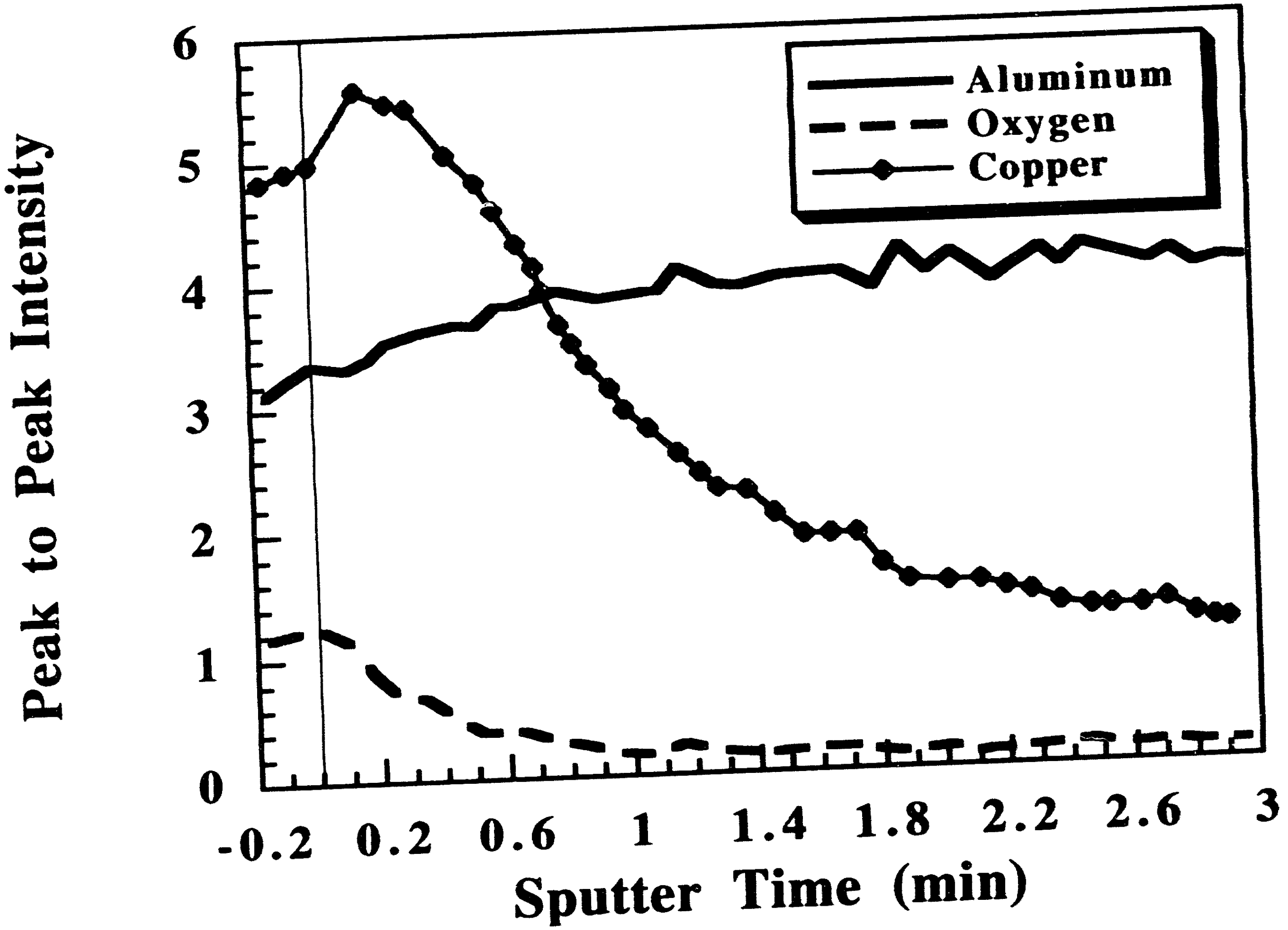
IMMERSION RINSE

CONVERSION COAT

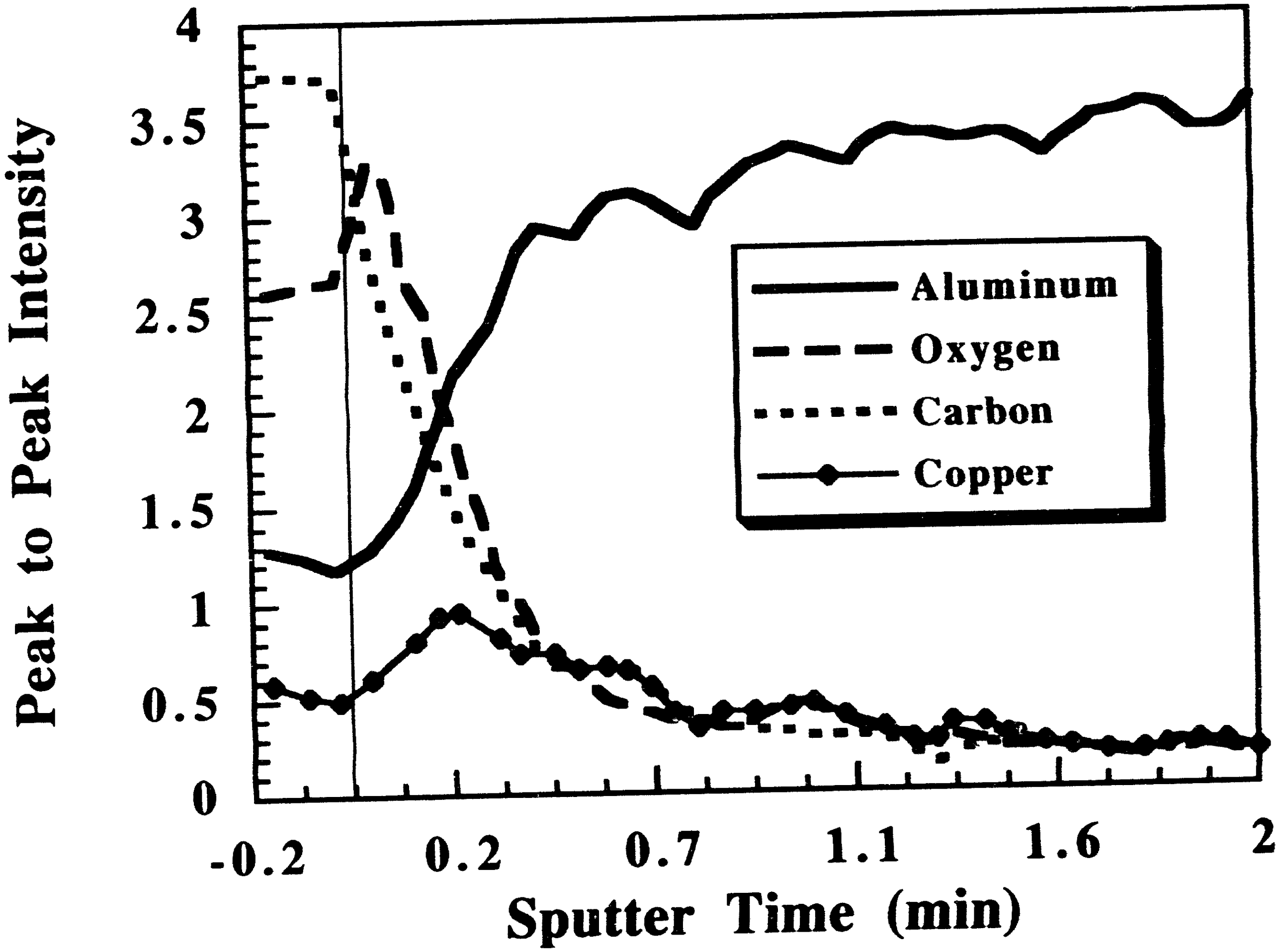
Al 2024 degreased

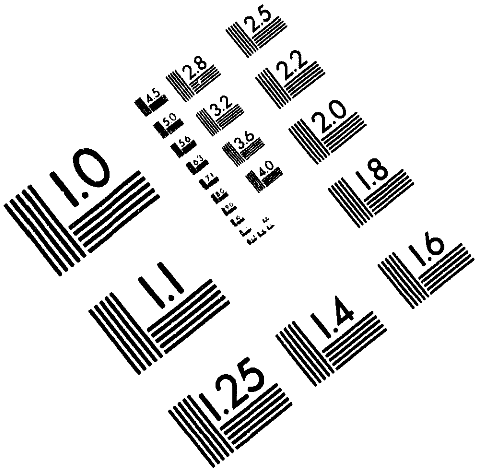


Al 2024 de-oxidized



Al 1100 de-oxidized in nitric acid containing Cu





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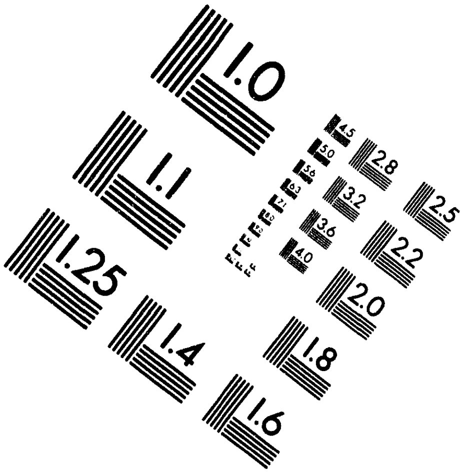

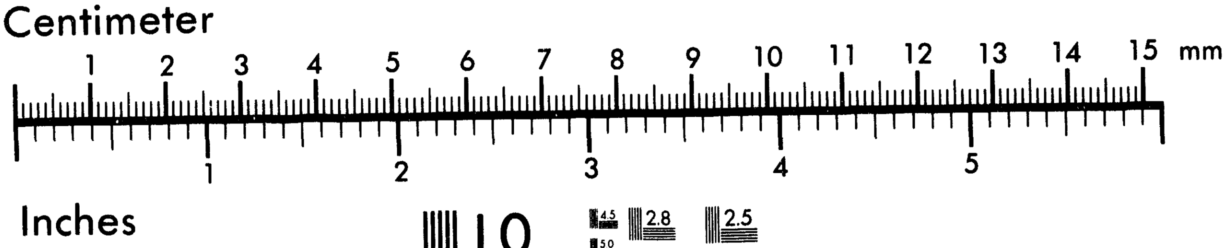

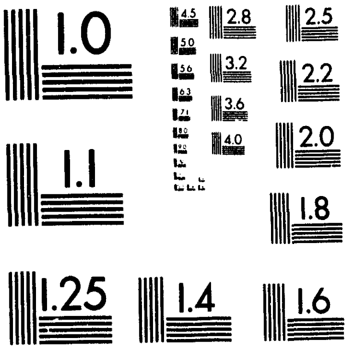

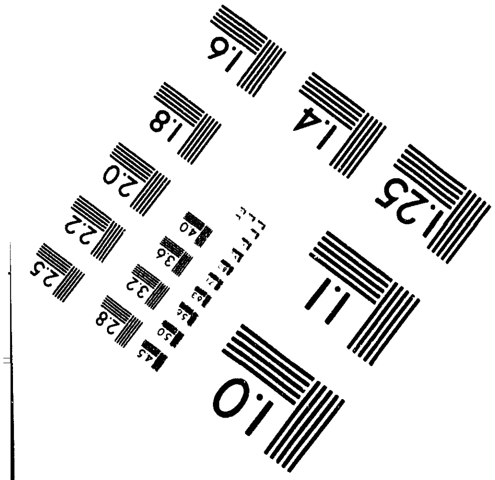

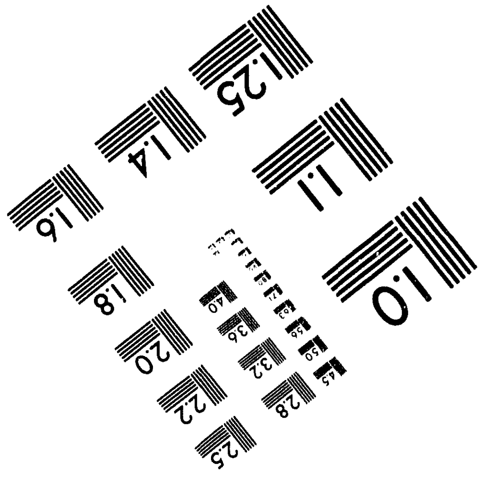

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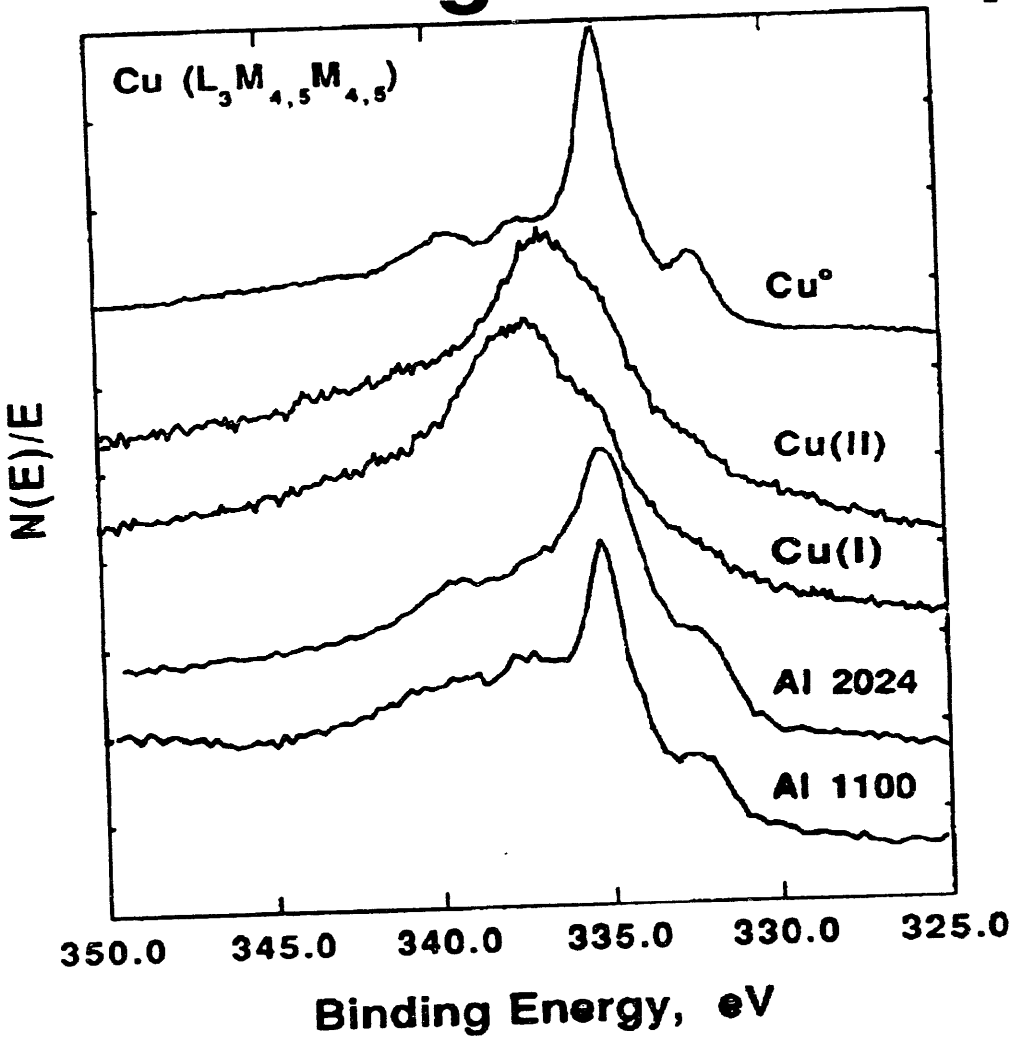
3 of 3

Auger Lineshape Profile

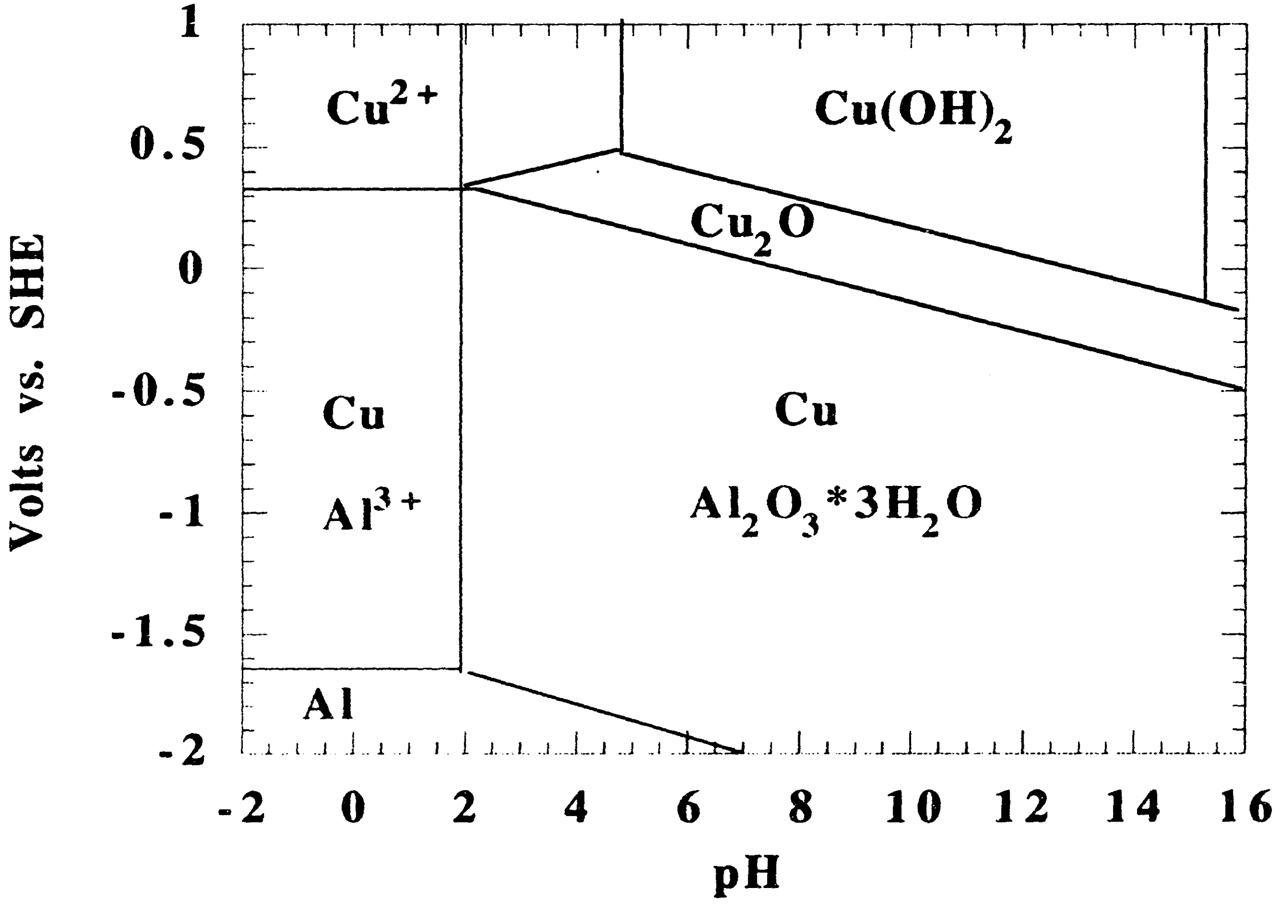


Auger Parameter
Cu($2p_{3/2}$) vs. Cu($L_3M_{4,5}M_{4,5}$)

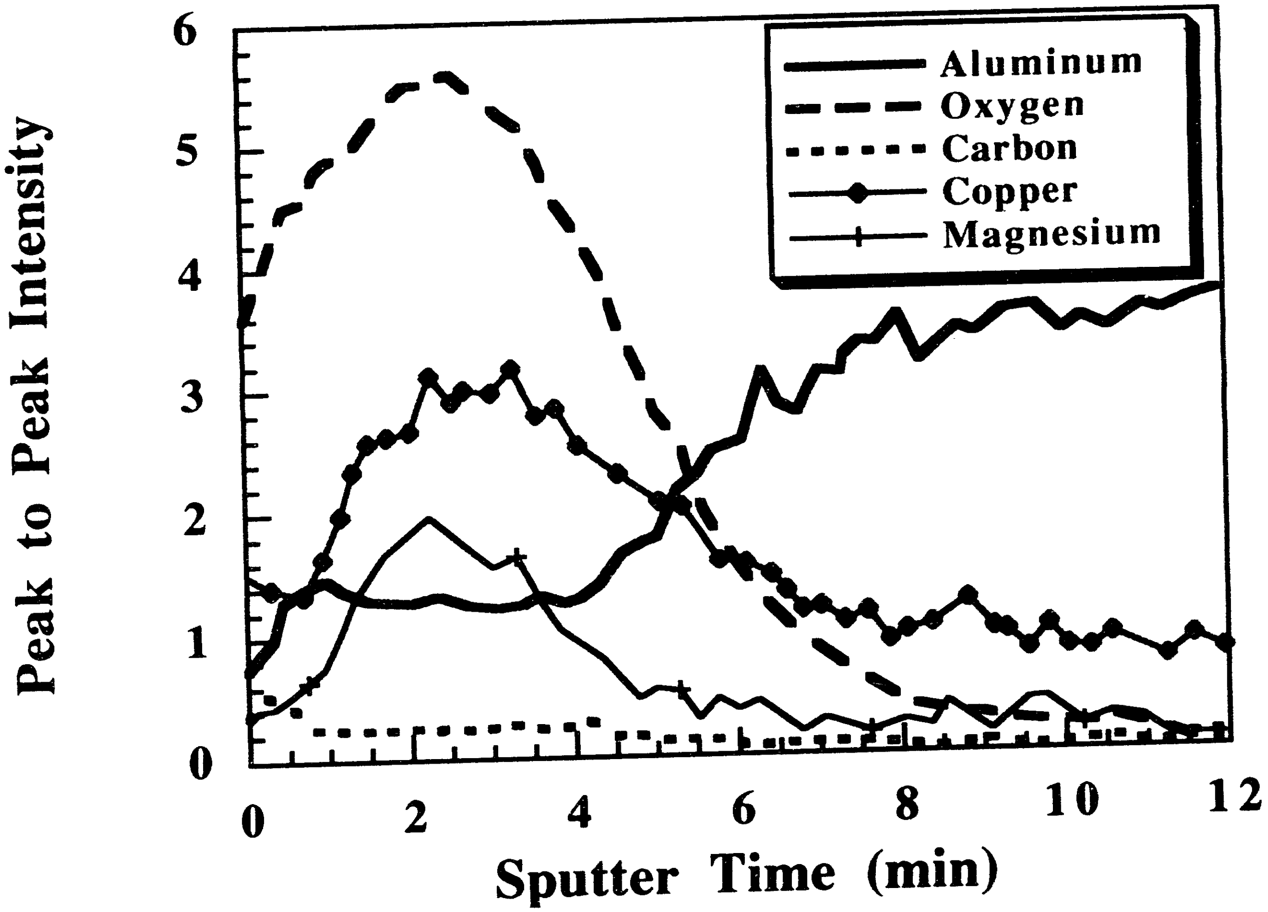
	α + hν (eV)
Cu°	1851.4
Cu(II)	1850.9
Cu(I)	1849.1
Al 2024	1851.2
Al 1100	1852.2

Pourbaix Diagram

–Potential vs. pH equilibria



Al 2024 coated with Hydrotalcite



Summary

- Surface enrichment of copper occurs on Al during de-oxidizing treatment
- Cu enrichment on Al 2024-T3 is on order of 3-4x Cu level in bulk material
- Cu exists in the zero valence state
- Enrichment occurs by copper deposition

Session IV:
Emerging Coatings Technology

Rudy Buchheit and Paul Chalmers
Moderators

Session Four: Emerging Coatings Technology

Moderators: Rudy Buchheit, Sandia National Laboratories
Paul Chalmer, National Center for Manufacturing Sciences

1:00 Ground Rules and Goals

1:05 **Sol-Gel Synthesized Polymetallosiloxane Coatings**
T. Sugama, Brookhaven National Laboratory.

1:30 **The Use of Intense, Pulsed Ion Beams for Material Surface Treatment**
R. Stinnett, D. McIntyre, R. Buchheit, B. Turman, E. Neau, Sandia National Laboratories,
J. Greely, M. Thompson, Cornell University, D. Rej, Los Alamos National Laboratory.

1:55 **Chromate-Free Talc Conversion Coatings for Aluminum**
R. Buchheit, C. Drewien, J. Finch, Sandia National Laboratories,
G. Stoner, University of Virginia.

2:15 Break

2:30 **Surface Modification of Stainless Steels by Electrochemical Methods**
F. Mansfeld, University of Southern California.

2:55 **Overview of the NCMS Chromate Alternatives Project**
P. Chalmer, National Center for Manufacturing Sciences.

3:20 Moderated Discussion.

4:00 Adjourn

In this session, we will examine some of the major classes of emergent chromate replacement technologies through representative presentations for:

- Sol-gel Methods
- Dry Methods (Pulsed Ion Beam Surface Treatment)
- Chemical Methods
- Electrochemical Methods

The objectives of this session are to:

- disseminate information to potential users of these technologies
- provide guidance to aid in structuring the development process so that useful processes are generated

Sol-Gel Derived Polymetallosiloxane Coatings For Corrosion Protection of Aluminum Substrates

Toshifumi Sugama
Energy Efficiency and Conservation Division
Department of Applied Science
Brookhaven National Laboratory
Upton, New York 11973

Summary

Various polymetallosiloxane (PMS) polymers, such as polytitanosiloxane (PTS), polyzirconosiloxane (PZS), polyborosiloxane (PBS), polyaluminosiloxane (PAS), polylanthanosiloxane (PLS), and polytinsiloxane (PTIS) were synthesized through the hydrolysis-polycondensation-pyrolysis route of two-step, acid-base catalyzed sol precursors consisting of N-[3-(triethoxysilyl)propyl-4,5-dihydroimidazole (TSPI) as monomeric organofunctional silane, metal alkoxides, $M(OR)_n$ [M: Ti, Zr, B, Al, La, and Sn, R: CH_3, C_2H_5, and C_3H_7, n: 2, 3, or 4], methanol, and water, at pHs from 7.1 to 7.9. The synthesized PMS polymers were then evaluated as corrosion-protective coatings of aluminum (Al) substrates. The PMS-coated Al specimens were prepared by dipping the alkali-etched Al into the sol precursor solutions, then pre-heated at 100°C to form xerogel films. Subsequently, xerogel-coating films were pyrolyzed in air at 300°C for 30 min.

A microstructural geometry of 300°C-treated PMS coating surfaces, in which fractal clusters were linked together, was characteristic of PTS, PZS, PAS, and PTIS coatings, while no fractal features were seen on the PBS and PLS coatings. The surface microstructure for the latter films showed a wrinkled and grained texture caused by thermal shrinkage of film and the formation of oxidized particles in the film layers, respectively.

The following four factors played an essential role in improving the protective ability of PMS coatings on Al substrates; 1) the increase in densification of M-O-Si linkages in the PMS network structure with an increased treatment temperature from 100° to 300°C, 2) the minimum susceptibility of film surfaces to water-wetting behavior, 3) the interlocking morphology between cluster units consisting of symmetrical fractal branches, and 4) the dense microstructure of clusters of ~ 2 μm entirely covering the metal substrate. The major contribution of factors (3) and (4) was to minimize the stress generated by the shrinkage of films, so that there was no crazing nor peeling. Polytitanosiloxane (PTS) was identified as the most effective cluster-coating film which exhibited all of these important factors.

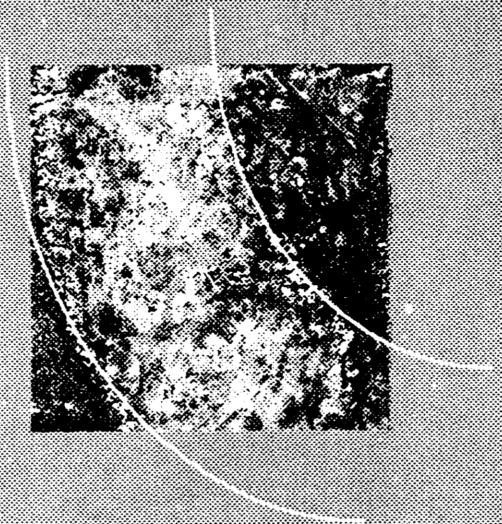
Corrosion Resistance: Results and Plans

Contributors:

R.G. Buchheit, L.M. Maestas
G.A. Poulter, N.R. Sorensen

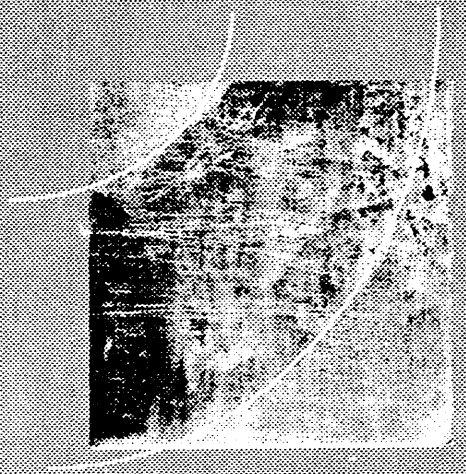
Mechanical and Corrosion Metallurgy Department
Sandia National Laboratories

Salt spray exposure testing of beam treated Al sheet stock.



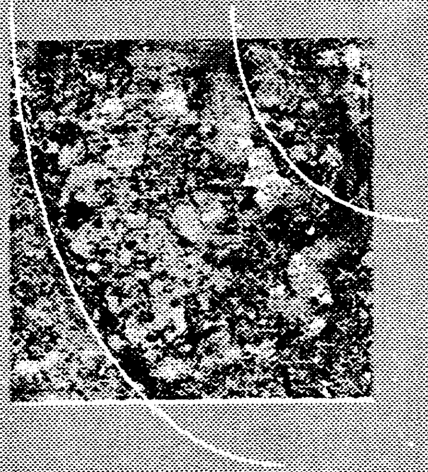
2024-T3

Al_2Cu	940 C
Al_6Mn	450 C
Al_3Fe	1147 C
Al_2CuMg	550 C
Al_7Cu_2Fe	545 C



6061-T6

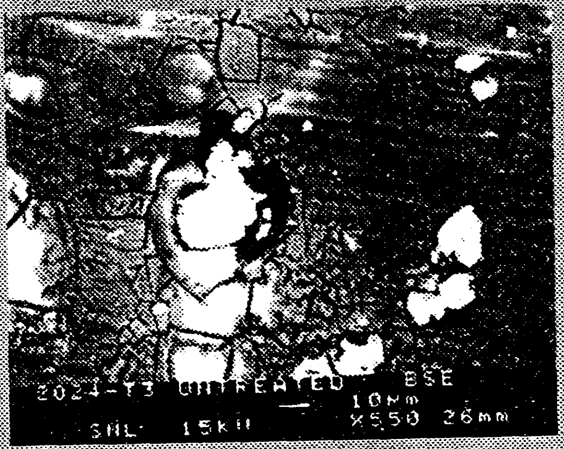
Mg_2Si	**2790 C**
$Al_9Si_2Fe_2$	< 750 C



7075-T6

$MgZn_2$	590 C

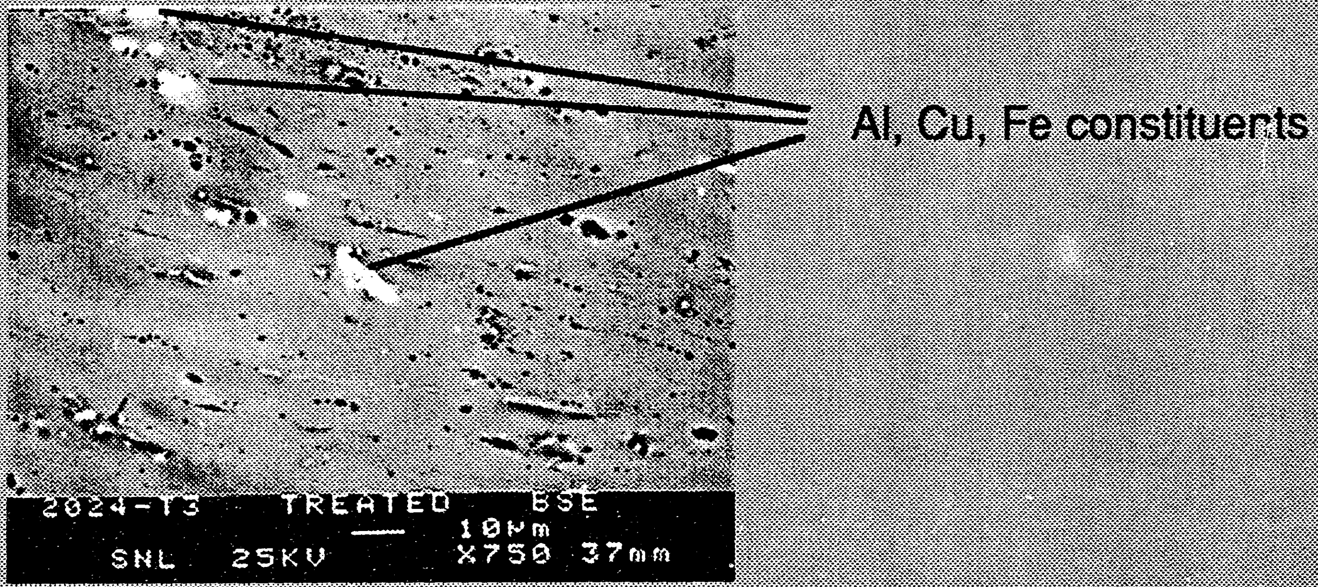
Pitting can be surpressed by ion beam treatment.



Pitting due to an Al,Fe,Cu constituent on untreated 2024-T3 exposed to salt spray

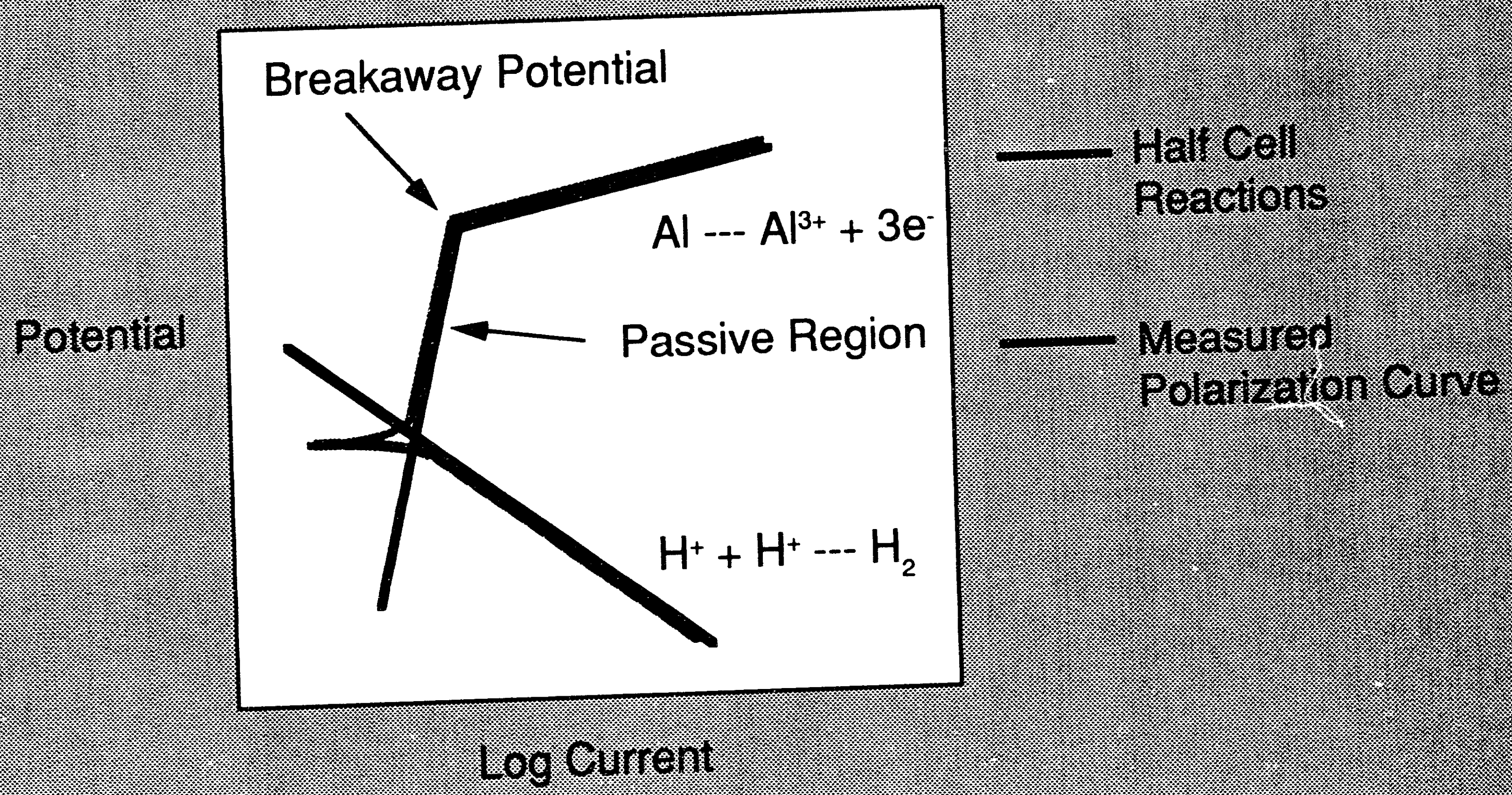
No pitting is observed after salt spray on treated surfaces where constituents are fully dissolved

Un-optimized treatment schedules leave pit initiating constituents at the treated surface.



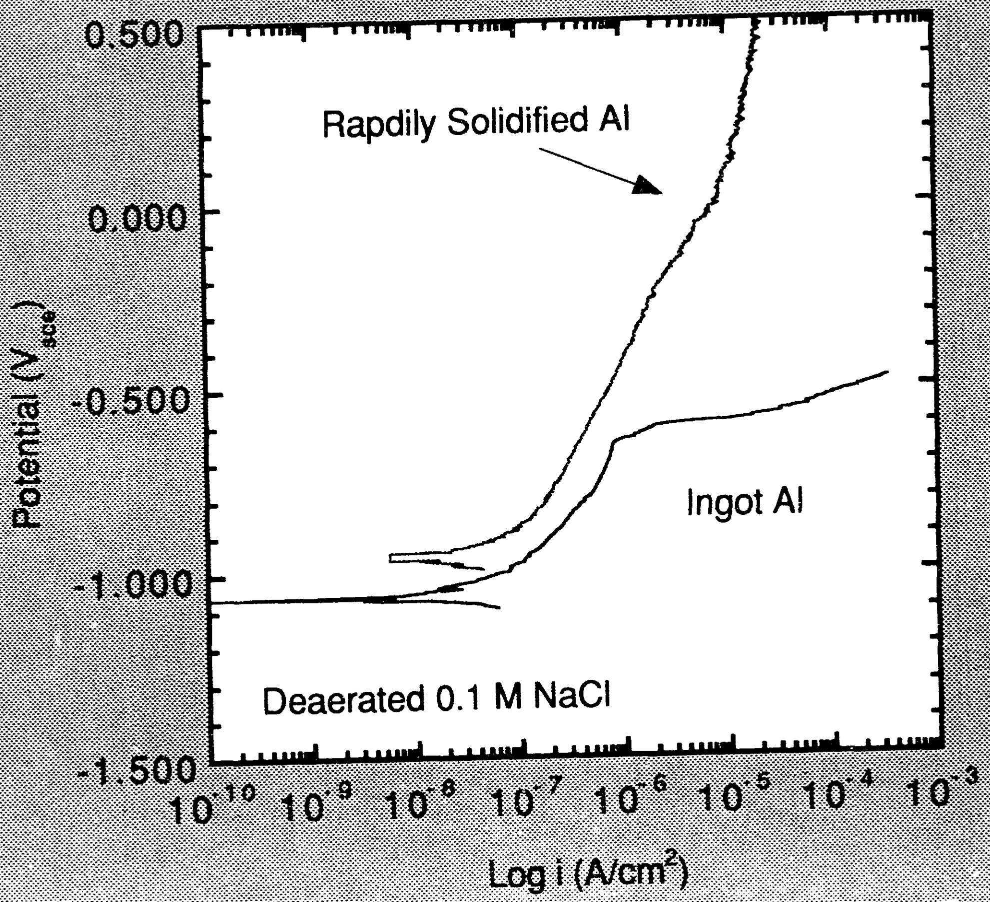
Beam Treated 2024-T3

Interpretation of Polarization Curves.



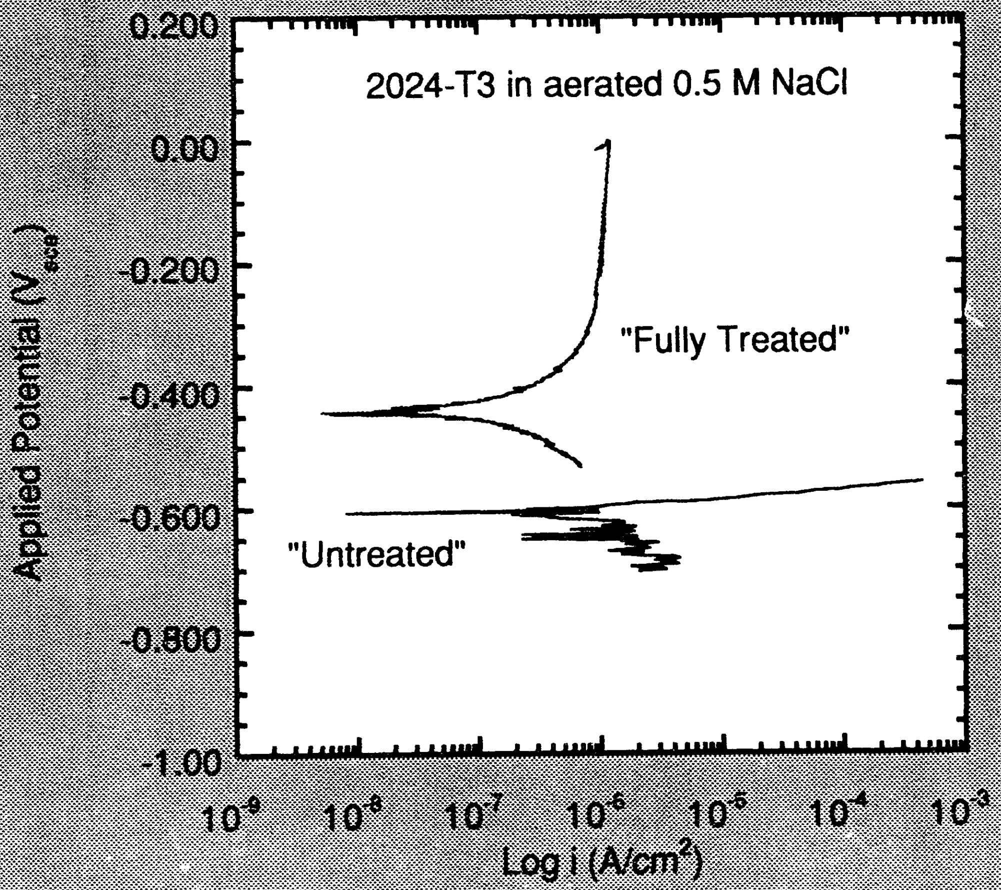
What can we expect to gain by ion beam treatment?

Anodic Polarization of Rapidly Solidified and Ingot Aluminum



The absence of film breakdown indicates improved resistance to localized corrosion.

Corrosion Resistance of 2024-T3 can be significantly enhanced by beam treatement.



Proposed Tasks.

1.) Optimization of treatment parameters for Al alloys.

   - identify necessary treatment depth
   - identify energy input required to fully dissolve particles

2.) Surface Alloying to produce non-equilibrium Al-transition metal alloys with high corrosion resistance (e.g. Al-Ta, Al-Cr, Al-W, Al-Mo, Al-Zr).

   - sputter deposit transition metal, then ion beam treat

3.) Explore effects of ion beam treatment on aqueous and atmospheric corrosion response of Fe-base, Ti-base, and Cu alloys for

4.) Surface hardening.

5.) Fatigue crack initiation resistance.

Non-Chromate Talc Conversion Coatings for Aluminum

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Abstract

We have developed a method for forming an inorganic conversion coating on aluminum that is procedurally similar to chromate conversion coating methods. This new method, however, does not use or produce hazardous or toxic chemicals. The coating forms by a precipitation mechanism involving Al^{3+}, Li^{+}, OH^{-}, CO_3^{2-}, and possibly other anions present in the bath as impurities. This polycrystalline coating is continuous, conformal and persistent in aggressive environments. Coating thicknesses range from several tenths to ten micrometers depending on the substrate alloy composition and the coating process conditions. The outer portions of the coating are porous, but pores do not penetrate to the coating-substrate interface. These coatings, as currently fabricated, do not match the levels of performance offered by commercially available chromate conversion coatings, but are capable of meeting many of the corrosion resistance, conductivity, and paint adhesion requirements established in MIL-C-5541E "Chemical Conversion Coatings on Aluminum and Aluminum Alloys".

In this presentation, methods for producing the talc coating on 6061-T6 will be described and compared to traditional chromate conversion coating methods. The resulting coating structure and composition will be briefly described. Additionally, performance data for the talc coatings in MIL-C-5541E required tests will be presented along with comparative data for a commercial chromate conversion coating.

This work has been sponsored by the U.S. Department of Energy under contract no. DE-AC04-76DP00789.

Talc Coating as a Metal Finishing Process

- Non-electrolytic Method
- Desirable Properties Exhibited
- Low Toxic Hazard

Contributors:

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Primary Goal:

A method for fabricating inorganic coatings with attractive properties that does not use or produce hazardous substances.

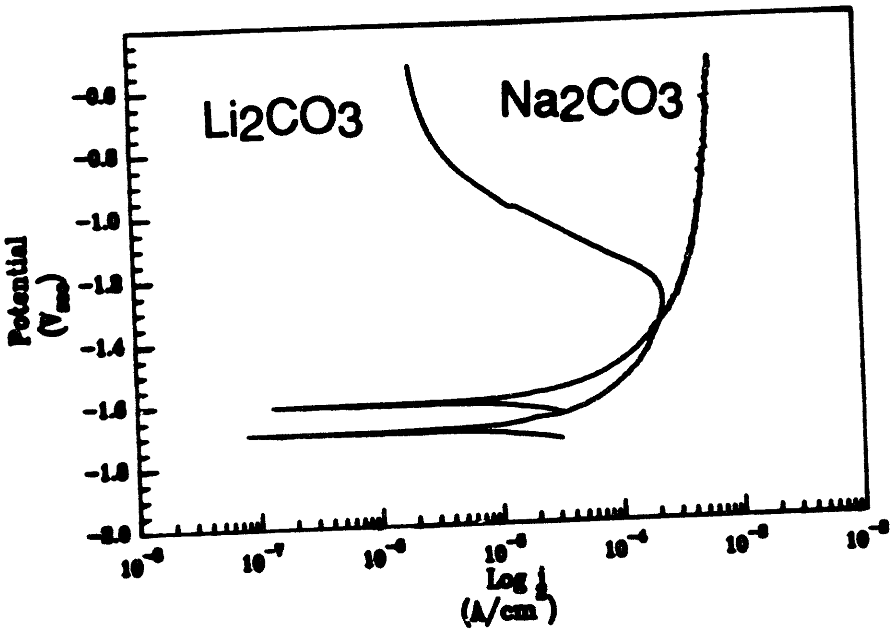
Project Guidelines:

* coating procedure is similar to existing methods;
processing time and cost are reasonable

* desirable properties are offered:
corrosion resistant - conductive - adherent

* compatible in relevant systems environments

Passivation in 0.1M Li2CO3 plus 0.6M NaCl at pH 10: Anodic Polarization



1100 Al

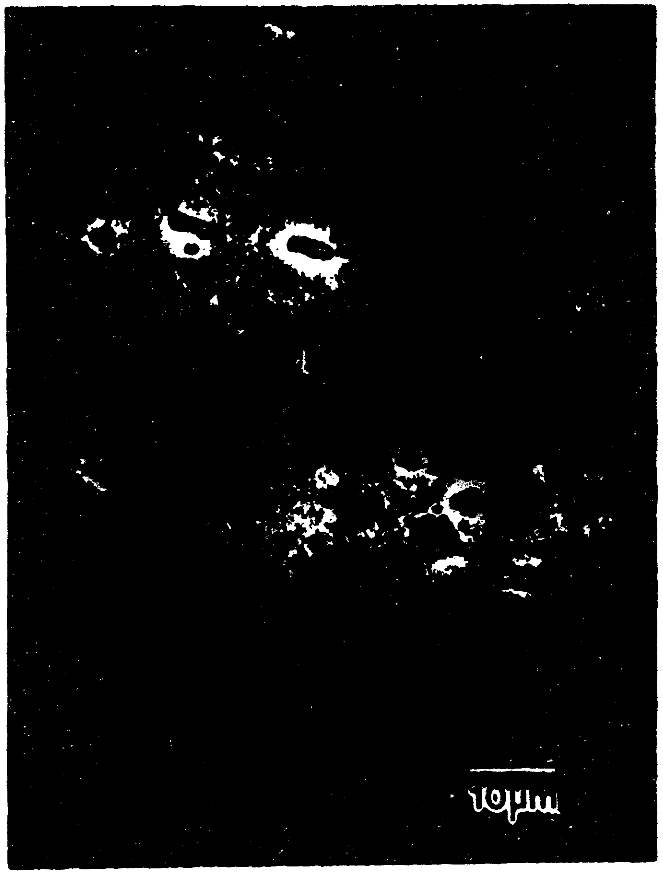
Talc Conversion

Degrease
Alkaline non-etch cleanse
Acid Deoxidize

Coat:
< 15 minutes
Li_2CO_3 plus LiOH
$11.5 < pH < 13.5$
$20^\circ C < T < 70^\circ C$

Post Coat Age:
3 to 24 hours

Talc Coating Morphology
on 1100 Al (Al-1.0(Fe,Si,Cu))



Talc Films

- 0.1 to 10 µm in thickness
- bilayered: poorly crystalline, Li-poor inner layer
  crystalline Li-rich outer layer
- conformal and continuous
- exhibits barrier properties
- persistent in aggressive environments

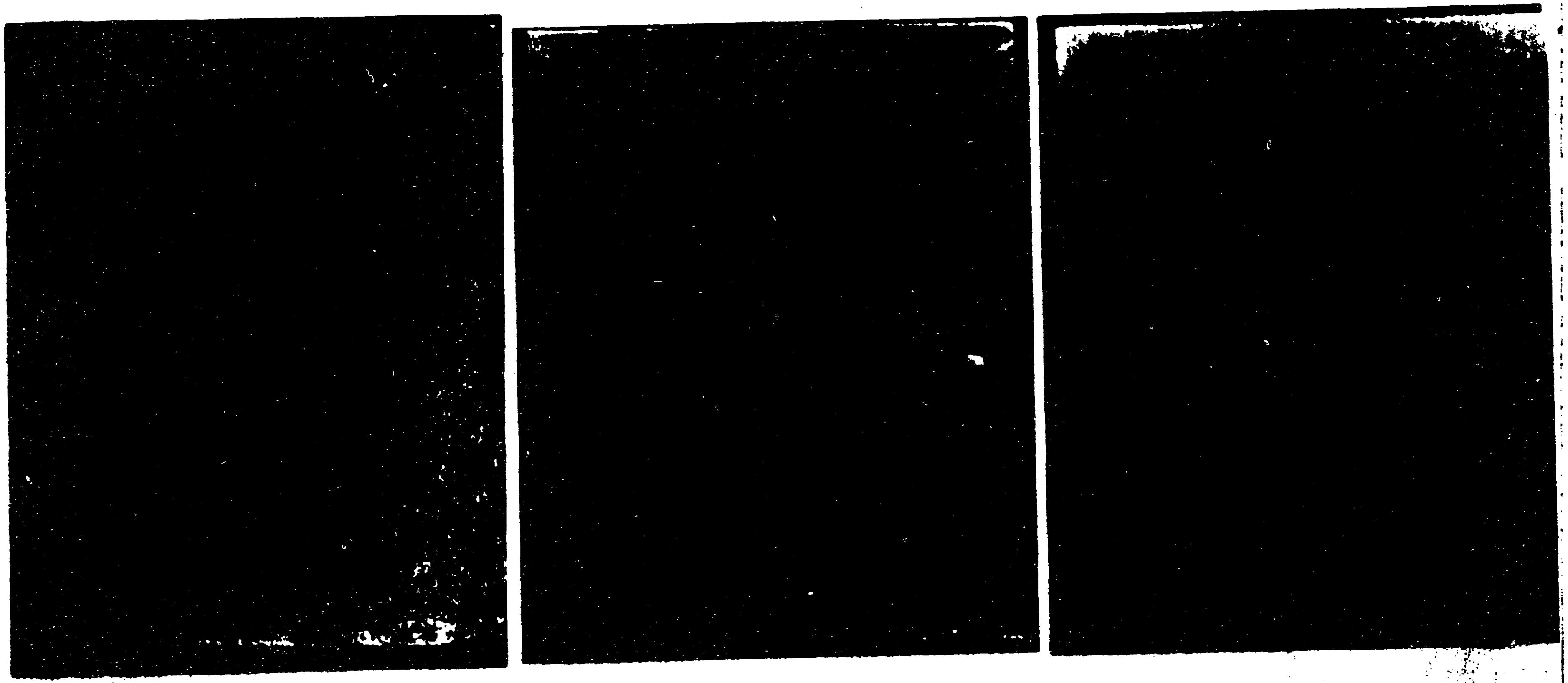
Performance Assessed per: MIL-C-5541E "Chemical Conversion Coatings for Al and Al-Alloys"

Corrosion: Salt Spray (Fog) Exposure

Resistivity: Contact Resistance under an impinging load

Paint Adhesion: Adhesion of paint after aqueous exposure and scribing

Talc Coated 6061-T6



As-Coated

After 168 h Salt Spray

Uncoated
After 168h
Salt Spray

Corrosion Resistance After Exposure to Elevated Temperatures

	Hydrotalcite				Alodine			
	1100		6061		1100		6061	
T (°C)	A	B	A	B	A	B	A	B
25	F	F	F	P	P	P	P	P
70	P	P	P	F	P	F	P	P
115	P	P	P	F	F	F	P	F
160	P	P	P	P	F	F	P	F
205	F	P	P	P	P	F	P	P
250	P	P	P	P	P	P	P	P
300	P	P	P	P	P	P	F	F

Coated coupons subjected to salt spray exposure per MIL-C-5541D & ASTM B117; exposure time : 168 hours

P = pass

F = fail

A,B refer to coupon numbers

Talc Coated 6061-T6

	Resistivity (mohm/in^2)	
	Before Salt Spray	After Salt Spray
Specification	< 5	< 10
Talc 22° C	1.11±0.47	3.81±1.86
Talc 50° C	*5.26±2.72*	1.74±0.69

	Paint Adhesion (high solids white urethane paint)
Specification	no delamination
Talc 22° C	*fail*
Talc 50° C	*fail*

Conductivity Data

Four Point Probe Coating Resistances (in milliohms)

Alloy	Alodine 1200 S	Talc (as-coated)	Talc (aged 160° C)	Uncoated
1100 Al	0.31±0.053	0.23±0.022	0.27±0.049	0.34±0.047
2024-T3	0.32±0.060	0.23±0.064	0.23±0.010	0.31±0.051
6061-T6	0.36±0.043	0.37±0.039	0.34±0.062	0.36±0.045
7075-T6	0.28±0.055	0.25±0.030	0.23±0.048	0.33±0.099

Mercury Probe Coating Resistances (in ohms)

Alloy	Alodine 1200 S	Talc (as-coated)	Talc (aged 160° C)	Uncoated
1100 Al	1.0×10^{10}	1.67×10^{9}	2.56×10^{9}	3.0
2024-T3	2.4	5.7×10^{4}	8.3×10^{6}	1.6
6061-T6	30.0	2.21×10^{9}	6.6×10^{9}	5.0
7075-T6	33.0	3.9×10^{9}	2.3×10^{10}	2.7

Advantages

- Simple
- Rapid
- Low cost
- Some desirable properties offered
- Low toxicity

Disadvantages

- unfamiliar technology
- corrosion resistance inferior to chromate processes
- adequate paint adhesion is unproven
- process is not optimized

Summary

- Talc-like barrier films can be formed on Al by immersion in alkaline Li-salt solutions
- Films are conformal, continuous, and persistent in aggressive environments
- A simple immersion method has been devised for producing these coatings
- Coating operation is rapid and low cost, with a low toxic hazard
- The coating exhibits desirable properties and meets many standardized performance criteria

NATIONAL CENTER FOR MANUFACTURING SCIENCES
ENVIRONMENTALLY CONSCIOUS MANUFACTURING

Presentation to Chromate Replacement Workshop
Sandia National Laboratories, September 16, 1993

Abstract

The National Center for Manufacturing Sciences (NCMS) is a consortium of over 160 United States and Canadian manufacturing companies dedicated to improving the global competitiveness of its members. Its Technology function, which organizes and manages cooperative research projects involving precompetitive technology development, divides its activities among six Strategic Initiative Groups, including Environmentally Conscious Manufacturing (ECM). Currently active environmental projects within ECM span program areas ranging from materials substitution issues (CFC and lead replacement) and pollution prevention in surface finishing operations to remediation of industrial waste sites.

NCMS' Technology agenda is industry-driven, responding primarily to member requests to explore potential interest and initiate projects in a particular area. One such project, initiated in late 1992, was originally stimulated by the possibility that a member company might be willing to offer for cooperative development a process, developed so far on a laboratory scale, which could serve as the basis for a chromium-free alternative for chrome conversion coating of aluminum.

As with many NCMS projects, the first step was to put a notice in *Executive Briefing*, a publication circulated widely among the NCMS membership, requesting input from potentially interested individuals who might want to participate in a workshop on chromium alternatives. In this case, there was an immediate indication of widespread interest from a broad spectrum of NCMS member companies. Accordingly, a workshop was held in January, 1993. Participants compared their specific interests, explored possible areas of cooperation, and in the end developed the outlines of an introductory project intended to assess the present status of potential alternatives for the specific requirements represented by the members represented there, and to serve as a springboard for subsequent projects aimed at developing promising candidates to the point where they could be substituted for members' current processes.

In subsequent communications and meetings, the scope of the assessment and some of the procedural details were worked out, a statement of work was generated, and a project agreement drawn up. A copy of the work statement is included among the viewgraphs.

This project serves as a good prototype for the project formation process at NCMS. Member companies with common interests, in this case the need to solve a common environmental problem, find it advantageous to combine their resources to avoid duplication of effort, and to leverage their individual contributions, in an area which does not involve direct competition among the participants. Although it is still somewhat new to U. S. industry, this mode of operation is rapidly becoming a useful option in the quest for global competitiveness.

Environmentally Conscious Manufacturing Strategic Initiative Group

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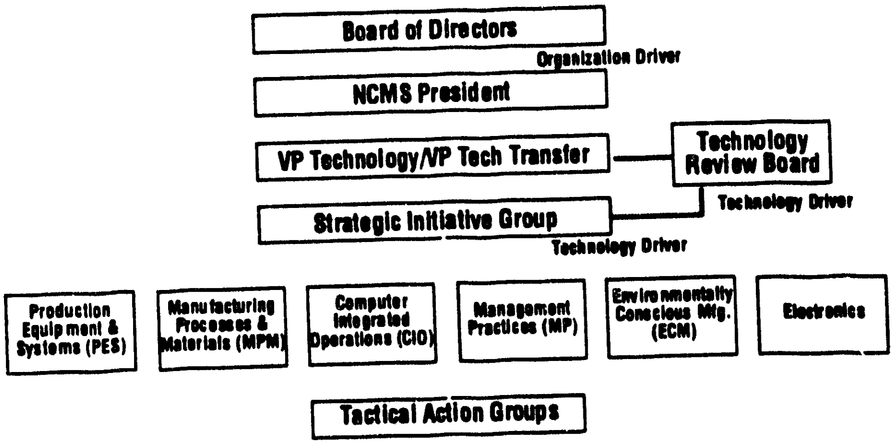
NCMS Member Company Structure



Project Specific Participation

1993 Planning Committee

- Wayne France, General Motors Corporation, Chair
- Neil Sbar, AT&T, Vice Chair
- Angelo Decrisantis, United Technologies Corporation, Secretary
- Jim Anderson, Ford Motor Company
- Paul Arbesman, Allied Signal
- Mike Leake, Texas Instruments Incorporated
- Karen Salveta, Digital Equipment Corporation
- Ralph Worden, Kingsbury Corporation
- Vic Schaefer, Cincinnati Milicron
- Ed White, Eastman Kodak

- Steve Lingle, Environmental Protection Agency
- Gary Vest, United States Air Force
- Don Walukas, National Defense Center for Environmental Excellence

Vision

- Environmental stewardship through development and implementation of Environmentally Conscious Manufacturing to enhance global competitiveness of U. S. and Canadian manufacturing

Mission

- Establish and implement an advanced and innovative portfolio of science and technology research and development programs to ensure and facilitate environmentally conscious manufacturing
- Leverage member company resources and dual-use technologies to achieve these objectives
- Disseminate to industry, government, academia, the public sector, and the marketplace, the results of the NCMS environmentally conscious manufacturing research and development
- Be the best source of environmentally conscious manufacturing science and technology for the industries and members served, consistent with the goals of the NCMS organization

Program

- Life-Cycle Design for Environmental Compatibility
- Manufacturing Solvents and Their Substitutes
- Reduced Lead Use in Manufacturing
- Environmentally Conscious Manufacturing Packaging Initiatives
- Emissions from Surface-Finishing Operations
- Sensors for Environmentally Conscious Manufacturing Processes
- Remediation of Industrial Wastes
- Handling and Disposal of Metal-Working Fluids

Strategy

- Focus and leverage resources to cost effectively achieve environmentally conscious products and processes
- Streamline the administrative processes at NCMS and member companies to achieve timely project agreements and program implementation
- Select projects with due consideration to the following prioritized environmental issues: prevention, minimization, treatment, and remediation
- Implement the Air Force and EPA Memoranda of Understanding for enhanced interactions between government and industry

Collaborative Activities with Other Organizations

- Related Organization
    - Center for Waste Reduction Technologies - AIChE
    - National Association of Metal Finishers
    - Institute for Interconnecting & Packaging Electronic Circuits (IPC)
    - American Automobile Manufacturers Association
    - Association of Electro Platers and Surface Finishers
    - Microelectronics and Computer Technology Corporation
    - Electric Power Research Institute

Current Projects

- Environmental Impact Assessment - Solvent Database
- Material Compatibility Testing
- Definition & Measurement of Clean - Electronic Components
- Environmental Impact Assessment - Monitoring & Modeling
- Component Compatibility Testing - Electronic Components
- Assessment of Plating Emissions Control Technology
- Development of Alternatives to Lead Based Solders
- Assessment of Remediation Applications
- Advanced In-Situ Bioremediation Developments
- Alternative Mechanical Interconnects - Conductive Adhesives

NCMS

Emerging Projects

1993 Starts

- Design Optimization of Metal Working Fluid
- Alternatives to Chromium for Metal Finishing
- Mold Release and Tool Preparation
- Pollution Prevention Implementation - Plating Industry

1994 Starts

- Life Cycle Design
- Continuous Monitoring of Specific Volatile Compounds
- EPA Priority Substance Elimination/Minimization
- Environmentally Conscious Packaging

NCMS

NATIONAL CENTER FOR MANUFACTURING SCIENCES
ENVIRONMENTALLY CONSCIOUS MANUFACTURING

ALTERNATIVES TO CHROMIUM FOR METAL FINISHING

STATEMENT OF WORK

Contents

I. Purpose of Project

The use of chromium in surface finishing applications carries environmental, as well as health risks. This project is intended to survey existing alternatives to the use of chromium in metal finishing processes. Project participants use chrome on a variety of surfaces, for a variety of different applications, but all are very interested in finding suitable alternatives.

Several alternatives using materials other than chromium have been investigated, although most are still in the laboratory stage. Typically, while a certain amount of characterization has been done on coating properties during the course of their development, many alternatives have not been tested specifically for applications of interest to participants.

The project will take advantage of the fact that most participants are set up to do routine testing of coating properties in conjunction with their manufacturing activities. Samples of several alternative coating types will be prepared, and will be distributed to participants for evaluation in test series most meaningful for their particular applications. In this way, a broad spectrum of comparative results will be generated, and will be used to identify areas for targeted development of the most promising candidates in subsequent projects.

II. Background

Metal finishing processes involving chromium are in widespread use, in applications ranging from decorative finishes on ordinary hardware to hard and corrosion resistant coatings for demanding aerospace applications. Chrome finishes are applied to aluminum and steel, as well as magnesium and zinc. Processes can be dip coatings or electrochemical, and may involve downstream operations such as additional coatings or paint.

The major health and environmental problem with chromium arises with the hexavalent oxidation state, which has been shown to be carcinogenic in animal studies. Processes using chromium in lower oxidation states have been developed. While such processes may be preferable from the standpoint of operator safety, the residues from any process containing chromium will continue to pose an environmental problem. The conversion of chromium to the hexavalent form in nature cannot be ruled out, so the disposal of chromium in any form is likely to become increasingly difficult. Therefore, many current users of chromium-based processes have become interested in exploring chrome-free alternatives.

One problem with the commercial development of suitable alternative processes is the fragmentation of the potential market. If the market were dominated by a few large customers, or a few universally used processes, suppliers of chromium-free alternatives could target those applications and be reasonably certain of a sizable volume once an alternative is identified. However, with a large number of users, each with a particular mix of requirements, it becomes unclear which choice of application is likely to lead to a commercially successful product. As a result, while a few chrome-free processes have reached the point of commercial availability, many of the potential alternatives have been developed in a laboratory setting, and have not undergone widespread evaluation by potential customers.

This represents an area in which a cooperative research project can make a significant contribution. Project participants have developed test procedures finely tuned to their specific applications. If provided with samples of alternative processes, participants will be in a good position to provide valuable feedback on the capabilities and shortcomings of those samples. Such a program can identify where suitable alternatives already exist, and can also identify those areas in which further development is most essential. Such a comprehensive overview would be difficult for any single company, acting alone, to generate or to justify.

III. Summary of Project Tasks

A. Select Coatings, Substrates and Tests for Study

The Project Steering Group will appoint a committee to select the coatings and substrates to be tested, and to determine the tests which will be performed. Criteria for selection will include:

- suitability for applications of interest to project participants
- expected cost of final process
- amount of development needed for commercially viable process

Substrates: In preliminary discussions, the project participants have identified five substrates as representative of the range of alloys of interest. The final selection may be revised by agreement of the Project Steering Group, should sample coupons be unavailable within the resource of time constraints of the project, or should other information be developed indicating that a revision of the list would better meet the interests of the participants. All of these substrates are aluminum alloys. They are listed below, together with the rationale for their selection.

- 2024-T3, to represent the high copper structural alloys of primary interest for aerospace applications
- 6061-T6, of intermediate coating difficulty
- 7075-T6, relatively easy to coat
- 3005, a nearly pure aluminum, similar to the common 3003 alloy used for beverage can stock (for which a great deal of information has already been collected), and having good general corrosion resistance to begin with. None of the participants currently uses 3003; at least one uses 3005.
- 356, to represent cast alloys

Coatings: A list of potential coatings has also been prepared. The list is intended to serve as a preliminary reference, and to indicate the wide variety of candidate processes already available or under investigation. Any particular item may or may not be selected for inclusion in the study. In order for a particular coating to be selected, at least one potential source must be identified who agrees to provide the required number of samples. The list may be supplemented by other candidates identified by the selection committee. The list includes:

1. Cerium (Australian process)
2. Cerium (GM process)
3. Cerium/molybdenum
4. Alodine (phosphate + organic)
5. Alodine (Cobamine)
6. Betz Metchem process
7. Sanchem process
8. Turco process
9. Hughes process

10. Lithium (Sandia)
11. Lithium + nickel acetate (Sandia)
12. Northrup (Si)
13. Northrup (Mo)
14. Oakite (Okemcote)
15. University of Connecticut process (polymer)
16. Check QPL (MIL-C-81706) for other possible candidates from vendors of qualified products

Tests: A variety of tests have been considered for inclusion in the study. In preliminary discussions, the broad range of possible tests has been split into two tiers. The "primary" tests are those considered to be particularly indicative of overall coating performance, and/or are widely accepted as standards. The remaining possibilities are designated as "follow-up" tests, to be performed as indicated by the results of the primary test series.

Primary tests will be carried out under carefully validated conditions. For each primary test, a lead lab will take responsibility for setting the standards, for ensuring that its own testing adheres to the standards, and for assisting other participants who perform confirmation testing in keeping the test conditions as consistent as possible from one lab to another.

Follow-up testing will be performed by those participants interested in generating the data and equipped to run the tests. The follow-up work is expected to generate valuable information, but the specification of methods and validation criteria are not necessarily intended to be as rigorous as in the case of the primary tests.

Four tests have been designated as primary:

1. Corrosion testing: salt spray (scribed, neutral), per ASTM B117
2. Corrosion testing: potentiostatic (RPI method)
3. Conductivity, per MIL-C-81706
4. Adhesion, per MIL-C-81706

The following have been listed as possible follow-up tests:

- Acid fog
- "Real life" exposure testing (long term)
- Impedance spectroscopy
- Addition adhesion tests
- Humidity-temperature cycling
- Paint and bake tests
- Reworkability tests (method to be determined)

In addition, it was recommended that various items of information and recommendations be obtained from the suppliers of the coated samples, including:

- Coating weight
- Target characteristic for which coating was optimized
- Time required for application of coating
- Number of steps required for application of coating
- Cleaning procedure required for preparation to coat

The selection committee will review these tests and their designations as "primary" and "follow-up", and may recommend changes if appropriate. The Project Steering Group will make the final decision concerning the tests to be performed.

A preliminary list of participants capable of performing each of the primary tests has also been assembled. The list follows, with possible lead labs for each test indicated by an asterisk:

1. Salt spray: TI*, Sandia*, Kodak, Allied Signal
2. Potentiostatic: RPI*, Sandia (limited), GM-HR
3. Conductivity: Sandia*, TI*, Kodak
4. Adhesion: Kodak*, TI, Sandia, Allied Signal (can supply painted samples and do backup testing)

In addition, UTC can act as gatekeeper and can prepare the database, while RPI can lead in experimental design, in preparing the environmental assessment, and in producing the final report.

The selection committee will assemble a detailed schedule of testing to be performed by each participant. The final selection of substrates, coatings and tests, together with test methods and statistical validation procedures, will be presented to the Project Steering Group at a project meeting. Upon approval by the group, the testing phase of the project will begin.

B. Prepare, Distribute, and Test Samples

Upon approval of the final list and schedule by the Project Steering Group, preparation of samples will be arranged. This will involve procuring blank coupons of the appropriate alloys in sufficient quantity, labeling the coupons by stamping or other means, and applying the coatings to be tested. Developers of the processes to be tested, or vendors of those processes where commercially available, will be given the opportunity to supply the coatings. Those agreeing to supply materials to the project will be informed of the tests to be performed, and will be given the opportunity to comment on the test methods, and to designate the specific characteristics for which their process is intended to show optimal performance. Preference will be given to work which can be done in part or entirely as a cofunding contribution to the project. Before distribution to project participants for testing, a preliminary round of tests may be done on subsets of each sample set to verify quality and consistency. The Project Steering Group will decide on the criteria to be applied to the preliminary round, and the extent of testing to be done.

After having successfully completed the preliminary testing round, samples will be distributed among project participants for full testing. As far as possible, the identity of alloys and coatings will not be revealed to the groups performing the testing until after the testing has been completed. The lead lab for each particular test will coordinate the distribution of samples and will monitor the status of the testing for that test. The Project Steering Group will delegate responsibility for collecting the test results, and for tabulating and distributing them to project participants. The UTC group has indicated willingness to act in a gatekeeper role for these activities.

C. Select Promising Candidates and Analyze Environmental Consequences

The Project Steering Group will review the results and select candidate processes for further analysis based on:

- performance results in the testing, as compared with processes currently in use
- range of applicability as compared with the interests of project participants
- estimates of eventual acceptance by manufacturers (considering both performance and economics)

A contract will be awarded to perform a preliminary analysis of the environmental consequences of replacing processes currently using chromium with the potential replacements. The RPI group has proposed to carry out this analysis. The study will identify the issues involved in a full life-cycle analysis of the alternatives, and will carry out the analysis in sufficient detail to provide a preliminary indication of whether the alternative is likely to be preferable to chromium from an environmental (as well as a health and safety) standpoint.

D. Prepare Final Report

The Project Steering Group will delegate responsibility for collecting the assembled information, together with explanatory and other supplementary material, into a final report. The RPI group has proposed to generate this report. The report will be reviewed by the Project Steering Group, and upon acceptance will be released for distribution to NCMS membership and to U.S. and Canadian industry within the time frame specified in the Project Agreement.

IV.

Specific funding levels for this project from NCMS member participants are listed in Appendix B.

V. Project Schedule

Target completion dates for the tasks associated with each section are listed below. Numbers refer to months following start of project.

Task	Subtask	Completion
A. Selection	Appoint selection committee	
	Prepare final plan	1
B. Samples	Procure and prepare coated coupons	3
	Complete primary tests	6
	Complete follow-up tests	9
C. Analysis	Award environmental analysis contract	7
	Complete analysis	10
D. Report	Complete final report	12

Distribution:

MS 0342	Org. 1824	M. R. Keenan
MS 0342	Org. 1824	M. J. Kelly (5)
MS 0340	Org. 1832	R. J. Salzbrenner
MS 0340	Org. 1832	R. G. Buchheit (20)
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