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ENVIRONMENTALLY COMPLIANT COATINGS USING NON-CHROMATED SYSTEMS



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14 ABSTRACT

Conversion coatings and primers used for the corrosion protection of aluminum alloy components in aircraft are based, almost exclusively, on chromate systems that are on the Environmental Protection Agency List of hazardous materials. Chromium is targeted for elimination from the workplace. This effort is part of a research program to develop a suitable replacement for chrome in coatings technology. This effort focused on the use of cerium chemistry to provide the corrosion inhibition for aluminum alloys used in the aircraft industry. The primary tasks were the development of a non-chromated conversion coating and surface treatment and a non-chromated primer coating system for military aircraft. This report presents the development, characterization, and evaluation of inorganic coatings that can serve as potential replacements for current chromate coatings. This effort was performed by the Materials Research Center at the University of Missouri-Rolla and the Boeing Corporation.

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ENVIRONMENTALLY COMPLIANT COATINGS USING NON-CHOROMATED SYSTEMS

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ABSTRACT

The conversion coatings and primers used for the corrosion protection of aluminum alloy components in aircraft are based, almost exclusively, on chromate delivery systems. The chromates are universally accepted as the most efficient and cost effective chemicals available for minimizing metal corrosion. Even when this highly successful system is used, the cost to the Federal Government for painting and re-painting aircraft exceeds one billion dollars per year. Unfortunately, chromate may be banned or become prohibitably expensive to use in the future because of its high toxicity. Currently listed as one of the 17 most toxic substances on the EPA list of hazardous materials, chromium is targeted for elimination from the workplace in the near future. As a result, it is imperative that non-chrome based materials be developed for applications associated with the U.S. aircraft industry, both from a technical and an economic point of view.

In an effort to develop a suitable replacement for chrome in coatings technology, a multi-faceted research program was initiated at University of Missouri-Rolla (UMR), in conjunction with the cooperative support of Boeing-St. Louis. The focus of the program was on the use of cerium chemistry to provide the corrosion inhibition for aluminum alloys used in the aircraft industry. The primary tasks identified for this project were the development of (1) a non-chromated conversion coating and surface treatment and (2) a non-chromated primer coating system for military aircraft.

The principal program requirement was the development, characterization and evaluation of inorganic coatings that can serve as potential replacements for the chromate based corrosion preventative coatings presently in use. Excellent progress has been made in attaining the stated goals, as will be described in more detail in this report. The following major accomplishments have been achieved: (1) the development of an electrolytic cerium conversion coating which has a 85% success rate in passing two week salt fog corrosion tests, (2) the design of a new dip (immersion) cerium coating that is nearly three times more effective in retarding corrosion than original conversion films produced using the dip process, which in some isolated tests a number of specimens have given good corrosion resistance in a 1 to 2 week time frame and (3) a promising organic primer coating that incorporates cerium salts as inhibitors into the organic carrier to provide corrosion protection to the aluminum alloys.

The main sections of the report will describe each of these accomplishments in detail. In addition, characterization of the films produced, including physical, morphological, chemical and electrochemical testing, will be presented.

SECTION I. INTRODUCTION

The use of hexavalent chromium (Cr^{6+}) in the corrosion protection of aluminum alloys in military and commercial aircraft has been an established corrosion inhibiting surface treatment procedure for decades. The chromium compounds have been shown historically to be the best technical choice, and are highly cost effective as well. Unfortunately, the chromates have now been identified as possible carcinogens and Cr^{6+} is a confirmed human carcinogen. Therefore, a major effort is in place to replace the current conversion coatings and primers with non-toxic substitutes as the exposure limits to chrome continue to decrease. OSHA's guidelines for "Occupational Exposure to Hexavalent Chromium" are expected to significantly increase the cost of compliance, which will serve as a catalyst for change in the surface treatments used for aluminum. Clearly, the need to develop an effective substitute for chrome in corrosion protection applications is a critical issue that must be addressed in the very near term.

There are a number of features or properties commonly associated with an effective inhibitor. The desirable characteristics include (1) limited solubility in the system or environment of use, (2) serve as a good intermediate bonding layer for paint or other organic finishes, (3) continuous in bulk phase and impervious to gases and liquids, (4) able to "self-heal" areas where minor abrasion has occurred, (5) doesn't accelerate attack of base metal, and (6) low cost. Almost all of them are inherent in the chrome coatings and any suitable replacement would be expected to exhibit similar behavior. This, of course, assumes a similar mechanism for protection of the base metal.

There are any number of systems that have been proposed as alternatives to chrome based systems, and the more promising ones will be outlined in Section. II. One of the more recent additions to the list of potential replacements involves the use of rare earth metal salts. Compounds of cerium, one of the more common rare earths, are the basis for the coatings under development at UMR. The processes developed using cerium salts in conversion coatings and primers and the results of their effectiveness will be the main topic of this report.

The primary tasks of this project are (1) to develop a non-chromated conversion coating that can meet the requirements in MIL–C–81706, and (2) develop a primer

containing non-chrome inhibitors that can meet the requirements in MIL–P–23377, MIL–P–85582 and Boeing-St. Louis specification MMS–423.

Cerium conversion coatings were developed using two different deposition techniques. One was electrolytic, or non-spontaneous, and required a power source to make the coating. The other process was spontaneous and deposition occurred upon dipping the aluminum substrate in the appropriate chemical solution. The coatings were tested and characterized extensively, with the ASTM B–117 test of 336-hour salt fog exposure being the major evaluation of coating quality. In general, the electrolytic process produced coatings that were very successful in passing the salt fog corrosion tests. At present, the pass rate for these coatings is in excess of 85%. The dip process is less advanced, but recent process modifications have produced coatings which perform nearly three times better than the specimens deposited during the initial trials.

As the conversion coatings were developed, the unit processes which emerged as most critical to performance were (1) pretreatment and cleaning steps, (2) coating deposition, and (3) post-treatment or sealing step. The effects of the various chemicals and operating parameters evaluated in these steps will be described. The conditions which gave the best conversion coatings and the effects of the different process parameters or variables will also be given. These data will be supplemented by pertinent characterizations, including physical, chemical, morphological and electrochemical evaluations.

Primer development has also advanced well. Two complete generations of primer formulations have been tested and a third generation is now in test at Boeing-St. Louis. The spraying of the fourth generation is scheduled for completion in the near future, with subsequent testing to be completed by the end of summer 2001. A summary of the testing results obtained by Boeing-St. Louis is given as an attachment. A more detailed technical description on each task is contained in the following sections.

Section II. Literature Review of Non-chromate Conversion Coatings

Abstract

Conversion coating treatments that have been or are being evaluated as replacements for chromates are reviewed. Included are coatings produced from anodizing, molybdates, permanganates, sol-gels, hydrotalcite, zirconium salts, cerium/molybdate coatings, and rare earth salts. Many coating systems are hybrids of coatings from the preceding list. Special emphasis is placed on those that contain rare earths, especially cerium.

II.1. Introduction

High strength aluminum alloys are commonly used in aerospace applications due to their low density, high strength, ease of fabrication, and corrosion resistance. The favorable strength to weight ratio of aluminum alloys makes them preferable to ferrous metals in the aircraft industry where structural weight and corrosion resistance are of concern due to human safety and economics [1]. Corrosion is a commonly occurring problem in military aircraft, and structural components made from these high strength aluminum alloys, such as 7075-T6 and 2024-T3, are particularly susceptible to corrosion (Compositions: 2024 is 4.4% Cu, 0.6% Mn, 1.5% Mg, with the balance Al and impurities. 7075 is 1.6% Cu, 2.5% Mg, 0.23% Cr, 5.6% Zn, with the balance Al and impurities [2]). These components are exposed to aqueous corrosive environments, which result from the naturally humid air in which aircraft fly or condensation within structural cavities. To protect metal from corrosion in such environments, protective coatings including a variety of paints, chromate conversion or anodized coatings, or even the metal's naturally forming oxide film are used. Of these, chromating is the most commercially used surface pre-treatment stage for the corrosion protection of aluminum alloys in the aircraft and aerospace industries. Hexavalent chromium, which is a known carcinogen, is a primary component in this process. Other toxic chemicals, such as cyanides and fluorides, can also be present in commercial chromate conversion baths [3]. Major reasons for the widespread use of chromium-based protective coatings are their self-healing nature, excellent corrosion resistance, and their ease of application [4]. However, current environmental legislation is making the use of hexavalent chromium unattractive because of worker protection and waste disposal costs. Due to tightening regulatory pressure to reduce the hazardous waste of chromium, many attempts are being made to develop non-toxic alternative methods of corrosion protection.

II.2. Anodizing

Anodizing is a process for the corrosion protection of aluminum alloys that is commonly used in structural applications where fatigue is not a major concern. Anodizing builds an oxide layer which passivates the alloy's surface. The resulting aluminum oxide film provides corrosion resistance similar to that of chromate conversion coatings. However, it behaves more as a barrier and can not self-heal once the oxide layer is compromised. The aluminum oxide that forms during anodizing grows from the base metal and imparts good adhesion for primers, but also changes the mechanical properties of the alloy. One severe consequence of anodizing is a reduction in fatigue strength. Economically, most anodizing processes are ten times more expensive than the chromate conversion coating process.

One anodizing process, a sulfuric acid/boric acid anodizing (SBAA) treatment developed by Boeing, does offer comparable corrosion protection at a similar cost to that of chrome conversion coatings [5]. The process provides excellent paint adhesion and corrosion protection for aluminum, and may prove to be a possible replacement for chrome conversion coatings on some parts. However, because the process is anodic in nature it may not be a universal replacement for all parts, especially parts that may entrap fluids, such as welds, sharp edges, and crevices, or parts having steel inserts. Since the non-toxic alternative to chromating should not compromise the mechanical properties of the alloy, these problems would limit the use of SBAA as a universal alternative to chromating.

There are other methods of obtaining a corrosion resistant coating using an oxide layer that is built up in a controlled manner on an aluminum substrate. One is a derivative of the "talc" coatings (described later) where an immersion in boiling water causes a "reversion" of the talc coating to bayerite [6].

II.3. Molybdates

Initial research for the replacement of chromium conversion coatings focused on the use of metal oxyanion analogues of chromates. Examples of such include tungstates, vanadates, permanganates, and molybdates [7]. Similar to chromates, these compounds have the ability to form metallic oxide/hydroxide films on metal surfaces. Molybdates are the most widely investigated of these compounds, due to their non-toxic nature. However, even though several

different molybdenum oxide films have been developed on different metal substrates, they do not protect against corrosion as well as chromate coatings. It is well known that the corrosion protection offered by molybdates can be improved by combining them with other inhibitors, such as nitrates, citrates, zinc sulfates, and phosphates. One conversion coating with good adhesion that was based on molybdates was developed by Kurosawa *et al.* [7]. The conversion coating was produced on steel by immersion in a 0.1M Na_2MoO_4 solution acidified with orthophosphoric acid. The coatings exhibited significant corrosion protection when exposed to salt spray tests. Tang *et al.* [8] patented a conversion coating process where zinc is immersed into a molybdate and phosphate solution.

The resulting coatings were said to have better corrosion protection than chromates at lower pH, equal to chromates in outdoor weathering exposure tests, but not as good as chromates in neutral tests, such as neutral salt spray. Even though testing was focused on zinc and steel substrates, the same synergistic effects may also apply for aluminum. One example would be the use of a molybdenum/cobalt-based conversion coating for the corrosion protection of aluminum alloys [8]. Results at Boeing show that the coating meets the requirements for corrosion resistance and paint adhesion characteristics, but that the process is not as easy to use as chromating.

II.4. Permanganates

Permanganate oxyanions are not known to be effective corrosion inhibitors for aluminum alloys [7]. However, a conversion coating developed by Bibber, which is based on the use of potassium permanganate, is reported to be very effective in protecting aluminum alloys [9,10]. The process calls for successive immersions in boiling water, an aluminum nitrate/lithium nitrate solution, and a permanganate/borax solution. These successive immersion stages result in the thickening of the aluminum's native oxide layer. The final step in the process involves sealing the porous oxide coating in a potassium silicate solution. This permanganate conversion coating provides a significant level of corrosion protection for aluminum alloys, including 336 hours in ASTM B-117 neutral salt spray.

II.5. Sol-gels

Sol-gel coatings are being evaluated as corrosion inhibitors due to their barrier properties and because they provide bonding between the substrate and the primer [11]. It is also worth

noting that this treatment method is already being commercialized by coatings companies such as Lord. The silica-based sol-gel coatings are, in general, formed from alkoxysilanes that are hydrolyzed to form a hydrolyzed silanol. This is followed by condensation reactions that then increase molecular weight [11]. Some of the most recent refinements and improvements on these types of systems include mixed silicon/zirconium systems [12], doping with cerium salts [13], and avoidance of thermal cure by use pre-formed particles [11]. The latter modification, called a SNAP (self-assembled nano-scale particle) system, uses gel particles that have been formed in solution prior to application to a substrate that has been pretreated with coupling agents.

A recent summary by Bierwagen on the status of sol-gel coatings indicates that products such as Boegel-EP provide good adhesion with primers [14]. However, non-Cr primers on the non-Cr conversion coatings perform poorly in salt spray.

II.6. Hydrotalcite coatings

Hydrotalcite coatings derive their name from a class of clays which they resemble [15]. The stoichchiometry of a typical coating is believed to be $Li_2Al_4CO_3(OH)_{12}\bullet 3H_2O$ [15]. The coatings are precipitated onto an aluminum panel when it is immersed in a lithium carbonate–lithium hydroxide solution that is saturated with aluminum. At least two patents have been granted that are closely related to this process [16,17]. One of these patents claims sealing in rare earth containing solutions as part of the process [17].

II.7. Rare earth metal salts

The use of rare earth metal salts as potential corrosion inhibitors was first demonstrated in 1984 [18]. The most significant corrosion protection was observed with cerium salts. The immersion of aluminum in baths containing 200-1000 ppm cerium reduced the rate of corrosion by at least one order of magnitude. The basis of the protection is believed to be the formation of cerium oxide on the metal's surface. The degree of corrosion protection greatly depended on the immersion time where at least 100 hours was required to achieve any significant protection [18]. Further investigation by Hinton *et a.l* [19] showed that a cerium oxide film could be produced on the surface much faster electrolytically by polarizing an aluminum alloy in an aqueous or organic solution containing cerium salts. However, the resulting cathodic coatings did not offer as much corrosion protection as the longer time immersion process did.

To overcome these practical problems, a process was developed and patented by Wilson and Hinton in which the metal substrate was immersed in an aqueous solution of cerium chloride and hydrogen peroxide [20]. The process covered a range of metals, including aluminum, galvanized steel, steel, zinc, cadmium, and magnesium. However, the resulting coating prepared by this process was still inferior in corrosion protection compared to the longer, 100 hour minimum immersion process. The inferior corrosion resistance of this coating process was thought to be a result of the heavily cracked morphology of the deposited film that left the underlying metal surface exposed. While this specific coating has not replaced chromate conversion coatings, the work helped initiate more interest in rare earth conversion coatings. This has resulted in several patents [21-26] that are relevant to the ongoing work on conversion coatings at UMR.

Literature has reported a mechanism of deposition and how the coatings protect high copper content aluminum alloys [27-36]. The general consensus is that deposition is brought about by a localized pH increase at cathodic sites, which causes a precipitation of cerium oxides or hydroxides onto the substrate [32,34,36]. The resulting barrier then should inhibit the cathodic reactions of the corrosion process [36].

II.8. Ce-Mo process

Another approach is the synergistic effect of combining cerium salts with molybdates. The Ce-Mo process involves both chemical and electrochemical steps for the deposition of a coating [37]. The first step is the immersion of the substrate in a 10 mM $Ce(NO_3)_3$ solution for 2 hours, followed by a second immersion in a 5mM $CeCl_3$ solution for an additional 2 hours. The second step involves an electrochemical treatment where the substrate is polarized in deaerated 0.1 M Na_2MoO_4 at a potential of +500 mV vs. SCE for 2 hours. Aluminum 6013-T6 coated with this process successfully passed ASTM B-117 salt spray, and after 60 days immersion in 0.5 M NaCl alloy 6061 showed no sign of significant localized corrosion. A sample of pure aluminum coated with this process which was then scratched exhibited no localized or uniform corrosion in the scratched area after 25 days exposure to NaCl. For untreated samples, or samples coated using only the molybdate solution, pits began to form within the first day of exposure. This suggests that the improved corrosion resistance of these alloys is a result of the synergistic effects between the cerium and molybdate treatments. However, when this Ce-Mo process was

applied to copper-containing aluminum alloys, such as 7075-T6 and 2024-T3, the results were less satisfactory, perhaps due to the presence of copper precipitates in the metal's outer surface layer which affect the corrosion behavior of the Ce-Mo modified surfaces, making them more susceptible to localized corrosion [38]. A patent based on this process has been granted [39].

II.9. Zirconium salts

Another possible replacement for toxic chromates is the development of a protective conversion coating based on zirconium oxide [7]. Developed out of necessity as a chromate replacement by the canning industry, this process consists of immersion of the substrate in an aqueous solution containing a soluble zirconium salt, such as zirconium ammonium acetate or fluorozirconic acid, and a polymeric material, such as polyacrylic acid. The treatment can be applied to tin, galvanized steel, and aluminum substrates.

One advantage of using zirconium oxide coatings is the ease of application. Treatment times of less than a minute allow the coatings to be applied by rolling or spray, which is extremely important for a continuous production line.

Several patents using zirconium salts have been granted, but the one most relevant to UMR's work is U.S. Patent 5,964,928 [40]. This patent takes advantage of a supposed synergistic effect with rare earth salts such as cerium.

II.10. Other Substitutions

Other candidates for the replacement of chromate conversion coatings include phosphates [41], titanates [7], cobalt oxides [42], and surfactant treatments [43]. Each of these coating processes have shown to provide some corrosion protection for aluminum alloys, but further development is needed.

II.11. Summary

There are many non-chrome conversion treatments that are in development, but there are none ready to completely replace chromates. Rare earth treatments remain some of the most promising methods. This is substantiated by the use of rare earths in other conversion coating processes.

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Section III. Electrodeposition of Cerium-Based Conversion Coatings

Abstract

The primary goal of the research and development was to deposit, characterize and evaluate conversion coatings for aluminum alloys based on cerium corrosion inhibitors to replace chromate conversion coatings. This phase of the work focused on the process to deposit cerium conversion coating using a current driven cathodically induced precipitation process. A promising electrolytic cerium coating process has been developed at UMR that has an 85% pass rate after two weeks of salt fog corrosion testing. The operating parameters used in producing this conversion coating will be discussed. Critical factors that influenced coating quality included current density, potential, bath pH, coating time and additive concentration. System optimization studies will continue and concentrate on improving coating consistency and corrosion resistance. A proposed mechanism for the deposition and treatment processes will also be presented.

III.1. Introduction

Though cerium is a reasonably good inhibitor, long term protection of the metal is sometimes lacking. Generally, the two mechanisms attributed to decrease in corrosion protection provided by cerium cathodic coatings are (1) incomplete coverage of the substrate due to hydrogen evolution or cracking, and (2) non-uniform coating composition. The second mechanism has been studied by Davenport [2] with the use of XANES for determining the oxidation states of cerium. Exposing the film to sodium chloride solution for at least seven days converted the Ce^{3+} oxidation state to the Ce^{4+} oxidation state. Apparently, the precipitation of $Ce(OH)_3$, which is less stable than $Ce(OH)_4$, was possible because the cathodic process generated alkaline conditions at the aluminum surface. If the solution pH is sufficiently high, cerium (IV) hydroxide will precipitate. Previous work at UMR relied on this mechanism to cathodically deposit $Ce(OH)_4$ films that serve as a conversion coating on aluminum alloys [3]. Recently, the UMR group has improved the cerium based coating for 7075-T6 that shows considerable promise.

III.2. Process Description

III.2.1. *Materials*

The majority of the panels used were 7075-T6 aluminum alloy sheet manufactured by Kaiser. Cerium nitrate hexahydrate of 99% purity from Aldrich was used in the electrolyte. The hydrogen peroxide (30%, A.C.S. Certified), sodium phosphate ($Na_3PO_4 \bullet 12H_2O$, A.C.S. Certified, Tribasic) and animal gelatin (Type A Bloom 275, lab grade) were obtained from Fisher.

III.2.2. Substrate Pretreatment

Pretreatment of the aluminum alloy was done in accordance with Boeing-St. Louis specifications. Specimens, with dimensions 1" X 3" (small panels) or 3" X 6" (large panels) were first rinsed with acetone, then immersed in a 5 wt% Turco alkaline cleaner for 5 to 10 minutes at 43±5 °C. Degreased panels were then rinsed with tap water followed by deionized water prior to electrodeposition.

III.2.3. Electrodeposition of Cerium Conversion Coating

Standard electrolyte (about 250 ml of solution) was prepared by dissolving 3.20g $Ce(NO)_3 \bullet 6H_2O$ (7.4 millimoles) in 200 ml deionized water and adjusting the pH to 1.98 with concentrated nitric acid. Animal gelatin (0.750g of the electrolyte) was dissolved in 40 ml water. The animal gelatin solution was then added to the cerium solution; the pH was 2.12. The pH is not affected when 10 ml of 30% hydrogen peroxide was added to the solution.

Direct current (DC) plating, with a dimensionally stable anode (DSA) or a platinum wire mesh of equal size to the aluminum cathode, was used to deposit the cerium coating (Figure III.1). The aluminum panels were partially immersed in the electrolyte during the electrodeposition process. The standard process applied a current density of 11 mA/cm^2 until a final potential of 30 volts was attained. The coating time was in the range of 60-90 seconds. Immediately after deposition, the panels were rinsed with deionized water and sealed. Sealing was done by immersing the sample for 5 minutes in a boiling (99±5 °C) solution of 2.5 wt% $Na_3PO_4 \bullet 12H_2O$ with an adjusted pH of 4.5 using phosphoric acid.

Several variables in the electrodeposition step were adjusted to improve the salt fog corrosion testing results including pH, additive concentration, coating time, potential and current density. The inclusion of a gelatin additive was instrumental in improving corrosion resistance.

Other organic additives were evaluated but the results were all unfavorable. The other additives studied included fish gelatins, D,L-Proline, cis-4-Hydroxy-D-Proline, and trans-4-Hydroxy-L-Proline.

III.2.4. Coating Evaluation

A Hitachi S-4700 scanning electron microscope SEM), equipped with an energy dispersive spectroscopy x-ray detector (EDS), was used to determine the surface morphologies and chemical compositions of the films. Analyses for composition profiles were done with a Physical Electronics Model 545 Auger Emission Spectrometer (AES). Argon ion sputtering, at an approximate sputter rate of 6 to 10 nm per minute with a voltage of 3 kV and an emission current of 1 mA was used to depth profile the samples.

III.2.5 Salt Spray Test

Salt spray testing in accordance with ASTM B117-90 was conducted on the electrolytic cerium coated panels. The salt fog chamber atomized 5 wt% sodium chloride solution at a temperature of 35 °C. Each coated aluminum (7075-T6) panel was taped on the backside, i.e. the side facing away from the anode, and edges before placing in the salt fog chamber. Specimens were removed from the salt spray cabinet at or before two weeks (336 hours) depending on performance. These panels were then subjected to visual and microscopic examinations. A Salt Fog Rating from zero to ten was assigned; with ten being the best, seven being the minimum passing and below seven failing.

III.3 Results and Discussion

III.3.1 Electrodeposition

The first UMR process (U.S. Patent# 5,932,083) [1] using glycol as a major component and a solution pH of 1.0 gave reasonable salt fog corrosion results for two weeks but did not give good reproducibility. The decision was made to use an aqueous electrolyte containing a low concentration of an organic additive, such as gelatin, to improve coating uniformity and corrosion resistance. At very low pH values (1.0/1.2) the coatings were not uniform and black spots appeared on the coated surface after one week of salt fog. These black spots did not show salt tails but appeared to be an early form of corrosion. EDS analysis showed less cerium in these areas than on the standard coating (Table III.1). The current density used to make these coatings was about 18 mA/cm^2 and the deposition time was about 90 seconds. As the thickness

of the coating increased, the voltage increased rapidly as a passive resistive, film was formed on the surface. Electrolysis was not extended beyond 35 volts due to supply limitations. As the pH of the electrolyte was increased to 2.1, the coatings performed better during the salt fog testing and the current density to form a coating decreased (Figure III.2). The use of gelatin to replace the organic-based electrolyte markedly improved the corrosion resistance of the coatings, the reproducibility of salt fog performance, and primer adhesion.

III.3.2 *Deposition Mechanism*

The mechanism for the electrolytic formation of the cerium films has been proposed previously by Lin [3]. The assumption is that the cathodic process generates sufficient alkalinity at the electrode surface to precipitate cerium (III) hydroxide,

$$Ce^{3+} + 3OH^- \rightarrow Ce(OH)_3$$

but this colorless film is not an effective inhibitor. When hydrogen peroxide was added, a precipitation reaction again occurred at the electrode surface but cerium (IV) was the dominant phase. A locally increased pH is achieved by the cathodic reduction reactions in which hydrogen ions consumed by hydrogen evolution and hydrogen peroxide is reduced.

$$2H^+ + 2e^- \rightarrow H_2$$

$$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$$

$$H_2O_2 + 2e^- \rightarrow 2OH^-$$

As the pH increases, the Ce^{3+} ions in the vicinity of the cathode are oxidized to Ce(IV) by hydrogen peroxide

$$2Ce^{3+} + 2OH^- + H_2O_2 \rightarrow 2Ce(OH)_2^{2+}$$

and eventually ceric hydroxide precipitates on the cathode by the reaction

$$Ce(OH)_2^{2+} + 2OH^- \rightarrow Ce(OH)_4$$

Using a previously published form of an E-pH diagram by M. Pourbaix, the indicated pH for $Ce(OH)_4$ precipitation is 10.4 at a cerium concentration of 30 mM [4]. A new diagram has been constructed at UMR that shows precipitation can occur at much lower pH values (see Section V.2.6). It is postulated that nucleation occurs initially at the hydrogen evolution sites where the pH is sufficiently high for the cerium compounds to precipitate. The front face of the

cathode was observed to nucleate a continuous cerium coating instantly upon application of current. With time the back side coated as well, but only the front face was corrosion tested.

III.3.3 Post-treatment

Following deposition by the standard electrolytic process, the cerium film was sealed in a boiling solution of sodium phosphate at pH 4.5. The corrosion resistance, but not the surface morphology was improved after sealing. The coating changed color from orange to yellow during drying. The film adhesion to the substrate was very good after the sealing step. It has been postulated that the sealing stage promotes diffusion between the substrate and the coating, giving improved interfacial integrity.

During the sealing step inhibiting phosphate compounds may form [5] by the following anodic process

$$Al + 3H_2PO_4^- \rightarrow Al(H_2PO_4)_3 + 3e^-$$

followed by secondary reactions.

$$2\ Al(H_2PO_4)_3 \leftrightarrow 2AlPO_4 + 4H_3PO_4$$

Several variations to the sealing procedures were attempted for the standard process but these gave poor corrosion resistance. When the pH of the phosphate solution was increased to 7.9, the coatings became more uniform but the corrosion resistance was poor. Sealing in hot water did not improve corrosion protection. In other experiments, two organic additives (polyethylene imine and triethylene tetramine) were evaluated at two different pH values (6.0 and 11) and two different temperatures (25 °C and an unmeasured boiling temperature). These changes were not effective in improving the corrosion resistance.

III.3.4 Surface Morphology

Immediately after deposition or sealing, the coating appeared uniform, but became more mottled in appearance as drying occurred. Observation with a light microscope indicated that cracks appeared during drying and after several days at room temperature the cracking became more extensive. The extensive network of random cracks may be due to excess shrinkage in conjunction with poor ductility. Unsealed specimens also show a color change during drying, possibly indicating the change from cerium (IV) hydroxide to cerium oxide. Preliminary SEM and EDS studies showed that white particles on the surface (Figure III.3a) were higher in cerium content than the rest of the surface. At higher magnification, the white particles appeared to be

an agglomeration of smaller particles of different shapes (Figure III.3b). The agglomerations may be the sites for hydrogen evolution, causing an increase in pH which led to precipitating cerium compounds. The phosphate compounds that were formed consist of aluminum, cerium, or both. A cross section of the film showed a layered structure for both sealed and unsealed samples but their significance is yet to be determined (Figure III.4).

III.3.5 Chemical Composition

EDS analyses (Table III.1) showed that corroded sealed cerium conversion coatings had less carbon, cerium, phoshorus and oxygen and more aluminum than those that were not exposed to the salt fog. The removal of a significant amount of carbon during the sealing process is important and further studies are necessary to explain this phenomenon. Sealed specimens had similar amounts of cerium and more oxygen than unsealed coatings. As expected, unsealed films did not contain phosphorus. Unsealed specimens did not have any aluminum at the surface while sealed specimens did have measurable aluminum signal. Analyses of specimens that passed the salt fog test contained similar amounts of cerium, phosphorus and aluminum unexposed sealed specimens. The indication is that there was limited degradation to the higher quality films and a decrease in the coating solubility.

Auger depth profiles were made on sealed specimens prepared at various deposition times and a constant current density of 6.6 mA/cm^2 using a standard electrolyte. All these coatings were similar in chemical composition with a range of thickness from 540 nm to 1700 nm. The coating thickness generally increased with deposition time. Figure III.5 shows a typical depth profile compared with a standard cerium oxide powder. There is a relatively constant amount of cerium, oxygen, and phosphorus in the film, which decreased rapidly at the interfacial region.

III.3.6 Salt Spray Evaluation as a Function of Deposition Parameters

The ASTM B-117 standard procedure was used to evaluate the corrosion resistance of the cerium conversion coated aluminum alloy (7075-T6) specimens. The electrolytic deposition process exhibited good reproducibility, with 97% (45/47) passing for one week and 85% (40/47) passing for two 2 weeks (336 hours) in the salt spray. The salt fog results were duplicated by Boeing-St. Louis, where five 1" X 3" standard samples were tested, all of which passed for two weeks (336 hours).

Coatings made using the standard conditions for 1.5 minutes but at lower current density, (6.6 mA/cm^2) gave 50% salt fog passing for one week and 24% passing for two weeks (336 hours). Increasing the coating time from 1.5 min (27 coulombs, 780 nm) to 2.5 min (45 coulombs, 1200 nm) gave good salt spray results when the lower current density was used (Figure III.6) & (Figure III.7). The number of coulombs was similar to that of the standard process and may be an indicator of how to vary current density and time to obtain a desired corrosion resistance. If the current density was too high, polarization occurred very quickly and the coating formed was too thin to pass the salt fog test. Also, if the current density was too low (Figure III.7), little or no precipitation occurred when the deposition time was similar to that used for the standard process. A longer deposition time may be necessary to make a corrosion resistant coating at very low current densities.

When the electrolyte pH was kept constant at 1.1, salt fog results varied with the amount of animal gelatin present, with an optimum value in the range of 0.3 wt%. It was also observed that as the pH increased up to 2.1 fewer samples had black spots after salt fog testing and more samples passed the corrosion test. At higher pH values (2.1), the current density necessary to deposit a coating decreased (2.2 – 11 mA/cm^2).

Various organic additives, fish gelatin, d,l-Proline, cis-4-Hydroxy-D-Proline and trans-4-Hydroxy-L-Proline were used in the electrolyte at pH 1.1 at several current densities. These specimens did not do as well in the salt fog test as those made in electrolyte containing animal gelatin. In addition, these other organic additives used in the electrolyte did not cause polarization to occur as quickly as animal gelatin. If the conditions were tailored for the different additives, better results may be attained and additional testing is needed in this area.

III.4 Summary

The electrolytic cerium conversion coatings made from a standard electrolyte containing animal gelatin at a current density of 11 mA/cm^2 were very reproducible and 85% passed the two weeks (336 hours) of salt fog corrosion testing. The cerium coatings adhered to the substrate and primer adherence to the coatings was also good. The coating process includes a standard pretreatment step similar to that followed by Boeing-St Louis, followed by deposition from the electrolyte containing animal gelatin by the optimized parameters previously described. The sealing step in boiling phosphate solution enhanced corrosion resistance. The standard

coating thickness was about 780 nm but the morphology was mottled in appearance when gelatin was used.

The following variables were found to be important when designing the conversion coating process: pH, current density, coulombs, coating time, coating thickness, potential and additives. To optimize the process, the interaction and synergism among these parameters must be considered in addition to their absolute values.

Some preliminary work with the lower current density of 6.6 mA/cm^2 has produced some encouraging results and further investigations are planned. The role of organic additives must be explored in more depth to gain a better understanding of their vital role to the integrity of the deposited coating.

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Table III.1 EDS Analysis in atomic percent for various cerium conversion coatings prepared by the electrolytic method.

Elements (atomic %)	Corroded Film	Unsealed Film	Sealed Film	Sealed/Passed Salt Fog	Black Area
C	1.2	48.4	20.8	0	0
Ce	0.5	12.9	11.5	12.4	1.6
O	4.9	35.8	49.5	59.2	64.9
P	0.7	0	13.7	15.3	2.1
Al	85.9	2.0	1.0	1.5	23.2

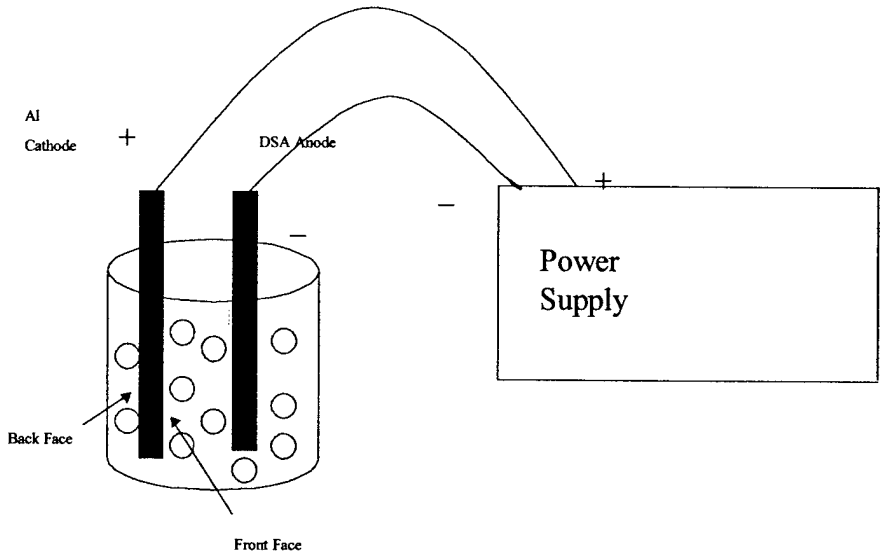


Figure III.1. Apparatus for the electrolytic deposition process.

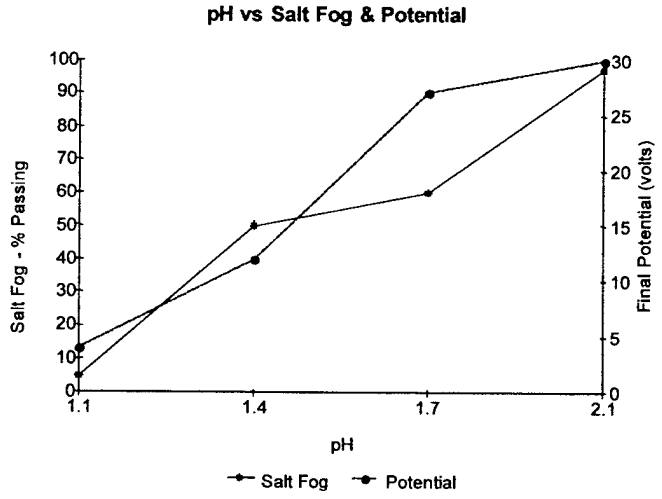
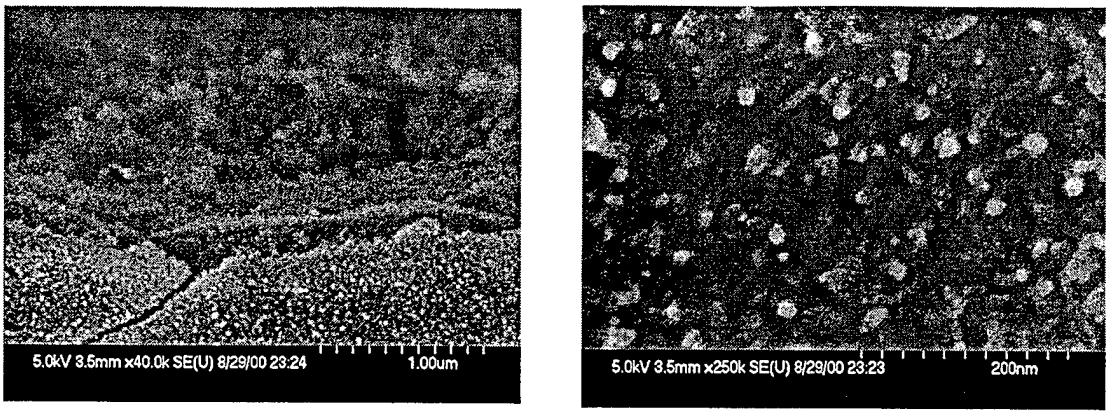
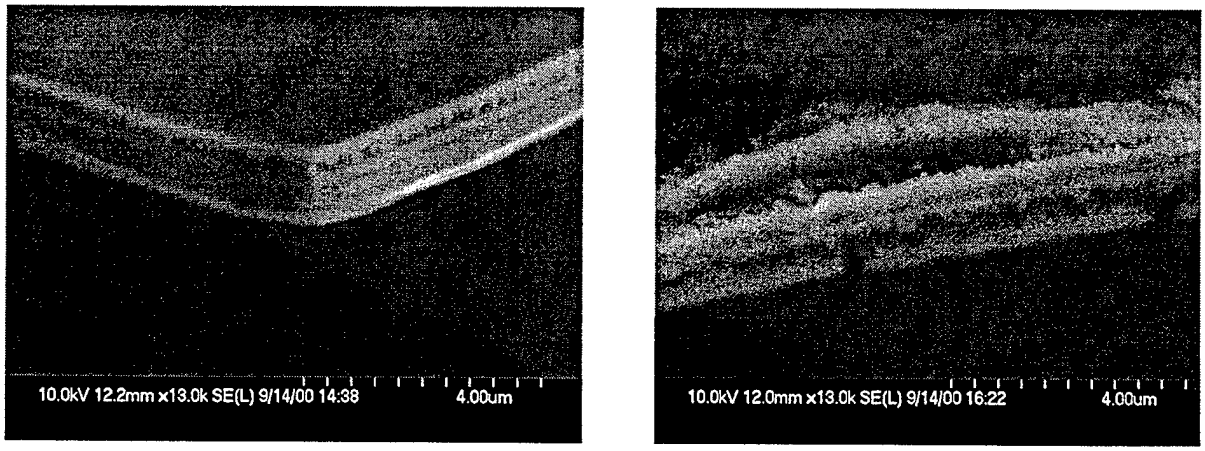


Figure III.2. Effect of solution pH on corrosion resistance and final cell potential of sealed electrolytic conversion coatings.



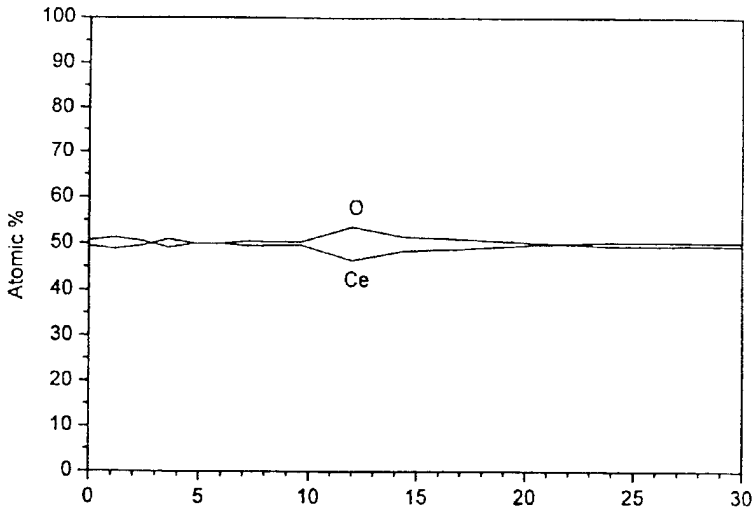
(a) (b)

Figure III.3. Surface of a typical sealed electrolytic cerium conversion coating (a) cerium-rich white particles (b) white particles, approximately 20 nm in diameter, at higher magnification.

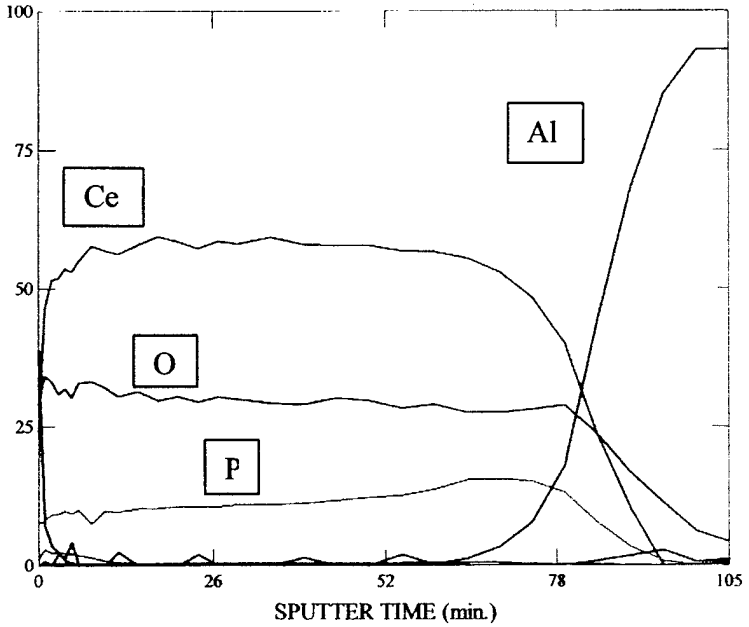


(a) (b)

Figure III.4. Edge view of electrolytic cerium conversion coatings (a) unsealed specimen (b) sealed specimen.



(a)



(b)

Figure III.5. AES depth profile (atomic composition - %) of (a) CeO_2 powder (b) sealed electrolytic cerium conversion coating on Al alloy 7075-T6.

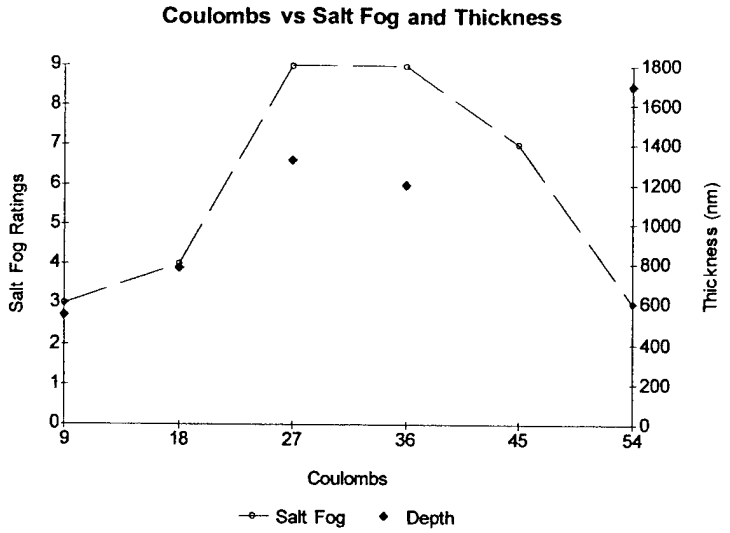


Figure III.6. The thickness and salt fog rating for sealed electrolytic cerium conversion coatings prepared from the standard electrolyte. A constant current density of 11 mA/cm^2 and various coating times were used. The salt fog ratings are for one week of testing.

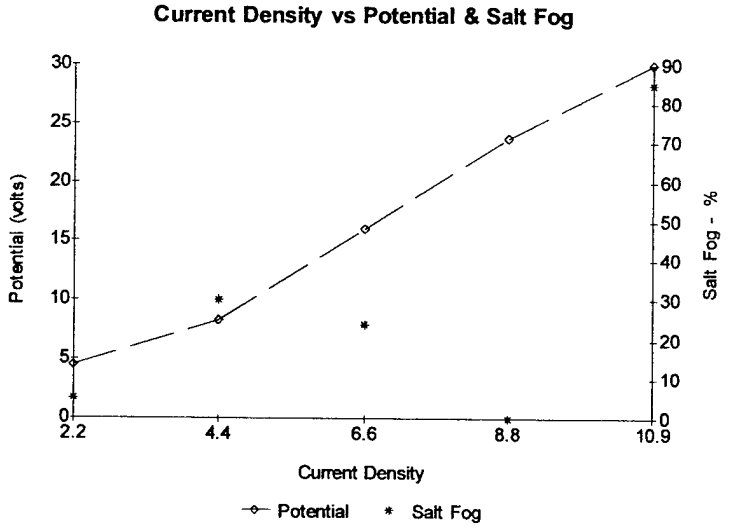


Figure III.7. The final deposition potential and percent samples passing salt fog for sealed electrolytic cerium conversion coatings prepared from a standard electrolyte but changing the current density. The salt fog results are for 2 weeks (336 hours).

Section IV. Spontaneous Cerium Dip Conversion Coatings for the Corrosion Protection of Aluminum Alloys

Abstract

The primary goal of this portion of the project was to develop a spontaneous cerium dip coating process for aluminum alloys. The effects of pre-treatment, electrolyte composition, deposition time and sealing were studied. The chemical composition, morphology and corrosion resistance of the deposited films were evaluated as a function of these variables. A cerium conversion coating with improved corrosion resistance compared to previous cerium dip deposits has been developed. It was found that high temperature alkaline cleaning (55 - 63^{0}C) in conjunction with sealing the cerium deposits in boiling sodium phosphate greatly improved the corrosion resistance of these coatings. The electrolyte composition and processing parameters necessary for promising four to seven day ASTM B-117 salt fog results have been identified.

IV.1. Introduction

The search for non-toxic alternative corrosion inhibitors has led to the development of a number of novel coating processes, but to date none are recognized as being equivalent to chromium. One of the most promising of these new conversion coating systems is based on rare earth elements [1]. One process involves the immersion of an aluminum alloy in 1000 ppm $CeCl_3$ for several days to provide significant corrosion protection upon subsequent exposure to a NaCl solution [2,3]. The protective action is imparted by the formation of a hydrated oxide film containing cerium in the oxidation states of both 3^+ and 4^+ [4]. The latter is known to be much more stable than trivalent cerium [5] and is considerably less soluble than aluminum compounds at high pH [6]. This immersion coating, with the presence of tetravalent cerium, provided a barrier against the passage of electrons and the diffusion of oxygen to the metal surface, thus reducing the rate of cathodic reactions and thereby inhibiting corrosion.

Cerium-rich coatings have also been formed by cathodic treatment in aqueous or in organic solutions containing cerium ions [7,8]. However, the cathodic process did not form a coating with the same degree of protection against pitting. This was attributed to the predominance of Ce(III) compounds and poor surface morphology. Although a patented process call "cerating" has been developed to chemically produce CeO_2 coatings using hydrogen peroxide [9], the corrosion performance of the deposited films was still poor. Observations have confirmed the existence of heavily-cracked regions which were wider than the average thickness of the film [10].

To develop a protective cerium conversion coating, the preference is to deposit Ce(IV) compounds with good surface coverage and adhesion. This has previously been accomplished electrochemically at UMR using a Ce(III) electrolyte containing hydrogen peroxide and gelatin as an organic additive. It is believed that cerium ions in the vicinity of the aluminum cathode were oxidized by peroxide from 3^+ to 4^+ due to an increase in pH, and then precipitated as hydrated Ce(IV) oxide [11]. The controlled cathodic deposition produced films with uniform coverage and good adhesion after a final aqueous sealing treatment. As a result, these cerium-based conversion coatings exhibited superior corrosion performance in both chemical and electrochemical tests compared to unsealed samples. Electrolytic cerium coatings on 7075-T6 aluminum provided corrosion resistance comparable to chromate conversion coatings in standard salt spray testing.

However, the use of an electrolytic process is more costly than a standard dip surface treatment, and the current driven cerium process is not feasible in aerospace applications where field maintenance is desired. This made the development of a cerium dip conversion coating desirable. The development of the spontaneous process used UMR's electrolytic process as the basis for the new dip process.

IV.2. Experimental Procedures

Aluminum alloy (AA) 7075-T6 test panels used in this study were manufactured by Kaiser; lot number 243911. The pre-treatment of the alloy was in accordance with Boeing-St. Louis specifications that included immersion in five weight percent Turco 4215 NCLT alkaline cleaner at 43 ± 5^0C for five to ten minutes. An optional surface activation step, consisting of immersion in 0.05 M sulfuric acid containing 0.02 M thiourea at ambient temperature for ten minutes, would follow the alkaline cleaning in some instances. Another optional pre-treatment step was when the aluminum substrates were deoxidized using a solution containing two point five weight percent Amchem #7 and ten volume percent nitric or sulfuric acid at ambient temperature for five minutes. In all cases, the panels were thoroughly rinsed with deionized water prior to coating.

The electrolyte was prepared by dissolving ten grams $CeCl_3$ into a solution containing 40g $NaClO_4$, 0.45g hydrogen peroxide (30%), and 200g distilled deionized water. The resulting pH of the solution was typically about four point five. The dip solution may contain additional

additives, in varied concentrations from 0.01 to 0.11 wt%. Defoaming agents (Surfonyl's DF-75, Air Products) and surfactants (Triton CF-10 and X-100, Rohm & Haas) were used as additives.

For buffering studies, borate was chosen because it would not form an insoluble precipitate under the conditions used for the standard dip coating process. The source of the borate was boric acid, which upon addition to the standard cerium dip electrolyte did not change the initial pH of the solution significantly. In studies on the effect of solution Al^{+3} concentration on the coating, $AlCl_3$ was used. This was used to keep from introducing a different anion to the solution. The change in chloride concentration would be negligible.

The AA substrates were immersed in the cerium electrolyte at room temperature for five to twenty minutes, with ten minutes being optimum. The substrate was oriented in the beaker containing the cerium solution at a 45^0 angle. The side of the aluminum panel which faced down was referred to as the bottom side. Similarly, the side which faced up was referred to as the top side. After deposition, the cerium coatings were rinsed with deionized water. Immediately after rinsing, some coatings were sealed at 120^0C by immersion in a two point five weight percent Na_3PO_4 solution at a pH of four point five for five minutes. The panels were then double rinsed with distilled water and allowed to air dry.

The surface morphologies and compositions of coated specimens were studied using either a Hitachi S-4700 or JEOL T330A scanning electron microscope. The goal was to correlate variations in the structure to processing conditions.

The corrosion resistance of the cerium conversion coatings was evaluated in accordance with ASTM B-117 neutral salt fog. The typical sample size was 1.5" x 3" x 0.04" panels. The edges and backsides of the panels were covered using a non-conductive tape after deposition, and exposed to salt fog for 336 hours.

IV.3. Results and Discussion

IV.3.1. Optimized Cerium Dip Coating Process

A spontaneous cerium dip process which can improve the corrosion resistance of an aluminum alloy substrate has been developed. The best corrosion resistance was obtained using a high temperature alkaline cleaning step in conjunction with a boiling sodium phosphate seal. The alkaline cleaning step consisted of immersion in a solution of Turco 4215 NCLT at an

increased temperature of 55-63^{0}C for five minutes. The AA 7075-T6 panels were immersed in the standard cerium electrolyte for ten minutes. After cerium deposition, the panels were rinsed with distilled water and sealed at 120^{0}C using a two point five weight percent Na_3PO_4 solution at a pH of four point five for five minutes. The cerium conversion coatings prepared using this process had a passing rate of 90% for four days, 60 % for seven days, and 20 % for two weeks after neutral salt fog exposure. To date, no other spontaneous cerium conversion coating process has provided as much corrosion protection while still being easy to top coat. The following is a detailed description of variables that were evaluated and characterized which lead to the development of the current spontaneous cerium conversion coating.

IV.3.2. Substrate

To minimize the effect of substrate variation often observed from different lots, several sources of aluminum were screened and a large quantity from a single lot was purchased. The lot for this research was manufactured by Kaiser; lot number 243911. The AA surface was relatively smooth and free of excessive, deep roll marks. Energy dispersive spectroscopy (EDS) elemental analysis indicated that the substrate had the specified amounts of alloying elements present. Screening of the substrate using the standard cerium dip coating evaluated in neutral salt fog indicated that the source of aluminum was acceptable for the project.

IV.3.3. Pre-treatment

One of the most important parts of a coating process is how the initial starting substrate is cleaned, or pre-treated. Though a substrate may be pre-treated in several ways based upon the conversion coating to be deposited, the most favorable surface pre-treatment for the cerium dip process is immersion in an alkaline cleaner. The cleaner used initially was Turco's 4215 NCLT at 43$\pm$5^{0}C for five to ten minutes. The cleaner removes much of the grease and shop oils without etching or excessive surface attack as shown in Figure IV.1. More recently, the temperature was increased, which improved corrosion resistance.

After degreasing, an optional surface activation step may be used to accelerate the deposition process by slightly etching the metal surface. The substrate is activated by immersion in a 0.05 M sulfuric acid solution containing 0.02 M thiourea at ambient temperature for ten minutes. The activation step is particularly useful when a low etch de-oxidation is desired. The resulting surface is only slightly etched, as shown in Figure IV.2. This mild attack of the

aluminum surface is believed to remove some of the native oxide layer and increase the surface area of the substrate allowing for cerium to deposit much quicker. Figure IV.3 shows that activating the substrate prior to immersion in the cerium solution allows for a thicker coating to deposit. In some cases the activation step accelerated the cerium deposition process too much, resulting in an uniform coating with poor adhesion. Inhibitors/additives, such as thiourea, have been incorporated into the activation solution to passivate exposed intermetallics on the surface, which allows for a slightly slower, more uniform cerium coating to grow.

In place of activation, the substrate may be deoxidized after alkaline cleaning using a solution containing two point five weight percent Amchem #7 and ten volume percent nitric or sulfuric acid at ambient temperature for five minutes. Though this pre-treatment is necessary for the nucleation and growth of a good chromate conversion coating, the extent of surface attack and exposure of grain boundaries (Figure IV.4) as well as the residual acidic pH seems to be undesirable for the cerium deposition process based on the salt fog corrosion pass rate of cleaned/deoxidized/coated panels.

IV.3.4. Mechanism for Cerium Deposition

The mechanism for nucleation and growth of the cerium dip coatings is similar to that of the electrolytic process in the sense that hydrogen is evolved, the local pH at the aluminum surface rises, and cerium precipitates. However, where the electrolytic process evolves hydrogen by cathodically polarizing the working electrode, in the cerium dip process the presence of chloride attacks the aluminum surface forming local anodes which becomes the driving force to evolve hydrogen at local cathodes. Figure IV.5 provides an SEM sequence of cerium nucleation and growth.

To better understand the initiation of the coating, a piece of AA 7075-T6 was immersed in the standard cerium dip solution for three seconds. Nucleation sites were identified visually on the SEM, and characterized using EDS for elemental analysis. The areas identified as nucleation sites would give a measurable cerium (Ce) content. Ce was not detected on the areas that did not appear to have a coating. The most important thing in these analyses is the composition of the substrate. Due to variable amounts of oxide (partly depending on whether or not a Ce conversion coating was present), oxygen (O) was removed along with Ce from the analyses and the data was normalized, as shown in Tables 1 and 2. After doing this, copper (Cu)

seems to be the only major alloying element whose concentration seems to correlate with the nucleation of the cerium conversion coating. The Cu concentration in Table 2 is quite variable. This can be explained as variation in size of Cu containing intermetallic sites. Size of intermetallics is comparable to activation volume for EDS, so Al, O, and alloying elements are detected in addition to Ce and underlying intermetallic precipitates. Nucleation was favored at Cu rich sites since they were usually cathodic to the surrounding substrate.

IV.3.5. Solution Chemistry

The standard electrolyte for the spontaneous cerium dip process consisted of 0.16 M (4 wt%) $CeCl_3$, 1.1 M (16 wt%) $NaClO_4$ and 0.05 M (0.18 wt%) hydrogen peroxide. The resulting pH of the solution was typically about four point five. Once the substrates were properly pre-treated, they were rinsed with distilled, deionized water and immersed in the cerium electrolyte for deposition times between five to twenty minutes, with ten minutes being optimum based on film thickness (~ 250 nm) and adhesion to the substrate. The presence of $NaClO_4$, a second oxidizing agent, allowed for the coatings to grow more uniformly.

Though the deposited coatings were uniform, they failed in less than three days exposure to salt spray. One plausible reason was thought to be due to hydrogen evolution sites, where the H_2 bubbles would stick to the surface, preventing a sufficient coating to grow in its place. This led to the incorporation of additives into the electrolyte in an attempt to change the surface tension of the solution and modify the nucleation and growth of the cerium deposits.

The first additive used was a defoaming agent, Surfonyl DF-75, which was employed to lower the surface tension and remove bubbles from the aluminum surface which would improve cerium transport at the substrate/solution interface. This resulted in the formation of an organic/cerium residue which spontaneously deposited on the bottom side of each test panel. The bottom side became extremely hydrophobic due to the formation of an organic layer on the substrate's surface along with the cerium. As shown in Figure IV.6, the resulting surface is less cracked/dehydrated compared to cerium deposits made with no defoamer present in the electrolyte.

Other surfactants, such as Triton CF-10 and X-100, were used in the electrolyte in place of the DF-75 in an attempt to remove bubbles from the surface and improve cerium transport. The resulting coatings were not hydrophobic, and also failed in salt fog.

Gelatin, which was very successful in improving the electrolytic cerium deposits, was added to the cerium solution in an attempt to modify the nucleation and growth rates. The addition of gelatin was not successful, because the gelatin precipitated the cerium excessively upon addition of hydrogen peroxide into the electrolyte prior to introducing the metal substrate to be conversion coated.

Chelating agents, such as ethylenediaminetetraaceticacid (EDTA), which could bind cerium preferentially based upon valence at specific pH ranges were used to prevent excessive build up of cerium precipitates, that form at sites other than the aluminum surface in the standard dip process. Inhibition of precipitation is needed because cerium in the solution will easily precipitate at pH values near four point five in the presence of hydrogen peroxide altering the cerium concentration during the coating process. Formation of a water soluble complex between EDTA and Ce^{+3} prevented undesirable cerium precipitation in the bulk solution. The EDTA complex is stable up to a pH of eight to nine, where sufficient OH^- anions were present to weaken the Ce/EDTA ligands. Under the alkaline conditions present at the aluminum surface, the Ce/EDTA complex became unstable and cerium was released. However, initial salt spray results for Ce/EDTA-based conversion coatings were not promising. More research will be done with EDTA and other such complexing agents.

The affect of the anion on the solution chemistry and coating performance was also evaluated. A halide free cerium electrolyte has been developed to remove $NaOCl_4$ and replace

$CeCl_3$ with $Ce(NO_3)_3$. The morphology of the coatings produced from Cl-free solutions changes greatly when $Ce(NO_3)_3$ was used (Figure IV.7). The cerium precipitates were less spherical and more gelatinous.

Buffering the electrolyte also affected coating morphology and performance. Since the deposition of the cerium conversion coating is driven by pH, it was decided to try controlling deposition by adding a buffer to the solution. Borate was used because it will not form an insoluble precipitate with cerium as phosphate would under the conditions used for the dip coating.

Visually, the higher buffer concentrations seemed to slow the coating rate. Using SEM, morphology was seen to change going from a concentration of one point four to thirteen grams per liter boric acid in the dip solution (Figure IV.8). Salt spray results were poorer for the highest borate concentration, which seems to correlate with the SEM images of the morphology change.

The concentrations of Al^{+3} in solution can greatly change coating performance and morphology, as well (Figure IV.9). It is believed that the anodic reaction of the dip coating process involves dissolution of aluminum. The question then becomes what effect does increasing Al^{+3} concentration in the solution have on the cerium conversion coating. A set of experiments was carried out that showed a significant change in morphology when going from an Al concentration of eight to seventy five parts per million. Negative salt spray results correlated with the changes in morphology seen by SEM as aluminum concentration was increased. At the 270 ppm level, large (several microns across) crystalline deposits were observed. EDS analysis of these areas showed them to be aluminum chloride.

IV.3.6. Sealing

Sealing at 120^0C in a two point five weight percent Na_3PO_4 solution at a pH of four point five for five minutes was found to be a critical step for ensuring good corrosion resistance for the electrolytic process. The idea was to "seal" the cerium deposit, as well as any bare aluminum surface, similar to what is done for anodized aluminum processes. For the electrolytic cerium process, the sealing step was absolutely necessary for obtaining good salt spray performance. For the cerium dip coating process where the temperature of the alkaline cleaner is 43 ± 5^0C, the use of a sealing step is not necessary. When the substrate was cleaned at 43^0C, there was no

clear improvement in corrosion resistance with sealing the cerium deposit. However, when the pre-treatment step using Turco 4215-NCLT was modified by increasing the cleaning bath temperature from 43^{0}C to 55 - 63^{0}C, the sealing of the resulting cerium deposit greatly improved the corrosion resistance of the spontaneous cerium conversion coating.

IV.3.7. Neutral Salt Fog Evaluation

The corrosion protection of the cerium-based deposits were evaluated by exposing them to neutral salt fog in accordance with ASTM B-117 for 336 hours. Samples were removed from salt fog, rinsed, and evaluated at four, seven, and fourteen day intervals in order to record their performance.

The spontaneous cerium conversion coatings were easily top coated with a primer; however, the cerium conversion coating by itself had very poor corrosion resistance, failing salt fog in less than three days. Cerium coatings prepared using defoaming agents performed much better in salt fog testing. This hydrophobic/organic layer, if undisturbed, could pass 336 hours in salt fog. In fact, it could last for as long as three to four weeks before the nucleation of pits occurred. However, the hydrophobic layer was oily and adhesion of the top coat using a water based primer was poor. The only ways to successfully top coat the hydrophobic protective layer would be to mechanically swab it away, which would destroy its corrosion resistance, or to raise the viscosity of the paint.

Cerium conversion coating prepared using an elevated alkaline cleaning temperature of 55 - 63^{0}C for five minutes, immersion in the standard dip solution for ten minutes, and sealed in a boiling sodium phosphate solution for five minutes had a passing rate of 90% for four days, 60 % for seven days, and 20 % for two weeks after neutral salt fog exposure. The resulting cerium conversion coatings exhibited excellent paint adhesion, and prevented the nucleation of blisters near the scribe, as well as in the field.

IV.4. Summary Of Spontaneous Cerium Conversion Coating Process

A spontaneous process to form cerium conversion coatings that can successfully pass four days neutral salt spray has been developed. By determining the proper pre-treatment step, the types of additives present in the electrolyte, and the sealing steps, the rate of nucleation and growth, as well as the morphology of the resulting coatings, can be controlled. The ultimate goal was to obtain a pre-treatment, electrolyte, additive, and/or sealing step which minimized any

undesired effects of substrate alloying resulting in a cerium conversion coating which can pass 336 hours salt fog.

Use of an elevated alkaline cleaning temperature of 55 - 63^{0}C in conjunction with a sodium phosphate sealing step greatly improves the corrosion resistance of the spontaneous cerium conversion coatings.

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Table IV.1. Concentrations in atomic % for bulk uncoated surface with O removed from the EDS analyses.

Element	Al	Mg	Cu	Zn
Area 1	94.4	2.6	0.7	2.3
Area 2	93.3	3.6	0.7	2.5
Area 3	94.3	2.7	0.8	2.2
Area 4	95.0	2.4	0.7	2.0
Area 5	94.8	2.7	0.6	1.9

Table IV.2. Concentrations in atomic % for nucleation sites with Ce and O removed from the EDS analyses.

Element	Al	Mg	Cu	Zn
Area 1	92.6	2.9	1.6	2.3
Area 2	92.7	2.8	2.1	2.3
Area 3	93.4	2.8	1.3	2.3
Area 4	91.5	4.0	1.6	2.6
Area 5	93.9	2.7	1.1	2.3

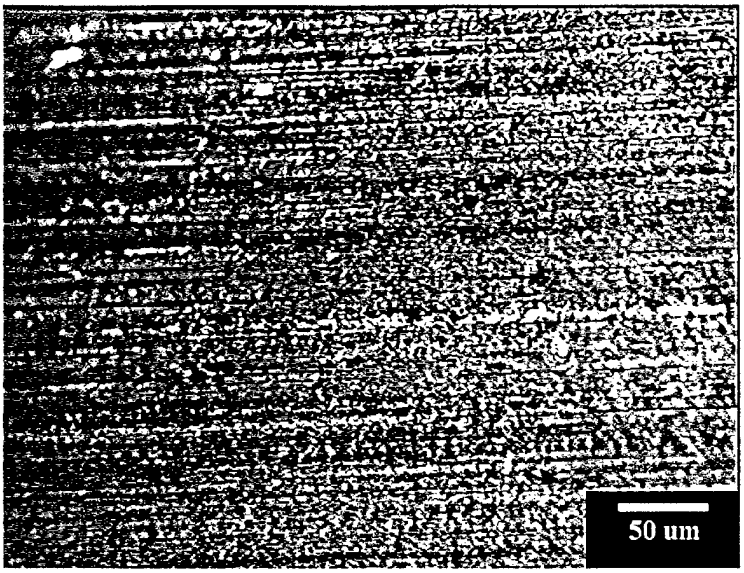


Figure IV.1. Aluminum alloy 7075-T6 surface cleaned using Turco 4215 NCLT At 43°C for 5 minutes.

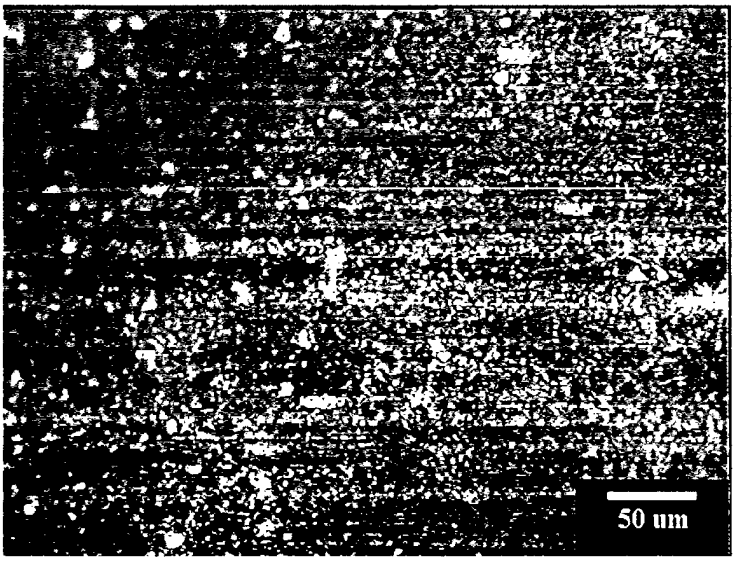
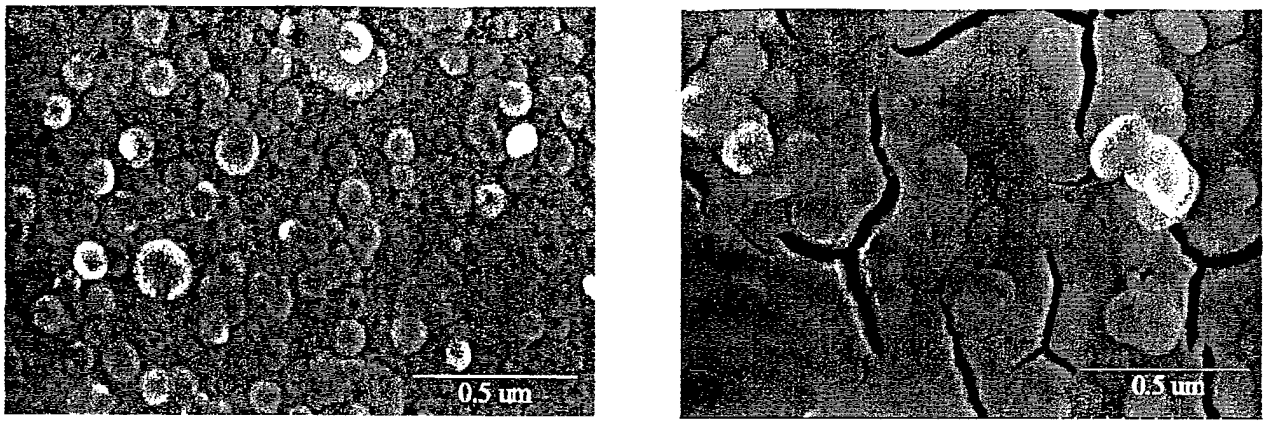


Figure IV.2. Aluminum alloy 7075-T6 surface activated using 0.05M sulfuric acid containing 0.02 M Thiourea at 25°C for 10 minutes.



(a) (b)

Figure IV.3. SEM micrographs illustrating the effect of activation on surface morphology and film formation by spontaneous method: (a) 10 minute deposition on cleaned only AA 7075-T6; (b) 10 minute deposition on cleaned, acid-activated AA 7075-T6.

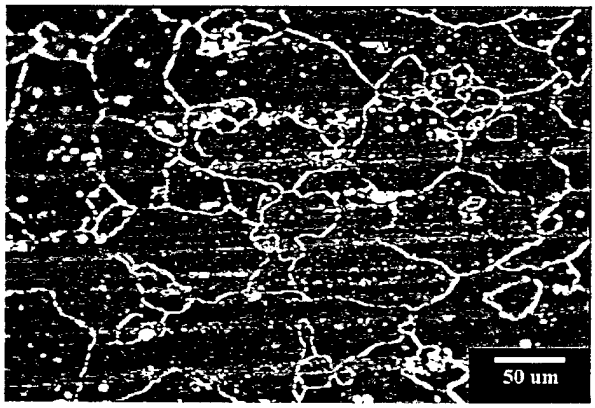
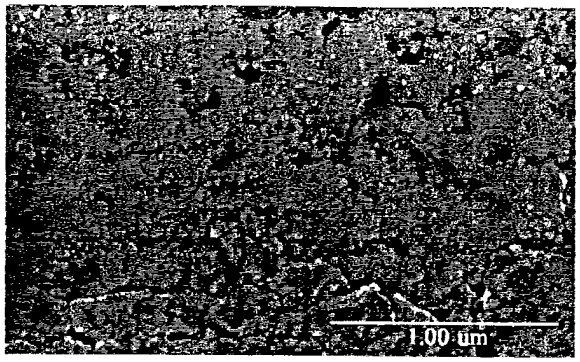
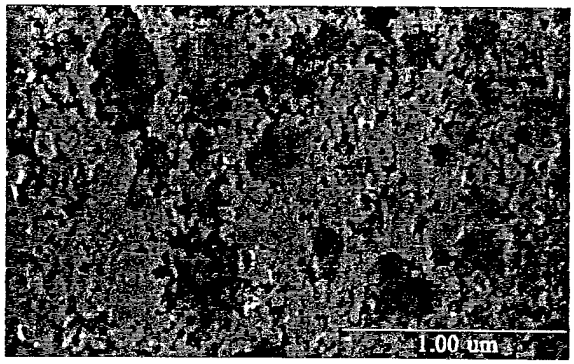


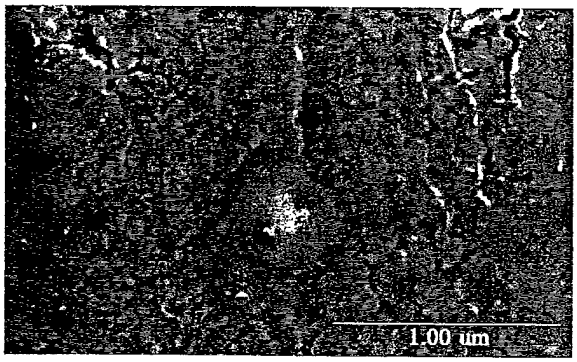
Figure IV.4. Aluminum alloy 7075-T6 surface de-oxidized using Amchem 7 At 25°C for 5 minutes.



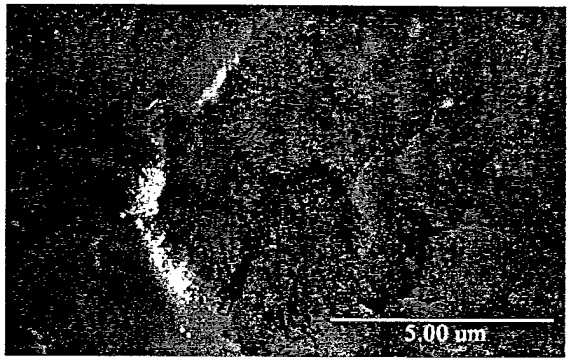
(a)



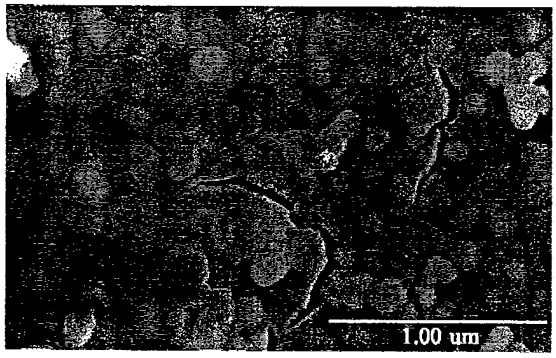
(b)



(c)

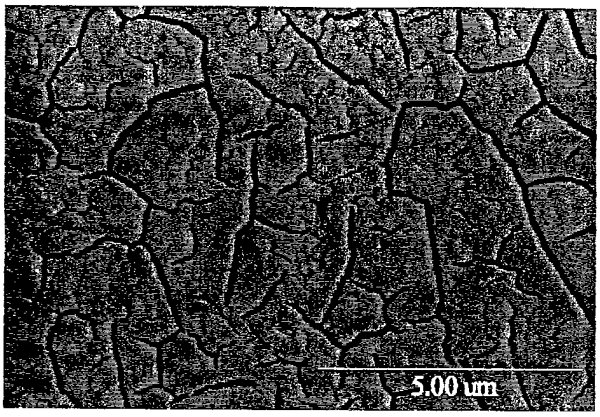


(d)

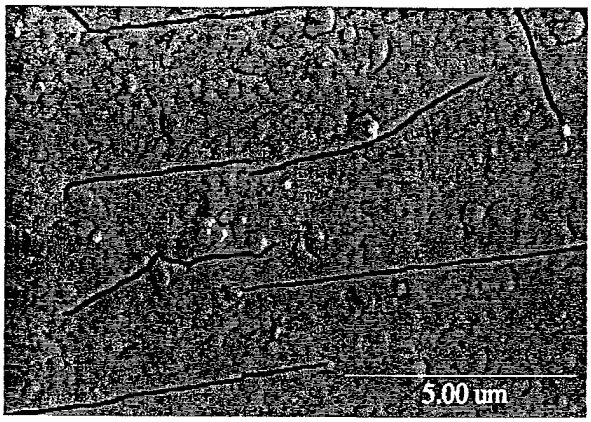


(e)

Figure IV.5. SEM micrographs illustrating the deposition morphology for the spontaneous cerium conversion coating on AA 7075-T6 at: (a) 0; (b) 3; (c) 6; (d) 60; and (e) 600 seconds immersion.

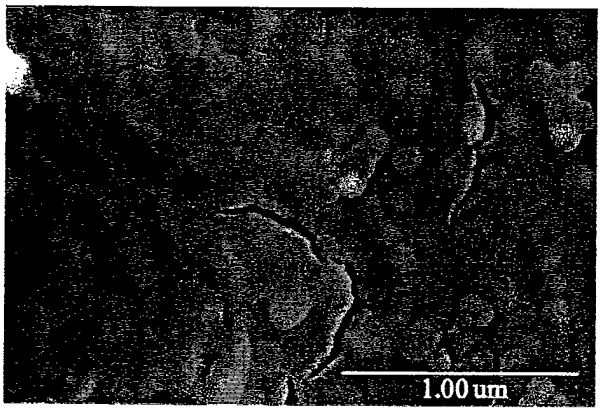


(a)

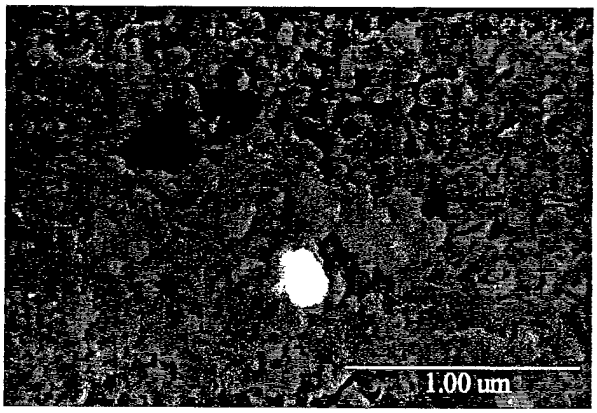


(b)

Figure IV.6. SEM micrographs illustrating the effect of additives on surface morphology and film formation by spontaneous method: (a) 10 minute deposit with no additive; (b) 10 minute deposit with additive in dip solution.



(c)



(d)

Figure IV.7. SEM micrographs illustrating the effect of anions on surface morphology and film formation by spontaneous method: (a) 10 minute deposit using $CeCl_3$; (b)10 minute deposit using $Ce(NO_3)_3$ in dip solution.

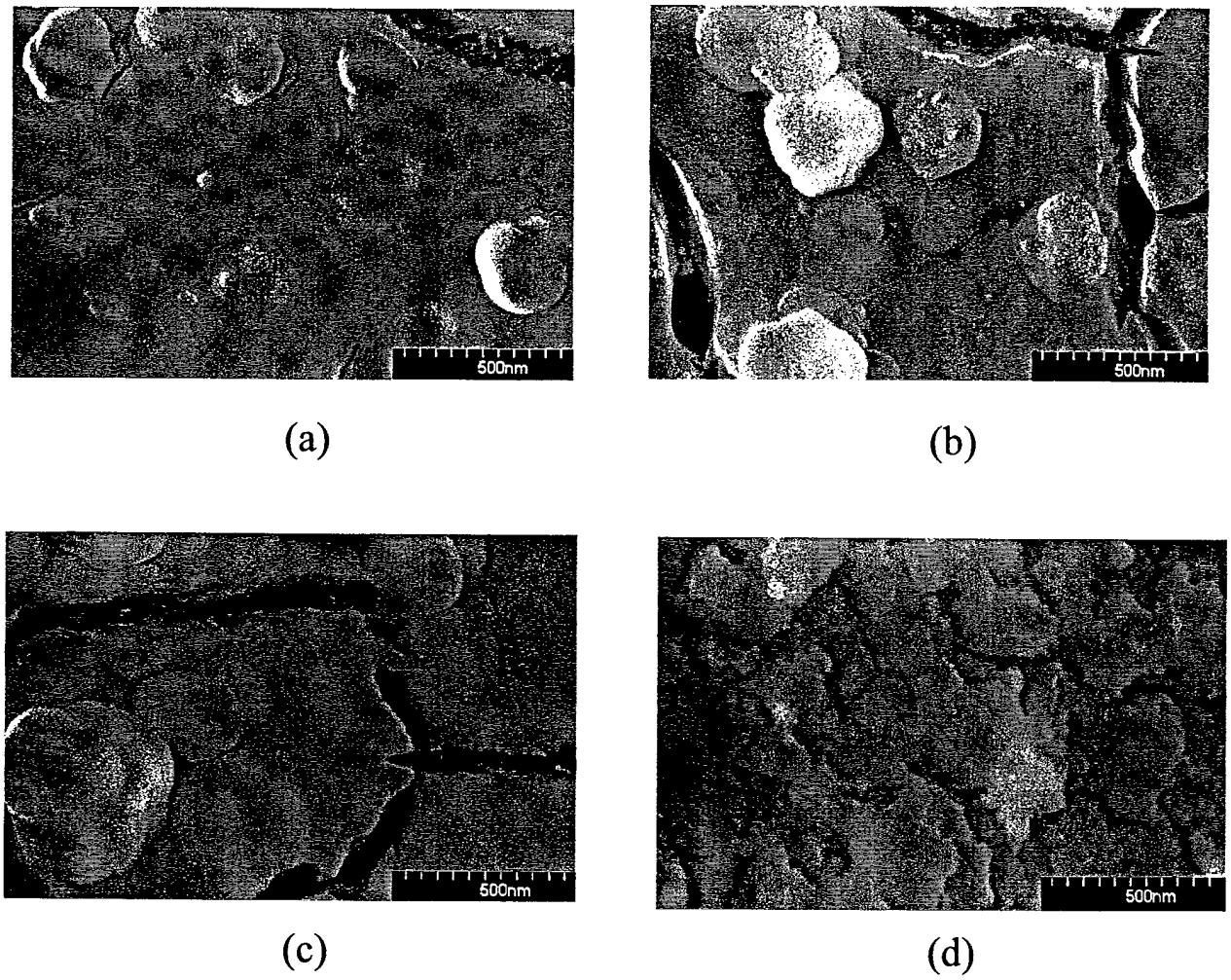


Figure IV.8. Effect of borate (added as boric acid, H_3BO_3) additions to dip coating solution. Boric acid concentrations are: (a) 0 g/L boric acid, (b) 0.1 g/L, (c) 1.4 g/L, and (d) 13 g/L.

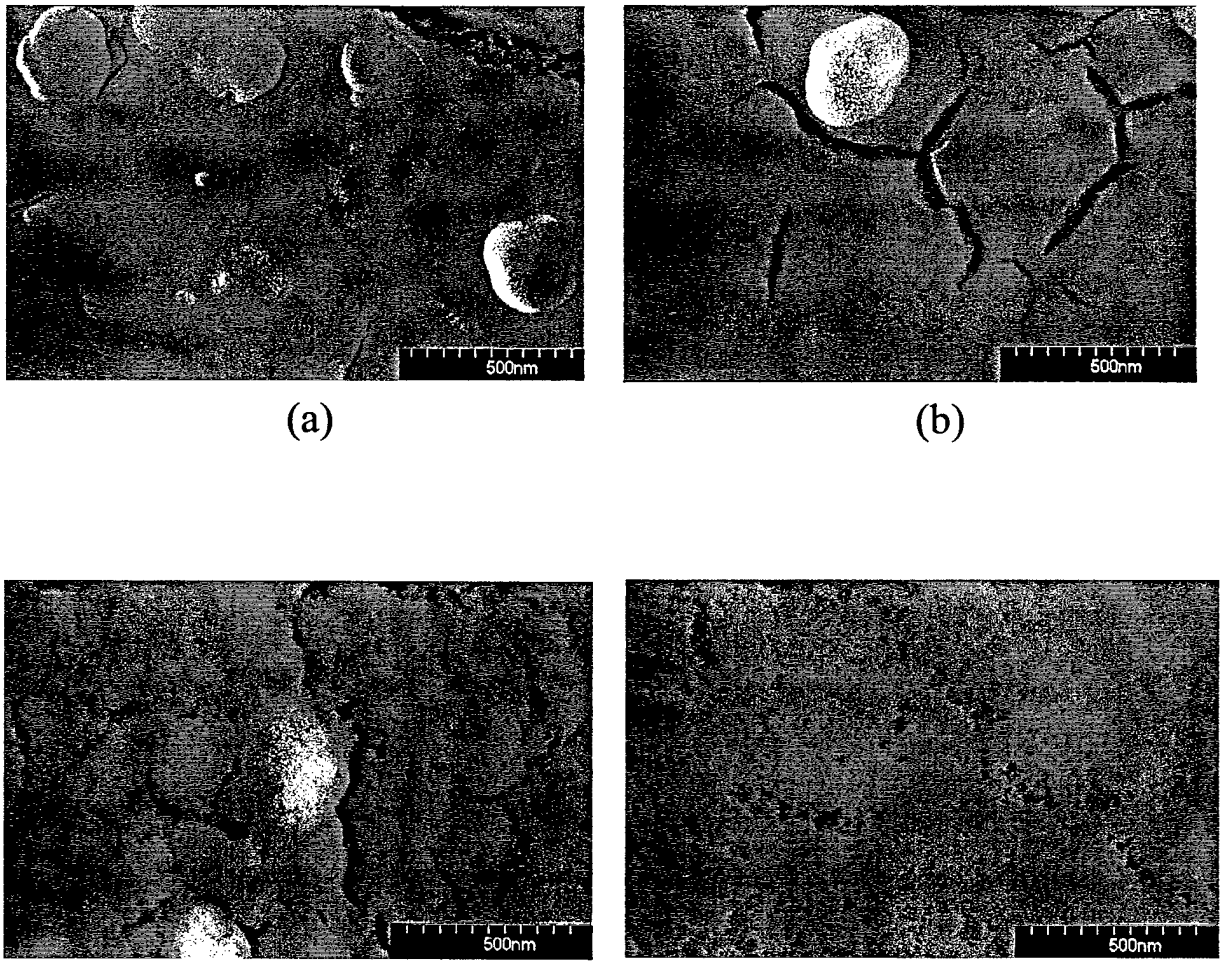


Figure IV.9. Effect on coating morphology from additions of Al^{3+} to the coating solution. Concentrations of aluminum used to produce each morphology: (a) 0 ppm, (b) 8 ppm, (c) 75 ppm, and (d) 270 ppm.

Section V. Characterization of Cerium-Based Conversion Coatings

The broad aims of the characterization effort have been to correlate the structure and composition of cerium-based conversion coatings to salt fog corrosion performance and to understand the effect of substrate pre-treatment on the deposition, structure and performance of cerium-based coatings. This document summarized results of scanning electron microscopy (SEM) with energy dispersive spectroscopy (EDS), x-ray photoelectron spectroscopy (XPS), and electrochemical evaluation of 7075-T6 test panels and cerium-based conversion coatings. Dr. John Grant of UDRI/AFRL performed all of the XPS analysis and contributed significantly to XPS analysis.

V.1. Physical Characterization of Cerium-Based Conversion Coatings

Abstract

Cerium-based conversion coatings were deposited on aluminum alloy substrates by three different methods, a current-driven (electrolytic) process, a spontaneous dip reaction with a solution, and sputter deposition. Coating morphology was examined using SEM and coating chemistry was characterized using XPS. It was found that coating adhesion depended on proper surface pre-treatment (i.e., alkaline degreasing or alkaline degreasing plus deoxidation). Spontaneous coatings grew by a nucleation and growth process and their performance in salt fog testing was improved by proper pre-treatment and sealing. Sputter deposited coatings consisted of nano-crystalline CeO_2. As-deposited coatings produced by all three deposition methods contained mainly Ce^{4+}. For all coatings, sealing converted Ce^{4+} to Ce^{3+} and improved performance in salt fog corrosion testing.

V.1.1. The Effect of Surface Pre-treatment

The effect of surface pre-treatments on the morphology, composition, and performance of conversion coatings was investigated for spontaneous and sputter deposited coatings. Surface treatment affected the adhesion, surface morphology, and performance of conversion coatings. The pre-treatments that were examined were desmutting (acetone rinse), degreasing (alkaline cleaning with Turco NCLT), and deoxidation (standard deoxidation with Amchem 7 or an alternate process with an H_2SO_4-based acid activation).

The effect of pre-treatment on the surface chemistry of test panels was investigated by dipping panels into a suspension of CeO_2 spheres after various pre-treatments. This was a suspension of nano-sized crystalline CeO_2 particles, not a standard coating solution. The first

pre-treatment that was examined was a simple acetone rinse. Presumably, acetone has little effect on the chemical structure of the 7075-T6 surface; it simply removed physical deposits such as accumulated dust, oils, and inks along with any residual adhesive from the protective plastic coating that was applied by the manufacturer to prevent surface damage during shipping. After the acetone rinse, CeO_2 spheres attached to specific areas of the panel like the bottom of scratches (Figure V.1.1a) and other isolated areas around the surface (Figure V.1.1b). After acetone rinsing and cleaning followed by deoxidation or acid activation, the spheres were found distributed uniformly around the surface with no preferential deposition at any surface features. This test was an indication that deoxidation or acid activation altered the chemistry of the aluminum alloy surface and produced a much stronger interaction (presumably electrostatic in nature) with CeO_2. The more aggressive pre-treatment produced a more uniform surface.

Spontaneous and sputter deposition processes were used to form cerium-based coatings on Al 7075-T6 test panels after acetone rinsing. In both cases, adhesion was poor. Figure V.1.2a shows a spontaneous coating on an acetone-rinsed test panel. The coating had multiple cracks (present prior to insertion in the SEM) and areas where the coating had flaked off, revealing the underlying test panel. Figure V.1.2b shows a sputter deposited CeO_2 coating on an acetone rinsed test panel. Again, adhesion appeared to be poor and cracks were apparent in the coating. Adhesion of conversion coatings to test panels requires alteration of the composition or structure of the alloy surface, not just removal of contaminants.

Alkaline cleaning followed by deoxidation or acid activation significantly improved the adhesion of both spontaneous and sputter deposited coatings on 7075-T6 test panels. This more aggressive surface treatment also changed the morphology of coatings that were subsequently deposited. Comparison of the surface morphology of spontaneous coatings on an acetone rinsed test panel (Figure V.1.3a) to one on a panel that had been alkaline cleaned and acid activated (Figure V.1.3b) revealed striking differences (note that the images have significantly different magnifications). First, the coating on the cleaned/activated substrate was free of cracks and peeled areas. This was an indication that the coating had better adhesion to the substrate. The coating on the acetone-rinsed substrate nucleated preferentially at the tops of the roll marks. The lighter colored lines in Figure V.1.3a are composed of Ce-rich nodules. On acetone rinsed substrates, the nodules were present only on the tops of roll marks on the substrates. There was no preferential distribution of the Ce-rich nodules on cleaned, acid activated substrates. Coatings

on cleaned, acid-activated substrates also had superior corrosion resistance. Spontaneous dip coatings with an organic additive on cleaned, acid-activated substrates provided corrosion protection for the duration of a 336 hour test in salt fog, whereas coatings on acetone rinsed substrates always failed within 336 hours. Similarly, sputter deposited coatings had better adhesion and more uniform appearance on cleaned and acid activated substrates compared to acetone rinsed substrates.

V.1.2 Growth of Spontaneous Dip Coatings

The growth of spontaneous coatings on 7075-T6 substrates was characterized by SEM. Examination of spontaneous coatings on alkaline cleaned, acid activated 7075-T6 test panels indicated that coatings form by a nucleation and growth process. At very short coating times (30 seconds or less) small, Ce-rich nuclei are observed on panel surfaces (Figure V.1.4a). Small, distinct Ce-rich deposits are seen along with larger, "fuzzy" deposits. For surfaces that were treated by alkaline cleaning and acid activation, these deposits were uniformly distributed around the surface of the test panel. For surfaces that were only rinsed with acetone, nuclei were concentrated in specific areas, such as the tops of roll marks. Growth under the conditions that produce the nuclei observed in Figure V.1.4a produced a coating that was uniform, adherent, and, for the most part, crack free (Figure V.1.4b). The coating consisted of Ce-rich nodules in a cerium-containing matrix, as characterized by EDS. Cleaned, acid-activated substrates immersed in the spontaneous coating solution for 5 to 10 minutes provided the best corrosion protection.

The deposition of spontaneous coatings was affected by the orientation of the panel in the coating solution. Panel orientation during spontaneous coating is shown schematically in Figure V.1.5. During salt fog testing, the performance of the coating on the bottom or downward facing surface of the panel offered superior corrosion protection compared to the top or upward facing surface. A series of samples were prepared to examine the effect of panel orientation on coating morphology and performance. SEM samples were prepared from opposite surfaces of the same test panel to ensure that coating conditions and surface preparation were identical. Examination after coating for 30 seconds (Figure V.1.6) showed that nuclei had formed on both the top and bottom surfaces. The top surface had far fewer nuclei than the bottom. After coating for 10 minutes, the feature size observed on the top surface (Figure V.1.7a) was larger than that found on the bottom (Figure V.1.7b). The cerium-rich nodules in the top surface coating were ~600

nm in diameter, while those in the bottom coating were approximately 250 nm in diameter. There were also a larger number of cerium-rich nodules on the bottom side as compared to the top side.

Analysis using x-ray photoelectron spectroscopy (XPS) showed that most of the coatings prepared by the spontaneous process contained only Ce^{4+} (Figure V.1.8). However, a limited number of coatings contained a mixture of Ce^{4+} and Ce^{3+}, and one coating contained only Ce^{3+}. The cerium oxidation state appeared to be dependent upon processing parameters. The Ce oxidation states for coatings prepared by 3 different methods are shown in Figure V.1.8. However, no correlation was found between Ce oxidation state and salt fog performance. Some coatings that contained only Ce^{4+} performed well in salt fog testing, while others did not. Likewise some coatings containing a mixture of valence states performed well in salt fog testing while others did not. XPS analysis did show that the spontaneous deposition process rapidly covered the entire surface of 7075-T6 test panels. Examination at multiple spots showed a strong Ce signal and almost no Al signal after 30 seconds of coating (Figure V.1.9). Therefore, in addition to the Ce-rich nuclei observed in SEM (Figure V.1.4a), there was a thin, uniform cerium coating on the Al surface.

Some coatings formed by the spontaneous deposition process were sealed in a boiling solution of sodium phosphate. Sealing increased the proportion of Ce^{3+} in the coatings, but some Ce^{4+} also remained (Figure V.1.10). Sealing also increased the Al signal from the sample, in agreement with EDS analysis for the electrolytic coatings (Section III). Preliminary results have shown that sealing can improve salt fog performance, but more work is needed to understand the relationship among processing conditions, oxidation state, and salt fog performance.

V.1.3 Electrolytic Conversion Coatings

The morphology of cerium-based conversion coatings deposited by a current-driven process was investigated (Figure V.1.11). Electrolytic coatings had a mottled appearance to the naked eye and examination by SEM revealed large areas that were cracked and peeling. Figure V.1.11 shows a cracked area that had started to peel away from the underlying layers. The coating appeared to be composed of alternating layers of high and low density material. Examination at higher magnification showed that the coating was made up of spherical clusters around 200 nm in diameter that were composed of even smaller spheres that were less than 50 nm in diameter.

In the as-deposited state, XPS analysis found that electrolytic coatings contained only Ce^{4+} (Figure V.1.12). Aging the coating in air for up to two weeks did not alter the Ce oxidation state. Phosphoric acid sealing altered the predominant oxidation state, producing a coating that was predominantly Ce^{3+}. Once sealed, the Ce^{3+} state was detected on samples after up to 6 weeks in salt fog testing. Sealing also altered the aluminum signal in the XPS spectra. Sputter depth profiling confirmed observations by SEM that the coating thickness varied. Figure V.1.13 compares the sputter depth profiles for thick and thin areas in the same coating. The thickness of the two spots differed by a factor of ~5, but the coating composition was the same. Presumably, the thick spot was an unpeeled point and the thin spot was the bottom of a peeled area.

V.1.4 Sputter Deposition of CeO_2

Cerium oxide coatings were sputter deposited on a variety of substrates, including 7075-T6, glass microscope slides, a thin, pure Al sputter deposited coating on a glass slide, and a thin 7075 Al coating sputter deposited on a glass slide. In all cases, the CeO_2 coatings were polycrystalline with an average grain diameter of ~10 nm, determined by TEM analysis (Figure V.1.14a) and calculation from the peak width in x-ray diffraction using the Scherer formula. The formation of CeO_2 was confirmed by x-ray diffraction of coatings on 7075-T6 test panels and by selected area electron diffraction of TEM samples (Figure V.1.14b). The structure of sputter deposited coatings varied insignificantly with changes in deposition temperature and pressure. Nano-crystalline CeO_2 was the only phase detected in sputter deposited coatings. The deposition rate was 5 nm/min, regardless of the deposition temperature and pressure. These coatings offered little protection during salt fog testing. The apparent path of attack was through pinholes that were found in every sample examined by SEM (Figure V.1.15). Sealing produced slight improvement in salt fog performance, but the corrosion protection offered by sputtered coatings (a few days at best) was inferior to that produced by the other two coating methods.

XPS analysis of as-deposited samples showed that they contained only Ce^{4+} (Figure V.1.16), which is consistent with results from TEM and x-ray diffraction. Due to its thermodynamic stability and insolubility, it was thought that sealing would not affect sputter deposited coatings. However, XPS analysis indicated that sealing converted the sputter deposited coatings from Ce^{4+} to Ce^{3+} (Figure V.1.16). From this measurement, it was not possible to determine if the entire coating was converted, but examination at several locations around the surface found only Ce^{3+}, indicating that a continuous surface layer of Ce^{3+} was

formed. Sealing did not have a significant affect on the aluminum signal as it had in spontaneous and electrolytic coatings.

V.1.5 Summary of Physical Characterization of Cerium-Based Conversion Coatings

The effect of substrate pre-treatment on the surface morphology of spontaneously deposited cerium-based conversion coatings was studied using SEM. Coatings on acetone-rinsed test panels had poor adhesion, significant cracking, and poor performance during salt fog testing. Pre-treatment had a significant effect on the surface morphology of the coating. For coatings on acetone rinsed test panels, cerium-rich, light colored spheres (presumably related to sites of initial coating nucleation) were concentrated on the roll marks of the substrate. Test panels that were alkaline cleaned and acid activated had a much more uniform appearance. For the spontaneous deposition process, alkaline cleaning followed by acid activation provided the best balance of coating time, coating morphology, and the ability of the coating to provide corrosion protection.

Spontaneous deposition of cerium-based conversion coatings proceeded by a nucleation and growth process. Proper surface preparation was required for uniform distribution of nuclei. In addition, nucleation density and the resulting coating structure and cerium oxidation state were affected by process variables, such as panel orientation during deposition. It was found that coatings that were deposited on the downward-facing side of test coupons had a smaller physical feature size and superior performance in salt fog testing. As deposited coatings contained mainly Ce^{4+}. Sealing resulted in a mixture of Ce^{3+} and Ce^{4+}. Sealing improved salt fog performance for most coatings.

Electrolytic coatings always contained cracked and peeled areas. As deposited coatings contained only Ce^{4+} and performed poorly in salt fog testing. Sealing in phosphate solution converted the coating to Ce^{3+} and improved the salt fog performance, allowing coatings to protect for up to 6 weeks in salt fog corrosion testing.

Cerium oxide coatings were sputter deposited on a variety of substrates including 7075-T6 test panels, glass microscope slides, and pure Al or 7075 Al coated glass microscope slides. The coatings were nano-crystalline CeO_2, but always contained pinholes that allowed for rapid attack in standard corrosion testing. These samples indicate that pure, dense, crystalline CeO_2 offers only barrier protection to corrosion. Sealing converted the surface of the coating from Ce^{4+} to Ce^{3+}.

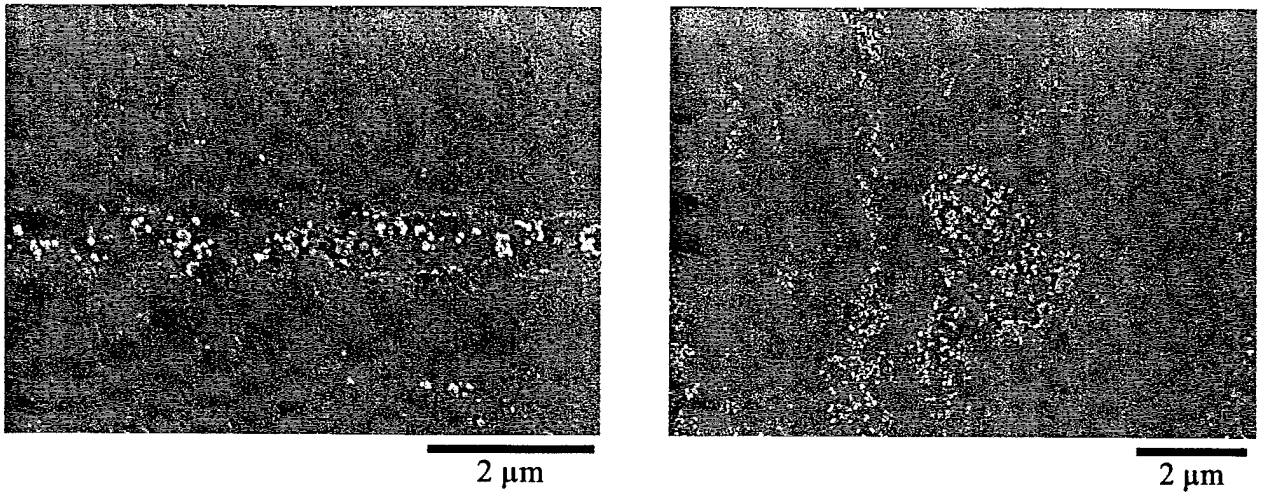


Figure V.1.1. CeO_2 spheres deposited on an acetone rinsed 7075-T6 test panel surface.

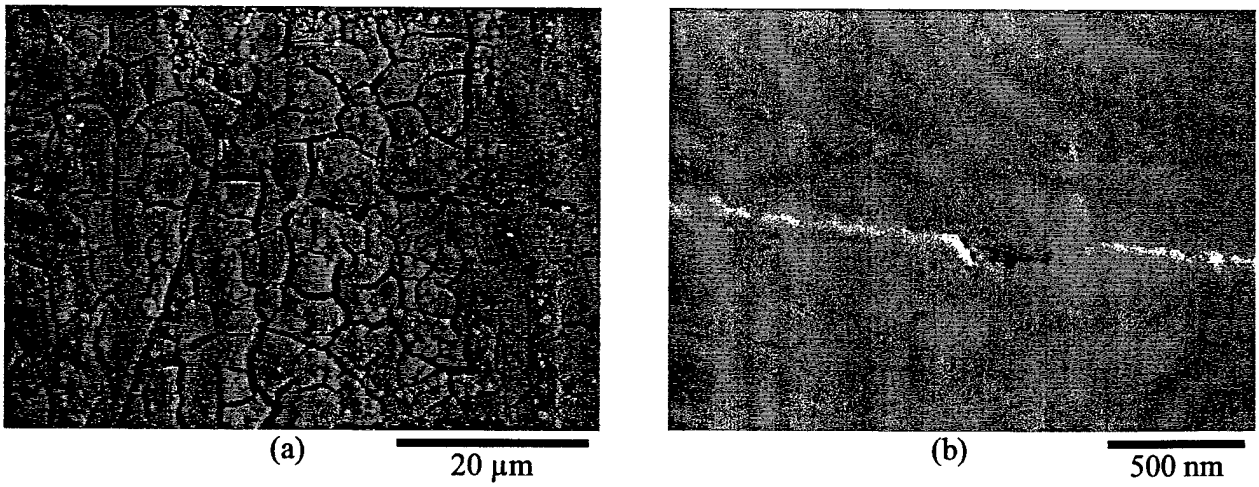


Figure V.1.2. Surface morphology of cerium-based conversion coatings prepared by (a) spontaneous coating and (b) sputter deposition on acetone-rinsed 7075-T6 test panels.

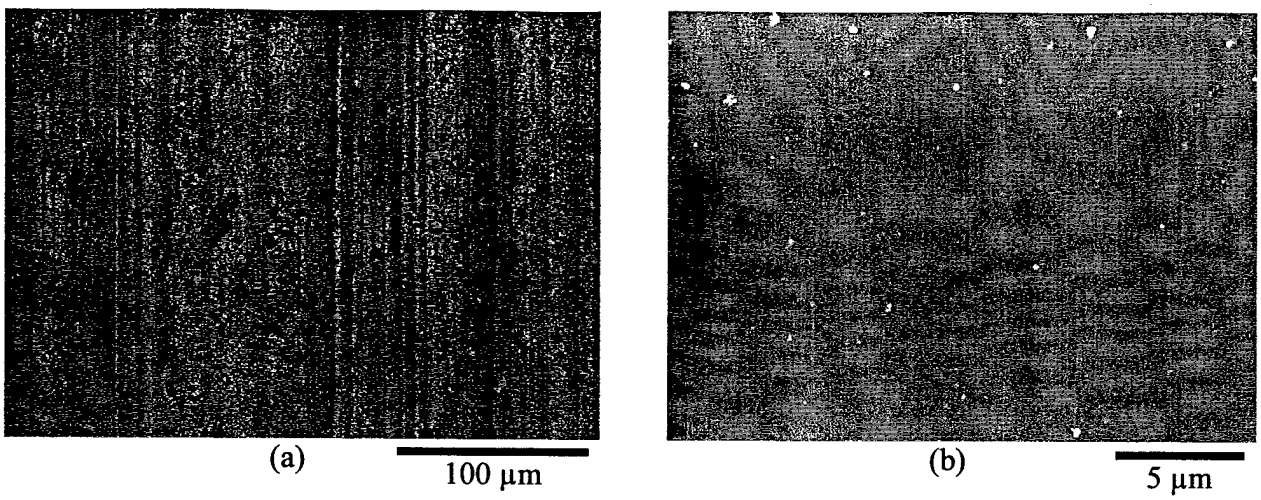


Figure V.1.3. Surface morphology of spontaneous coatings on 7075-T6 test panels that were (a) acetone rinsed or (b) alkaline cleaned and acid-activated prior to deposition.

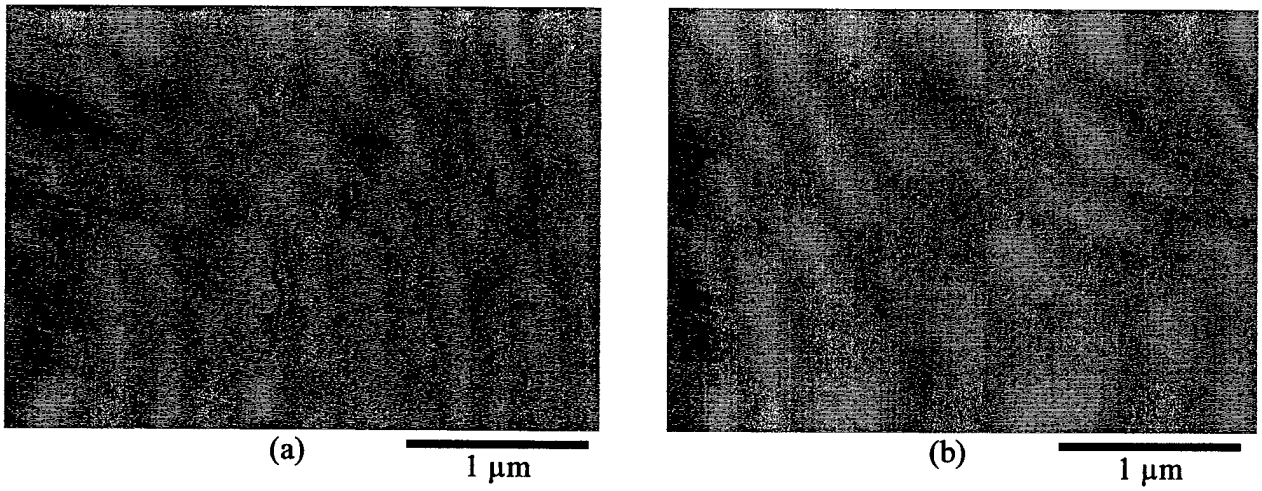


Figure V.1.4. Surface morphology of a spontaneous coating on a 7075-T6 test panel after immersion for (a) 30 seconds and (b) 5 minutes. The panels were alkaline cleaned and acid activated prior to immersion in the coating solution.

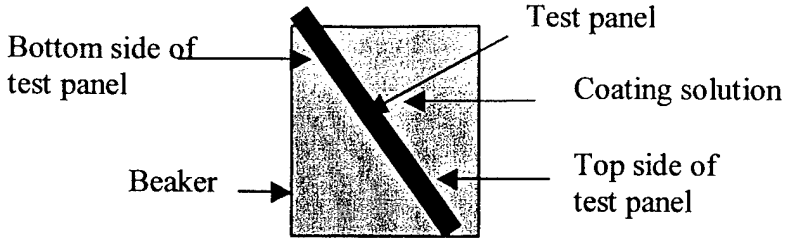


Figure V.1.5. Schematic diagram of the orientation of a test panel in the coating solution.

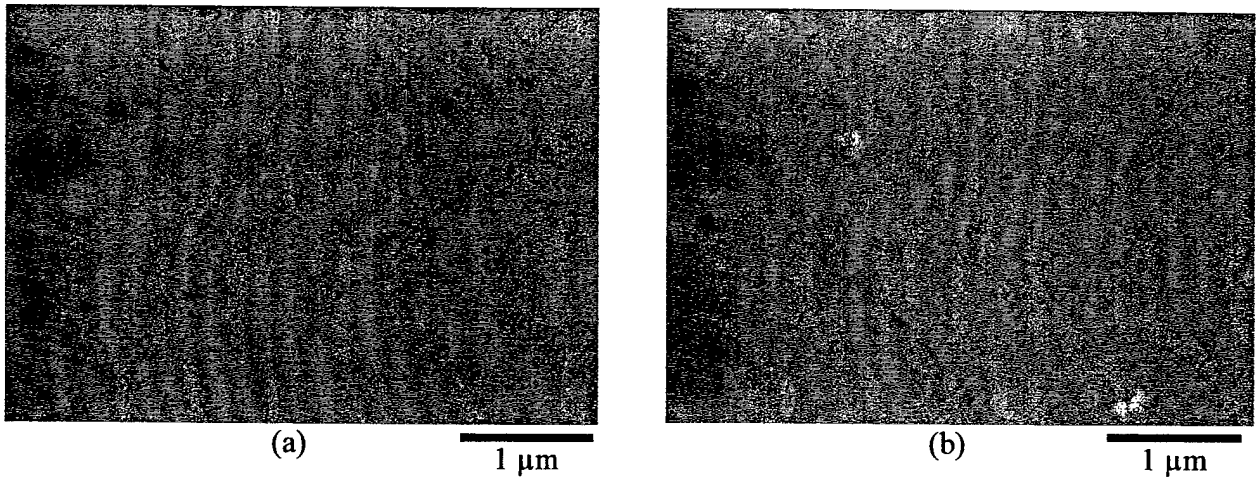


Figure V.1.6. Surface morphology of spontaneous cerium conversion coatings on 7075-T6 test panels after 30 seconds of immersion in a spontaneous coating solution, (a) top side of panel, and (b) bottom side of panel.

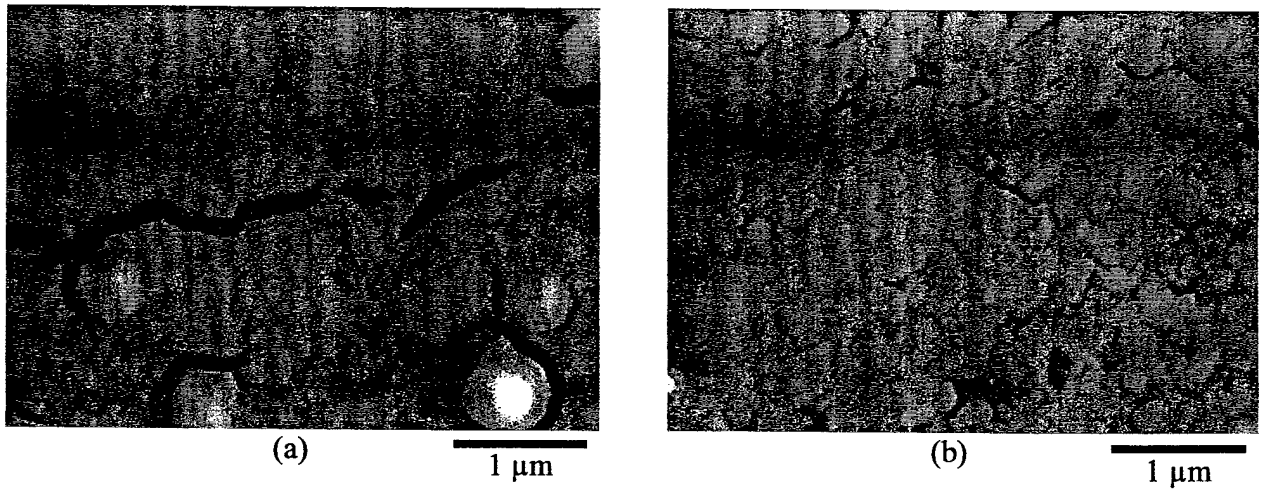


Figure V.1.7. Surface morphology of spontaneous cerium conversion coatings on 7075-T6 test panels after 5 minutes of immersion in a spontaneous coating solution, (a) top side of panel, and (b) bottom side of panel.

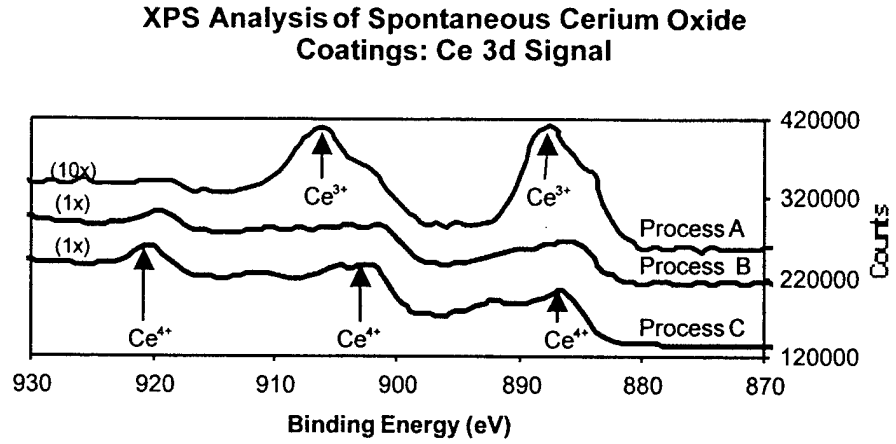
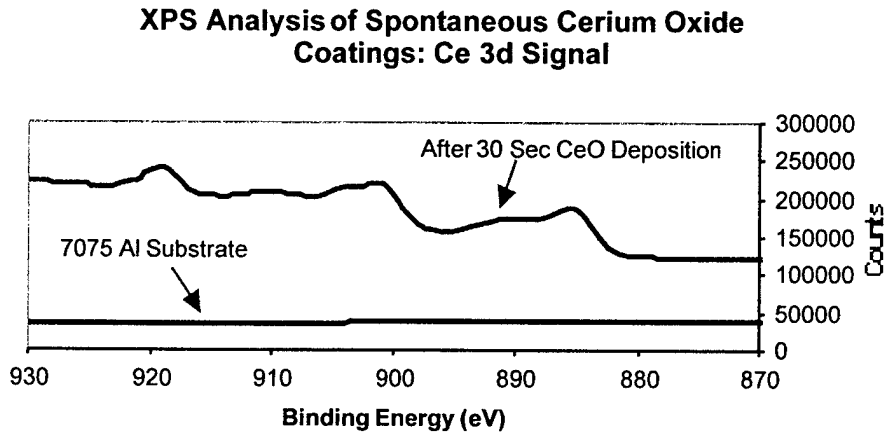


Figure V.1.8. XPS analysis showing the variation in cerium oxidation state in spontaneous cerium conversion coatings deposited under different conditions.



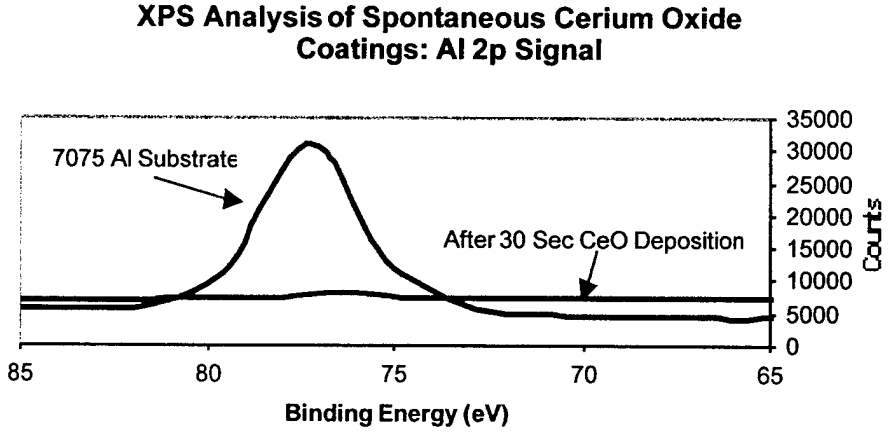


Figure V.1.9. XPS analysis of a 7075-T6 test panel bare (uncoated) and after immersion for 30 seconds in a spontaneous cerium conversion coating solution.

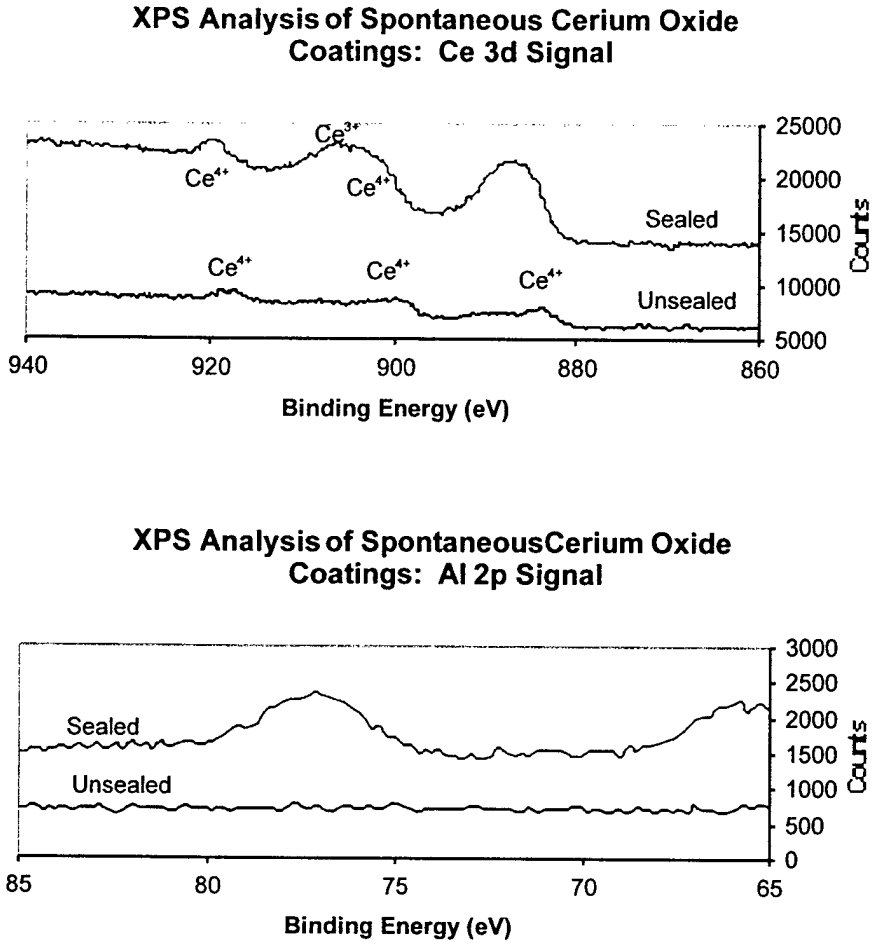


Figure V.1.10. Cerium 3d and Al 2p XPS spectra of spontaneously deposited cerium-based conversion coatings before and after sealing.

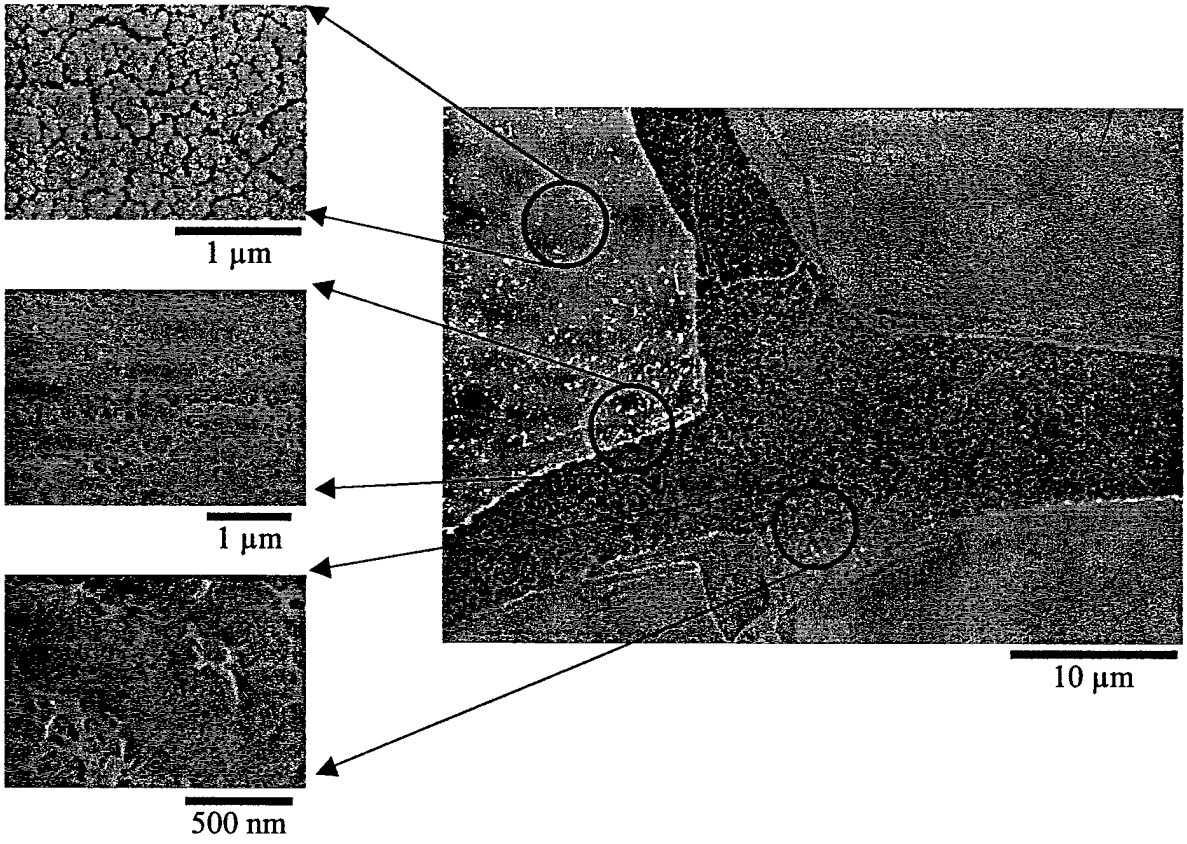


Figure V.1.11. SEM micrographs of a sealed cerium conversion coating deposited by the electrolytic method.

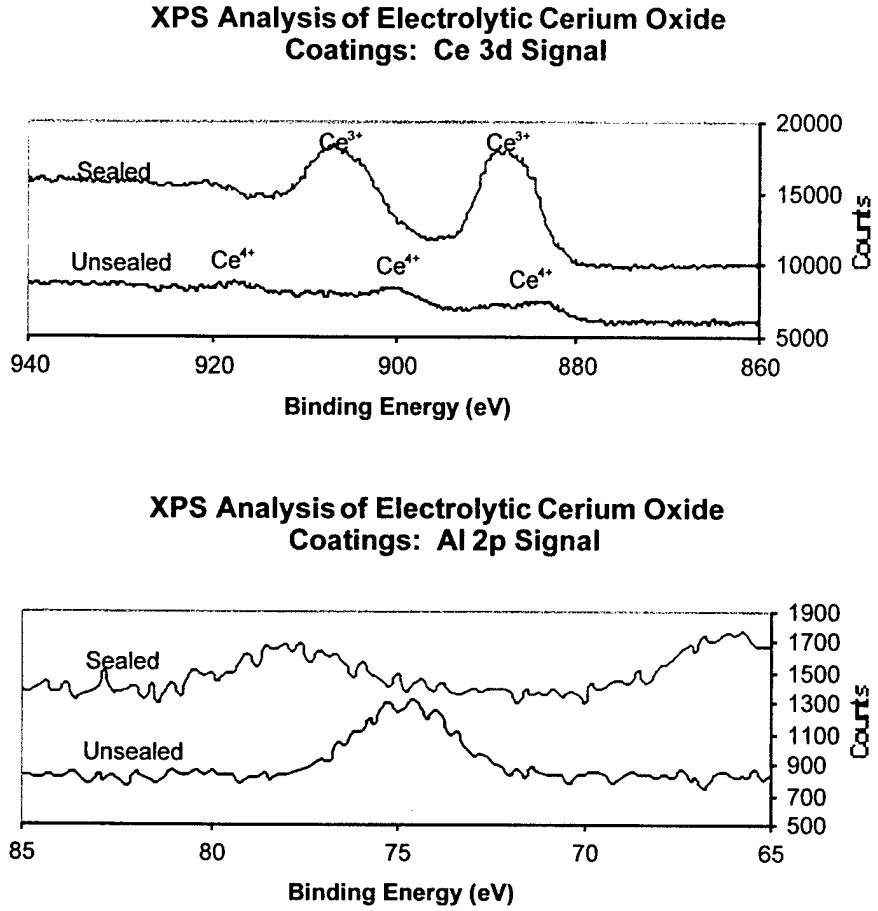
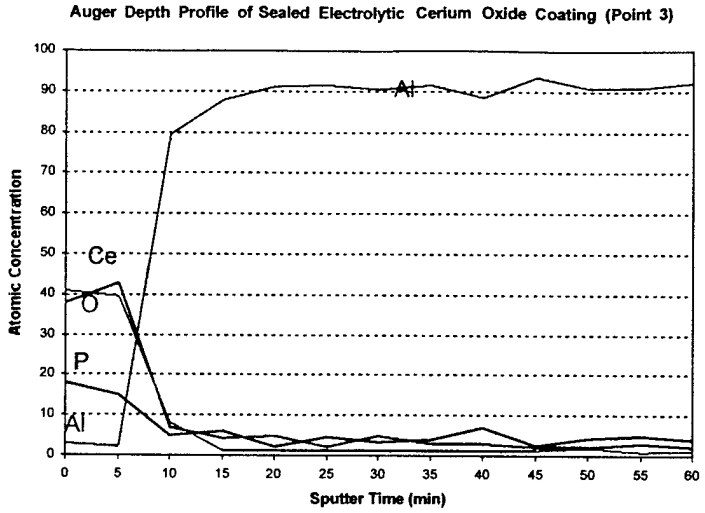
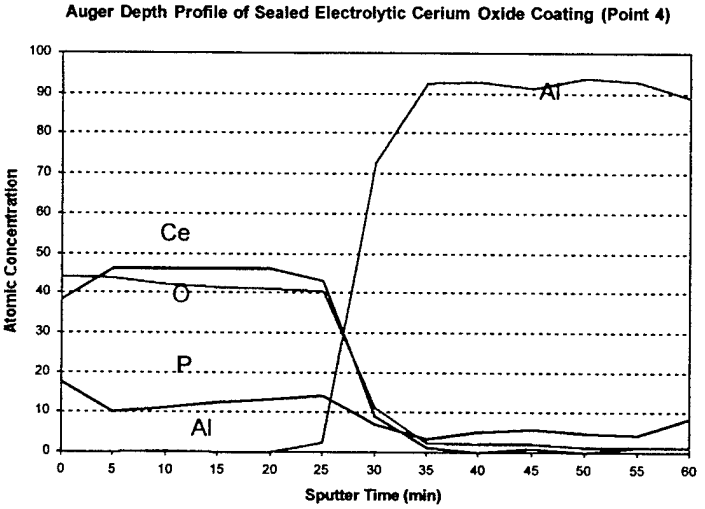


Figure V.1.12. Cerium 3d and Al 2p XPS spectra for electrolytic cerium conversion coatings



(a)



(a)

Figure V.1.13. Sputter depth profiling for (a) a thin region and (b) a thick region on an electrolytic cerium conversion coating.

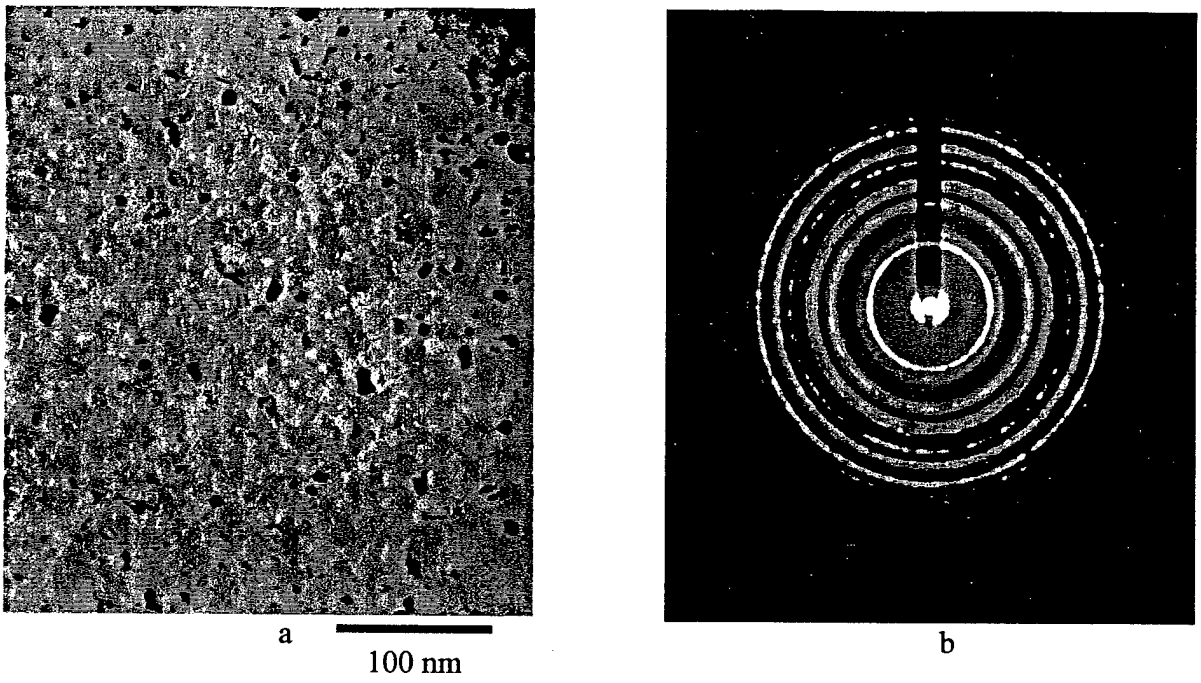


Figure V.1.14. Sputter deposited CeO_2 coating, (a) TEM image, and (b) selected area electron diffraction.

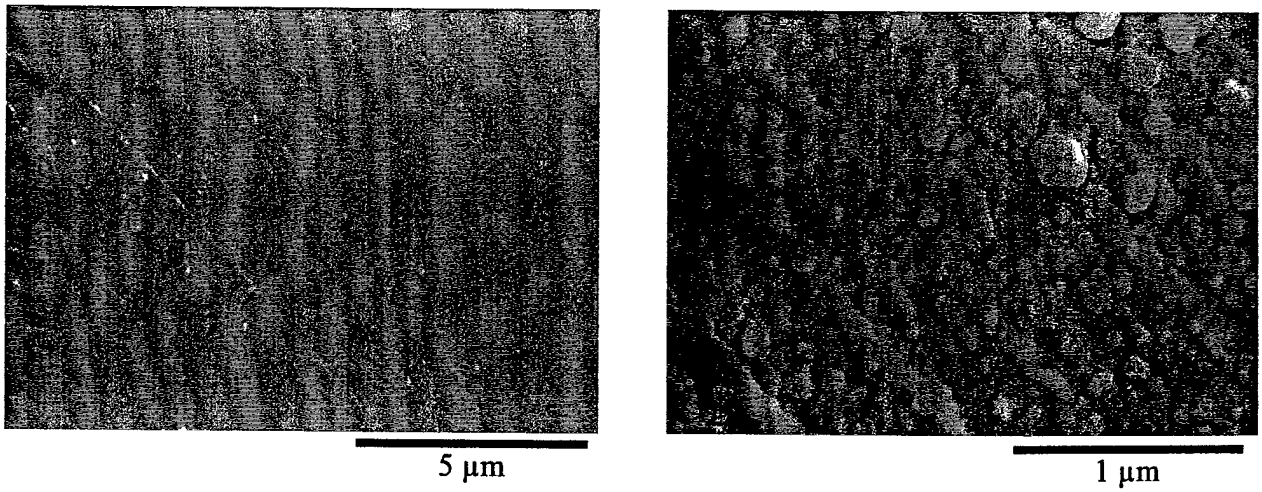
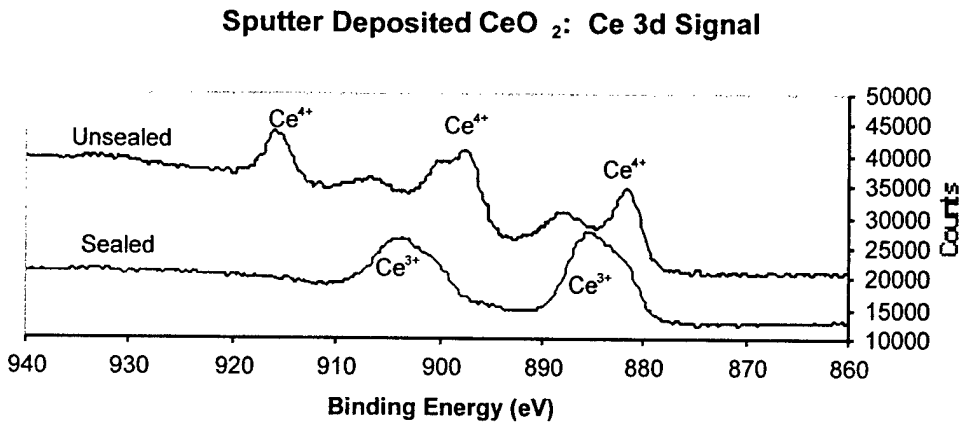


Figure V.1.15. Surface morphology of a sputter deposited CeO_2 coating on a 7075-T6 test panel that was alkaline cleaned and acid activated.



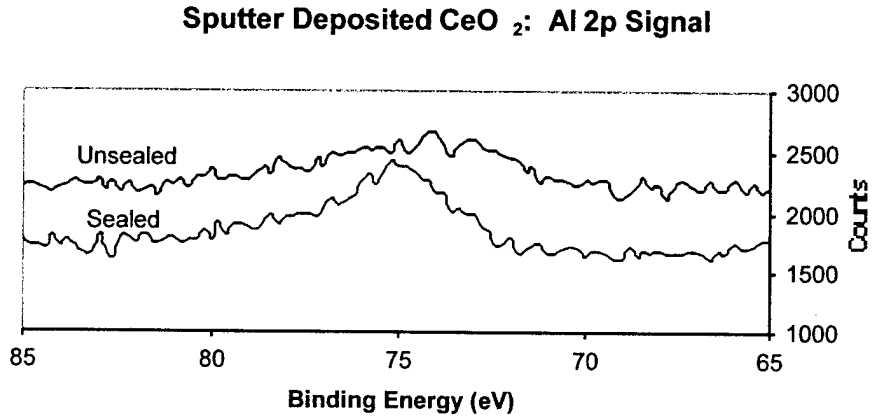


Figure V.1.16. XPS analysis showing cerium 3d and aluminum 2p signals from the surface of sputter deposited CeO_2 coating.

Section V.2. Electrochemical Characterization

Abstract

A number of different electrochemical techniques were used to characterize the aluminum specimens at various stages during the cerium deposition process. The objective was to correlate the electrochemical behavior to corrosion resistance. The tests used and the results obtained are presented in the following sections.

V.2.1. Electrochemical Techniques

The development and use of proper electrochemical techniques for characterizing and evaluating the cerium coatings and related substrates was one of the goals of the study. After extensive investigation, the following procedures were found to be beneficial in identifying trends in polarization response and their correlation with the salt fog results.

Anodic Polarization (DC-Pol) – This is a commonly used technique, but the electrolyte selected for use is critical in terms of sensitivity and ability to provide effective screening. A Prohesion solution (0.35 % $(NH_4)_2SO_4$ and 0.05 % NaCl) at ambient temperature appeared to be the best choice for most of the aluminum alloys with or without conversion coatings.

Cathodic Cyclic Voltammetry (Cath-CV) – The cathodic polarization pattern provided data that was sufficiently sensitive to allow screening of bath compositions for electrolytic cerium deposition. In particular, the amounts of organic additives and oxidizers, as well as pH and temperature effects, could be identified.

Electrochemical Impedance Spectroscopy (EIS) – The EIS tests were very useful in evaluating initial substrate condition, pretreatment efficiency and the corrosion resistance of coatings. It was found that for conversion coating evaluations a comparison of curves made before and after one day immersion in Prohesion electrolyte gave relatively consistent results that correlated well with salt fog performance. Similar techniques also showed good results for primer coated specimens with a "drilled pit" defect.

Anodic Chronopotentiometry (ACP-KS) – This technique was developed at UMR for the estimation of surface activities for both initial substrates and conversion coatings. A halogen free electrolyte, such as 5 % K_2SO_4 , was used. When a small anodic current, such as 0.1 to 1 mA/cm^2 was applied, the voltage would quickly increase to exceed the instrument limit on pure aluminum, indicating a high level of passivation. For alloys, the voltage rise was slower and

depended on the "active sites" on the alloy surface. Both the relative changes in voltage and rate of change at certain times were found to be significant.

Scanning Reference Electrode Technique (SRET) – The scanning reference electrode technique (SRET) has also been recently introduced into the coating study. A SVP 100 SRET system with an EG&G Potentiostat/Galvanostat Model 273 and a Fisher Wide Range Conductivity Meter was used. The test media was 100 mg of NaCl in 4 liters of DI water. By UMR's own convention, a bright color (red, orange and white) represents the intensity of anodic sites, and a dark color (green, blue and black) represents the intensity of cathodic sites. Most of the aluminum specimens tested were 7075-T6 from Kaiser. Pretreatment and coating of the specimens were the same as described in earlier sections of this report. The specimen surfaces were covered using electroplater's tape to expose a circular, 6 cm^2 area for the SRET testing. Artificial defects were "drilled" through the coating to the aluminum base using a 1/32" diameter end mill. The depth of these pits was sufficient to remove all traces of the coating and expose the underlying aluminum. Three pits were spaced 6 mm apart to form an equilateral triangle.

V.2.2. Substrate Screening

In the early stages of the development of the conversion coating process, inconsistent experimental results were frequently encountered. For example, significant differences in the corrosion protection were noted for 7075-T6 aluminum panels treated using the same coating process. It was later found that similar phenomena existed even for the commercial chromate conversion coatings. It was therefore assumed that the initial substrate could play a very significant role in ultimate performance.

A comprehensive study showed that not only could the 7075-T6 aluminum panels from different suppliers (e.g., Alcoa, Kaiser, Q-Panel, etc) be very different, but also panels from different batches from the same suppliers did not give reproducible behavior. Results showed that the initial resistance of the oxidized aluminum layer could be from 10^4 to 10^7 Ω cm^2 (Figure V.2.1) with the higher value being preferred. The pre-treatment processes could reduce the differences, but an order of magnitude difference in resistance was still common. It was found that the substrates with impedance greater than $10^{5.5}$ Ω cm^2 was necessary for a successful salt fog performance, whereas an impedance smaller than $10^{4.5}$ Ω cm^2 was likely have less successful salt fog results. More importantly, such differences affect the performance of the conversion coatings. For example, two chromate conversion coatings made by the same company on 7075-

T6 panels from two different sources showed over two orders of magnitude difference in resistance (FigureV.2.2). The one with high resistance passed two week salt fog, while the one with low resistance failed in two days. Similar tests and results were found with Ce conversion coatings (Figure V.2.3), although the initial EIS without immersion showed similar impedance values.

It was from these studies that the importance of insuring a uniform initial substrate condition was identified. Therefore, the need to optimize the pre-treatment processes to minimize differences in various starting substrates became a critical element in reproducing high quality conversion coatings. Monitoring these surfaces by a combination of EIS and DC polarization tests was then viewed as a desirable element of the characterization procedure.

V.2.3. Evaluation and Correlation of Conversion Coatings

The techniques which were found to show correlation with salt fog results included *DC-Pol*, *EIS* and *ACP-KS*. As indicated above, the test electrolytes and timing are important factors. Faulty information could be inferred without consideration of such factors. A simple EIS test could show similar results while salt fog testing could give very different results as shown in Figure V.2.3. The comparison of impedance change before and after one day immersion in Prohesion at ambient temperature showed good correlation with salt fog performance. With little or no change (Figure V.2.4) the specimen would probably pass after two week salt fog testing, while a drop of an order of magnitude or more (Figure V.2.5) indicated failure was probable.

V.2.4. Coating Process Studies

It was found that the electrolytic cerium coating process could be successfully characterized and evaluated with the *Cath-CV* technique. Results showed that the electrolyte pH, organic additive type and content, electrode potentials, oxidizer concentration, etc. were critical factors in providing a good cerium conversion coating. Figure V.2.6 (A) shows a curve which is consistent with a good and uniform coating. The change in the factors listed above could cause a significant change in the curve, resulting in a coating with unsatisfactory corrosion inhibition.

V.2.5. SRET Techniques

The SRET scan results on bare aluminum are shown in Figure V.2.7. It indicates the three drilled pit anode areas show up as red while the rest of the surfaces show up as cathodes, indicated by the green color using this convention. Although the anodic activities of the drilled

pits decreased after an hour, new anodic sites emerged. After several hours, the original drilled pits and the new sites become nearly equal in anodic activity and current density.

Figure V.2.8 shows the SRET scans for chrome conversion coated aluminum panels. One pit gave strong anodic activity and the remaining surface acted as the working cathode. However, this pit changed to a cathodic site after seven hours and eventually shut down in activity after 15 hours. A second drilled pit began to show cathodic activity after the first hour and remained cathodic for 15 hours, also eventually shutting down. The third drilled pit remained inactive until the first drilled pit area changed from anodic to cathodic. At this time, the third pit became anodic. Eventually all corrosion activity ceased.

Figure V.2.9 shows the SRET scans for cerium conversion coated aluminum alloy panels. At first, one drilled pit was highly anodic and the remaining two pits were cathodic. The one pit remained anodic throughout the entire process and did not shut down though the two cathodic pits shut down after some 30 hours. The new cathodic site adjacent to the anodic site was apparently an artifact of scan direction. The important feature of these results was that the original cathodic site shut down after 30 hours in agreement with the corrosion protection mechanism for cerium described in the literature.

V.2.6. Mechanism Studies

The cerium conversion coatings are deposited using either spontaneous (dip) or non-spontaneous (electrolytic) electrochemical processes. In either case the protective cerium oxide film forms by a precipitation mechanism that is very dependent on potential and pH (Figure V.2.10) as indicated by the E-pH diagram reported in the literature. The oxidation state and phase of the condensed cerium has been shown to be important to the corrosion protection properties provided by the film. Because of the strong influence of the solution chemistry and operating parameters on film performance, a basic knowledge of the thermodynamic stability of the system is essential. Towards this end, revised E-pH diagrams were developed for a few systems of interest in the formation of cerium conversion coatings. Some major differences were found when comparisons were made with the diagrams available in the literature. The revised diagram, shown in FigureV.2.11, provided a better explanation for the mechanism of the cerium coatings being developed at UMR.

A few small scale tests were also conducted to observe the phase changes occurring with variations in pH. The observed precipitation phenomena seemed consistent with the predictions

made using the new E-pH diagram, but a more in-depth analysis is needed.

A Ce-H_2O-$HClO_4$ system was chosen as an example system in which hydroxy ions are the only significant complexing species for the Ce ions. For a system exhibiting alternative complexing ions, the Ce-H_2O-H_2SO_4 system was used. Details on the construction of the diagrams are in progress and will be reported at a later date.

V.2.7. Summary

Electrochemical techniques provide an excellent complementary role in monitoring, evaluating and controlling the coating process. Results showed that substrate surface condition, pretreatment and coating bath composition all have important roles in the coating performance in salt fog testing.

The correlation studies using EIS in Prohesion showed that a value of greater than $10^{5.5}$ Ω cm^2 is necessary for a quality pre-coated substrate. Substrates with impedance value less than $10^{4.5}$ Ω cm^2 will probably fail in the salt fog test whether they are CeCC or CrCC.

For conversion coatings, a comparison of EIS results for specimens before and after 1-day immersion in Prohesion showed good correlation with the salt fog results. A conversion coating that passed salt fog testing showed little decrease in the low frequency impedance, with values around 10^6 Ω cm^2.

Cath-CV is very useful in evaluating the bath for E-CeCC process. The newly developed ACP-KS technique is promising in the evaluation/correlation studies as well as providing valuable mechanistic information. SRET can be employed to provide both qualitative and quantitative information in electrochemical activities on substrates and conversion coatings.

Preliminary studies in cerium phase and transformation mechanisms provided more insight in the coating process and the importance of E-pH predominance area diagrams was shown.

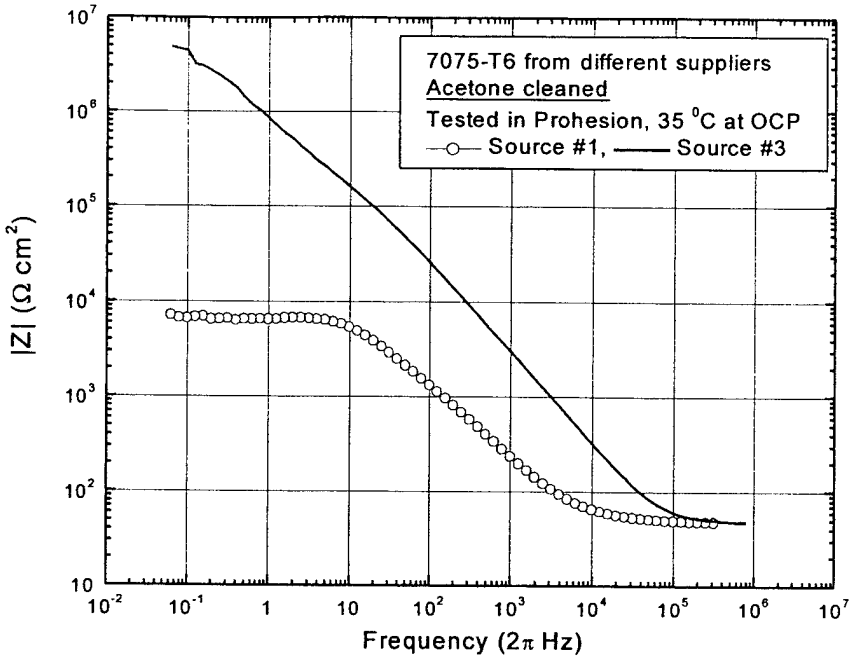
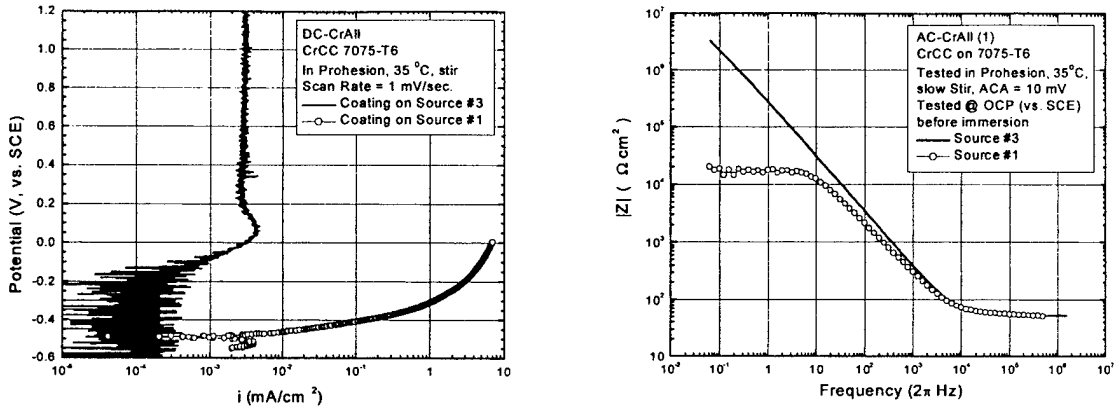
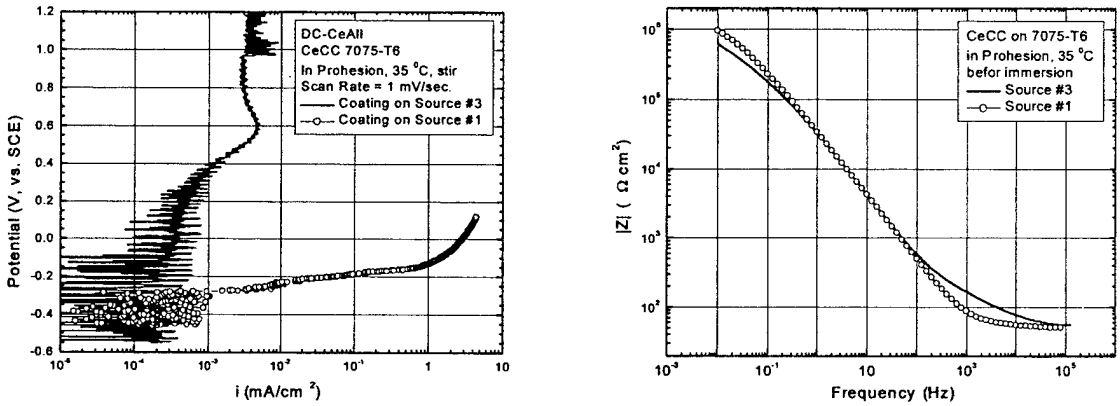


Figure V.2.1. DC polarization curves of aluminum 7075-T6 substrates from different suppliers.



(a) (b)

Figure V.2.2. DC polarization (a) and EIS (b) curves of chromate conversion coatings on 7075-T6 substrates from different suppliers.



(a) (b)

Figure V.2.3. DC polarization (a) and EIS (b) curves of cerium conversion coatings on 7075-T6 substrates from different suppliers.

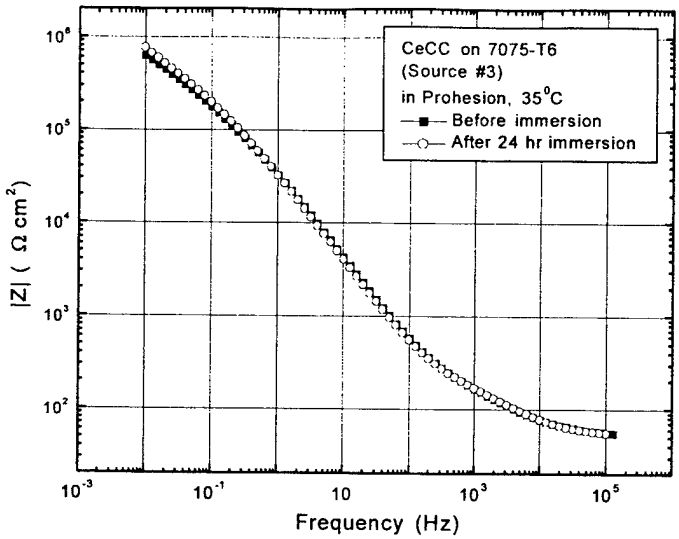


Figure V.2.4. EIS results of cerium conversion coatings on 7075-T6 substrates from Source #3. The coating passed two week salt fog testing.

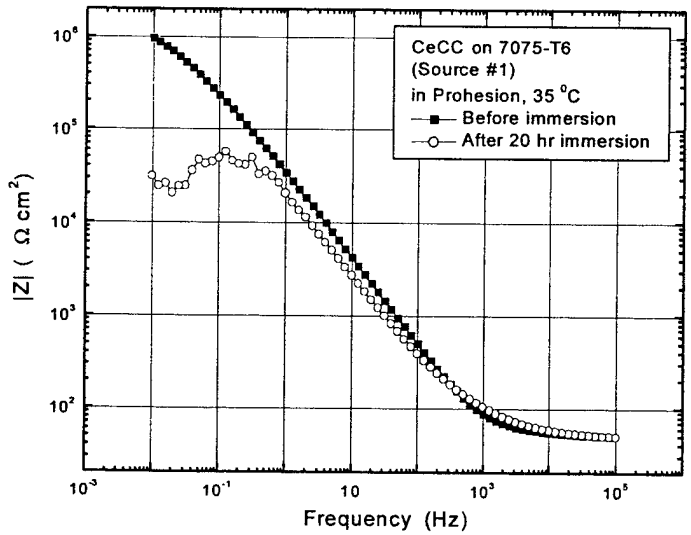
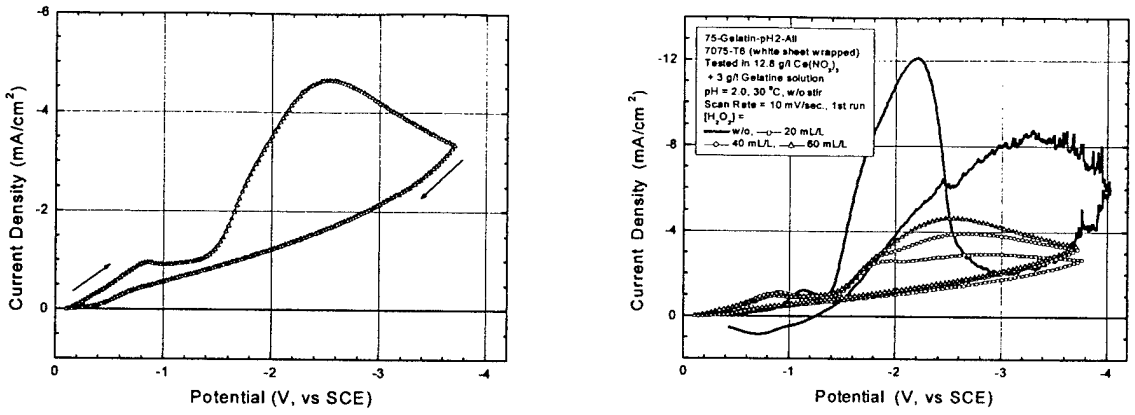


Figure V.2.5. EIS results of cerium conversion coatings on 7075-T6 substrates from Source #1. The coating failed in salt fog testing.



(a) (b)

Figure V.2.6. Cathodic polarization results of cerium conversion coatings process on 7075-T6 substrates with varied parameters. (a) A curve representative of a good coating. (b) Coating under different conditions.

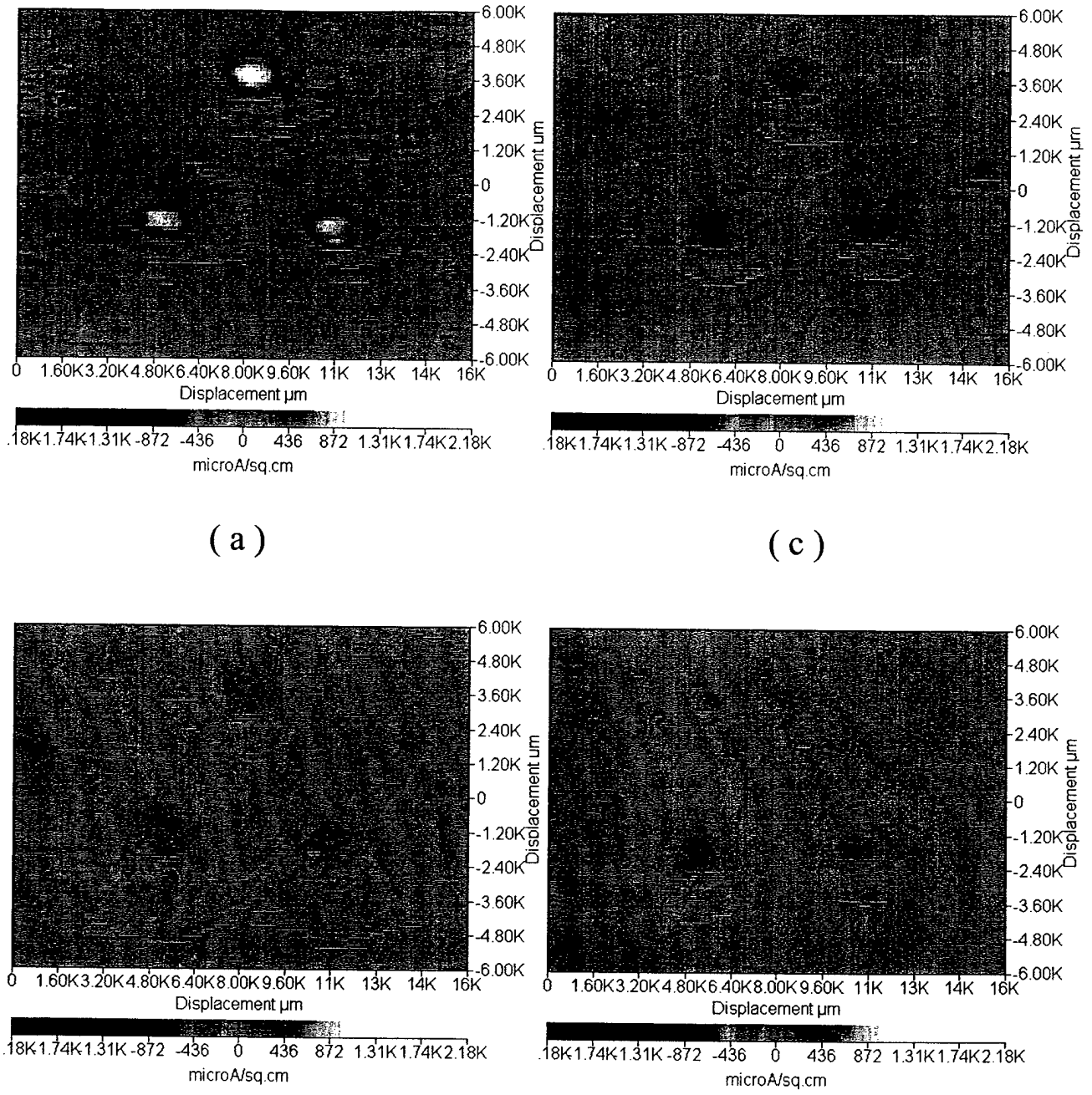
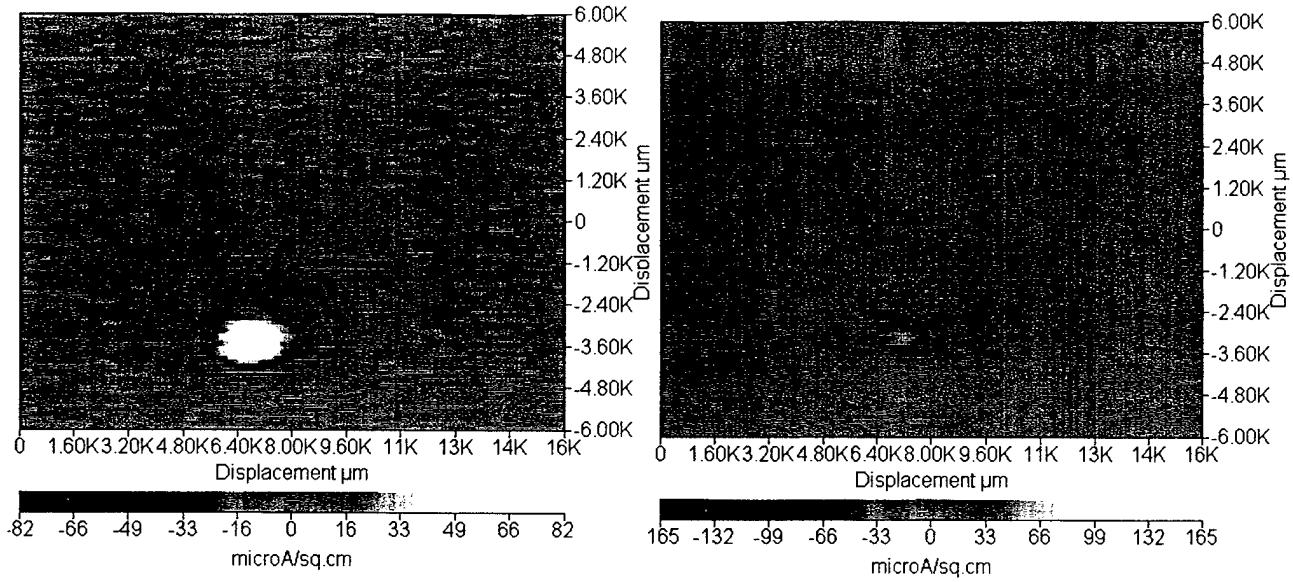
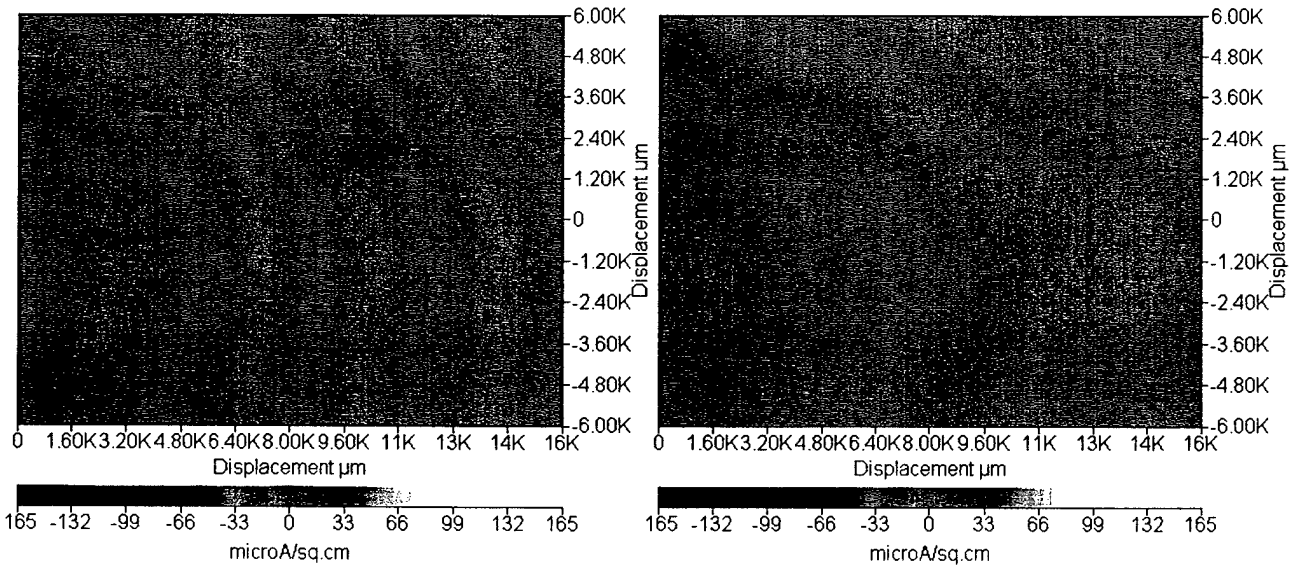


Figure V.2.7. SRET scans on cleaned 7075-T6 aluminum panels with three drilled pits in deionized water plus 25 mg/L NaCl. The immersion time was (a) 6 minutes; (b) 1 hour 6 minutes; (c) 9 hour 8 minutes; (d) 23 hour 11 minutes.



(a)

(b)



(c)

(d)

Figure V.2.8. SRET scans on CrCC 7075-T6 aluminum panels with three drilled pits in deionized water plus 25 mg/L NaCl. The immersion time was (a) 11 minutes; (b) 1 hour 11 minutes; (c) 8 hour 13 minutes; (d) 15 hour 14 minutes.

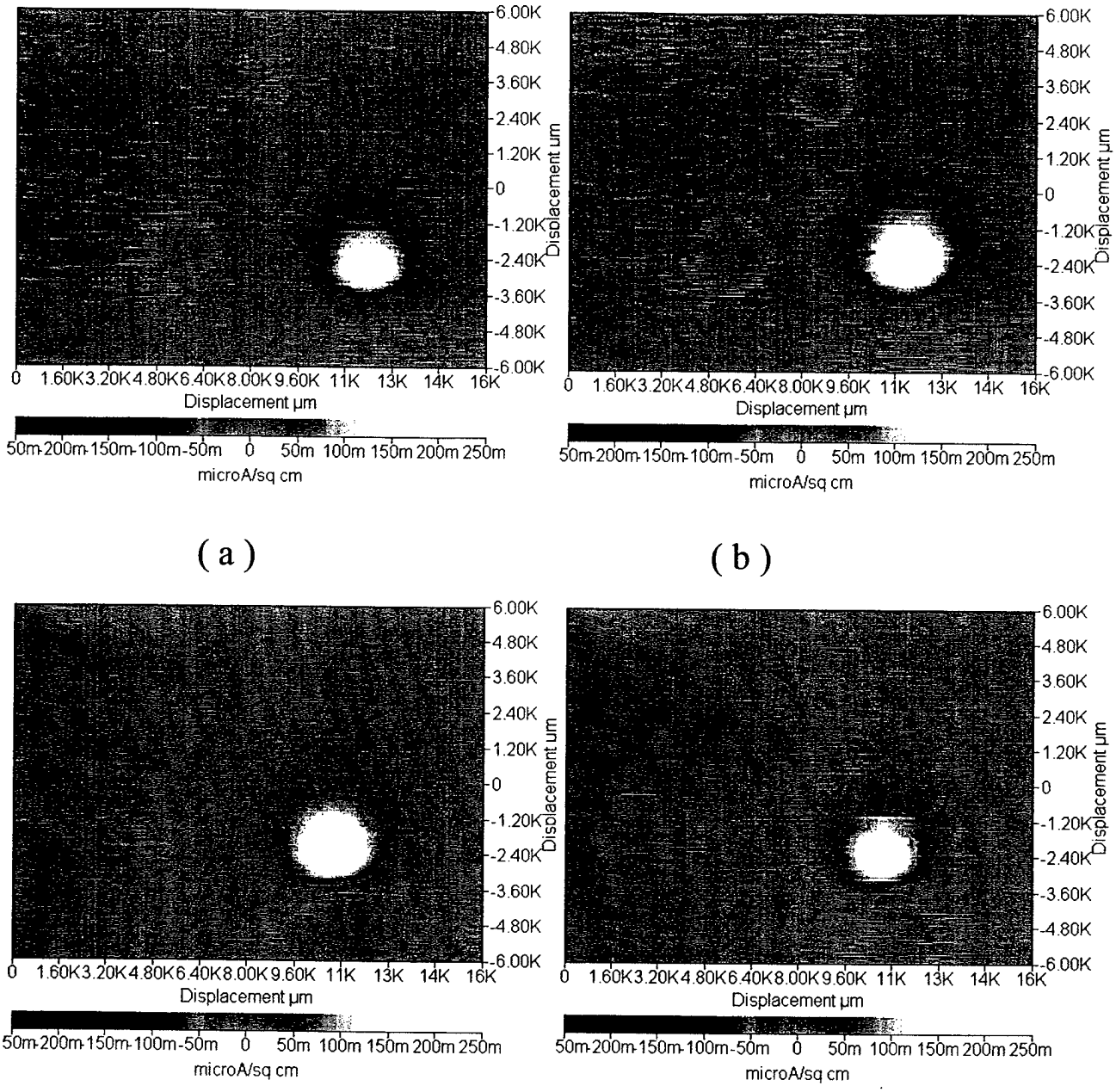


Figure V.2.9. SRET scans on CeCC 7075-T6 aluminum panels with three drilled pits in deionized water plus 25 mg/L NaCl. The immersion time was (a) 15 minutes; (b) 2 hour 39 minutes; (c) 32 hour 23 minutes; (d) 73 hour 15 minutes.

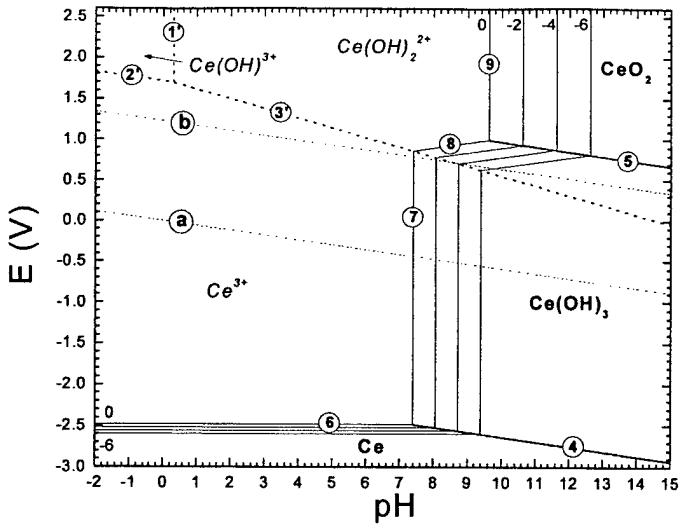


Figure V.2.10. Previous Pourbaix Diagram of Ce-$HClO_4$-H_2O system at 25 ^{0}C.

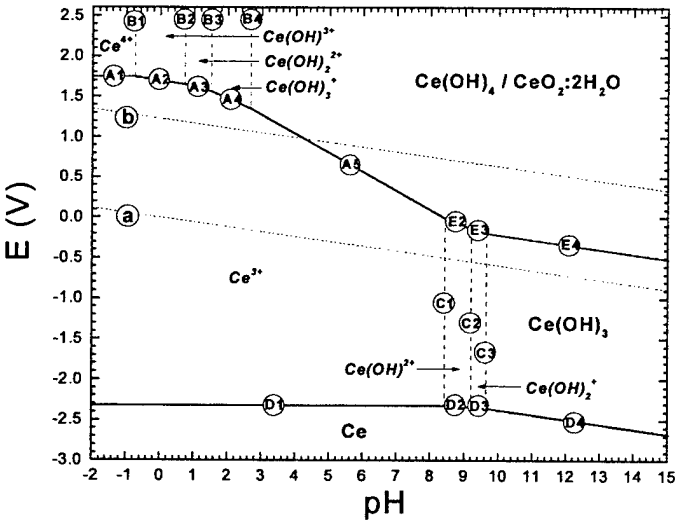


Figure V.2.11. Revised Pourbaix Diagram of Ce-$HClO_4$-H_2O system at 25 ^{0}C.

Section VI. Epoxy Polyamide Primers for Aluminum Alloy Corrosion Inhibition

Abstract

Previous literature reports on the effectiveness of cerium salts as inhibitors in epoxy polyamide paints, and the results of the first two test generations of cerium primer tests at UMR for this work, are disputable. Not until after this work was complexation of cerium inhibitor salts with coating resin observed and documented. Polyamide resin was observed to complex cerium salts regardless of anion composition or cerium valence state. The complexation has far-reaching effects, e.g., on curing development, paint stability, cerium ion solubility, inhibitor valence and redox behavior, and should affect inhibitor activity. New, complexed inhibitor nitrate and phosphate species of cerium were synthesized from EDTA, and N-propylamine, N-ethanolamine, N,N-diethanolamine, and N,N,N-triethanolamine. These inhibitors were incorporated into epoxy polyamide paints. Pre-complexing of the cerium salt rendered the cerium unreactive towards the polyamide resin and prevented interaction with polyamide and inhibition of curing. Preliminary corrosion, adhesion, and flexibility results obtained with the new, complexed cerium inhibitors appear promising.

VI.1. Introduction

In addition to recent surface conversions of aluminum for the prevention of corrosion, cerium has a long-standing history of being incorporated into organic coatings as a corrosion inhibitor [1]. Literature suggests cerium salts are effective inhibitors of aluminum corrosion but at active concentrations 10 times that of, e.g., strontium chromate ions [1a]. Soluble cerium ions, either (III) or (IV) in valence [1-4], are reported to inhibit the cathodic corrosion reaction and precipitate [4,5] onto cathodic sites by virtue of a high pH environment created at those sites such as by oxygen reduction in the presence of water.

Corrosion inhibition by cerium salts is observed to be counter-anion and concentration dependent,[1-4] but not necessarily valence state dependent. Recent data obtained by UMR on the phase diagram of cerium compounds as a function of pH (see section V.2.6, this report) shed new light on valence dependence of corrosion inhibition, particularly if inhibition is a precipitation mechanism induced by pH. However, no specific pattern of corrosion inhibiting efficiency has yet emerged with regard to the chemical or electrochemical properties of the counter-ion of cerium.

UMR examined the use of cerium compounds in organic, electrodeposited primer coatings. In initial UMR work, cerium nitrate salts were included as an additive to electrodeposited coating (E-coat) formulations [5], which demonstrated scribed and unscribed corrosion resistance similar to that of chromate-converted aluminum with E-coatings of proprietary inhibitor packages from major E-coating producers. Very high electrochemical impedance and corrosion resistances resulted. Auger spectroscopy sputter profiling through the cerium E-coating indicated that the cerium additive was first deposited as a conversion layer followed by a cerium containing, organic epoxy E-coating. Cerium salts in E-coatings were shown to effectively inhibit corrosion of both 7075-T6 and 2024-T3 aluminum alloys, thus suggesting application in traditional primer systems.

A new coating system design, consisting of a cerium conversion coating on aluminum followed by an organic primer coating containing a cerium inhibitor, was proposed. The traditionally designed organic surface primer coating containing cerium-based inhibitors may, then, re-supply and support the cerium-rich surface conversion layer in the event of coating damage. Two, now complete, phases of the proposed work formulated and tested cerium containing organic primers. These primer coatings were applied onto chromate or cerium converted aluminum alloy. Cerium salts were selected not only to reproduce and benchmark literature results but also to determine mechanism and level of inhibition by the cerium salts in the primer in comparison to chromate and literature results. Therefore, accelerated corrosion testing was used to ascertain, as a function of composition, whether cerium inhibitors could re-supply protection conveyed by cerium or chromate conversion coatings in the event of surface damage, such as a controlled scribe or pinhole defects. Other test regimen included SO_2 filiform resistance, primer wet adhesion, and chemical resistance to solvent.

VI.2. Experimental

Several cerium salts were selected, based on solubility and anion structure, for formulation into epoxy polyamide primer formulations as corrosion-inhibiting pigments. The salts selected for screening were cerium(III) nitrate hexahydrate, phosphate (anhydrous), sulfate hydrate, and cerium(IV) oxide and oxide hydrate. In addition, cerium(III) pentanedionate (acac), cerium(IV) nitrate, praseodymium(III) nitrate, and the co-inhibitor pigments barium metaborate and aluminum(III) phosphate (K-White) were examined as part of the initial studies. The control primer coatings for these studies was a chromate conversion of 7075-T6 alloy [6] followed by

either Deft #44-GN-072 waterborne chromated epoxy polyamide primer (MIL-P-85582B, type 1, class 2), or Deft #02-Y-040, a high solids chromated primer (MIL-P-23377G, type 1, class 2).

Salts were sized for incorporation into organic primers by either physically grinding the powders in a ball jar containing ½" ceramic ball media, by solution precipitation of the salt from water or acetone into tetrahydrofuran or methylene chloride, or physical grinding of the salts after incorporation into the primer resin (during the dispersion phase). The Hegman number was used as a convenient measure of effective maximum pigment particle size in the primers.

Three primer test sequences have been performed during this work period. UMR formulated primers that were based on standard, industrial strontium chromium(VI) oxide epoxy polyamide formulations of Deft, Inc. (Table VI.1), one waterborne and one solventborne type. The concentration of inhibitors (Table VI.2) in the primers was established on a weight-weight (Generation I) or a volume-volume (Generation II) replacement of chrome in the original formulation with an estimated overall pigment volume concentration (PVC) of about 26% for a waterborne, or 23% for a solventborne, system. Generation I primers were waterborne formulations that included the inhibitors cerium oxide and/or cerium nitrate, with co-inhibitors aluminum phosphate and barium metaborate, compared to a chromate primer control. Generation II primers tested the inhibitor salts cerium nitrate, cerium phosphate, and cerium pentanedionate, with co-inhibitors barium metaborate and aluminum phosphate, in waterborne or solventborne primer formulations and were compared with an analogous chromate control primer. Actual manufacture of the formulated primer millbases for Generations I and II occurred at Deft, Inc., Irvine, CA, with supplemental formulations and syntheses produced at UMR. A third primer test sequence (Generation III) was applied to chromated 7075-T6 and 2024-T3 alloys and electrolytic cerium coated 7075-T6 alloy at Boeing-St. Louis. Syntheses of both the inhibitors and primer coatings from the inhibitors for Generation III were performed at UMR using resin materials supplied by Deft, Inc. Pigments were dispersed into the polyamide portion of the formulation for waterborne coatings or the epoxy portion for solventborne coatings.

Coatings were manufactured from the millbases by addition of a curing agent letdown, which consisted of either an epoxy resin solution for waterborne or a polyamide resin solution for solventborne formulations, followed by a final letdown with water for waterborne systems to an appropriate viscosity for spray application. The viscosity for spraying was about 20 seconds (Zahn #2) or 18 centistokes. No additional letdown was required for solventborne coatings.

Spray applications onto either a chromate [6] or cerium[7] converted 7075-T6 or 2024-T3 alloy were made with high volume low pressure (HVLP) spray to achieve a dry film thickness of about 1 mil (25 μm). The Appendix reports additional method details and results obtained for the waterborne and solventborne primers.

VI.3. Results and Discussion

VI.3.1. Primer Generations I and II

Moderate results were obtained for primer Generations I and II (see Table VI.3 and Appendix), in general agreement with the quality of results reported in literature [1], but less effective than UMR E-coating results [5]. Primers were better or similar in effect to barium metaborate, better than aluminum phosphate, while combinations of a cerium salt with either non-cerium inhibitor gave no synergistic effect. In general, waterborne coatings outperformed their solventborne counterparts in corrosion resistance. Excellent SO_2 filiform corrosion results were obtained, as were results for wet adhesion, flexibility, and chemical fluid resistance. However, salt fog testing according to ASTM B-117 specified in MIL-P-85582B or MIL-P-23377G is the rigorous, testing focal point. It was here that results were moderate; varying from light salting in the scribe with no creepage, to salting and blistering with up to 1/16-1/8" creepage as a function of the cerium primer (see result summary Table VI.3 and Appendix). More soluble salts (nitrate) appeared to give better initial protection though less soluble salts gave longer lasting protection. Primers were difficult to synthesize and tended to display poor storage stability, often degrading in less than one week. In some instances hard settling was observed; in others, discoloration and loss of thermosetting properties were observed. In general, Generation I gave slightly better overall results compared with Generation II though the scope of Generations I and II was similar.

Rare earth blends have potentially synergistic corrosion inhibiting action [2]. UMR synthesized primers containing rare earth element salts (Figure VI.1), including praseodymium, neodymium, and samarium that either alone or blended with cerium gave results comparable to primer Generations I and II. The rare earth inhibitors, or blends, formulated into the waterborne epoxy polyamide showed salting, however slight, in the scribe of panels after 500-1000 hours ASTM B-117 exposure compared to a shiny, unaffected chromate scribe after similar exposure. Panels, like Generations I and II, had excellent appearance otherwise with no blister or pinhole corrosion.

Generation II primers were applied after longer in-can storage, up to 4 weeks compared to hours for Generation I primer coatings. Thus, storage stability issues may at least partially account for any discrepancy between the first and second test sequences. Storage stability is an issue that could prevent commercialization and use of any coating inhibitor technology, regardless of how effective. Organic primer coatings should, in practice, be useable up to a year or preferably more after the manufacture date, as specified in MIL-P-85582B and MIL-P-23377G.

Several Generation II primers applied onto cerium conversion coated 7075-T6 alloy, synthesized by the electrolytic method using cerium nitrate [7, see also section III this report], were observed to delaminate from the conversion coating during salt fog exposure. Delamination failures were not observed during Generation I testing. Cerium containing primers that were less prone to delamination were cerium salts of water reducible primers and cerium nitrate in high solids (solventborne) primers. Electrolytic conversion coatings of better consistency were developed between Generations I and II testing, thus the cerium conversion coatings were likely different between each generation. Delamination can result from poor surface wetting by the primer or reduced curing of the organic primer at the interface between the primer and the conversion coating.

VI.3.2. Cerium Complexation

A significant observation was made during synthesis of polyamide resin millbases containing pure cerium salts. The cerium-polyamide mixtures became dark yellow to reddish brown in color, emitted heat, and viscosified into gels. By our observations, all cerium compounds (simple salts and oxides) react with polyamide (amino) resin, and 1°, 2°, and 3° organoamines in general, though the rate of reaction depends on solubility and relative oxidative stability of the cerium salt. For example, the fastest reactions were observed with cerium nitrate and chloride salts, intermediate rate reactions with sulfates, and slower rate reactions with phosphate and oxide hydrate. The reaction appeared to be a complexation and not an ion-exchange reaction where the products were generally less soluble than the starting salt or amine. Complexes were synthesized from each starting cerium salt by the reaction of polyamide or a free amine, producing differently colored materials for each salt/ligand pair. The reaction was sensitive to air, which appeared to produce a less colored cerium(III) complex in the absence of air but converted to a darker colored cerium(IV) complex upon exposure to air. The type of

solvent also played a role in the complexation reaction since different colorations and reaction rates were obtained when the reactions occurred in the presence of water, ethanol, ether, or tetrahydrofuran. Literature supports these observations, showing that a rich complexation chemistry exists for cerium with organoamines [8,9] and oxo- species such as ethylenediamine-tetraacetic acid (EDTA) [10].

Of particular interest are changes in solubility, valence state, and reactivity of a cerium ion as a function of a complexing agent's chemical structure [9]. Solubility has been observed to decrease markedly after complexation regardless of the complexing agent involved. Decreased solubility can reduce effectiveness of the inhibitor through affected migration/leach rate properties. A "smart" release mechanism is still possible to allow for selective release of cerium due to a local change in pH at the onset of corrosion reactions. The possibility of smart release and design properties thereof are being assessed with the currently synthesized inhibitors (see below) via pH titration and measurement of electrochemical potentials. Electrochemical inhibition is expected to change as a function of the cerium valence and complexation states [11]. Valence oxidation state is being measured on Generation III inhibitors by x-ray photoelectron spectroscopy (XPS, Figure VI.2), cyclic voltammetry (CV), and electron spin resonanace (ESR) methods. XPS also indicated chemical differences in other atomic species, such as nitrogen, with and without the presence of cerium (Figure VI.3). Different reactivity of cerium ions, observed as a change in initiation rate, occurs as a function of the chemical structure of the complexing agent [9].

Three distinct coating performance concerns are raised by the observations, in conjunction with primer Generations I and II and literature-reported results: 1) Cure development of the thermosetting primer could be inhibited by cerium through formation of the cerium-polyamide complex, which may account for poor substrate adhesion for Generation II epoxy polyamide coatings to cerium salt conversion coatings. 2) The actual oxidation potential of the cerium inhibitor is questionable regardless of the starting salt composition, and thus inhibition activity, since the composition changed during synthesis of the millbase. A change in valence state could either enhance or retard the ability of the cerium ion to inhibit corrosion and would be expected to depend on a redox potential and solubility of the product complex. Based on these observations, it is understandable why no distinct difference or comparison between cerium(III) to cerium(IV) salts as corrosion inhibiting species currently exists. 3) Formulation stability was

adversely affected by complexation reactions producing hard settling or gelation such that neither mixing of the paint nor application could be made. A silver lining exists with respect to the complexation reactions. First and foremost, all prior conclusions with respect to cerium salt inhibitor mediocrity are immediately suspect due to unknown cure development, actual inhibitor composition, and oxidation state effects. Second, the variation of inhibitor activity as a function of the ligand chemical structure may allow tuning of the solubility and redox potential to mimic the electrochemical inhibition activity of chromates. Dual oxidation states of cerium, and the analogous property of chromate, allow for the possibility of tuned electrochemical behavior.

Cerium nitrate inhibited paints in the presence of EDTA were synthesized and tested by ASTM B-117 exposure. Results have been encouraging in that exposure times resulting in a shiny scribe have been extended to 1000 hours (Figure VI.4).

VI.3.3. Inhibitor Syntheses and Primer Generation III

One potential method to reduce the reactivity of cerium salts towards complexation with polyamide resin was to pre-complex the cerium ion with a ligand species. Preliminary results indicate complexation and reduced sensitivity to polyamide occurred for cerium nitrate when exposed to N-propylamine in ethanol. Neither color nor viscosity changes were observed by adding the solid cerium [di-N-propylamine] nitrate complex to polyamide resin. However, the N-propylamine complex had very poorly solubility, thus a series of complexes were synthesized with the goal of improving the solubility characteristics of the complexes. Similar complexations but slightly improved water solubility were observed in the order N-propylamine < N-ethanolamine < N,N-diethanolamine < N,N,N-triethanolamine. Further, the potentially exposed hydroxyl functionality was not expected to affect coating curing functions.

The inhibitor series was synthesized in a ceramic ball jar with ½" media and ethanol solvent from cerium(III) nitrate hexahydrate or cerium(III) phosphate salts. Nitrate and phosphate counter-ions were selected based on solubility and previous performance in primer Generations I and II. Complexes of each salt were made by milling the salt in the presence of either N-propylamine, N-ethanolamine, or N,N-diethanolamine to further control solubility of the resulting inhibitor. Inhibitors were recovered and washed with ethanol by a centrifugation method and dried in vacuo. Density of the complexes was measured by volume displacement of toluene by ~1 gram of dry product. Cerium concentration and stoichiometry was estimated by

XPS atomic percentages and carbon/hydrogen/nitrogen (CHN) and cerium (Ce) elemental analyses. Particle size of the complexes was observed by SEM.

Waterborne coating millbases were formulated to give 2%Ce by weight for each coating. Millbases were synthesized from the complexes and polyamide resin by cowls mixing of the components in the presence of 1mm ZrO_2 media, which were recovered by coarse filtration. No reaction including color or viscosity changes was evident during millbase syntheses. Millbases and epoxy resin (curing agent) solution were packaged in quart kits, MSDSs were then produced, and the packaged coatings shipped to Boeing for application onto chromate-converted 7075-T6 and 2024-T3 alloys, and cerium-converted 7075-T6 alloy, and subsequent testing which is underway.

VI.4. Summary

Primer salt fog corrosion test results of Generations I and II were moderate due to potential effects on curing development, solubility, inhibitor valence and redox behavior, and inhibitor activity. New, complexed inhibitor nitrate and phosphate species of cerium have been synthesized from EDTA, N-propylamine, N-ethanolamine, N,N-diethanolamine, and N,N,N-triethanolamine. The inhibitors, and epoxy polyamide coatings synthesized from the complexes, are being characterized for solubility in water, atomic composition, and metal ion valence state and their effect on the corrosion processes of aluminum. Pre-complexing of the cerium salt renders the cerium unreactive towards the polyamide resin and should allow curing to develop normally. Interfacial adhesion effects such as delamination, due to a possible interaction by the electrolytic cerium conversion coating, should not be affected by pre-complexation of paint-based cerium. Preliminary corrosion, adhesion, and flexibility results obtained with complexed cerium inhibitors appear promising.

VI.5. References

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Tables and Figures

Table VI.1: Epoxy polyamide primer coating formulations

Materials (By Volume)	Water Reducible	Solventborne (High Solids)
Epoxy resin	287	277
Polyamide resin	500	174
2-Butanol	112	95
Aromatic 100	0	33
Nitroethane	137	0
Dispersant	(Henkel Texaphor 963) 6	(Solsperse 20k) 15
Rutile titanium dioxide	49	17
Mistron Talc	93	30
Syloid silica	0	50
Inhibitor	70	53

Table VI.2: Primer generations I and II. Inhibitor concentrations in volume percent (PVC) and formulation type

Generation I	Form	Concentration (PVC)	Generation II	Form	Concentration (PVC)
Strontium chromate (control)	WR	6.3	Strontium chromate (control)	WR	6.3
$Ce(NO_3)_3$	WR	10.0	$CePO_4$	WR	7.9
$Ce(NO_3)_3$ / $BaBO_2$	WR	4.6 / 3.7	Ce(pentanedionate)$_3$	WR	8.1
$Ce(NO_3)_3$ / $AlPO_4$	WR	5 / 5	$BaBO_2$	WR	8.1
CeO_2	WR	8.4	Strontium chromate (control)	HS	8.0
$AlPO_4$ (K-White)	WR	9.4	$Ce(NO_3)_3$	HS	8.0
			$Ce(NO_3)_3$ / $BaBO_2$	HS	4.4 / 3.5
			$CePO_4$	HS	8.0
			Ce(pentanedionate)$_3$	HS	8.0
			$BaBO_2$	HS	8.1
			$AlPO_4$ (K-White)	HS	8.1

Notes: WR = water reducible (based on Deft 44-GN-072, 26 PVC); HS = high solids (based on Deft 02-Y-040, 23 PVC)

Table VI.3: Generation I and II primers salt fog testing results summary

Conversion/Inhibitor/Formulation	Neutral salt spray B-117	Salt-SO_2 spray
CrCC/Ce(III)$(NO_3)_3$/WR	Few scribe blisters	Pass
CeCC/Ce(III)$(NO_3)_3$/WR	Slight lift along scribe	Pass
CrCC/Ce(III)$(NO_3)_3$/HS	Few scribe blisters; 1/16 to 1/8" creep	Pass
CeCC/Ce(III)$(NO_3)_3$/HS	95% lifted	Pass
CrCC/$BaBO_2$/HS	White salt; no creep	Pass
CrCC/Ce(III)PO_4/HS	White salt; no creep	Pass
CrCC/Chrome(VI) oxide/WR	Dark/shiny scribe	Pass

Notes: CrCC = chrome conversion; CeCC = cerium nitrate conversion; WR = water reducible; HS = high solids

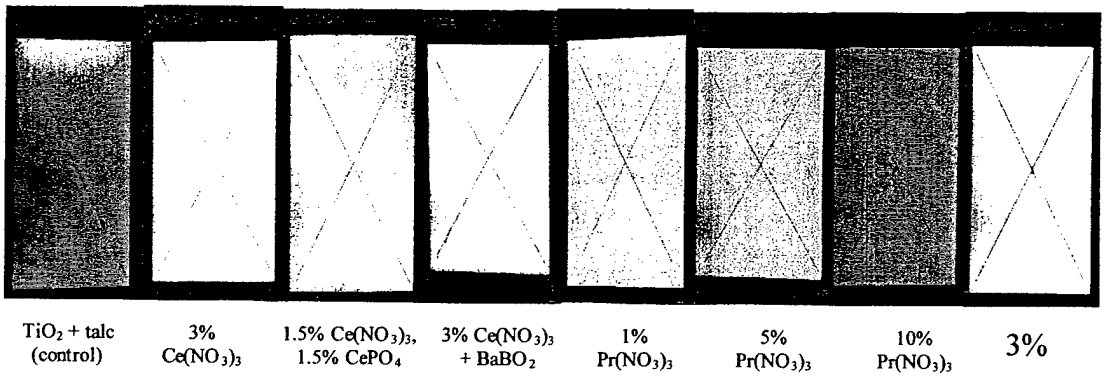


Figure VI.1: Rare earth elements in epoxy polyamide primers applied onto chromated 7075-T6 aluminum alloy after 500 hours ASTM B-117 exposure

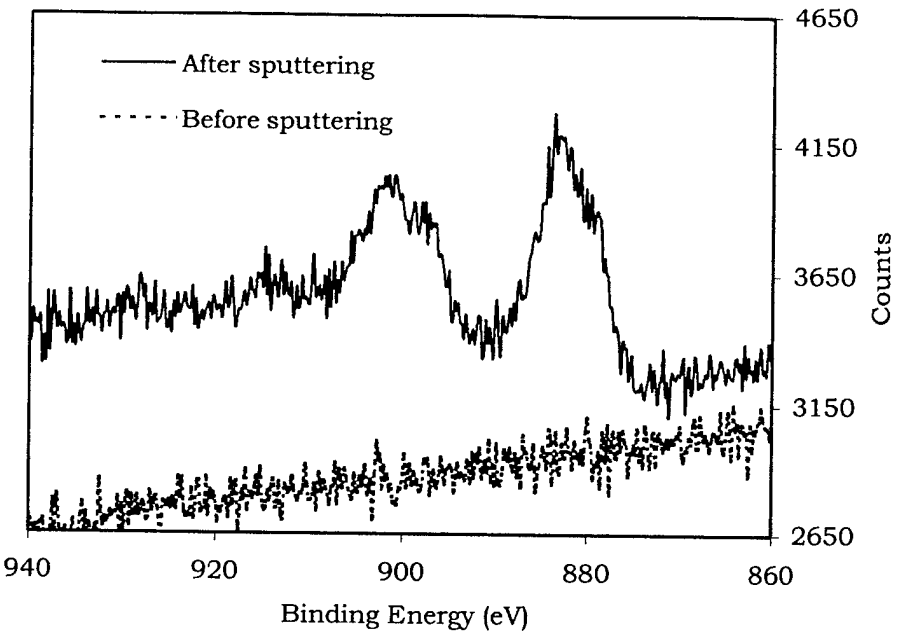


Figure VI.2: Ce 3d photoelectron spectrum of $Ce(III)(NO_3)_3$ polyamide surface (before and after sputtering)

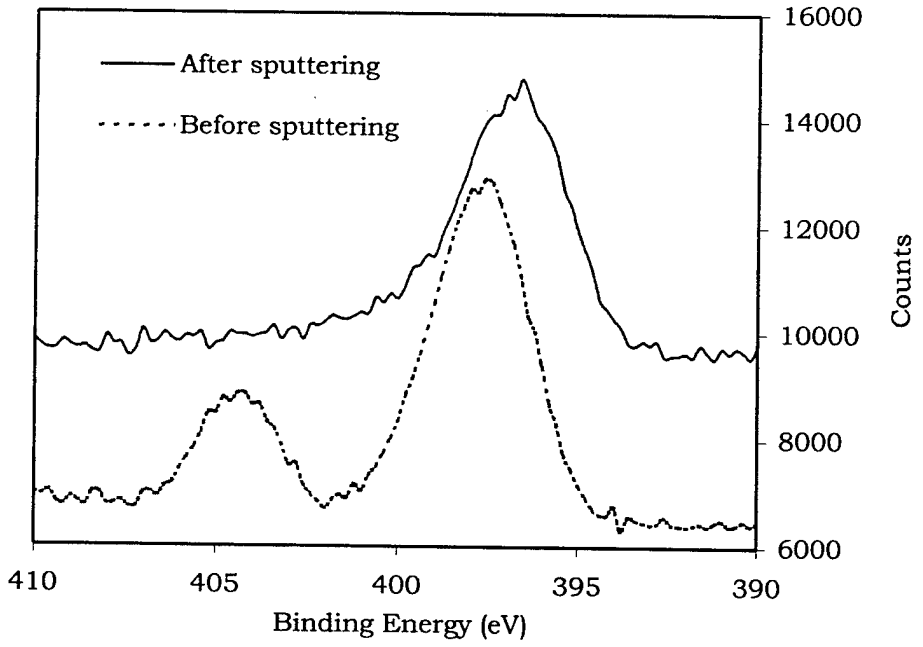


Figure VI.3: N 1s photoelectron spectrum of $Ce(III)(NO_3)_3$ polyamide surface (before and after sputtering)

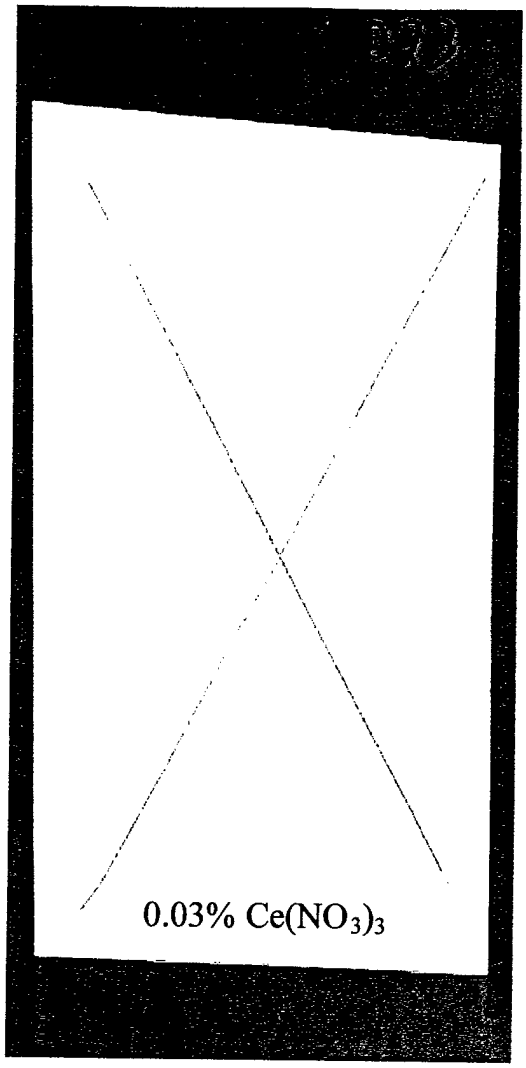


Figure VI.4: Preliminary result of $Ce(III)(NO_3)_3$ EDTA epoxy polyamide coatings on 7075-T6 aluminum alloy after 500 hours ASTM B-117 exposure with shiny scribe

GENERAL SUMMARY

The state of the development of the cerium electrolytic and dip conversion coatings has been presented. Progress in the design of a primer based on cerium inhibitors was also described. In general, advances in all three areas have been encouraging.

A standard process for the electrolytic coatings has been developed that is capable of giving an 85% pass rate in two week salt fog tests. The conditions are being optimized but additional research is needed to evaluate the pre-treatment step and organic additives. Other critical parameters that have been identified for more in-depth studies include current density, electrolyte pH and deposition thickness.

The current spontaneous cerium dip coating process produces coatings which are reproducible and uniform; capable of passing salt fog tests for a minimum of 4 days. In some isolated tests, number of specimens have given good corrosion resistance in a 1 to 2 week time frame. The major advances in improving the quality of the coatings have been related to the pre-treatment and sealing steps. Future developments will focus on optimizing these steps as well as evaluating additives as a means of extending corrosion protection.

In both cases, the characterization of the coatings will be expanded in an effort to correlate the coating properties with corrosion resistance and paintability.

Use of cerium as inhibitor in primers has been identified. Two generations of cerium-based primers formulated by UMR at Deft have been evaluated by Boeing-St. Louis. Testing of a third generation of cerium complexed primers at Boeing-St. Louis is currently underway. A fourth generation of primers will be based on promising candidates from previous Boeing-St. Louis testing as well as initial screening results from UMR. Future research will emphasize cerium complexes to control reactivity and mobility of cerium species within a primer matrix and evaluation of other rare earth salts.

TECHNICAL MEMORANDUM
ENGINEERING LABORATORIES

REPORT TYPE: FINAL

TECH MEMO: 254.00.0046.01
DATE: 14-JUN-00 REV:

TITLE: UNIVERSITY OF MISSOURI-ROLLA CERIUM INHIBITED PRIMER BASELINE TESTING

MODEL NO: CRAD MODEL TYPE: CRAD
REQ DOC: WR515-881
TEST ART DELIVERY: N/A
CHARGE NO: HX2-H1-501
SET-UP START: N/A
CONTRACT NO: R-5-33021/1
TEST START: 01-DEC-99
REQUESTING DEPT: 679N TEST COMP.: 21-APR-00
PART NUMBER: N/A
QUANTITY: TEARDOWN COMP.: N/A

DISTRIBUTION

NAME	DEPT
CHEMICAL PROCESS LAB	254
J.R. DEANTONI	679N
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R.J. SARGENT *	254W
DEPT. FILES*	254
ENGR. SUPPORT*/**	348

* PAGE 1 ONLY
** ORIGINAL REPORT

TEST ARTICLE DESCRIPTION: Cerium based conversion coating and primers applied to aluminum
MANUFACTURER: DEFT
TEST ARTICLE DISPOSITION: Returned to requester
TEST LOCATION/FACILITY NO.: CHEMICAL PROCESSES LAB, BLDG 102, ST. LOUIS
TEST CATEGORY: MATERIALS & PROCESSES
TUNNEL OCCUPANCY HOURS: N/A TEST RUNS/DATA POINTS: N/A
TYPE OF DATA ACQUIRED: RELATIVE CORROSION, ADHESION, FLUID RESISTANCE
NO. OF DATA CHANNELS: N/A
TEST VARIABLES AND CONDITIONS: Conversion coating and primer formulations, substrates, and substrate exposure methods.

OTHER LAB REPORTS: N/A
SUPPLEMENTARY REPORTS: N/A

KEYWORDS:
1. MATERIALS PROCESSING
2. ADHESION
3. ALUMINUM ALLOY 2024
4. ALUMINUM ALLOY 7075
5. CONVERSION COATING
6. CORROSION RESISTANCE
7. FLEXIBILITY
8. FLUID RESISTANCE

1. TEST OBJECTIVE: The purpose of this test is to perform baseline corrosion, adhesion, fluid resistance, and flexibility testing on cerium inhibited primers.

2. ABSTRACT OF RESULTS: Chromate conversion coated test panels showed superior corrosion resistance to cerium conversion coated test panels when coated with any of the cerium inhibited test primers. Deft 44-W-25 (cerium oxide) and Deft 44-W-28 (cerium nitrate) test primers were superior to Deft 44-W-27 (cerium nitrate w/K-white) test primer.

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MANAGER
CHEMICAL PROCESSES LABORATORY

RELEASED: N

3.0 INTRODUCTION

The USAF has issued University of Missouri-Rolla (UM-Rolla) a contract to develop cerium based conversion coatings and primers. UM-Rolla has subcontracted some of this work to Boeing-St. Louis. Boeing-St. Louis, UM-Rolla and Deft Coatings will work together to develop a cerium based non-chromated spray epoxy primer suitable for aerospace applications.

This is the first round of baseline testing of cerium inhibited primers. These formulations will explore cerium loading as well as various cerium compounds and combinations. This testing also includes baseline testing of current best non-chromated primer candidates leveraged from the Joint Group on Pollution Prevention (JG-PP) flight test program. Corrosion, adhesion, flexibility, and fluid resistance testing will be performed.

4.0 DESCRIPTION OF TEST ARTICLES

Test panels requiring cerium conversion coating were pre-treated by UM-Rolla while the remaining panels were pre-treated and coated by Boeing-St. Louis.

4.1 Alloy and Surface Treatment

4.1.1 7075-T6 bare aluminum, chromate conversion coated per P.S. 13209
4.1.2 7075-T6 bare aluminum, cerium conversion coated
4.1.3 2024-T3 alclad aluminum, chromate conversion coated per P.S. 13209
4.1.4 2024-T3 bare aluminum, chromate conversion coated per P.S. 13209
4.1.5 2024-T0 bare aluminum, chromic acid anodized per P.S. 13201, TY I

4.2 Primer Type

4.2.1 Deft 44-GN-72 Type I chromated epoxy **control** primer
4.2.2 U.S. Paint W4102/W3103 Type I non-chromated **baseline** primer
4.2.3 Dexter/Crown Metro 10PW22-2 / ECW-119 Type I non-chromated **baseline** primer
4.2.4 Spraylat/PRC-De Soto EWAE118 A/B Type II low IR non-chromated **baseline** primer
4.2.5 Deft 65-Y-002 non-chromated **test** primer
4.2.6 Deft 44-W-25 cerium based (cerium oxide) **test** primer
4.2.7 Deft 44-W-27 cerium based (cerium nitrate with K-white) **test** primer
4.2.8 Deft 44-W-28 cerium based (cerium nitrate) **test** primer

4.3 Topcoat Type

4.3.1 PRC-De Soto CA8201/F17925 / CA8200B (MMS 420) Fed. Std. 595 color 17925 gloss white topcoat

5.0 PROCEDURES AND RESULTS

Eight primers were tested in triplicate as described below. All of the panels were chromate conversion coated, per P.S. 13209, by Boeing-St. Louis or cerium conversion coated by UM-Rolla. All of the panels were primed per MMS 423B and topcoated per MMS 420, where applicable. MMS 420 polyurethane enamel topcoat was applied within four hours of primer application. All of the coated panels were air cured for 14-days before testing. Table 1 presents the coating application data as well as the resultant average thickness readings.

5.1 Corrosion Tests

5.1.1 Filiform Corrosion Resistance Test With MMS 420 Gloss White Topcoat for 1000 Hours (per MMS 423B)- Twenty-four alclad 2024-T3 aluminum panels were chromate conversion coated per P.S. 13209, primed and topcoated. A Hermes Vanguard 3400 engraving machine was used to scribe a "X" through the coated surface to the metal substrate of each panel. A spot test was performed, per P.S. 20004, to verify that the cladding had been penetrated. Each specimen's edge and back surface was covered with a protective tape. The panels were exposed to hydrochloric acid as prescribed in MMS 423B. Within 5 minutes of removal and without rinsing, the panels were transferred directly to a humidity chamber maintained at 104°F and 80% relative humidity for 1000 hours. MMS 423B requires that the panels exhibit no filiform corrosion extending beyond 1/4" from the scribe lines, and a majority of the filaments be less than 1/8" in length. Table 2 presents the 1000-hour filiform corrosion results.

All of the primers passed the 1000-hour filiform corrosion resistance test.

5.1.2 5% Salt Spray Corrosion Resistance Tests On 7075-T6 Aluminum for 3000 Hours (per MMS 423B)- Thirty-six bare 7075-T6 aluminum panels were supplied for testing. Twenty-four panels were chromate conversion coated per P.S. 13209 and twelve panels were cerium conversion coated. A Hermes Vanguard 3400 engraving machine was used to scribe a "X" through the coated surface to the metal substrate of each panel. Each specimen's edge and back surface was covered with a protective tape. All of the panels were exposed to 5% salt spray per ASTM B 117. The specimens were inspected at 1000, 2000, and 3000 hours and photographed at 2000 and 3000 hours. Table 3 presents the inspection results while Figure 1 presents the resultant photographs. MMS 423 requires that there be no signs of blistering, softening, lifting of the coating, or any corrosion extending beyond 1/32" from the scribe lines. After 3000 hours, each primer was ranked from best to worst. The coating was stripped from one panel from each primer group and the panels were re-ranked. Table 4 presents

the ranking results. Figure 2 presents a photograph of the stripped panels as a group. Photographs, at 1-power magnification, of the panels at each inspection interval are presented in Appendix A. Photographs, at 1-power magnification, of the stripped panels are presented in Appendix B.

All of the chromate conversion coated control/baseline primers and test primers passed the 5% salt spray corrosion resistance test per MMS 423B. However, only two of the four cerium conversion coated test primers passed the 5% salt spray corrosion resistance test per MMS 423B; Deft 44-W-28 (cerium nitrate) and Deft 44-GN-72 (chromated control). The two failed test primers, Deft 44-W-25 (cerium oxide) and Deft 44-W-27 (cerium nitrate w/ K-white), were dramatically less corrosion resistant when pre-treated with cerium conversion coating than chromate conversion coating.

The control/baseline primer panels were ranked higher than all of the test primers with the exception that the chromate conversion coated test primer Deft 65-Y-002 ranked higher than the chromate conversion coated baseline primer Dexter/Crown Metro 10PW22-2.

5.1.4 SO_2 Salt Spray Corrosion Resistance Tests On 2024-T3 and 7075-T6 Aluminum for 3000 Hours (per MMS 423B)- Twenty-four bare 2024-T3 aluminum panels, chromate conversion coated per P.S. 13209, were primed for testing. A Hermes Vanguard 3400 engraving machine was used to scribe a "X" through the coated surface to the metal substrate of each panel. Each specimen's edge and back surface was covered with a protective tape. All of the panels were exposed to SO_2 salt spray for 2-weeks, per ASTM G 85. The specimens were inspected at 1000, 2000 and 3000 hours. MMS 423 requires that there be no signs of blistering, softening, lifting of the coating, or any corrosion extending beyond 1/32" from the scribe lines. At the completion of the test, the panels were inspected, ranked, photographed, stripped, and re-photographed. Table 5 presents the inspection results while Figure 3 presents the photographs of the coated panels. Figure 4 presents a group photograph of the stripped panels. Photographs, at 1-power magnification, at each inspection interval are presented in Appendix C. Photographs, at 1-power magnification, of the stripped panels are presented in Appendix D.

All of the control/baseline primers passed the SO_2 salt spray corrosion resistance test except Spraylat/PRC-De Soto EWAE118 (non-chromated baseline). Test primers Deft 65-Y-002 (non-chromated) and Deft 44-W-25 (cerium oxide) passed, while test primers Deft 44-W-27 (cerium nitrate w/ K-white) and Deft 44-W-28 (cerium nitrate) failed the corrosion resistance test.

The control/baseline primer panels were ranked higher than all of the test primers, with the exception that Deft 65-Y-002 ranked higher than Spraylat/PRC-De Soto EWAE118.

5.2 Adhesion Tests

5.2.1 Scribed Wet Tape Adhesion Test (per MMS 420G)- Twenty-four alclad 2024-T3 aluminum panels, conversion coated per P.S. 13209, were primed for testing. A scribed wet tape adhesion test was performed on each panel per P.S. 21313. MMS 423B requires that the coating not exhibit any blistering and/or adhesion failures. The percentage of the coating removed was provided. Each panel was evaluated per Method A of ASTM D 3359 - 95. Table 6 presents the test results.

All of the primers passed the scribed wet tape adhesion test.

5.3 Fluid Resistance Tests

5.3.1 MIL-H-83282 Hydraulic Fluid Resistance Test at 150°F (per MIL-PRF-85582C)- Twenty-four bare 2024-T3 aluminum panels, conversion coated per P.S. 13209, were primed for testing. All of the panels were exposed to MIL-H-83282 hydraulic fluid in accordance with ASTM D 1308 at 150°F for 24 hours. MIL-PRF-85582C requires that there be no signs of softening, blistering, loss of adhesion, or other visually detectable deficiency four hours after removal from the hydraulic fluid. Discoloration of the coating is acceptable and shall not be cause for rejection. Table 7 presents the test results.

All of the primers passed the MIL-H-83282 hydraulic fluid resistance test.

5.4 Flexibility Tests

5.4.1 GE Reverse Impact Flexibility Tests (per MMS 423B)- Twenty-four bare 2024-T3 aluminum panels, conversion coated per P.S. 13209, were primed for testing. Reverse impact testing was performed on all of the panels per MMS 423B MMS 423B requires that the coating exhibit a minimum impact elongation of 10% when examined under 10-power magnification. Table 8 presents the test results.

Deft 44-GN-72 control/baseline primers passed and Deft 44-W-25 and Deft 44-W-28 test primers passed the ~~MIL-H-83282 hydraulic fluid resistance test.~~ GE reverse impact test

6.0 **SUMMARY**

The test results are summarized below and in Table 9.

Corrosion Tests:
Chromate conversion coated test panels showed superior corrosion resistance to cerium conversion coated test panels when coated with any of the cerium inhibited test primers.

For chromate conversion coated panels; 1) all of the control/baseline primers were superior to the cerium inhibited primers, 2) Deft 65-Y-002 (non-chromated) test primer was superior to the cerium inhibited test primers, and 3) there was no discernable difference between Deft 44-W-25 (cerium oxide) and Deft 44-W-28 (cerium nitrate) test primers, while Deft 44-W-27 (cerium nitrate w/ K-white) test primer was inferior.

For cerium conversion coated panels; there was no discernable difference between Deft 44-W-25 (cerium oxide) and Deft 44-W-28 (cerium nitrate) test primers, while Deft 44-W-27 (cerium nitrate w/ K-white) was clearly inferior.

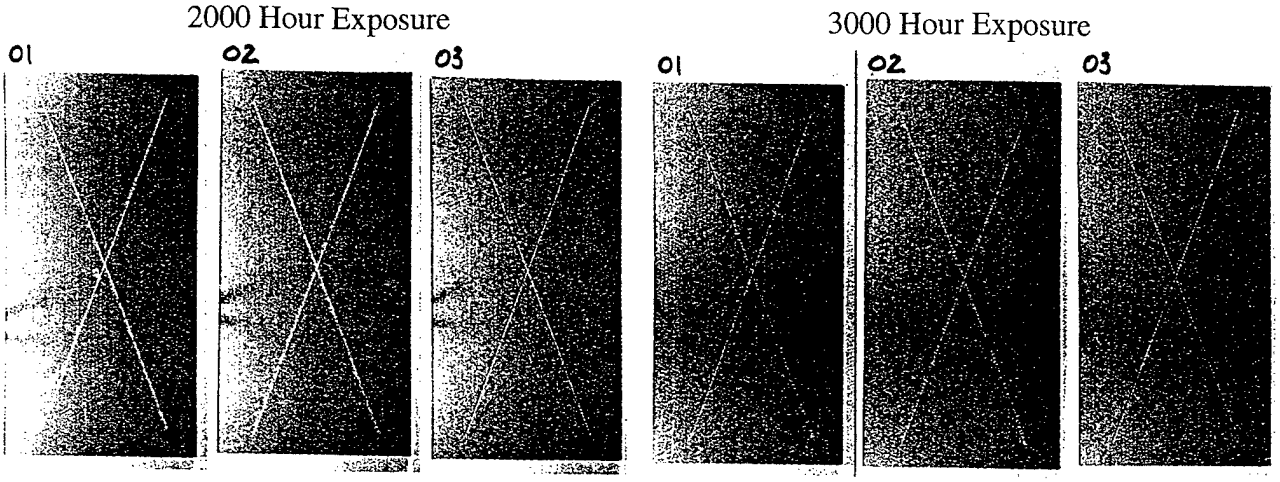
Adhesion Tests:
All of the primers showed excellent adhesion properties.

Fluid Resistance:
All of the primers showed excellent resistance to MIL-H-83282 hydraulic fluid.

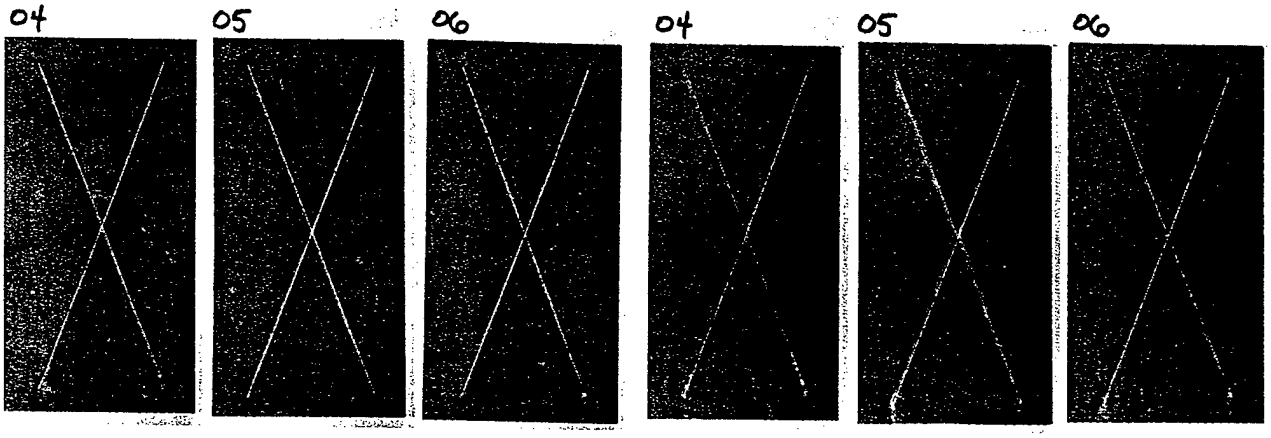
Flexibility:
Deft 44-W-25 (cerium oxide) and Deft 44-W-28 (cerium nitrate) test primers were more flexible than both Deft 44-W-27 (cerium nitrate w/ K-white) and Deft 65-Y-002 (non-chromated) test primers.

7.0 CONCLUSIONS

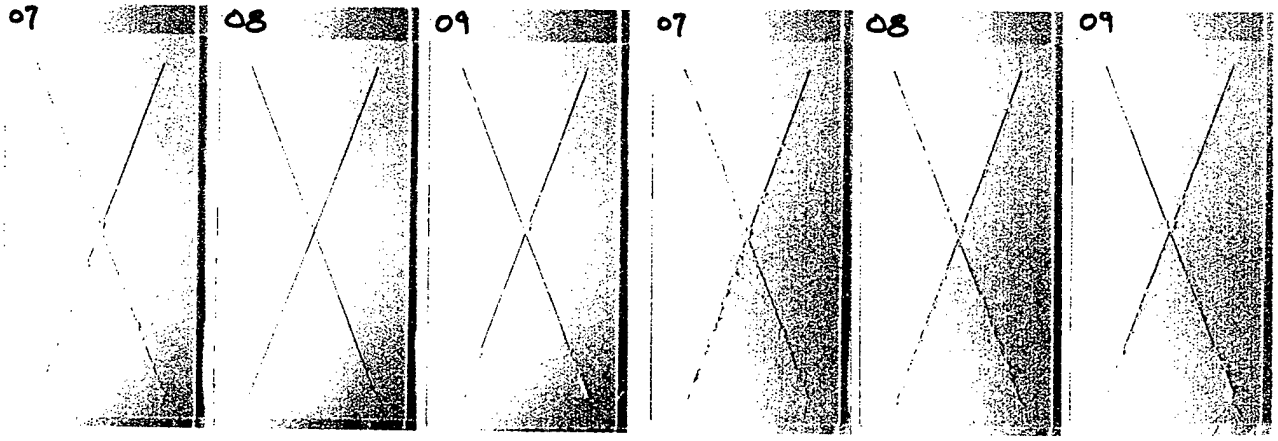
Chromate conversion coated test panels showed superior corrosion resistance to cerium conversion coated test panels when coated with any of the cerium inhibited test primers. Deft 44-W-25 (cerium oxide) and Deft 44-W-28 (cerium nitrate) test primers were superior to Deft 44-W-27 (cerium nitrate w/ K-white) test primer.



Specimens 1, 2, 3; Deft 44-GN-72 Primer Over Chromate Conversion Coating



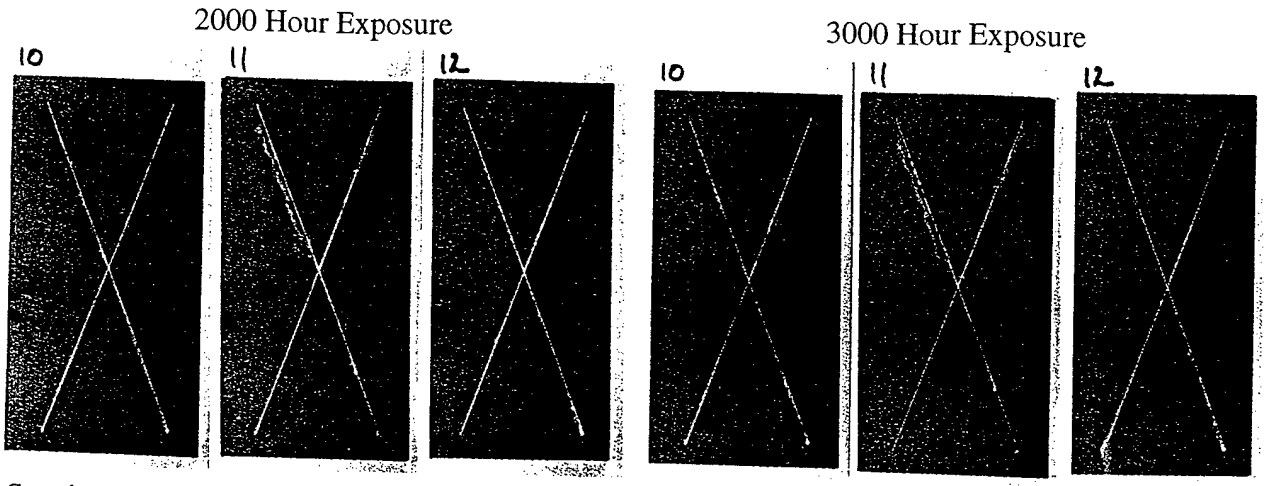
Specimens 4, 5, 6; U.S. Paint W4102 Primer Over Chromate Conversion Coating



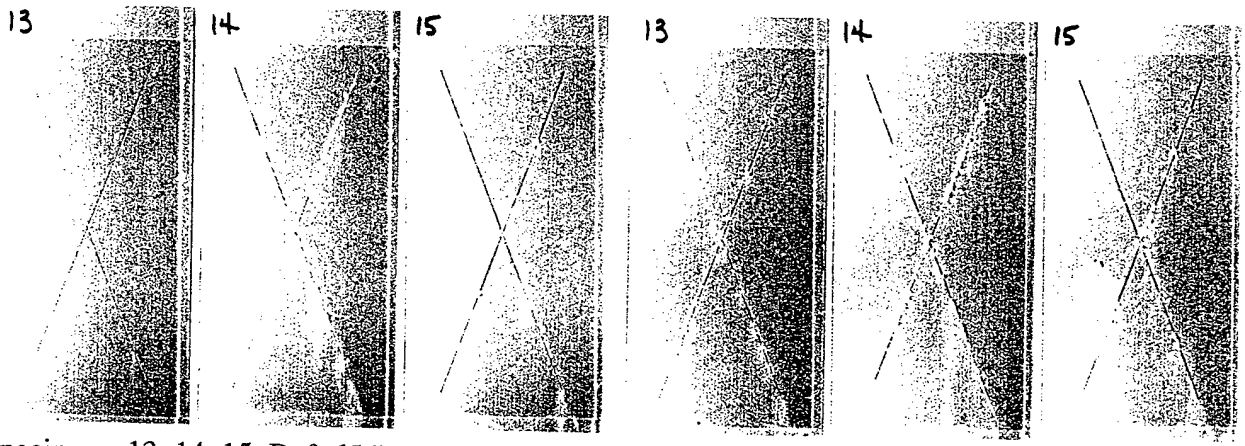
Specimens 7, 8, 9; Dexter 10PW22-2 Primer Over Chromate Conversion Coating

Figure 1 – Photographs of 7075-T6 Aluminum Panels Exposed to 5% Salt Spray at Interim Inspections (2000 and 3000 hours).

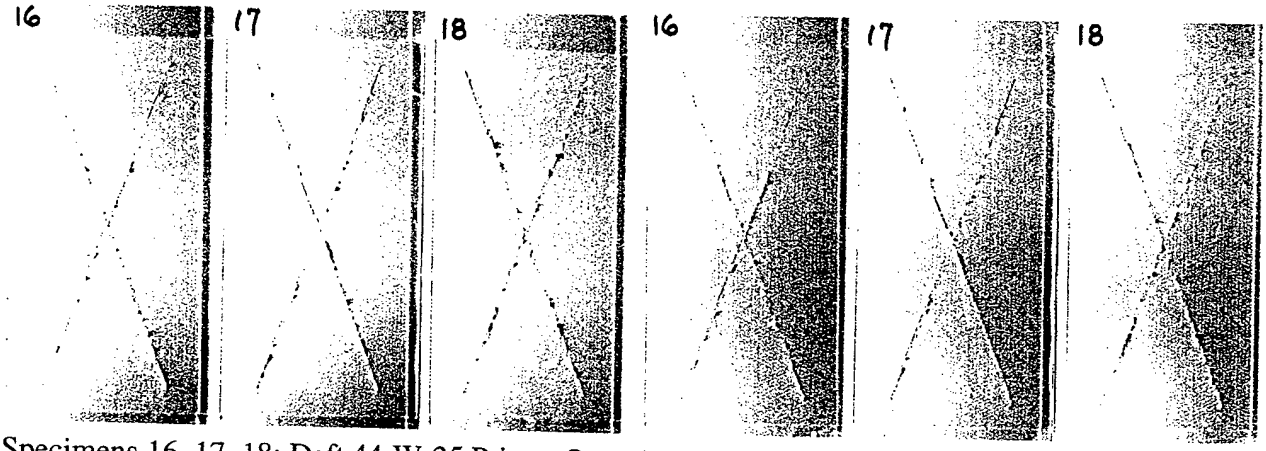
Figure 1 (cont.)



Specimens 10, 11, 12; PRC-De Soto EWAE118 Primer Over Chromate Conversion Coating



Specimens 13, 14, 15; Deft 65-Y-002 Primer Over Chromate Conversion Coating

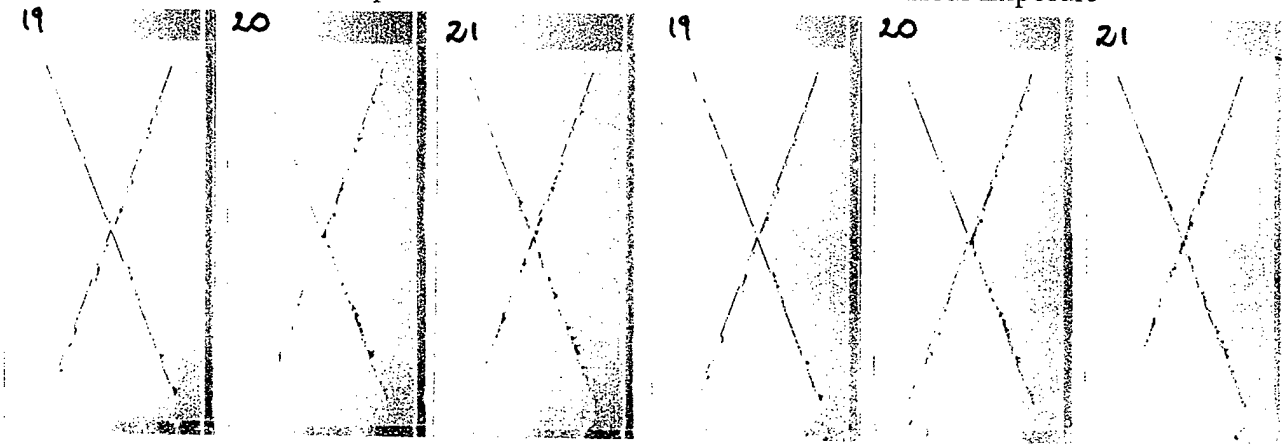


Specimens 16, 17, 18; Deft 44-W-25 Primer Over Chromate Conversion Coating

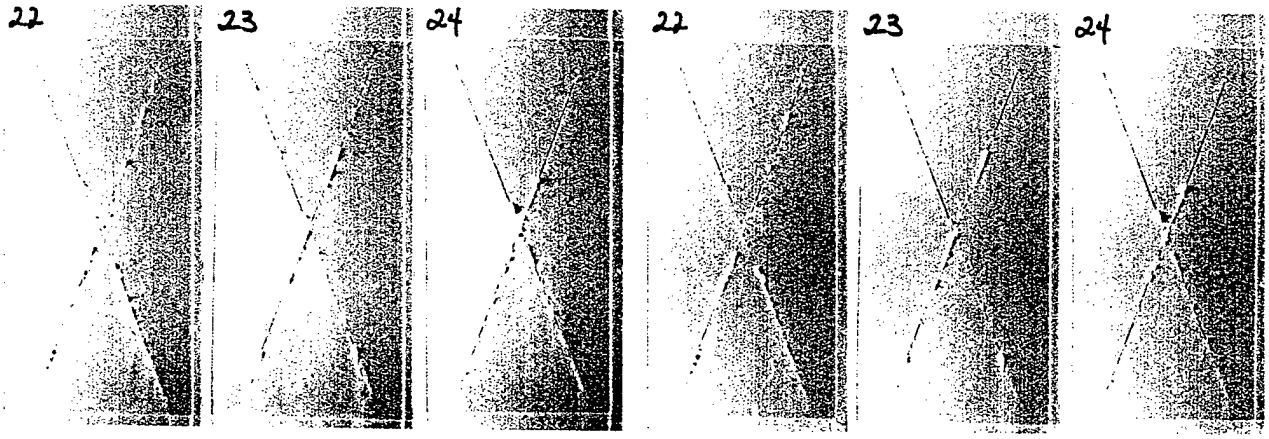
Figure 1 – Photographs of 7075-T6 Aluminum Panels Exposed to 5% Salt Spray at Interim Inspections (2000 and 3000 hours).

Figure 1 (cont.)

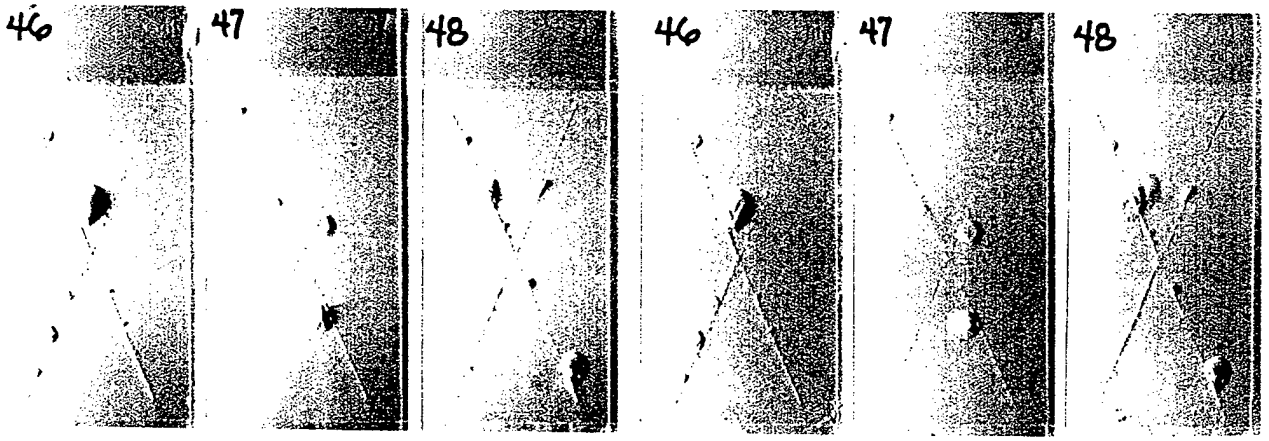
2000 Hour Exposure 3000 Hour Exposure



Specimens 19, 20, 21; Deft 44-W-27 Primer Over Chromate Conversion Coating



Specimens 22, 23, 24; Deft 44-W-28 Primer Over Chromate Conversion Coating

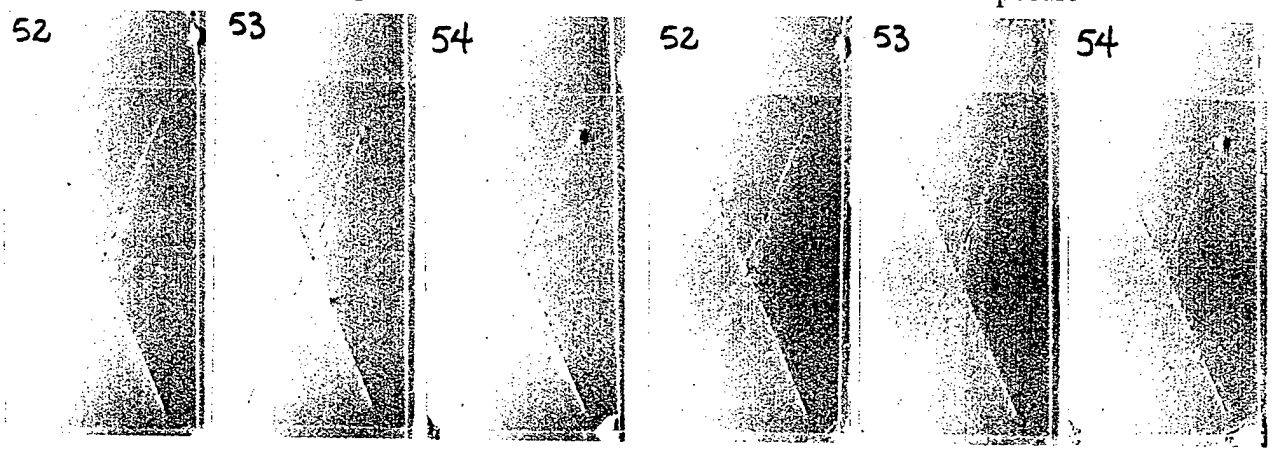


Specimens 46, 47, 48; Deft 44-W-25 Primer Over UM-Rolla Cerium Conversion Coating

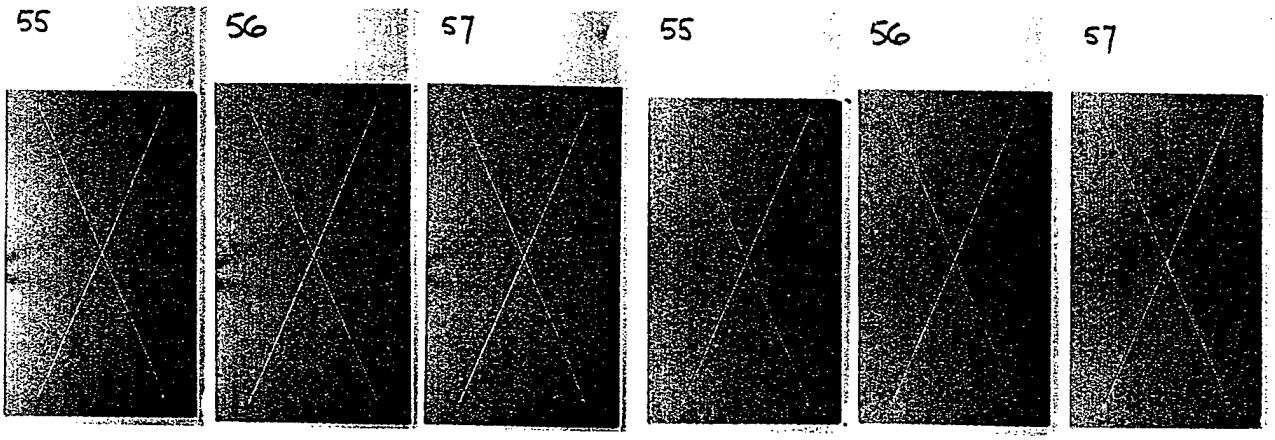
Figure 1 – Photographs of 7075-T6 Aluminum Panels Exposed to 5% Salt Spray At Interim Inspections (2000 and 3000 hours).

Figure 1 (cont.)

2000 Hour Exposure 3000 Hour Exposure

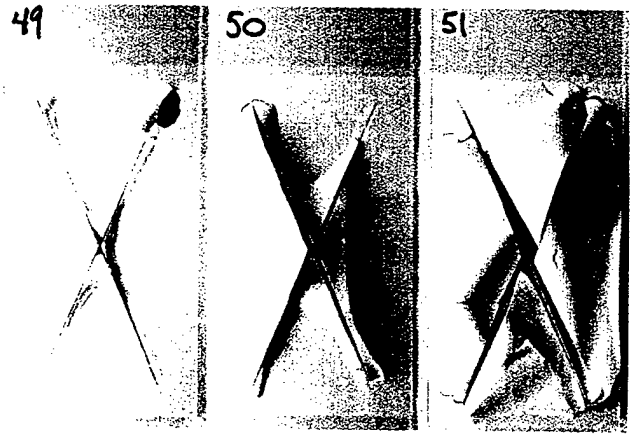


Specimens 52, 53, 54; Deft 44-W-28 Primer Over UM-Rolla Cerium Conversion Coating



Specimens 55, 56, 57; Deft 44-GN-72 Primer Over UM-Rolla Cerium Conversion Coating

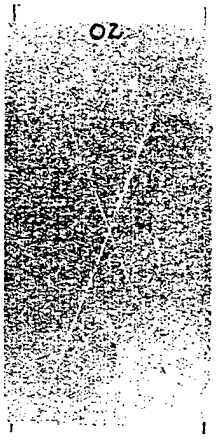
1000 Hour Exposure



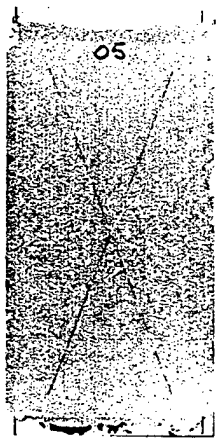
Specimens 49, 50, 51; Deft 44-W-27 Primer Over UMR Cerium Conversion Coating

Figure 1 – Photographs of 7075-T6 Aluminum Panels Exposed to 5% Salt Spray at Interim Inspections.

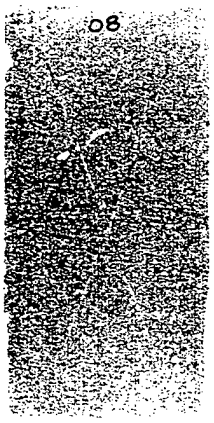
CHROMATE CONVERSION COATED



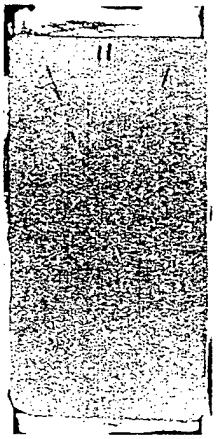
Deft 44-GN-72



U.S. Paint 4102

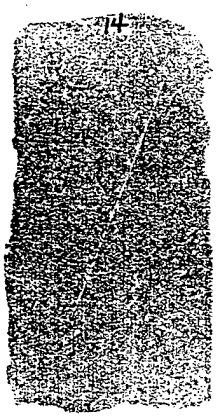


Dexter 10PW22-2

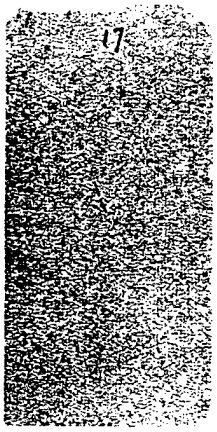


PRC-De Soto EWAE118

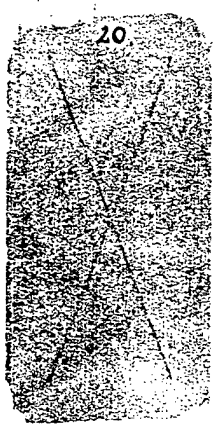
CHROMATE CONVERSION COATED



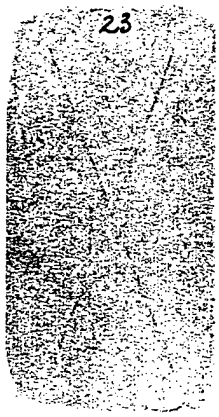
Deft 65-Y-002



Deft 44-W-25

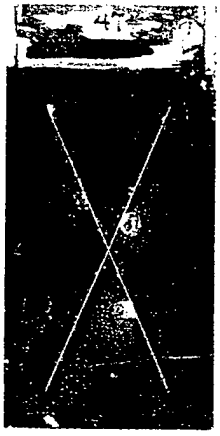


Deft 44-W-27

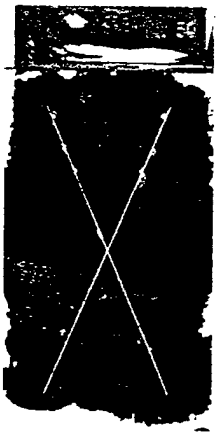


Deft 44-W-28

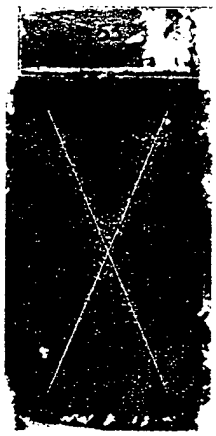
CERIUM CONVERSION COATED



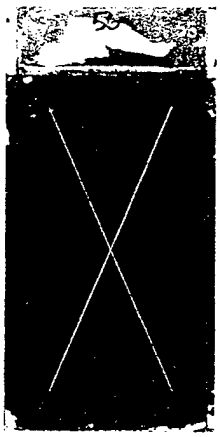
Deft 44-W-25



Deft 44-W-27

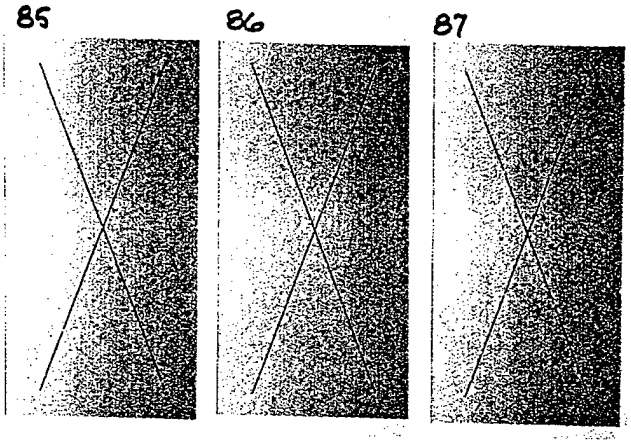


Deft 44-W-28

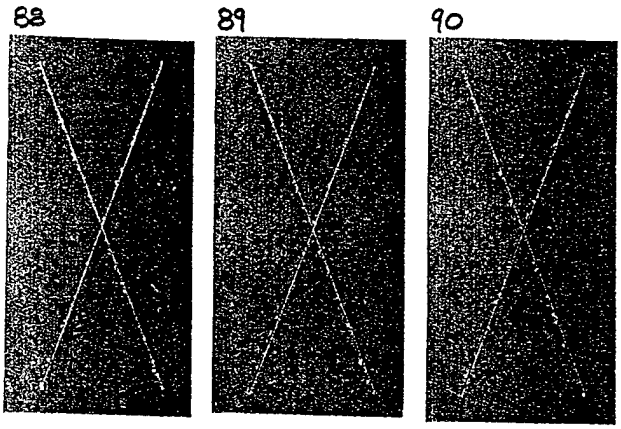


Deft 44-GN-72

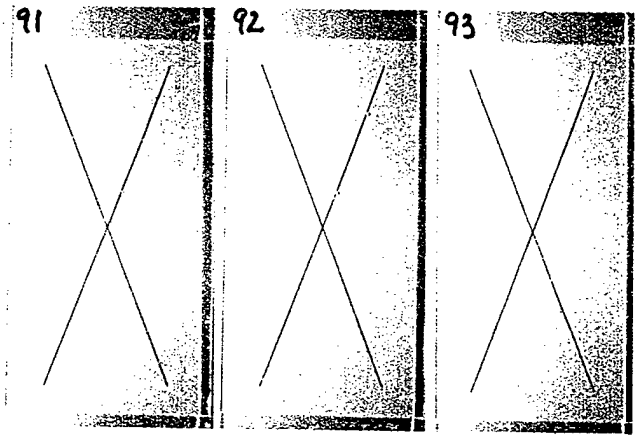
Figure 2 – Photographs of 7075-T6 Aluminum Panels Exposed to 5% Salt Spray for 3000 Hours, Then Stripped.



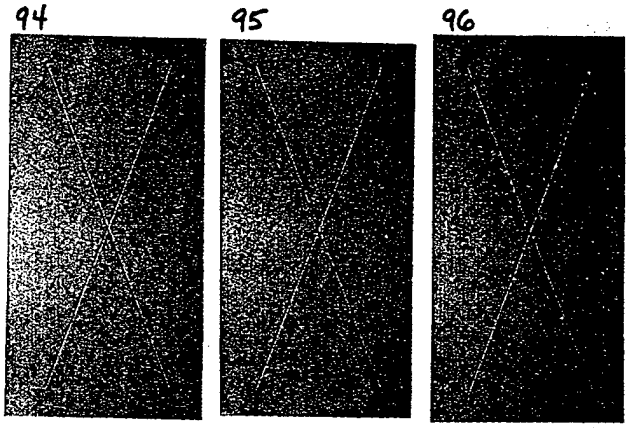
Specimens 85, 86, 87; Deft 44-GN-72



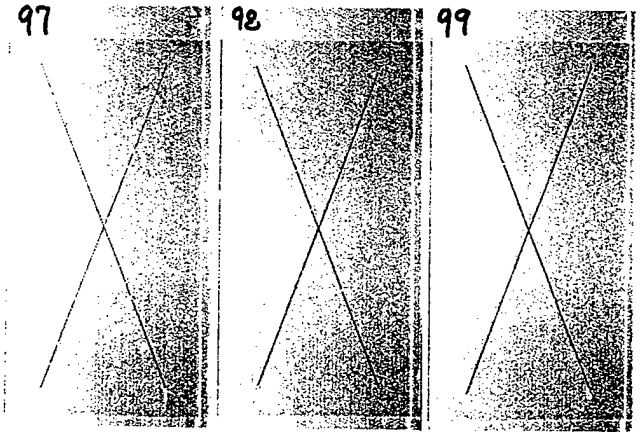
Specimens 88, 89, 90; U.S. Paint W4102



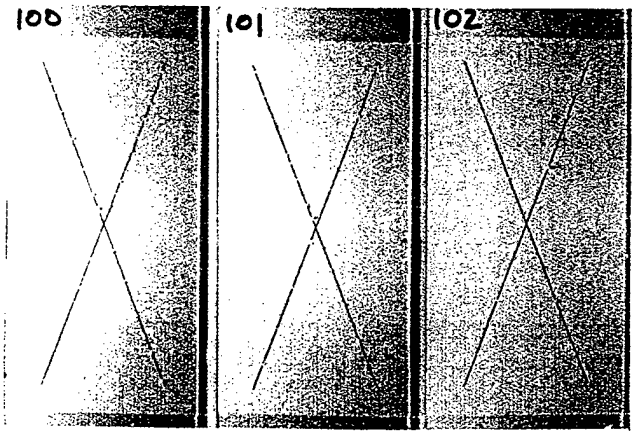
Specimens 91, 92, 93; Dexter 10PW22-2



Specimens 94, 95, 96; PRC-De Soto EWAE118



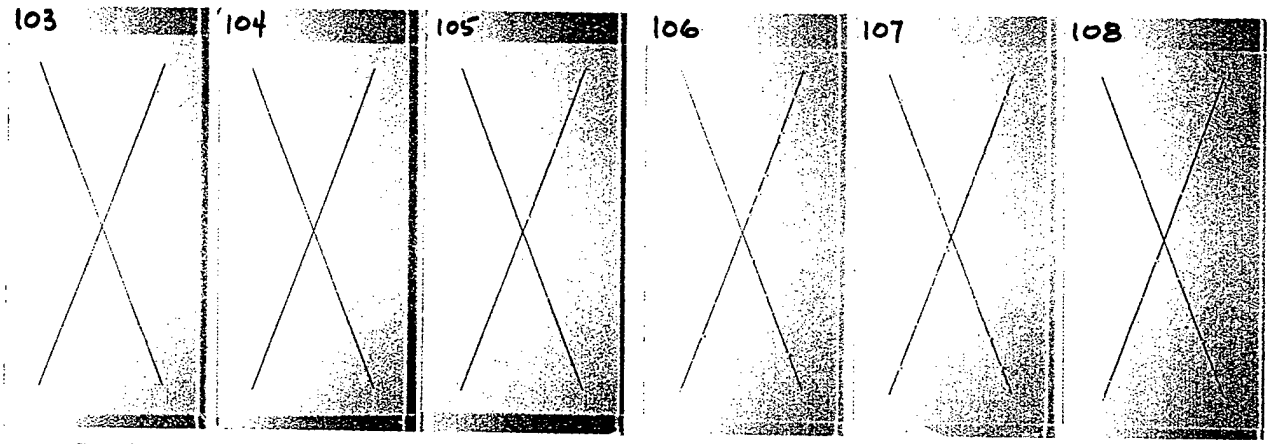
Specimens 97, 98, 99; Deft 65-Y-002



Specimens 100, 101, 102; Deft 44-W-25

Figure 3 – Photographs of Chromate Conversion Coated 2024-T3 Aluminum Panels Exposed to SO_2 Salt Spray for 2-Weeks

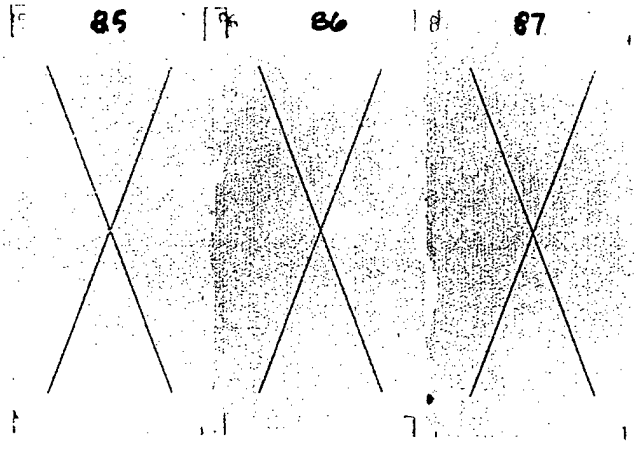
Figure 3 (cont.)



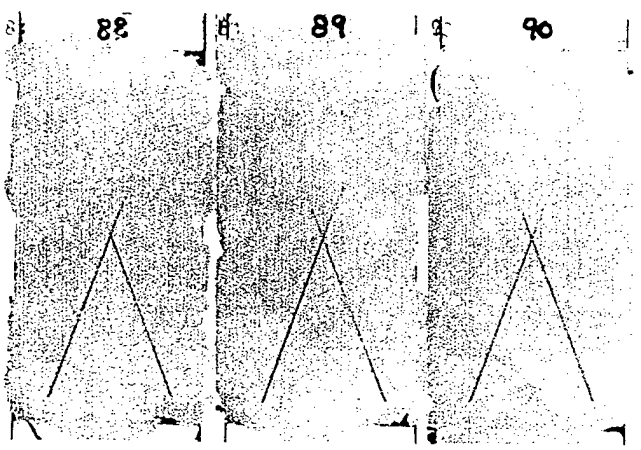
Specimens 103, 104, 105; Deft 44-W-27

Specimens 106, 107, 108; Deft 44-W-28

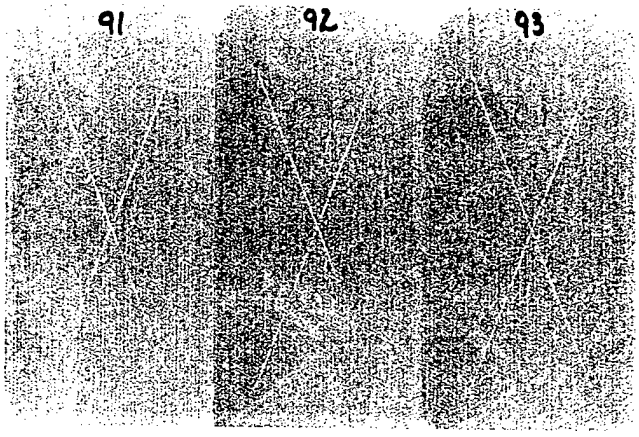
Figure 3 – Photographs of Chromate Conversion Coated 2024-T3 Aluminum Panels Exposed to SO_2 Salt Spray for 2-Weeks.



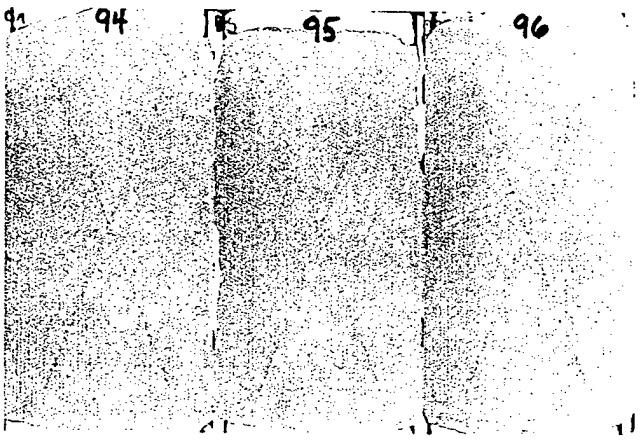
Specimens 85, 86, 87; Deft 44-GN-72



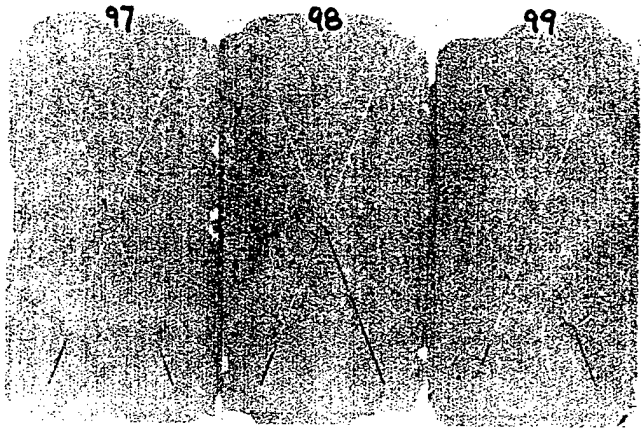
Specimens 88, 89, 90; U.S. Paint W4102



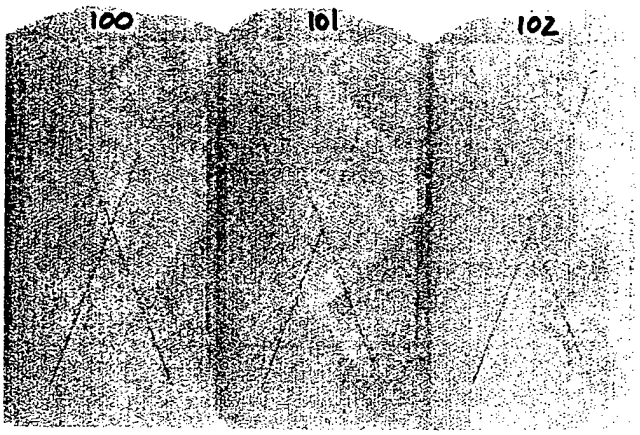
Specimens 91, 92, 93; Dexter 10PW22-2



Specimens 94, 95, 96; PRC-De Soto EWAE118



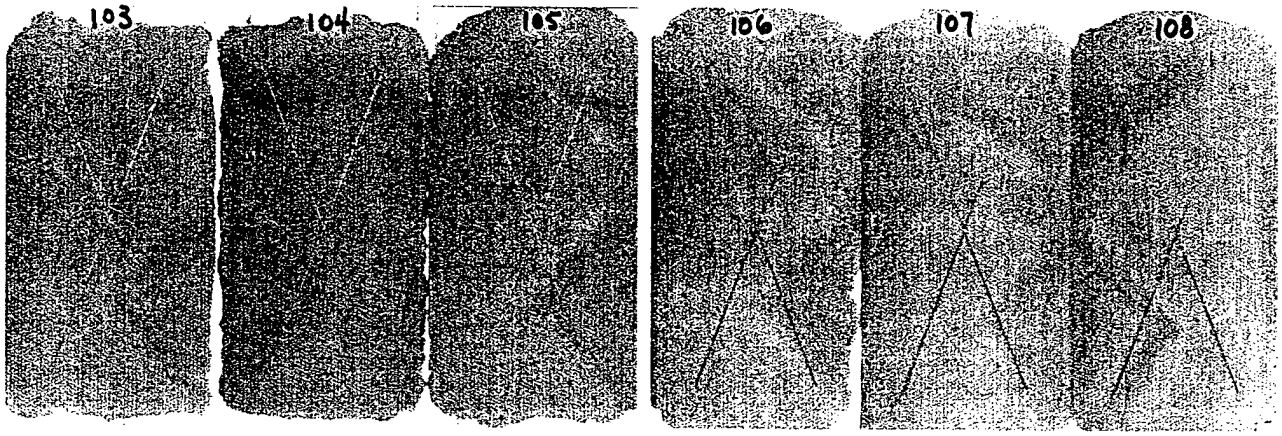
Specimens 97, 98, 99; Deft 65-Y-002



Specimens 100, 101, 102; Deft 44-W-25

Figure 4 – Photographs of Chromate Conversion Coated 2024-T3 Aluminum Panels Exposed to SO_2 Salt Spray for 2-Weeks, Then Stripped.

Figure 4 (cont.)



Specimens 103, 104, 105; Deft 44-W-27

Specimens 106, 107, 108; Deft 44-W-28

Figure 4 – Photographs of Chromate Conversion Coated 2024-T3 Aluminum Panels Exposed to SO_2 Salt Spray for 2-Weeks, Then Stripped

Table 1 - Coating Application Data

PAINT CODE	MANUFACTURER	BASE			CATALYST			SURFACE PRETREATMENT DATE	COATING APPLICATION			Average Primer Thickness (mils)	Thickness	
		PART NUMBER	BATCH NUMBER	MFG DATE	PART NUMBER	BATCH NUMBER	MFG DATE		DATE	TIME	VISC [1] (sec)		HI/Lo (inch)	Standard Deviation
CERIUM BASED PRIMERS														
1	Deft	44W25	L-13932	unkwn	44W25CAT	L-13933	unknwn	1-Dec-99	2-Dec	9:50 AM	16	1.10	1.45 / 0.87	0.05
2	Deft	44W27	L-13936	unkwn	44W27CAT	L-13937	unknwn	1-Dec-99	2-Dec	8:30 AM	18	1.58	1.79 / 1.20	0.07
3	Deft	44W28	L-13938	unkwn	44W28CAT	L-13939	unknwn	1-Dec-99	2-Dec	8:15 AM	22	0.97	1.15 / 0.81	0.06
NON-CHROMATED BASELINE PRIMERS														
4	U.S. Paint Type I	W4102	SF99041-14-1	Oct-99	W3103	SP99041-15-1	Oct-99	1-Dec-99	2-Dec	11:30 AM	26	0.88	1.07 / 0.73	0.05
5	Dexter Type I	10PW22-2	PD274-19	Oct-99	ECW-119	PD274-018	Oct-99	1-Dec-99	2-Dec	10:40 AM	20	1.24	1.57 / 0.95	0.06
6	Spraylat Type II Low I.R	EWAE118 A	B9022	Feb-99	EWAE118 B	F8102A	Feb-99	1-Dec-99	2-Dec	10:15 AM	35	1.50	1.75 / 1.21	0.08
7	Deft	65Y002 A	L-13868	unknwn	65Y002 B	L-13869	unknwn	1-Dec-99	2-Dec	10:05 AM	16	1.28	1.72 / 0.94	0.10
CONTROL PRIMER														
8	Deft Type I	44GN72 A	33972	Jun-99	44GN72 B	33973	Jun-99	1-Dec-99	2-Dec	9:00 AM	15	1.09	1.42 / 0.71	0.07
CONTROL TOPCOAT														
9	PRC-De Soto	CA8201 / F17925	525510	Sep-99	CA8000D	510582	Jul-99	1-Dec-99	2-Dec	2:45 AM	19	1.57	2.40 / 1.13	0.15

Notes:
[1] - Viscosity measurements were taken at room temperature with a #4 Ford cup

Table 2 - 1000-Hour Filiform Test Results

SUBSTRATE	PANEL ID	PRIMER	MMS 423B PASS/FAIL [1]	FILAMENTS LONGER THAN 1/8" (%)
Alclad 2024-T3 Aluminum With Chromate Conversion Coating per P. S. 13209				
	61	Deft (Chromated Control) 44-GN-72 A/B	P	None
	62			None
	63			None
	64	U. S. Paint W4102 / W3103 (Non-Chromated Baseline)	P	None
	65			None
	66			None
	67	Dexter / Crown Metro 10PW22-2 / ECW-119 (Non-Chromated Baseline)	P	None
	68			None
	69			None
	70	Spraylat / PRC-De Soto EWAE118 A/B (Non-Chromated Baseline)	P	None
	71			None
	72			None
	73	Deft 65Y002 (Non-Chromated)	P	None
	74			None
	75			None
	76	Deft 44-W-25 (Cerium Oxide)	P	None
	77			None
	78			None
	79	Deft 44-W-27 (Cerium Nitrate w/ K-white)	P	None
	80			None
	81			None
	82	Deft 44-W-28 (Cerium Nitrate)	P	None
	83			None
	84			None

Notes:

[1] - MMS 423A requires that he majority of filaments shall extend less than 1/8" from the scribe line and none may extend more than 1/4" inch from scribe line.

Table 3 - 3000-Hour 5% Salt Spray Corrosion Resistance Test Results

ALLOY	PRIMER	PANEL ID	WKS	CORROSION CODES [1]	MMS 423 [2]	COMMENTS
Bare 7075-T6 Aluminum Chromate Conversion Coated per P.S. 13209						
	Deft 44-GN-72 (Chromated Control)	1	6		P	No corrosion.
			12			
			18			
		2	6			No corrosion.
			12			
			18			
		3	6			No corrosion.
			12			No corrosion.
			18			
	U. S. Paint (Non-Chromated Baseline)	4	6		P	
			12			
			18			
		5	6			
			12			
			18			
		6	6			
			12			
			18			
	Dexter / Crown Metro 10PW22-2 (Non-Chromated Baseline)	7	6		P	
			12			Salt filling 40% of scribe.
			18			Salt filling 50% of scribe.
		8	6			
			12			
			18			Salt filling 50% of scribe.
		9	6			
			12			Salt filling 10% of scribe.
			18			Salt filling 30% of scribe.
	Spraylat / PRC-De Soto (Non-Chromated Baseline)	10	6		P	
			12			
			18			
		11	6			
			12			
			18			
		12	6			
			12			
			18			
	Deft 65Y002 (Non-Chromated)	13	6		P	
			12			
			18			Salt filling 10% of scribe.
		14	6			
			12			Salt filling 30% of scribe.
			18			Salt filling 40% of scribe.
		15	6			
			12			
			18			Salt filling 20% of scribe. Three 1/32" diameter blisters on field.

Table 3 (cont.)

Table 3 - 3000-Hour 5% Salt Spray Corrosion Resistance Test Results

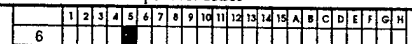
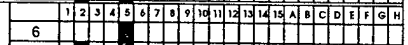
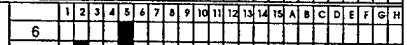
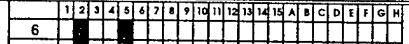
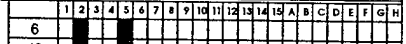
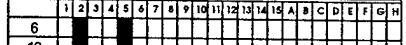
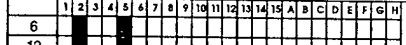
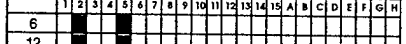
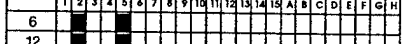
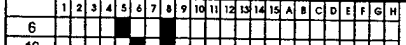
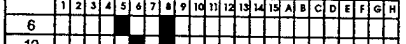
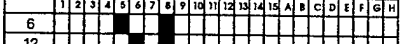
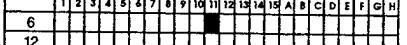
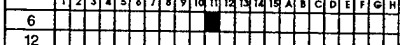
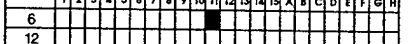
ALLOY	PRIMER	PANEL ID	WKS	CORROSION CODES [1]	MMS 423 [2]	COMMENTS
Bare 7075-T6 Aluminum Chromate Conversion Coated per P.S. 13209						
	Deft 44-W-25 (Cerium Oxide)	16			P	
			6			Salt filling 70% of scribe.
			12			Salt filling 70% of scribe.
			18			Salt filling 70% of scribe.
		17				
			6			Salt filling 60% of scribe.
			12			Salt filling 60% of scribe.
			18			Salt filling 60% of scribe.
		18				
			6			Salt filling 85% of scribe.
			12			Salt filling 90% of scribe.
			18			Salt filling 90% of scribe.
	Deft 44-W-27 (Cerium Nitrate w/ K-white)	19			P	
			6			Salt filling 30% of scribe.
			12			Salt filling 30% of scribe.
			18			Salt filling 30% of scribe.
		20				
			6			Salt filling 50% of scribe.
			12			Salt filling 50% of scribe.
			18			Salt filling 60% of scribe.
		21				
			6			Salt filling 50% of scribe.
			12			Salt filling 50% of scribe.
			18			Salt filling 50% of scribe.
	Deft 44-W-28 (Cerium Nitrate)	22			P	
			6			
			12			Salt filling 40% of scribe.
			18			Salt filling 50% of scribe.
		23				
			6			
			12			Salt filling 30% of scribe.
			18			Salt filling 30% of scribe.
		24				
			6			
			12			Salt filling 40% of scribe.
			18			Salt filling 40% of scribe.
Bare 7075-T6 Aluminum Cerium Conversion Coated by UM-Rolla						
	Deft 44-W-25 (Cerium Oxide)	46			F	
			6			Salt filling 95% of scribe. Largest blister propagated 0.32" from scribe.
			12			Largest blister propagated 0.48" from scribe.
			18			Largest blister propagated 0.48" from scribe.
		47				
			6			Salt filling 95% of scribe. Largest blister propagated 0.25" from scribe.
			12			Largest blister propagated 0.38" from scribe.
			18			Largest blister propagated 0.48" from scribe.
		48				
			6			Salt filling 90% of scribe. Largest blister propagated 0.31" from scribe.
			12			Largest blister propagated 0.34" from scribe.
			18			Largest blister propagated 0.41" from scribe.
	Deft 44-W-27 (Cerium Nitrate w/ K-white)	49			F	
			6			Test suspended after 1000 hours.
			12			
			18			
		50				
			6			Test suspended after 1000 hours.
			12			
			18			
		51				
			6			100% adhesion loss. Test suspended after 1000 hours.
			12			
			18			

Table 3 (cont.)

Table 3 - 3000-Hour 5% Salt Spray Corrosion Resistance Test Results

ALLOY	PRIMER	PANEL ID	WKS	CORROSION CODES [1]	MMS 423 [2]	COMMENTS
Bare 7075-T6 Aluminum Cerium Conversion Coated by UM-Rolla						
	Deft 44-W-28 (Cerium Nitrate)	52	6	1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 A B C D E F G H	P	Salt filling 95% of scribe.
			12			Salt filling 95% of scribe.
			18			Salt filling 95% of scribe.
		53	6			Salt filling 95% of scribe.
			12			Salt filling 95% of scribe.
			18			Salt filling 95% of scribe.
		54	6			Salt filling 90% of scribe. Two blisters: largest blister propagated 0.19" from scribe.
			12			Salt filling 90% of scribe. Two blisters: largest blister propagated 0.22" from scribe.
			18			Salt filling 90% of scribe. Two blisters: largest blister propagated 0.22" from scribe.
	Deft 44-GN-72 (Chromated Control)	55	6	1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 A B C D E F G H	P	
			12			
			18			
		56	6			
			12			
			18			
		57	6			
			12			
			18			

Notes:

[1] - Corrosion Test Finding Codes

Number	Description
1	Scribe line beginning to darken or shiny scribe.
2	Scribe lines > 50% darkened.
3	Scribe line dark.
4	Several localized sites of white salt in scribe lines.
5	Many localized sites of white salt in scribe lines.
6	White salt filling scribe lines.
7	Dark corrosion sites in scribe lines.
8	Few blisters under primer along scribe line. (<12)
9	Many blisters under primer along scribe line.
10	Slight lift along scribe lines.
11	Coating curling up along scribe.
12	Pin point sites/pits of corrosion on field (away from scribe) (1/16" to 1/8" dia.).
13	One or more blisters on field (away from scribe).
14	Many blisters under primer on field (away from scribe).
15	Starting to blister on field (away from scribe).
	Scribe line ratings
A.	No creepage
B.	0 to 1/64
C.	1/64 to 1/32
D	1/32 to 1/16
E.	1/16 to 1/8
F.	1/8 to 3/16
G.	3/16 to 1/4
H.	1/4 to 3/8
I.	Corrosion initiation/salt buildup at edge of scribe.

[2] - MMS 423B requires that there be no signs of blistering, softening, lifting of the coating, or any corrosion extending more than 1/32' beyond the scribe marks.

Table 4 - 5% Salt Spray Rankings After 3000 Hours of Exposure

		P.S. 13209 CONVERSION COATING [2] [3]				UM-ROLLA CERIUM CONVERSION COATING [1] [2] [3]			
		PANEL ID	Ranking (Coated)		Ranking (Stripped)	PANEL ID	Ranking (Coated)		Ranking (Stripped)
SUBSTRATE	PRIMER		Scribe	Field	Scribe		Scribe	Field	Scribe
Bare 7075-T6 Aluminum, Chromate Conversion Coated per P.S. 13209									
	Deft (Chromated Control) 44-GN-72 A/B	1	1	1	1	55	2	1	2
		2				56			
		3				57			
	U. S. Paint W4102 / W3103 (Non-Chromated Baseline)	4	4	1	3	No Primers Tested			
		5							
		6							
	Dexter / Crown Metro 10PW22-2 / ECW-119 (Non-Chromated Baseline)	7	6	7	5				
		8							
		9							
	Spraylat / PRC-De Soto EWAE118 A/B (Non-Chromated Baseline)	10	3	1	4				
		11							
		12							
	Deft 65Y002 (Non-Chromated)	13	5	8	6				
		14							
		15							
	Deft 44-W-25 (Cerium Oxide)	16	7	5	7	46	11	11	11
		17				47			
		18				48			
	Deft 44-W-27 (Cerium Nitrate w/ K-white)	19	8	10	9	49	12	12	12
		20				50			
		21				51			
	Deft 44-W-28 (Cerium Nitrate)	22	9	5	8	52	10	9	10
		23				53			
		24				54			

[1] - Panels 49 to 51 were suspended after 1000 hours of testing due to extreme adhesion loss.
[2] - At the complettion of the test, the panels were visually ranked 1 to 12 (best to worst)
[3] - One panel from each primer group was stripped, using Turco 5469, and visually ranked 1 to 12 (best to worst)

Table 5 - 2-Week SO_2 Salt Spray Corrosion Resistance Test Results

ALLOY	PRIMER	PANEL ID	WKS	CORROSION CODES [1]	MMS 423 [2]	RANKING [3]	COMMENTS
Bare 2024-T3 Aluminum Chromate Conversion Coated per P.S. 13209							
	Deft 44-GN-72 (Chromated Control)	85	1	2 3 4 5 6 7 8 9 10 11 12 13 14 15 A B C D E F G H	P	3	
			2	2 5			
		86	1	2 3 4 5 6 7 8 9 10 11 12 13 14 15 A B C D E F G H			
			2	2 5			
		87	1	2 3 4 5 6 7 8 9 10 11 12 13 14 15 A B C D E F G H			
			2	2 5			
	U. S. Paint W4102 (Non-Chromated Baseline)	88	1	2 3 4 5 6 7 8 9 10 11 12 13 14 15 A B C D E F G H	P	4	
			2	2 5			
		89	1	2 3 4 5 6 7 8 9 10 11 12 13 14 15 A B C D E F G H			
			2	2 5			
		90	1	2 3 4 5 6 7 8 9 10 11 12 13 14 15 A B C D E F G H			
			2	2 5			
	Dexter / Crown Metro 10PW22-2 (Non-Chromated Baseline)	91	1	2 3 4 5 6 7 8 9 10 11 12 13 14 15 A B C D E F G H	P	1	
			2	5			
		92	1	2 3 4 5 6 7 8 9 10 11 12 13 14 15 A B C D E F G H			
			2	5			
		93	1	2 3 4 5 6 7 8 9 10 11 12 13 14 15 A B C D E F G H			
			2	5			
	Spraylat / PRC-De Soto EWAE118 (Non-Chromated Baseline)	94	1	2 3 4 5 6 7 8 9 10 11 12 13 14 15 A B C D E F G H	F	8	
			2	2 5 15			
		95	1	2 3 4 5 6 7 8 9 10 11 12 13 14 15 A B C D E F G H			
			2	2 5 15			
		96	1	2 3 4 5 6 7 8 9 10 11 12 13 14 15 A B C D E F G H			
			2	2 5 15			
	Deft 65Y002 (Non-Chromated)	97	1	2 3 4 5 6 7 8 9 10 11 12 13 14 15 A B C D E F G H	P	2	
			2	2 5			
		98	1	2 3 4 5 6 7 8 9 10 11 12 13 14 15 A B C D E F G H			
			2	2 5			
		99	1	2 3 4 5 6 7 8 9 10 11 12 13 14 15 A B C D E F G H			
			2	2 5			
	Deft 44-W-25 (Cerium Oxide)	100	1	2 3 4 5 6 7 8 9 10 11 12 13 14 15 A B C D E F G H	P	6	
			2	2 5			
		101	1	2 3 4 5 6 7 8 9 10 11 12 13 14 15 A B C D E F G H			
			2	2 5			
		102	1	2 3 4 5 6 7 8 9 10 11 12 13 14 16 A B C D E F G H			
			2	2 5			
	Deft 44-W-27 (Cerium Nitrate w/ K-white)	103	1	2 3 4 5 6 7 8 9 10 11 12 13 14 15 A B C D E F G H	F	7	
			2	2 5 15			
		104	1	2 3 4 5 6 7 8 9 10 11 12 13 14 15 A B C D E F G H			
			2	2 5 15			
		105	1	2 3 4 5 6 7 8 9 10 11 12 13 14 15 A B C D E F G H			
			2	2 5 15			
	Deft 44-W-28 (Cerium Nitrate)	106	1	2 3 4 5 6 7 8 9 10 11 12 13 14 15 A B C D E F G H	P	5	
			2	2 5			
		107	1	2 3 4 5 6 7 8 9 10 11 12 13 14 15 A B C D E F G H			
			2	2 5			
		108	1	2 3 4 5 6 7 8 9 10 11 12 13 14 15 A B C D E F G H			
			2	2 5			

[1] - Corrosion Test Finding Codes

Number	Description
1	Scribe line beginning to darken or shiny scribe.
2	Scribe lines > 50% darkened.
3	Scribe line dark.
4	Several localized sites of white salt in scribe lines.
5	Many localized sites of white salt in scribe lines.
6	White salt filling scribe lines.
7	Dark corrosion sites in scribe lines.
8	Few blisters under primer along scribe line. (<12)
9	Many blisters under primer along scribe line.
10	Slight lift along scribe lines.
11	Coating curling up along scribe.
12	Pin point sites/pits of corrosion on field (away from scribe) (1/16" to 1/8" dia.).
13	One or more blisters on field (away from scribe).
14	Many blisters under primer on field (away from scribe).
15	Starting to blister on field (away from scribe).
	Scribe line ratings
A.	No creepage
B.	0 to 1/64
C.	1/64 to 1/32
D	1/32 to 1/16
E.	1/16 to 1/8
F.	1/8 to 3/16
G.	3/16 to 1/4
H.	1/4 to 3/8

[2] - MMS 423B requires that there be no signs of blistering, softening, lifting of the coating, or any corrosion extending more than 1/32' beyond the scribe marks.

[3] - At the complettion of the test, the panels were ranked 1 to 8 (best to worst)

Table 6 - Scribed Wet Tape Adhesion Test Results

SUBSTRATE	PANEL ID	PRIMER	PERCENTAGE OF PRIMER REMOVED IN TAPE TESTED AREA %	ASTM D3359 [1]	MMS 423 PASS/FAIL [2]
Alclad 2024-T3 Aluminum With Chromate Conversion Coating per P. S. 13209					
	109	Deft (Chromated Control) 44-GN-72 A/B	0	5A	P
	110				
	111				
	112	U. S. Paint W4102 / W3103 (Non-Chromated Baseline)	0	5A	P
	113				
	114				
	115	Dexter / Crown Metro 10PW22-2 / ECW-119 (Non-Chromated Baseline)	0	5A	P
	116				
	117				
	118	Spraylat / PRC-De Soto EWAE118 A/B (Non-Chromated Baseline)	0	5A	P
	119				
	120				
	121	Deft 65Y002 (Non-Chromated)	0	5A	P
	122				
	123				
	124	Deft 44-W-25 (Cerium Oxide)	0	5A	P
	125				
	126				
	127	Deft 44-W-27 (Cerium Nitrate w/ K-white)	0	5A	P
	128				
	129				
	130	Deft 44-W-28 (Cerium Nitrate)	0	5A	P
	131				
	132				

Notes:

[1] - ASTM D 3359 Criteria

- 5A - No peeling or removal
- 4A - Trace peeling or removal along incisions
- 3A - Jagged removal along incisions up to 1/16 inch on either side
- 2A - Jagged removal along most of incisions up to 1/8 inch on either side
- 1A - Removal from most of the area of the "X" under the tape
- 0A - Removal beyond the area of the "X"

[2] - The primer shall show no adhesion failure

Table 7 – MIL-H-83282 Hydraulic Fluid Resistance Test Results

SUBSTRATE	PANEL ID	PRIMER	PENCIL HARDNESS PRE-TEST/POST-TEST [1]	MIL-P-85582B PASS/FAIL [2]
Bare 2024-T3 Aluminum With Chromate Conversion Coating per P. S. 13209				
	133	Deft (Chromated Control) 44-GN-72 A/B	2H / 2H	P
	134			
	135			
	136	U. S. Paint W4102 / W3103 (Non-Chromated Baseline)	2H / 2H	P
	137			
	138			
	139	Dexter / Crown Metro 10PW22-2 / ECW-119 (Non-Chromated Baseline)	3H / 3H	P
	140			
	141			
	142	Spraylat / PRC-De Soto EWAE118 A/B (Non-Chromated Baseline)	H / H	P
	143			
	144			
	145	Deft 65Y002 (Non-Chromated)	3H / 3H	P
	146			
	147			
	148	Deft 44-W-25 (Cerium Oxide)	2H / 2H	P
	149			
	150			
	151	Deft 44-W-27 (Cerium Nitrate w/ K-white)	2H / 2H	P
	152			
	153			
	154	Deft 44-W-28 (Cerium Nitrate)	2H / 2H	P
	155			
	156			

Notes:

[1] - Scratch hardness values observed at up to 10X magnification.
Recorded value is the hardest pencil lead that would not scratch the coating.

[2] - The primer shall exhibit no softening, blistering, loss of adhesion, nor any other coating deficiency.

Table 8 - GE Reverse Impact Flexibility Test Results

SUBSTRATE	PANEL ID	PRIMER	PERCENTAGE ELONGATION [1]	MMS 423B Pass/Fail [2]
Bare 2024-T0 Aluminum With Chromic Acid Anodize per P. S. 13201, TY I				
	157	Deft	20	
	158	(Chromated Control)	20	P
	159	44-GN-72 A/B	20	
	160	U. S. Paint	1	
	161	W4102 / W3103	1	F
	162	(Non-Chromated Baseline)	1	
	163	Dexter / Crown Metro	2	
	164	10PW22-2 / ECW-119	2	F
	165	(Non-Chromated Baseline)	2	
	166	Spraylat / PRC-De Soto	5	
	167	EWAE118 A/B	5	F
	168	(Non-Chromated Baseline)	5	
	169	Deft	2	
	170	65Y002	2	F
	171	(Non-Chromated)	2	
	172	Deft	10	
	173	44-W-25	10	P
	174	(Cerium Oxide)	10	
	175	Deft	2	
	176	44-W-27	2	F
	177	(Cerium Nitrate w/ K-white)	2	
	178	Deft	10	
	179	44-W-28	10	P
	180	(Cerium Nitrate)	10	

Notes:

[1] - The 0.5% to 5% elongations were the result of dropping the impacter from a height of 6 inches. The 10% to 60% elongations were the result of dropping the impacter from a height of 26 inches. The impacter was not allowed to double bounce on the test specimen. Ten power magnification was used to detect fine surface cracking. The percentage elongation corresponding to the largest spherical impression at which no cracking occurred was recorded.

[2] - The primer shall exhibit a minimum impact elongation of 10% when examined under 10X magnification.

Table 9 - Test Data Summary

PRE-TREATMENT	PRIMER NUMBER	PRIMER	TEST TYPE PASS / FAIL [1] CORROSION: Filiform:MMS 420 Gloss White Topcoat	5% Salt Spray, 7075-T6 Al	SO_2 Salt Spray, 2024-T3 Al	ADHESION: Scribed Wet Tape	FLUID: MIL-H-83282 Hydraulic Fluid	FLEXIBILITY: GE Reverse Impact
Chromate Conversion Coating per P. S. 13209								
	1	Deft 44-GN-72 (Chromated Control)	P	P	P	P	P	P
	2	U. S. Paint W4102 (Non-Chromated Baseline)	P	P	P	P	P	F
	3	Dexter / Crown Metro 10PW22-2 (Non-Chromated Baseline)	P	P	P	P	P	F
	4	Spraylat / PRC-De Soto EWAE118 (Non-Chromated Baseline)	P	P	P	P	P	F
	5	Deft 65Y002 (Non-Chromated)	P	P	P	P	P	F
	6	Deft 44-W-25 (Cerium Oxide)	P	P	P	P	P	P
	7	Deft 44-W-27 (Cerium Nitrate w/ K-white)	P	P	P	P	P	F
	8	Deft 44-W-28 (Cerium Nitrate)	P	P	P	P	P	P
Cerium Conversion Coating by UM-Rolla								
	6a	Deft 44-W-25 (Cerium Oxide)	No Test	F	No Test	No Test	No Test	No Test
	7a	Deft 44-W-27 (Cerium Nitrate w/ K-white)	No Test	F	No Test	No Test	No Test	No Test
	8a	Deft 44-W-28 (Cerium Nitrate)	No Test	P	No Test	No Test	No Test	No Test
	1a	Deft 44-GN-72 (Chromated Control)	No Test	P	No Test	No Test	No Test	No Test

Notes:
[1] - Pass / Fail criterion defined in text of this report.

APPENDIX A

5% Salt Spray Corrosion Per ASTM B 117

Photographic Documentation of 7075-T6 Aluminum Panels at Inspection Intervals (2000, and 3000 hours)

DEFT 44-GN-72
CHROMATE CONVERSION COATING

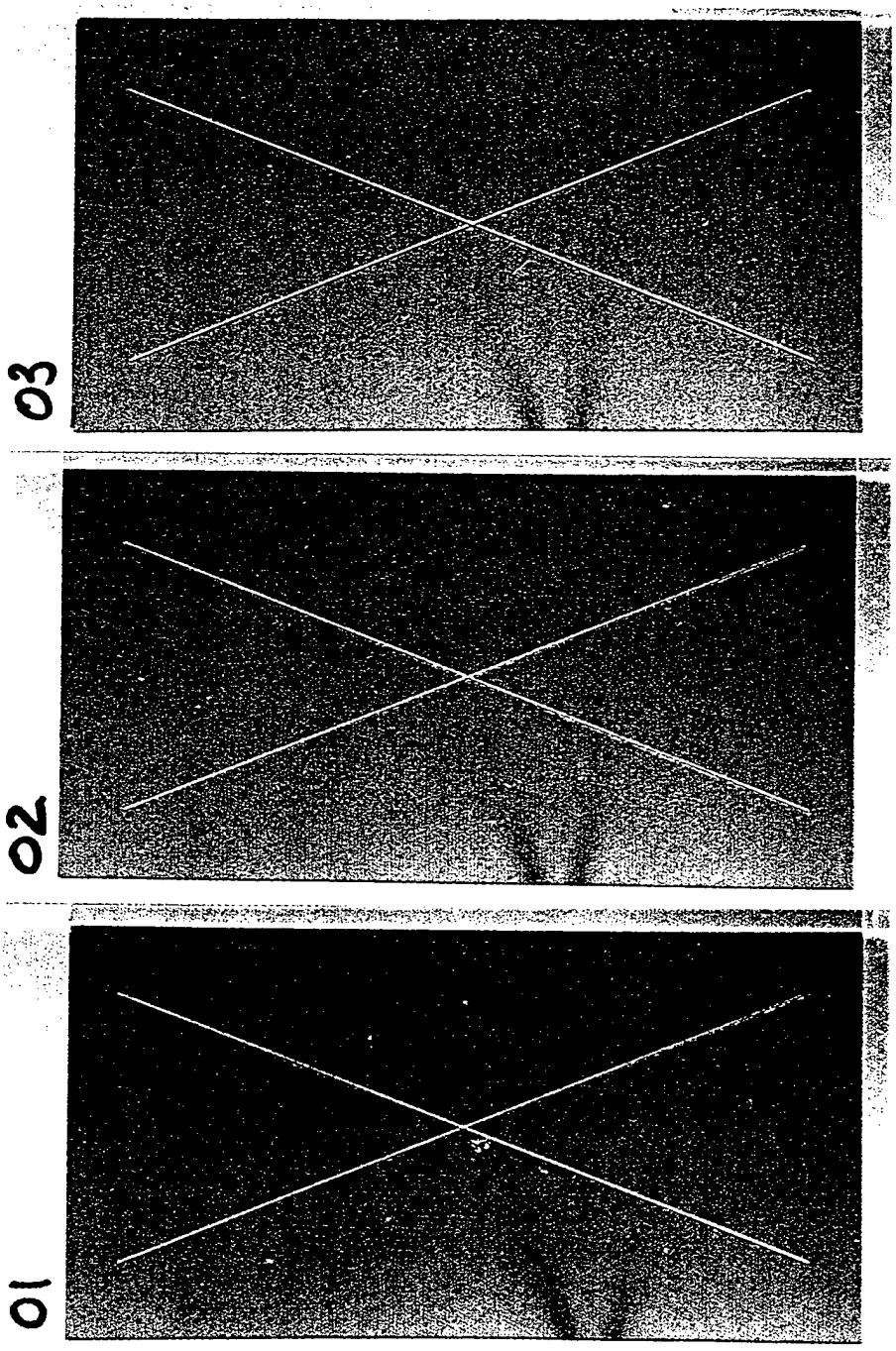


Figure A1 – Photographs of 7075-T6 Panels After Exposure to 5% Salt Spray For 2000 Hours.

U.S. PAINT W4102
CHROMATE CONVERSION COATING

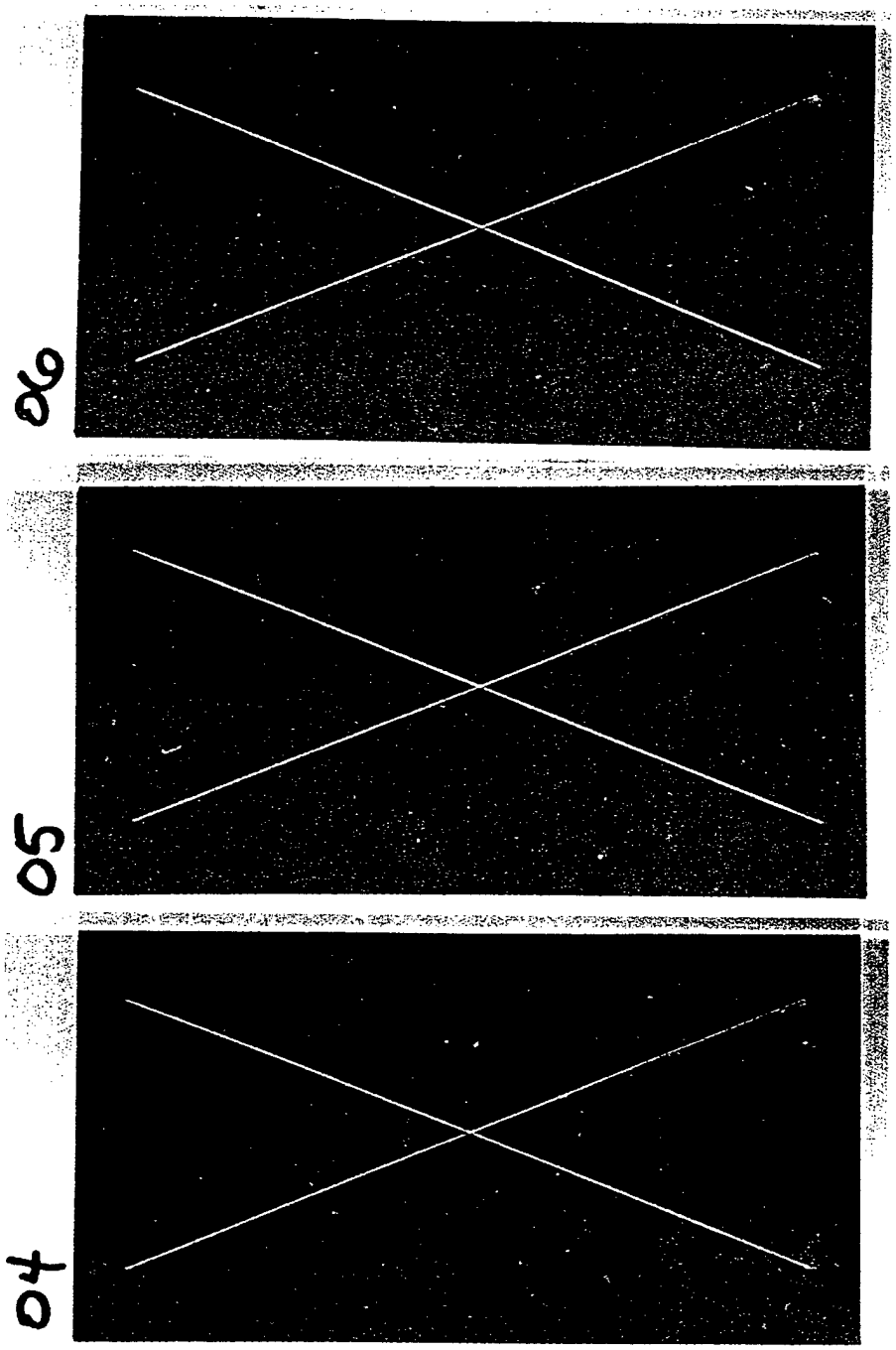


Figure A2 – Photographs of 7075-T6 Panels After Exposure to 5% Salt Spray For 2000 Hours.

DEXTER 10PW22-2
CHROMATE CONVERSION COATING

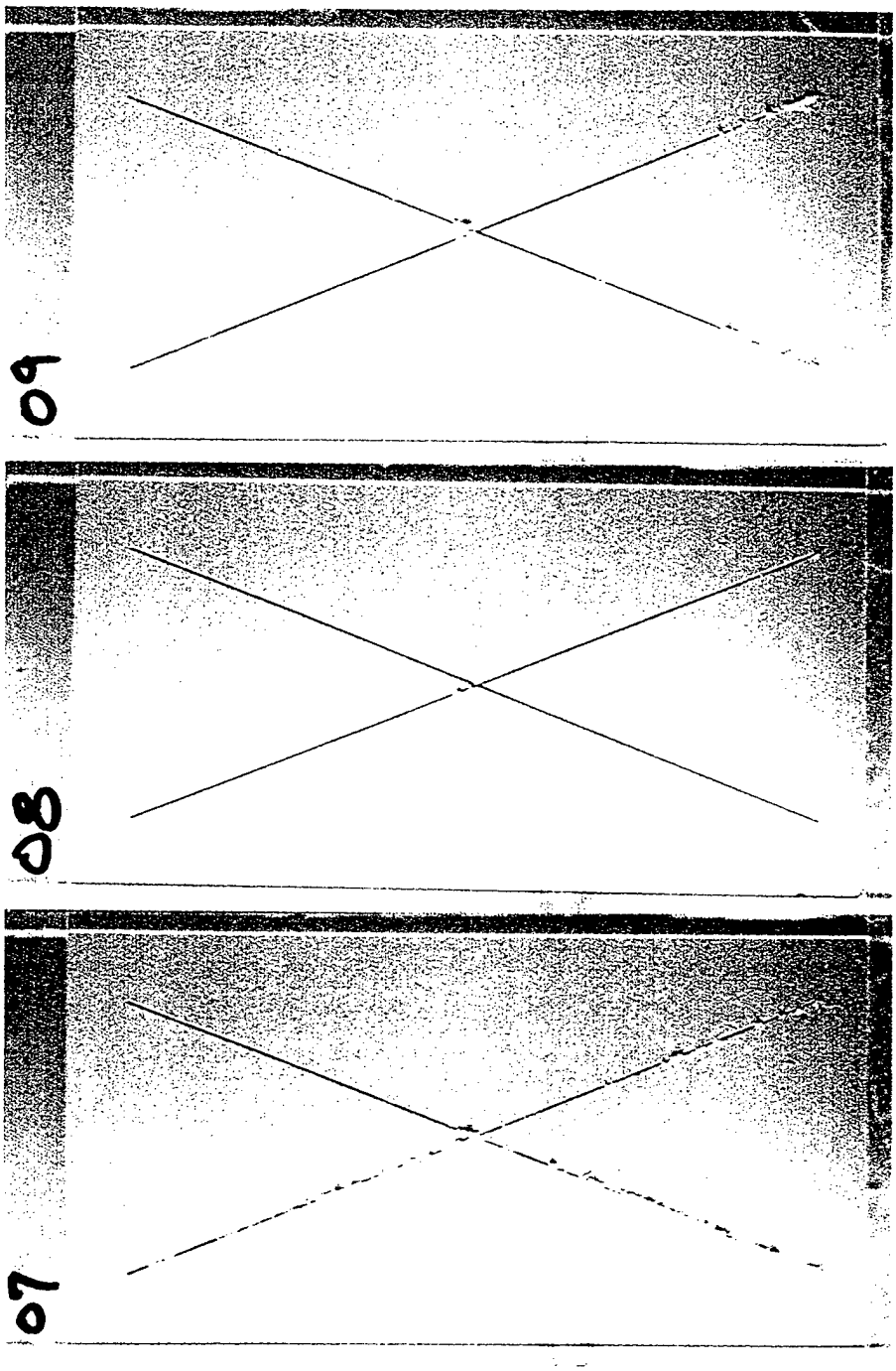


Figure A3 – Photographs of 7075-T6 Panels After Exposure to 5% Salt Spray For 2000 Hours.

PRC-DE SOTO EWAE118
CHROMATE CONVERSION COATING

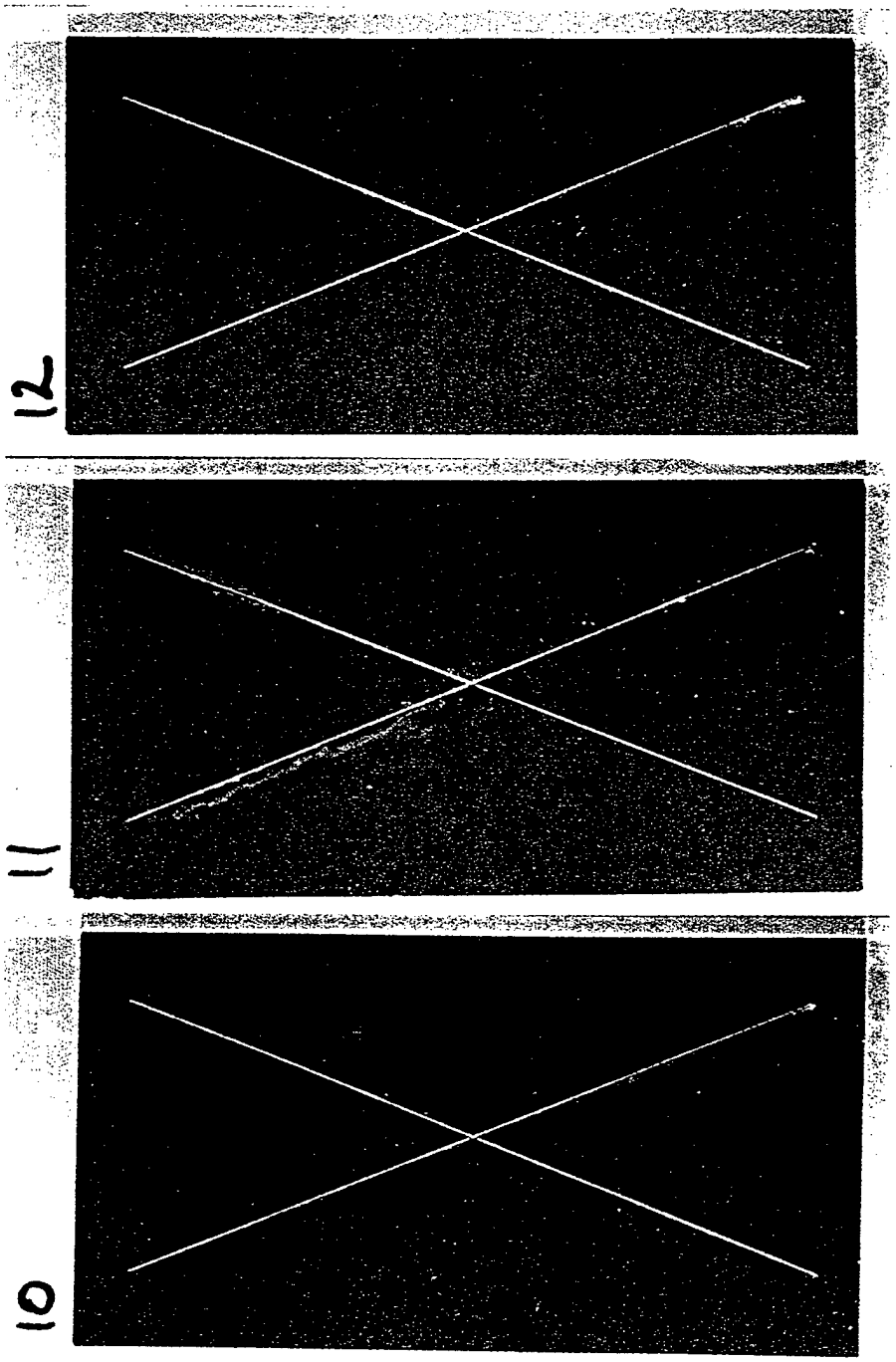


Figure A4 – Photographs of 7075-T6 Panels After Exposure to 5% Salt Spray For 2000 Hours.

DEFT 65-Y-002
CHROMATE CONVERSION COATING

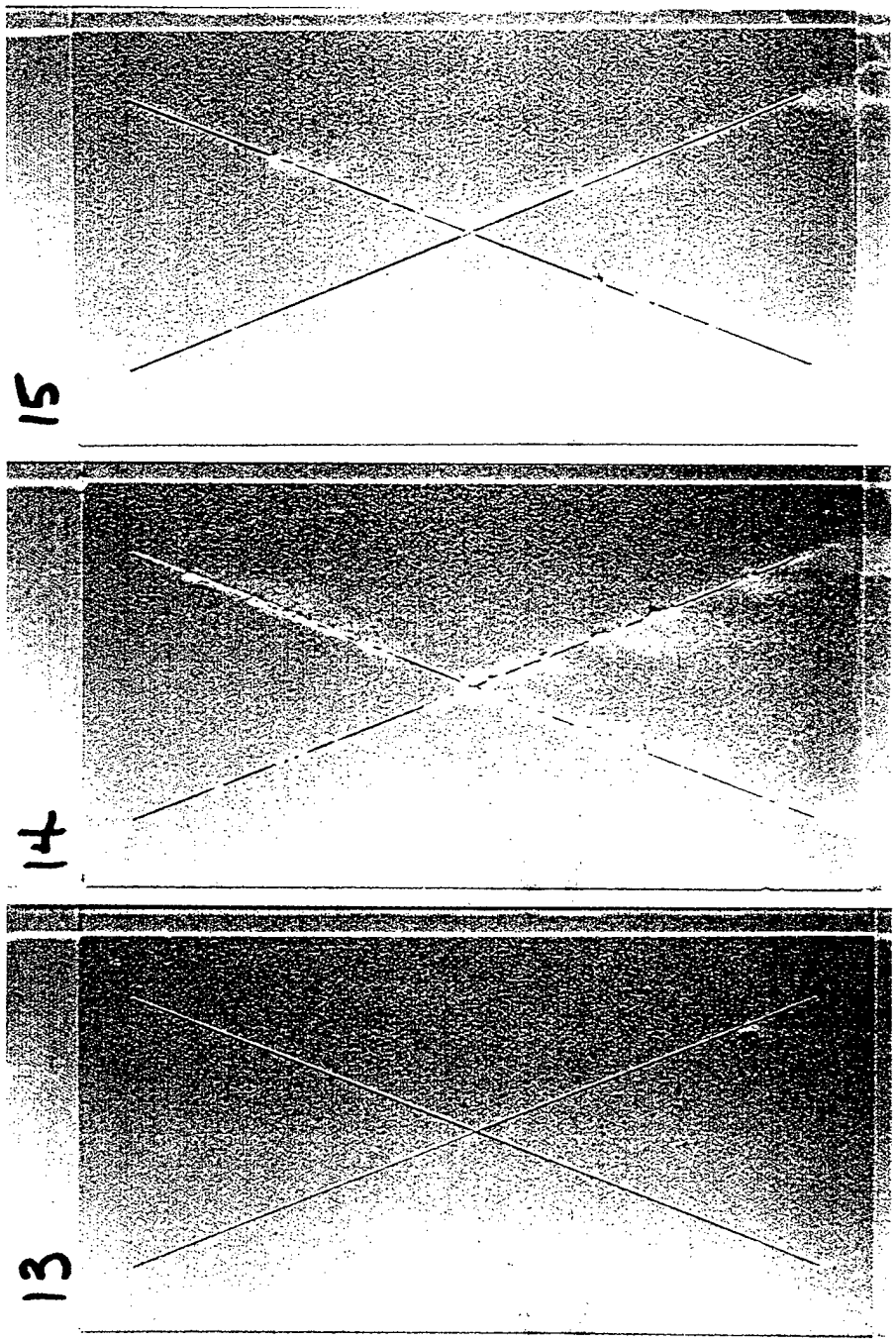


Figure A5 – Photographs of 7075-T6 Panels After Exposure to 5% Salt Spray For 2000 Hours.

DEFT 44-W-25
CHROMATE CONVERSION COATING

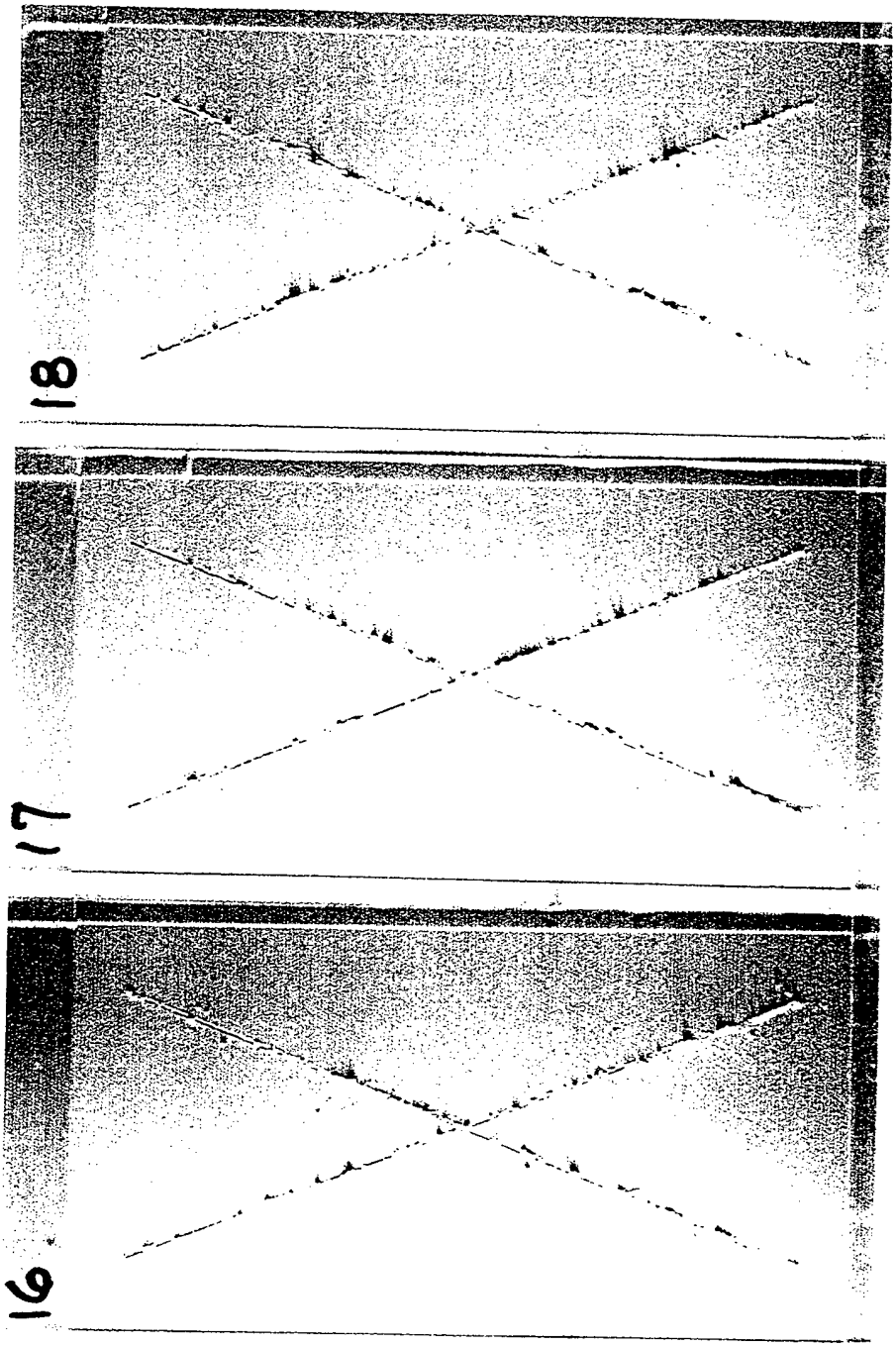


Figure A6 – Photographs of 7075-T6 Panels After Exposure to 5% Salt Spray For 2000 Hours.

DEFT 44-W-27
CHROMATE CONVERSION COATING

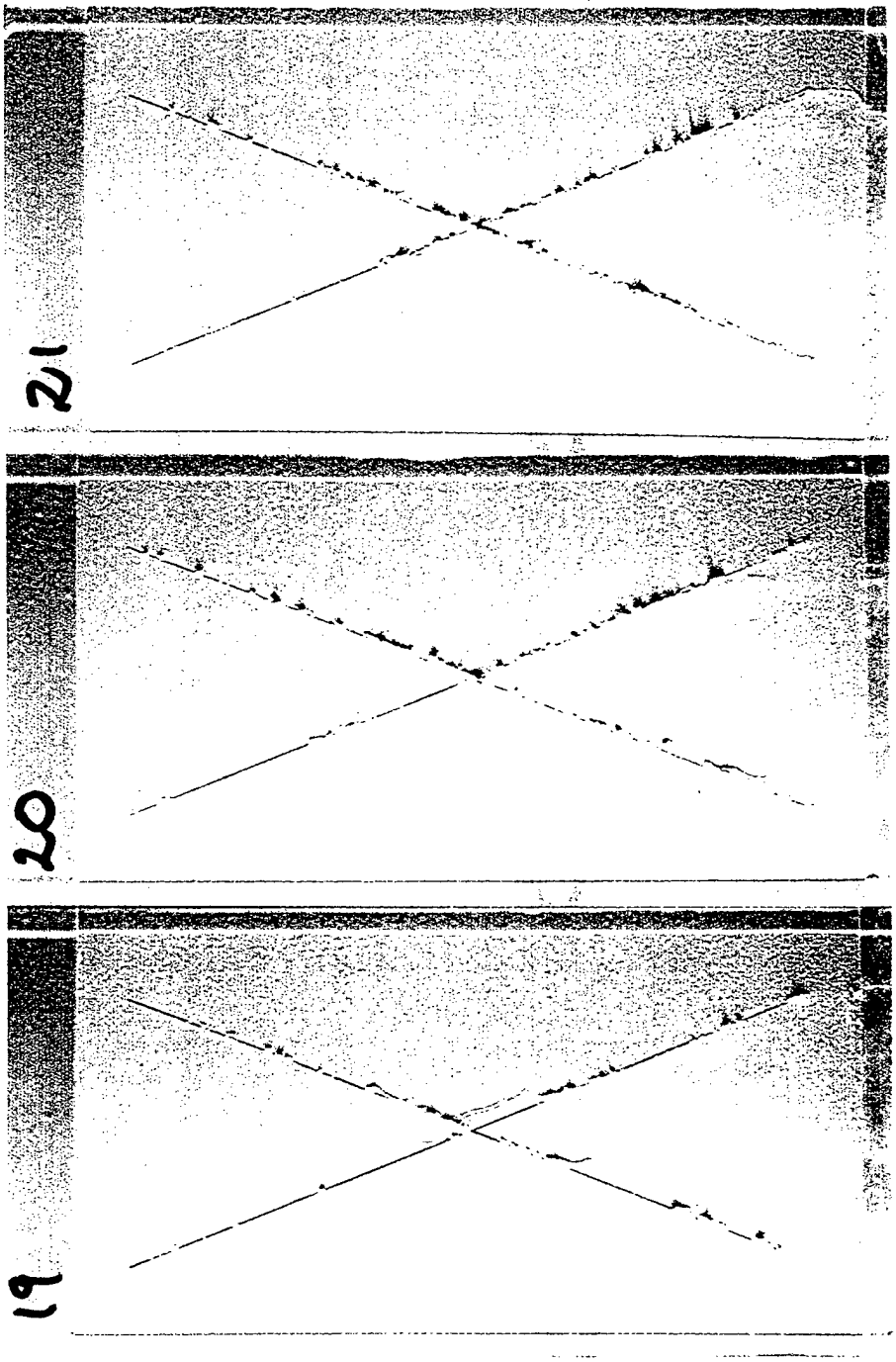


Figure A7 – Photographs of 7075-T6 Panels After Exposure to 5% Salt Spray For 2000 Hours.

DEFT 44-W-28
CHROMATE CONVERSION COATING

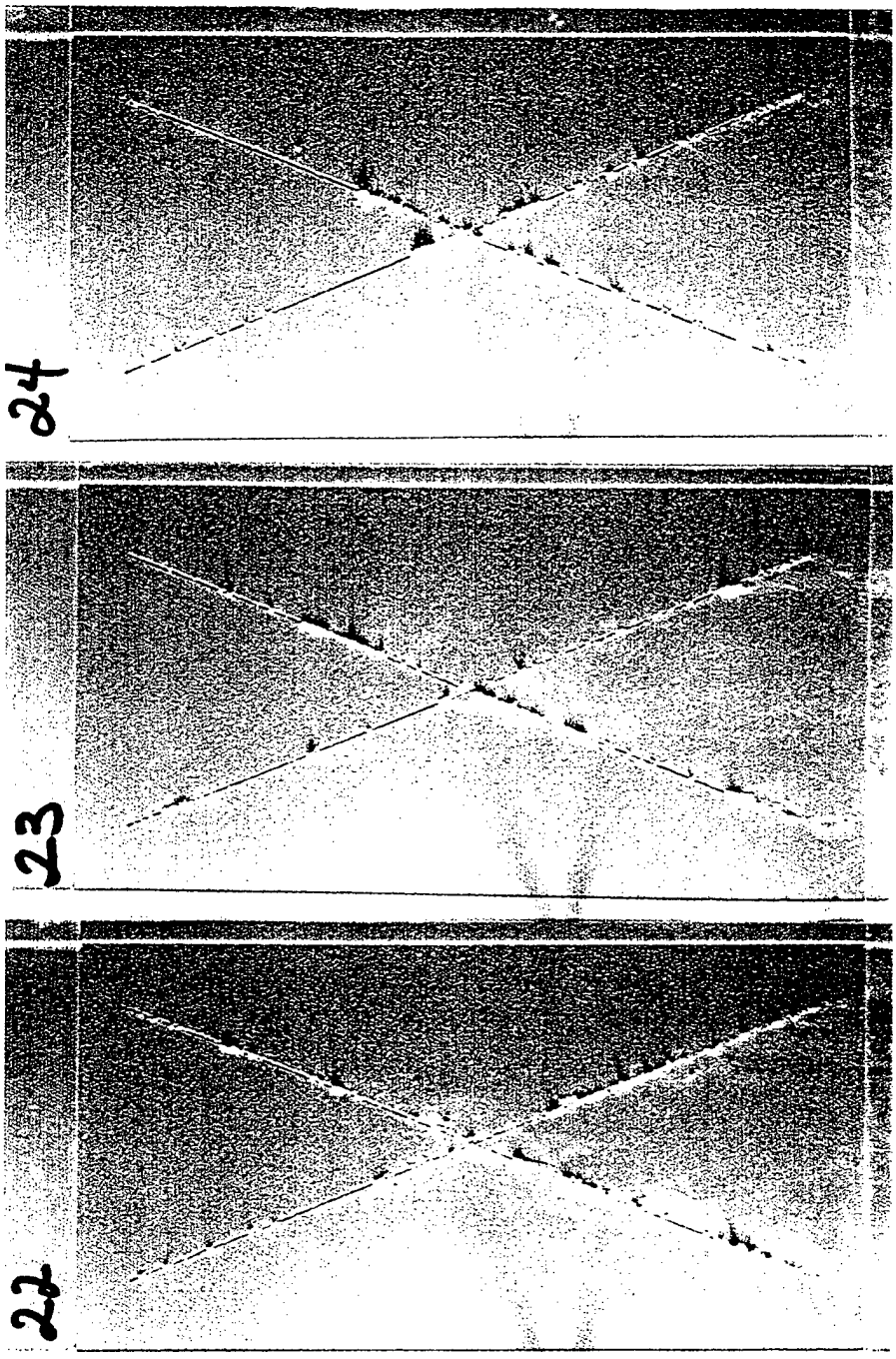


Figure A8 – Photographs of 7075-T6 Panels After Exposure to 5% Salt Spray For 2000 Hours.

DEFT 44-W-25
UM-ROLLA CERIUM CONVERSION COATING

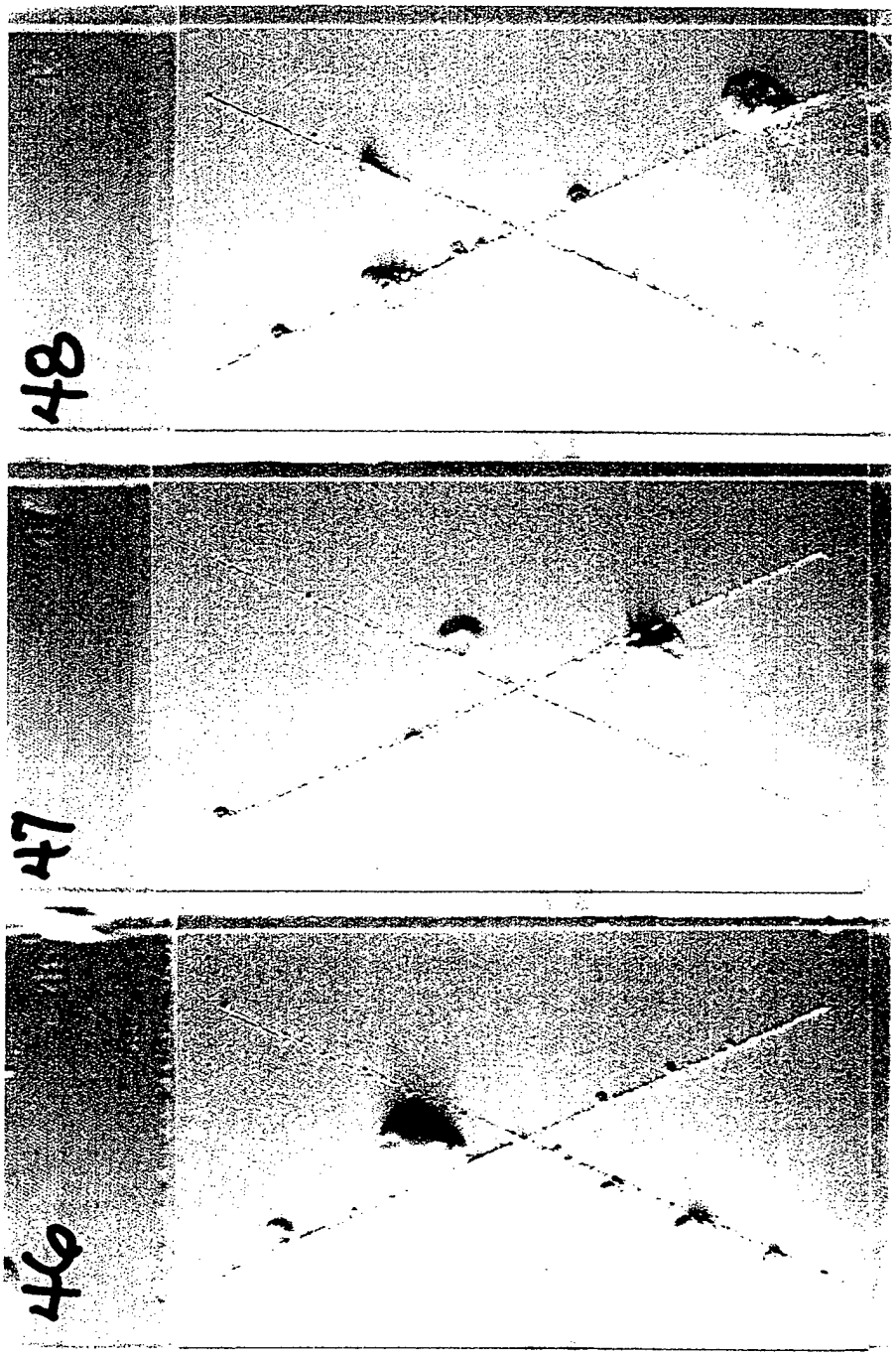


Figure A9 – Photographs of 7075-T6 Panels After Exposure to 5% Salt Spray For 2000 Hours.

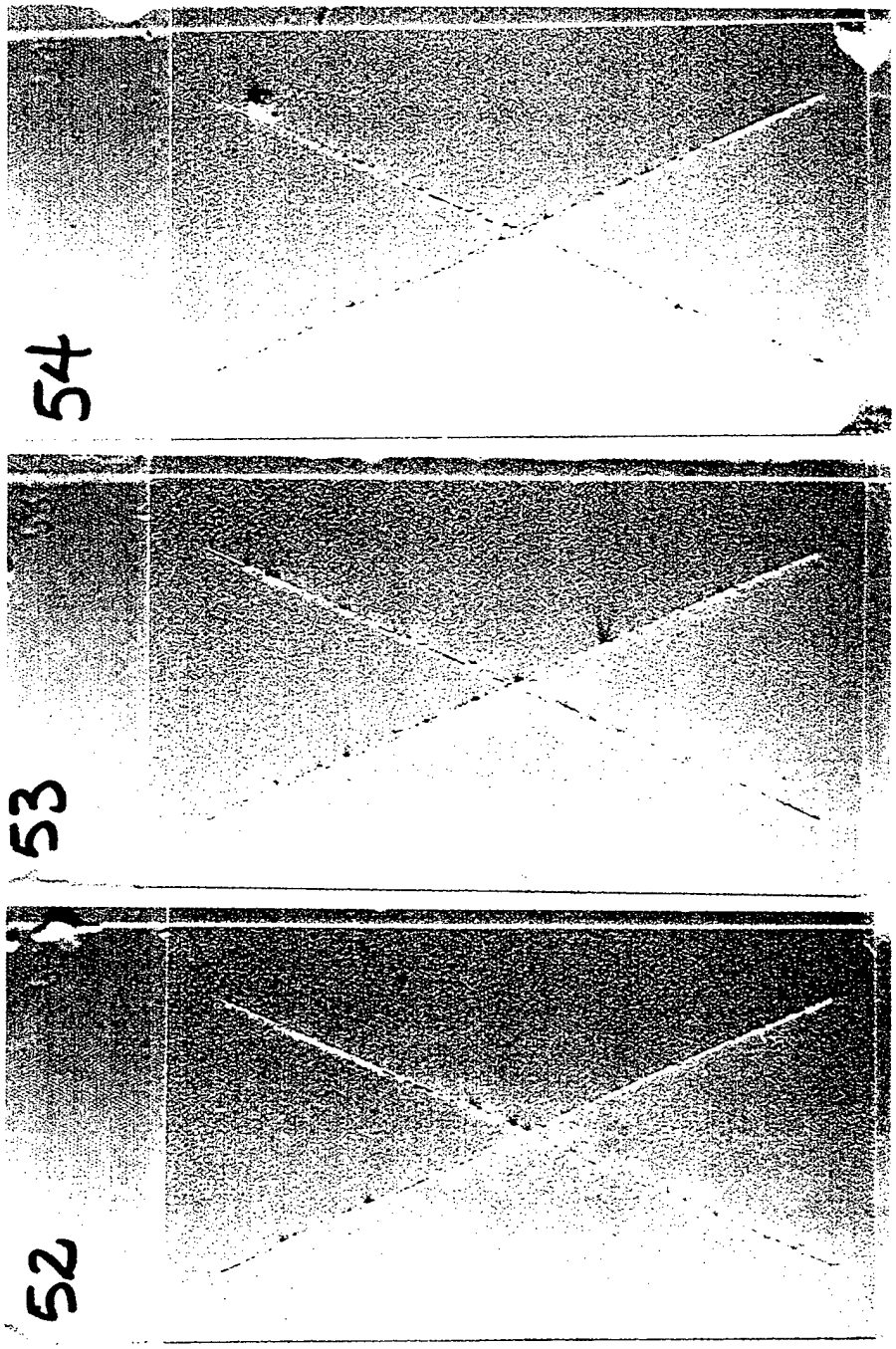


Figure A10 – Photographs of 7075-T6 Panels After Exposure to 5% Salt Spray For 2000 Hours.

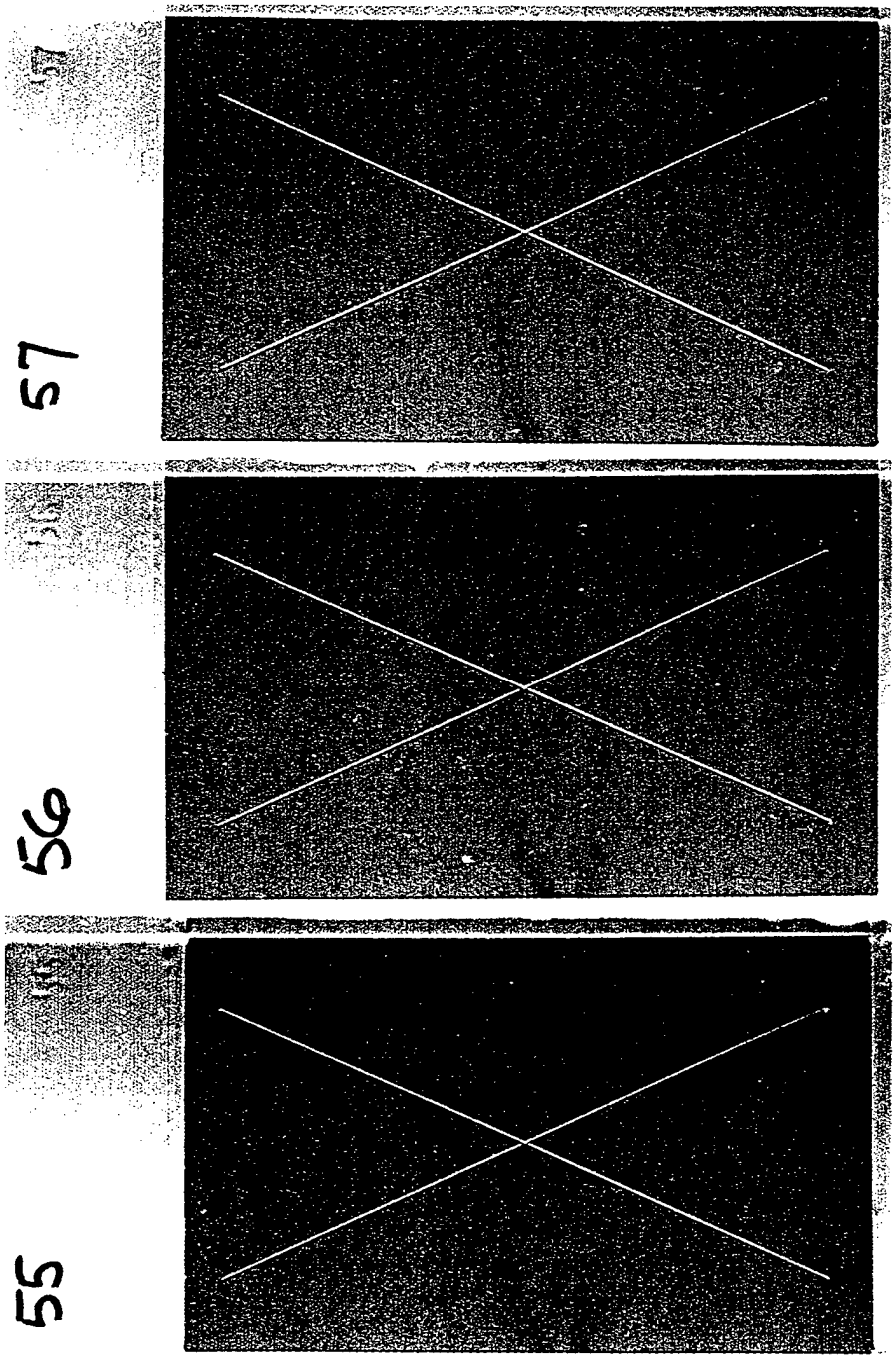


Figure A11 – Photographs of 7075-T6 Panels After Exposure to 5% Salt Spray For 2000 Hours.

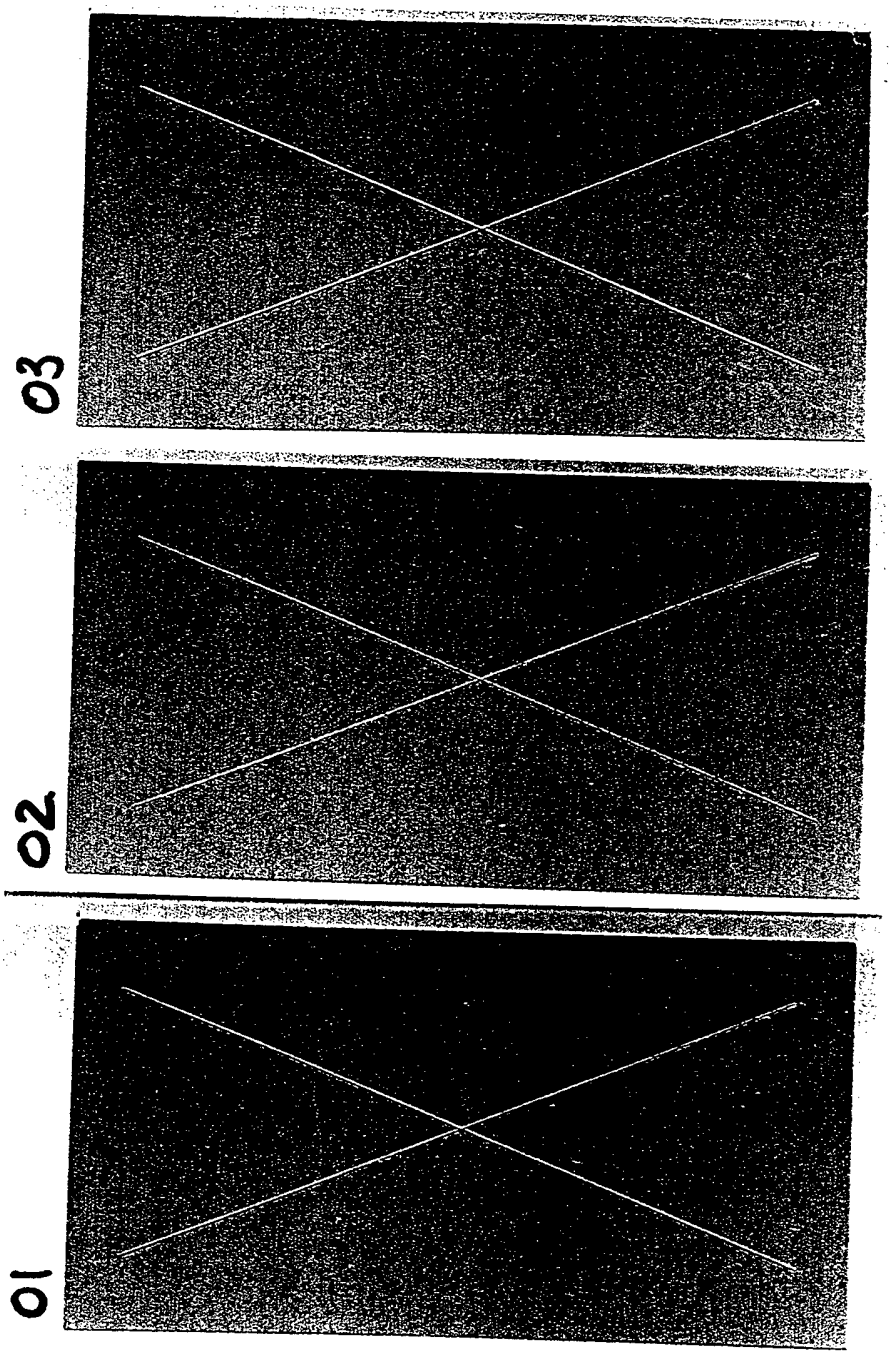


Figure A12 – Photographs of 7075-T6 Panels After Exposure to 5% Salt Spray for 3000 Hours.

U.S. PAINT W4102
CHROMATE CONVERSION COATING

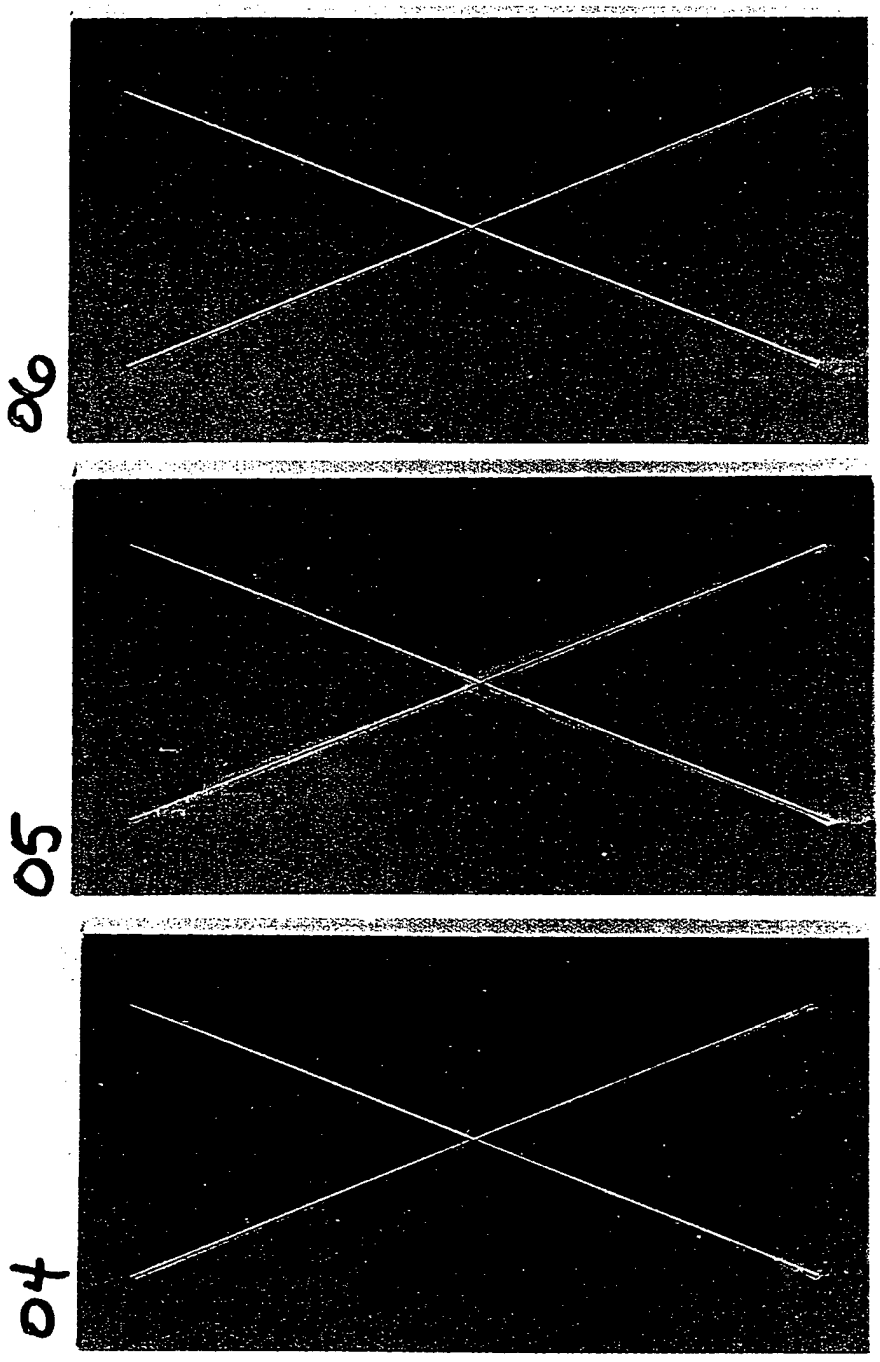


Figure A13 – Photographs of 7075-T6 Panels After Exposure to 5% Salt Spray for 3000 Hours.

DEXTER 10PW22-2
CHROMATE CONVERSION COATING

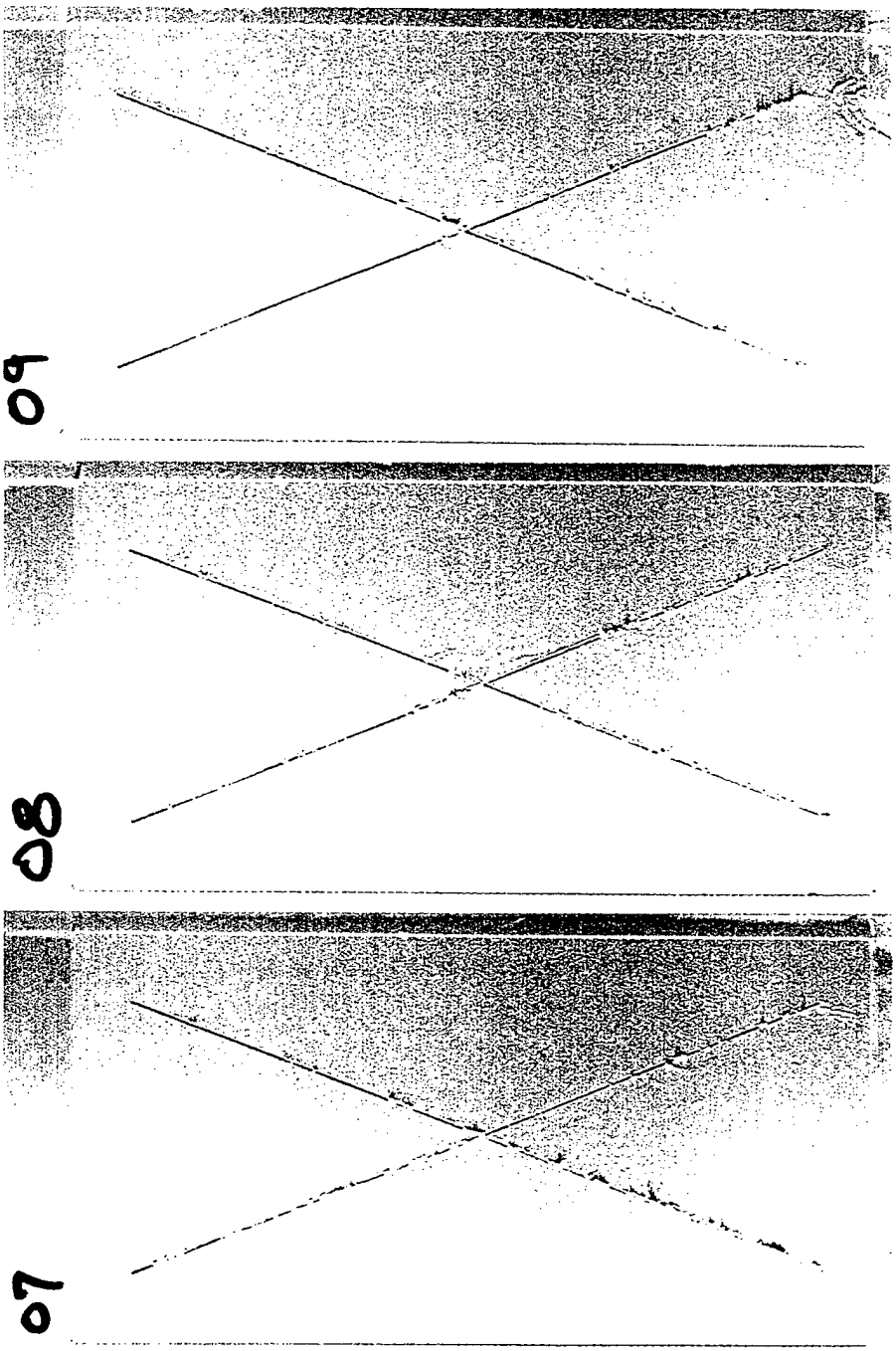


Figure A14 – Photographs of 7075-T6 Panels After Exposure to 5% Salt Spray for 3000 Hours.

PRC-DE SOTO EWAE118
CHROMATE CONVERSION COATING

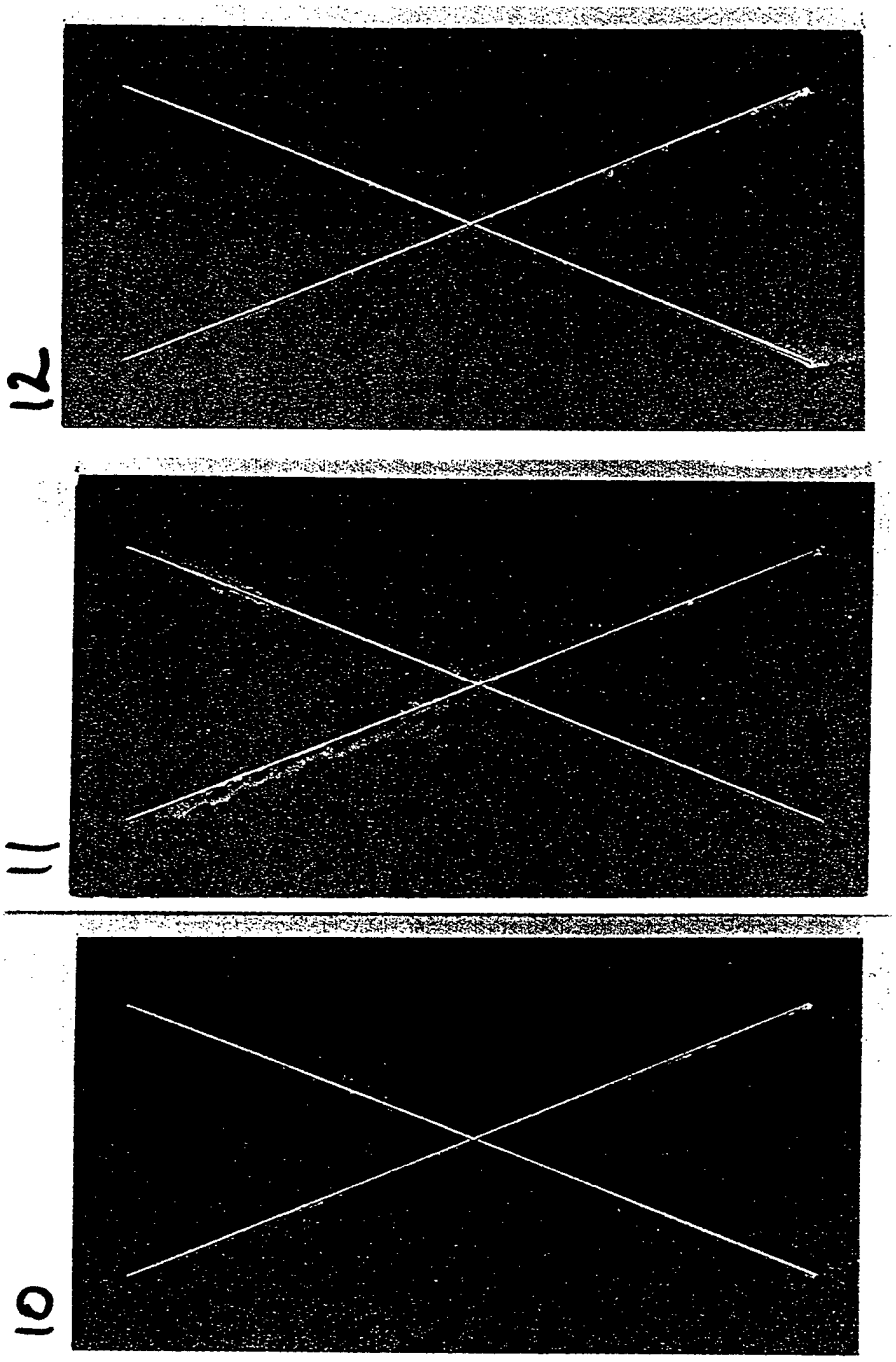


Figure A15 – Photographs of 7075-T6 Panels After Exposure to 5% Salt Spray for 3000 Hours.

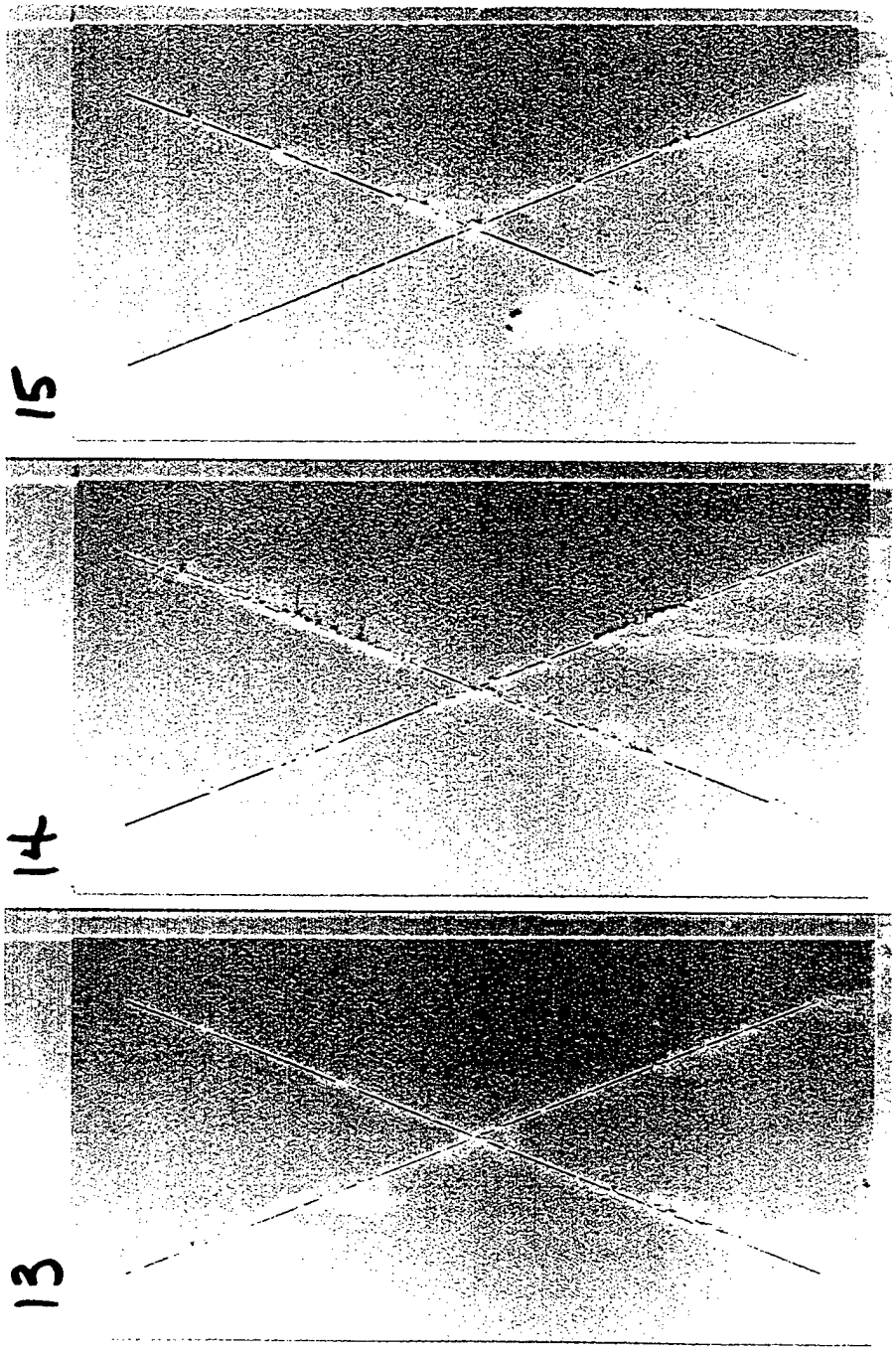


Figure A16 – Photographs of 7075-T6 Panels After Exposure to 5% Salt Spray for 3000 Hours.

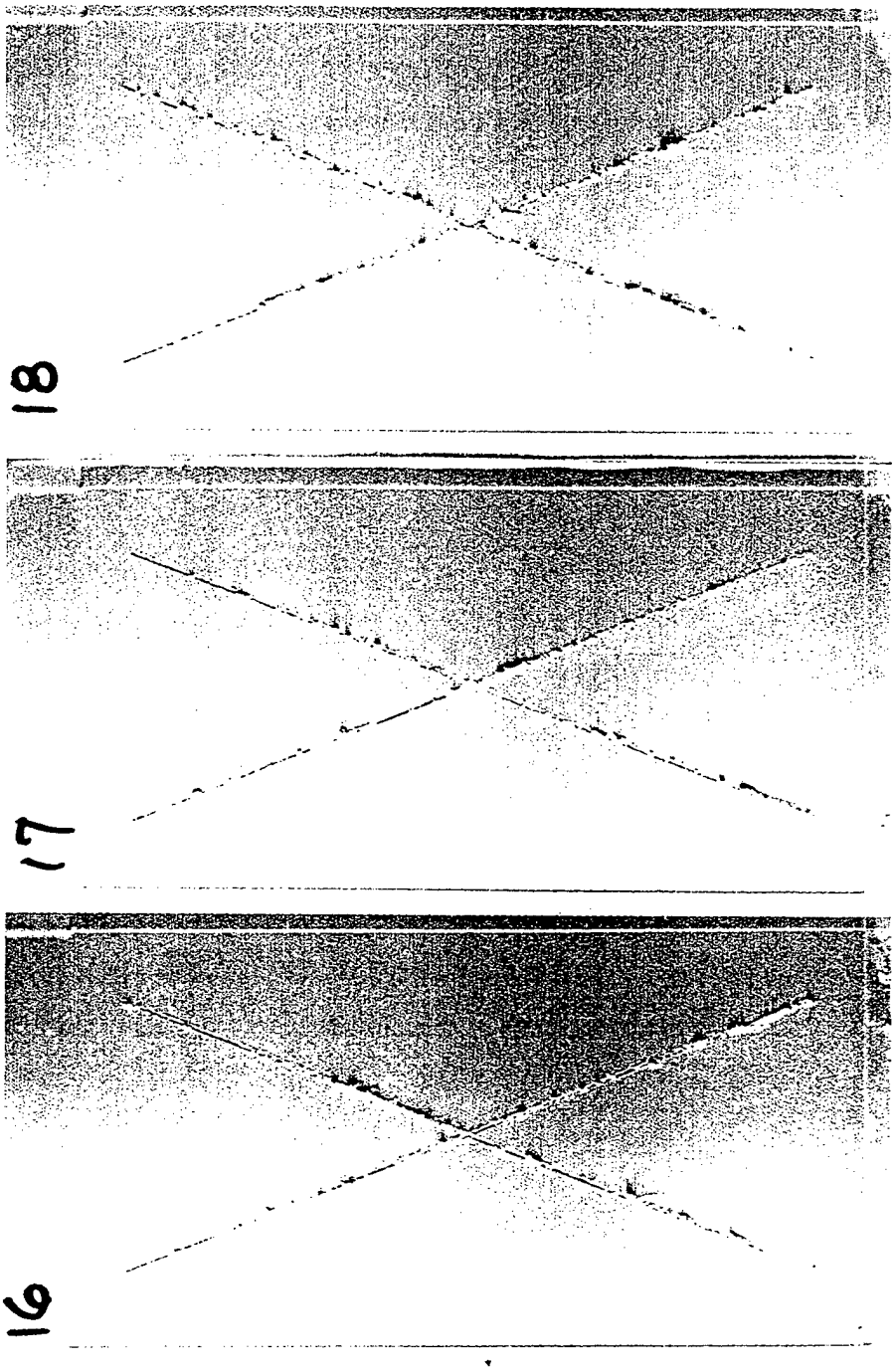


Figure A17 – Photographs of 7075-T6 Panels After Exposure to 5% Salt Spray for 3000 Hours.

DEFT 44-W-27
CHROMATE CONVERSION COATING

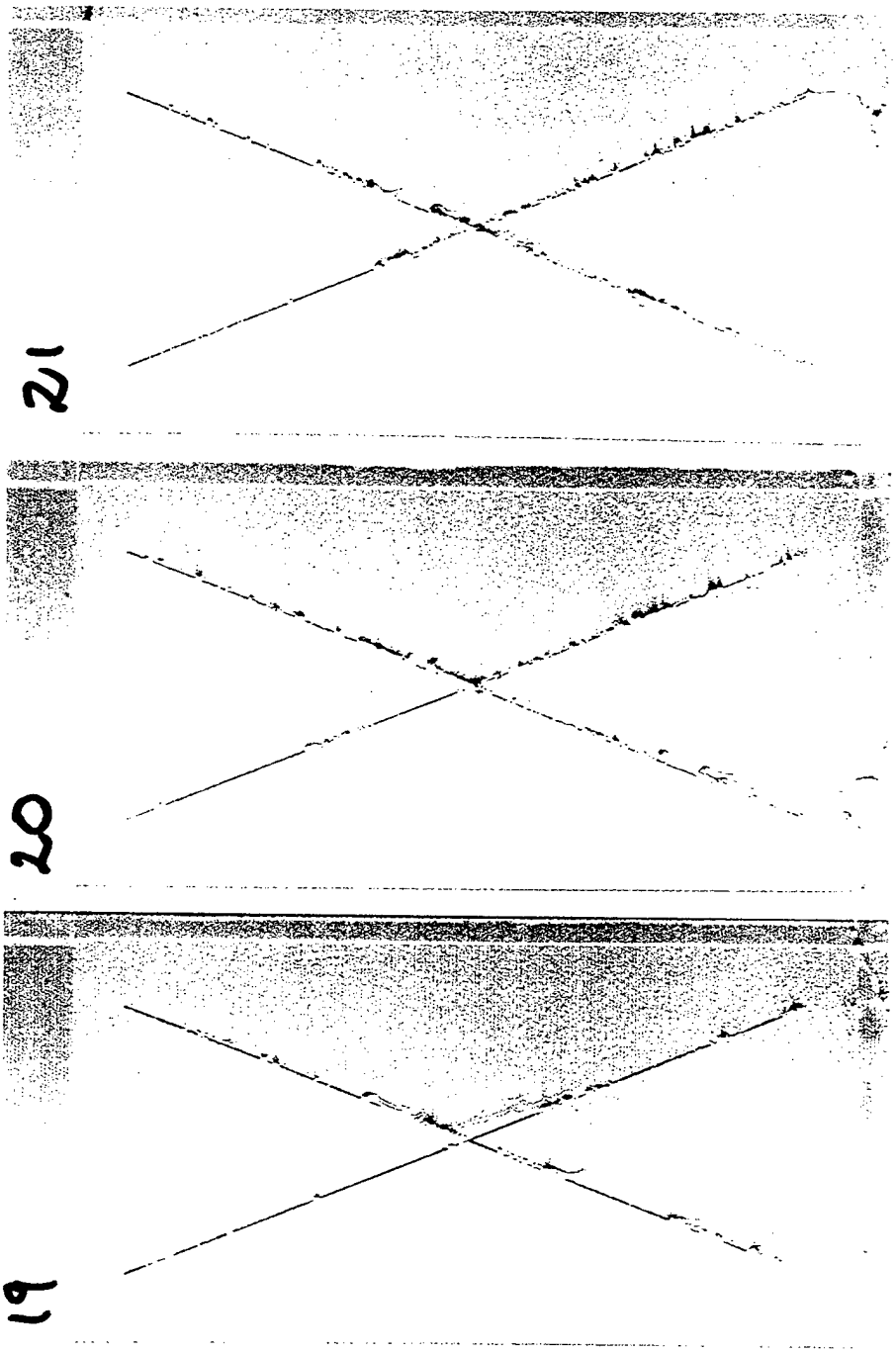


Figure A18 – Photographs of 7075-T6 Panels After Exposure to 5% Salt Spray for 3000 Hours.

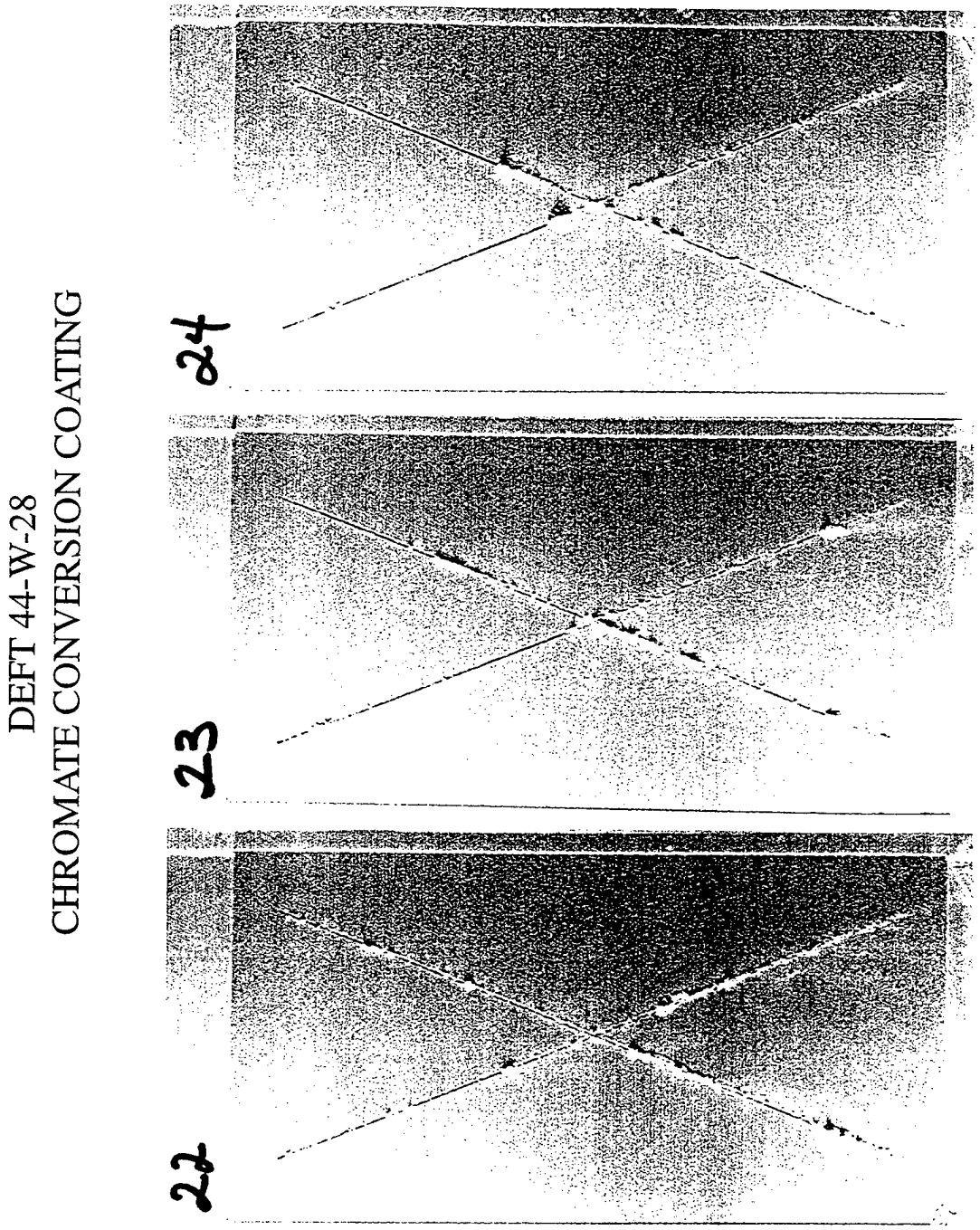


Figure A19 – Photographs of 7075-T6 Panels After Exposure to 5% Salt Spray for 3000 Hours.

Figure A19

DEFT 44-W-25
UM-ROLLA CERIUM CONVERSION COATING

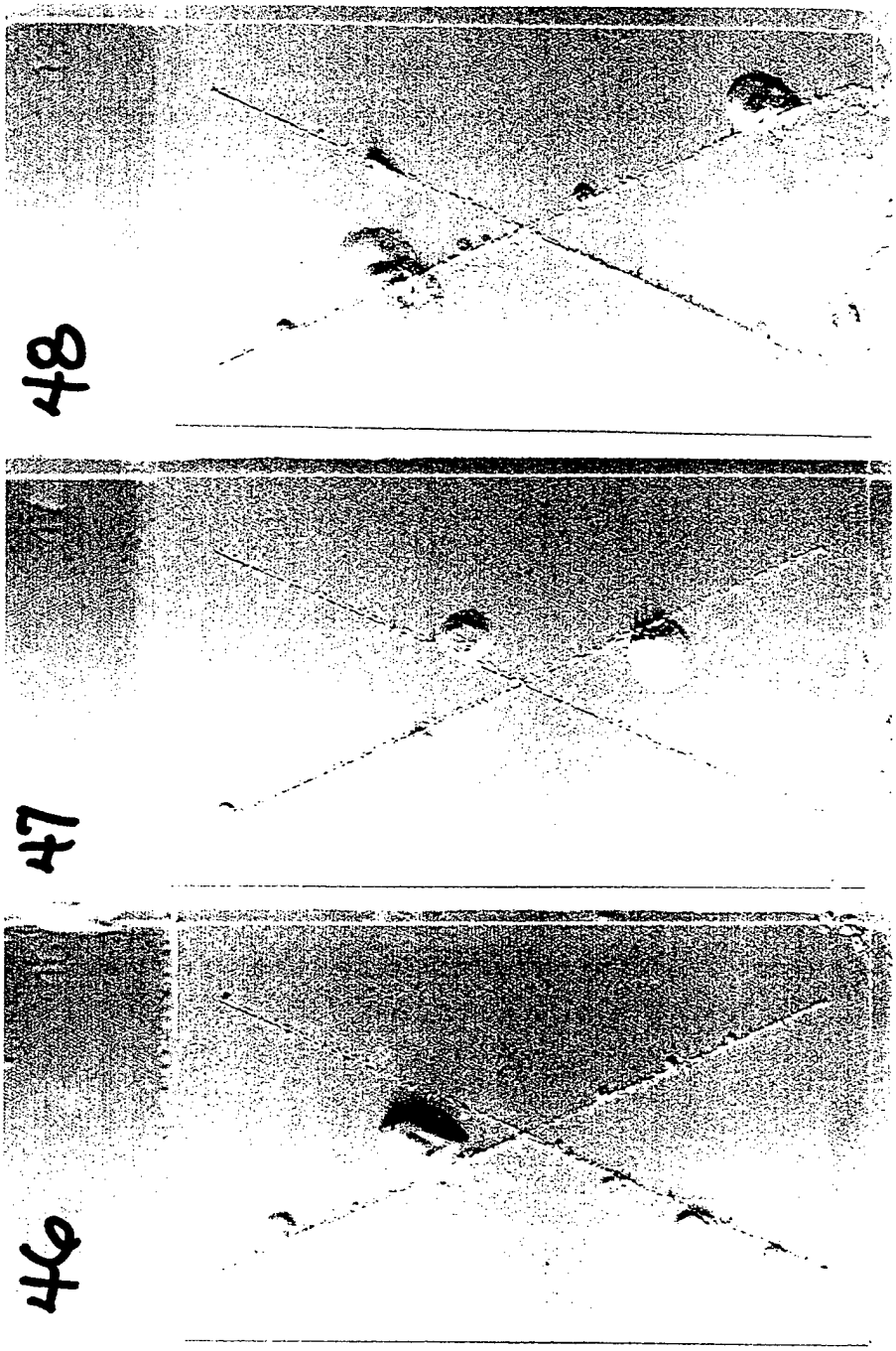


Figure A20 – Photographs of 7075-T6 Panels After Exposure to 5% Salt Spray for 3000 Hours.

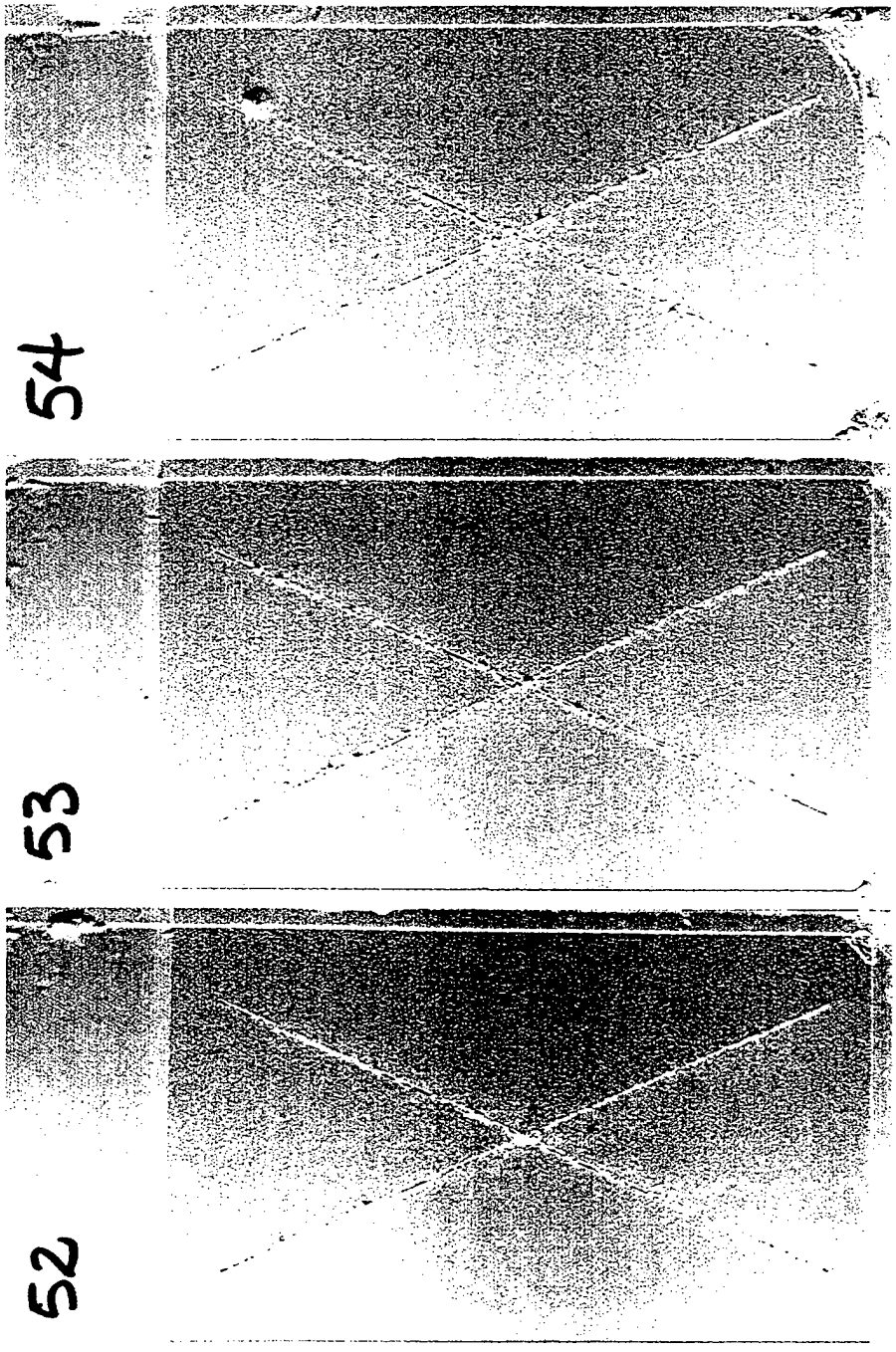


Figure A21 – Photographs of 7075-T6 Panels After Exposure to 5% Salt Spray for 3000 Hours.

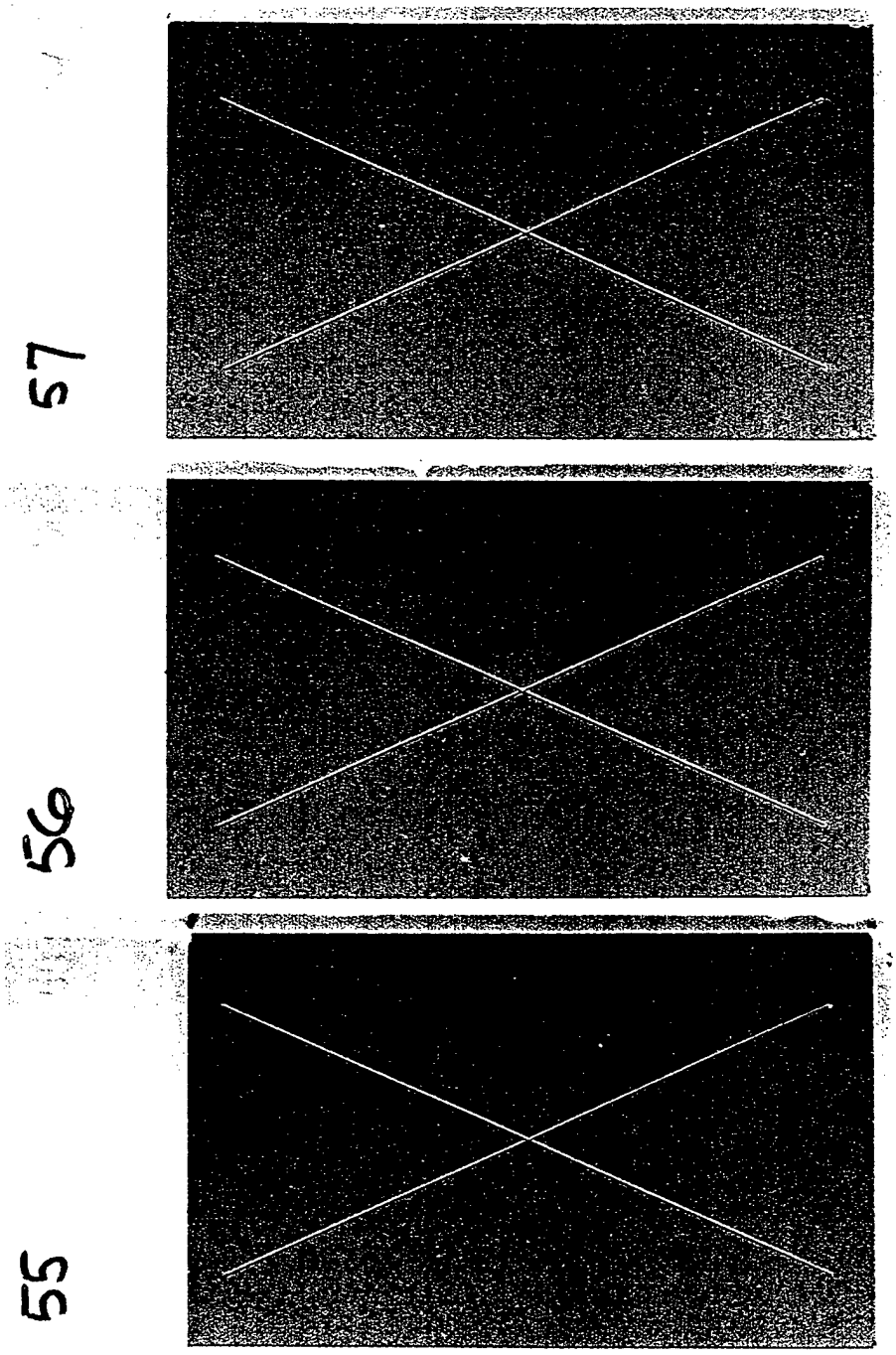


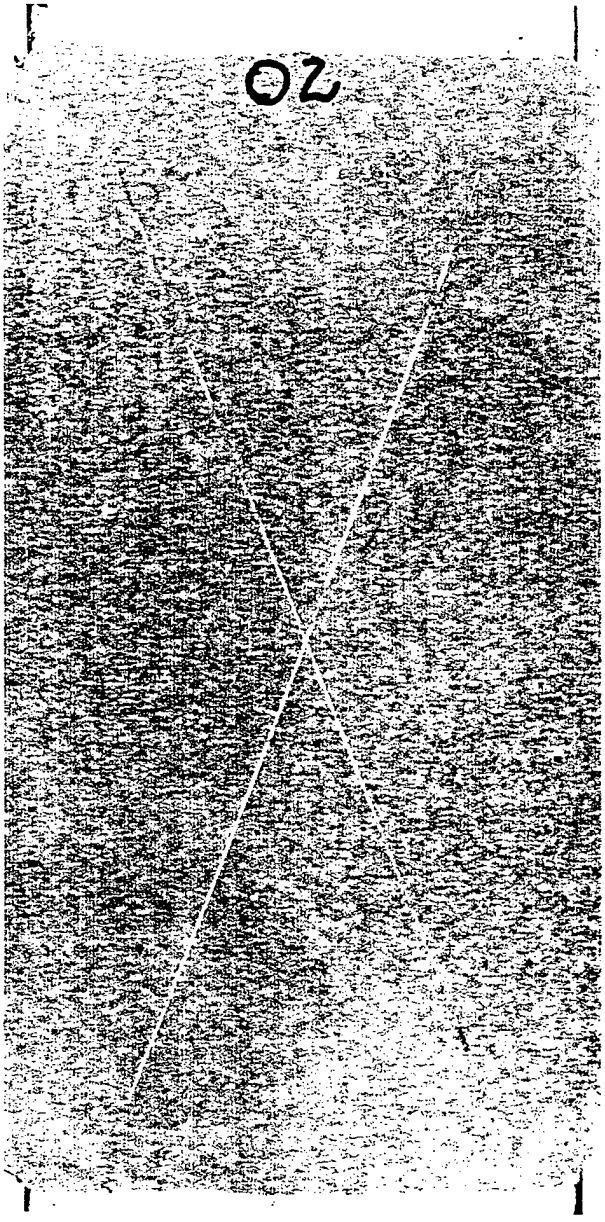
Figure A22 – Photographs of 7075-T6 Panels After Exposure to 5% Salt Spray for 3000 Hours.

APPENDIX B

5% Salt Spray Corrosion Per ASTM B 117

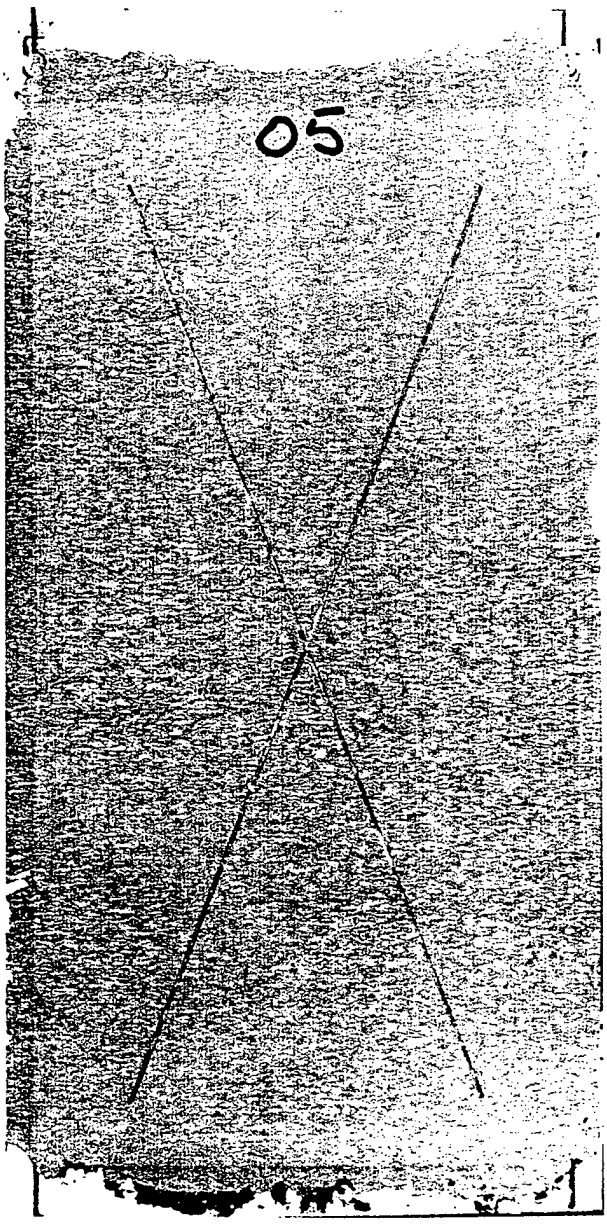
Photographic Documentation of 7075-T6 Aluminum Panels Exposed to 5% Salt Spray for 3000 Hours, Then Stripped.

DEFT 44-GN-72



Chromate Conversion Coated

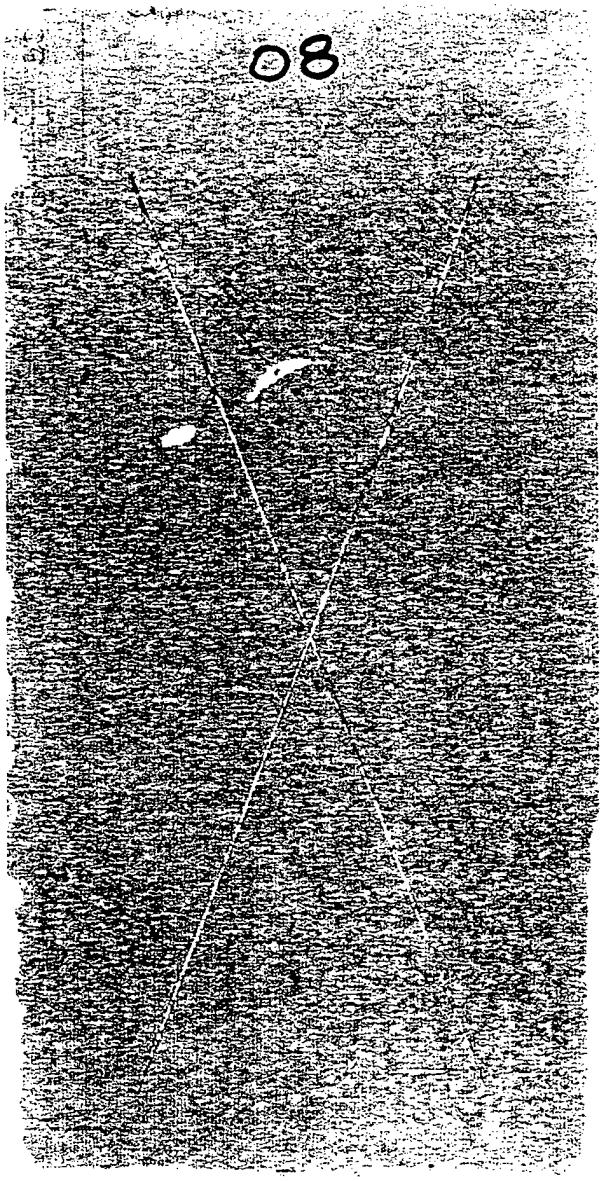
U.S. PAINT W4102



Chromate Conversion Coated

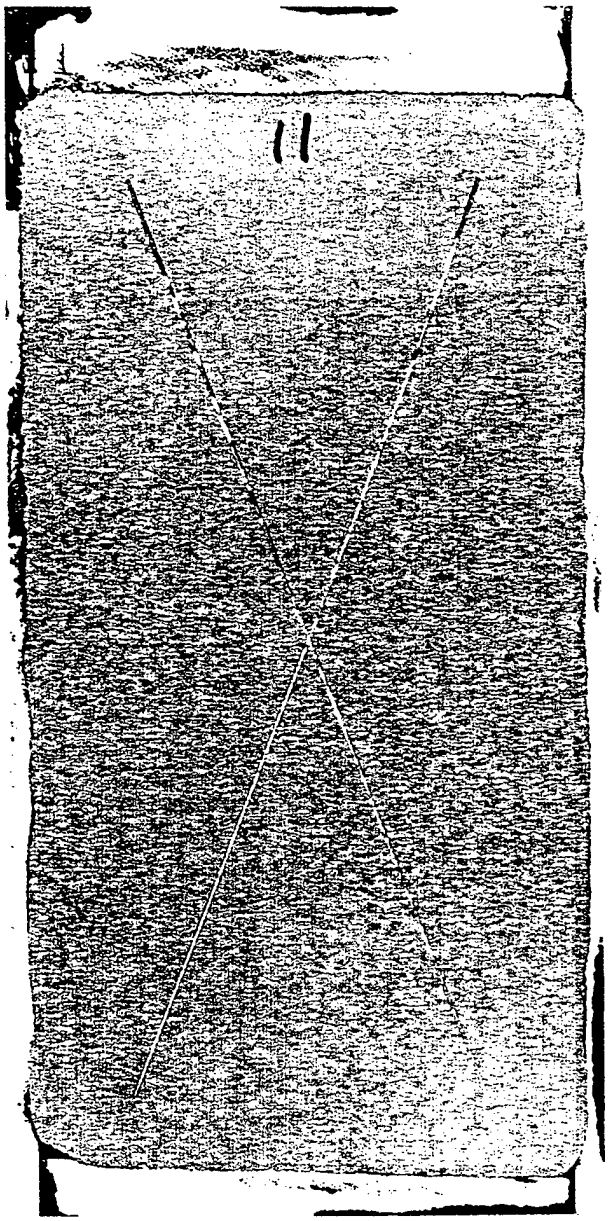
Figure B1 – Photographs of 7075-T6 Panels Exposed to 5% Salt Spray for 3000 Hours, Then Stripped.

DEXTER 10PW22-2



Chromate Conversion Coated

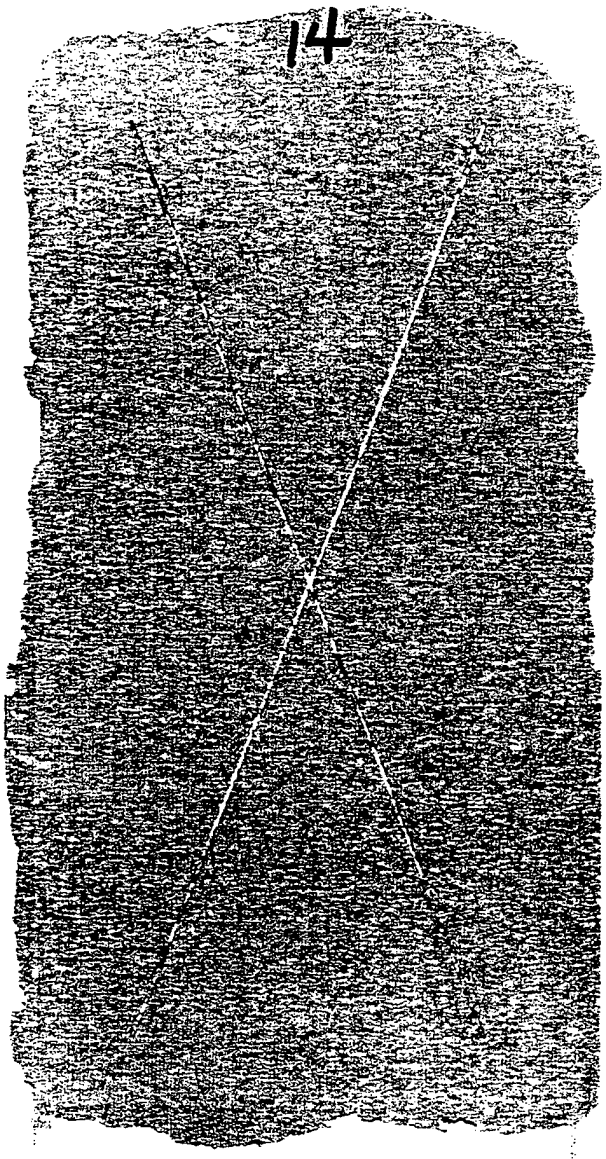
PRC-DE SOTO EWAE118



Chromate Conversion Coated

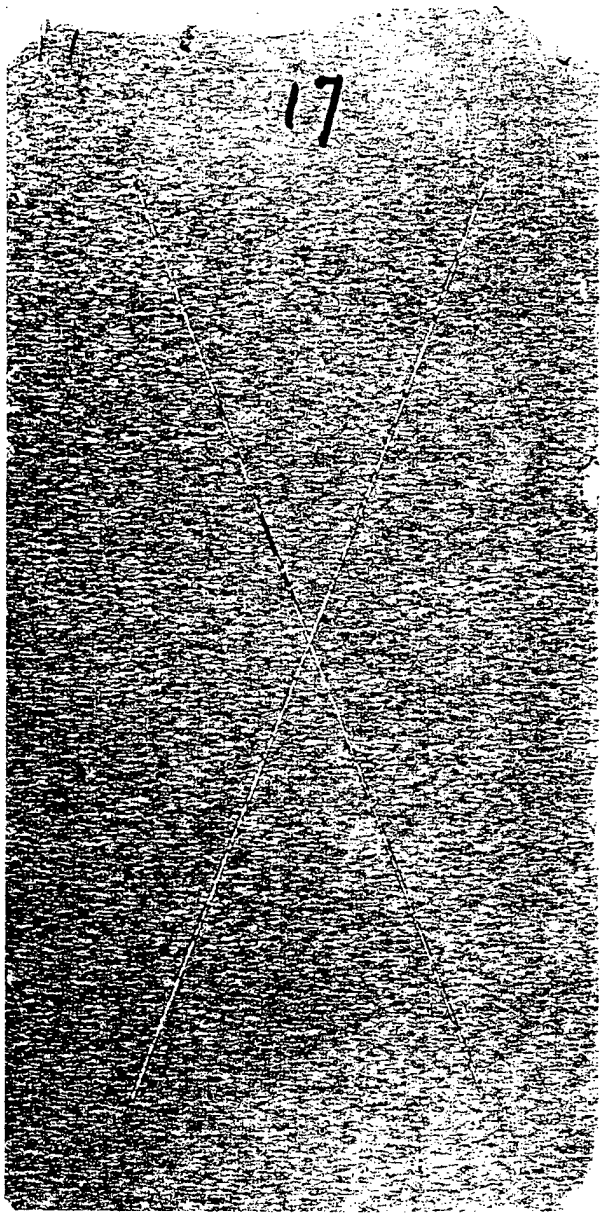
Figure B2 – Photographs of 7075-T6 Panels Exposed to 5% Salt Spray for 3000 Hours, Then Stripped.

DEFT 65-Y-002



Chromate Conversion Coated

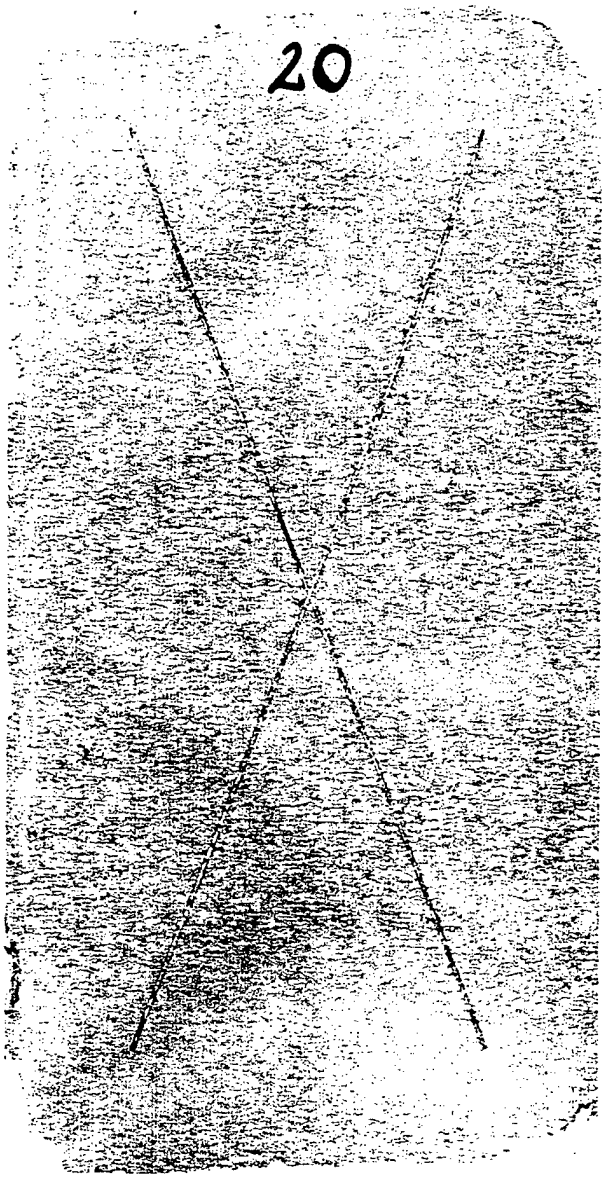
DEFT 44-W-25



Chromate Conversion Coated

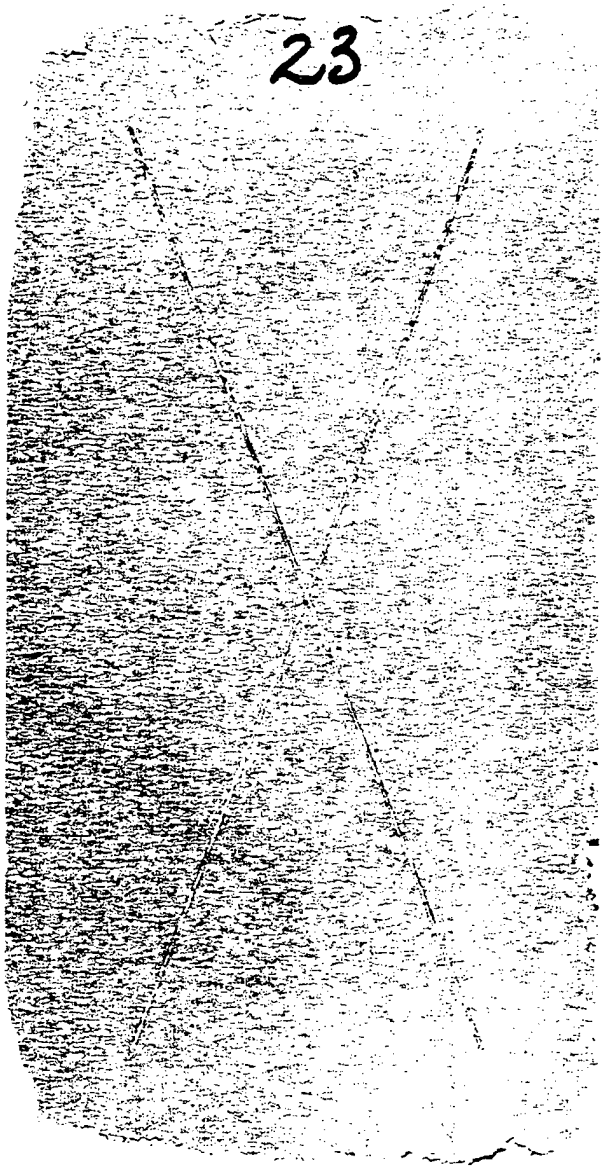
Figure B3 – Photographs of 7075-T6 Panels Exposed to 5% Salt Spray for 3000 Hours, Then Stripped.

DEFT 44-W-27



Chromate Conversion Coated

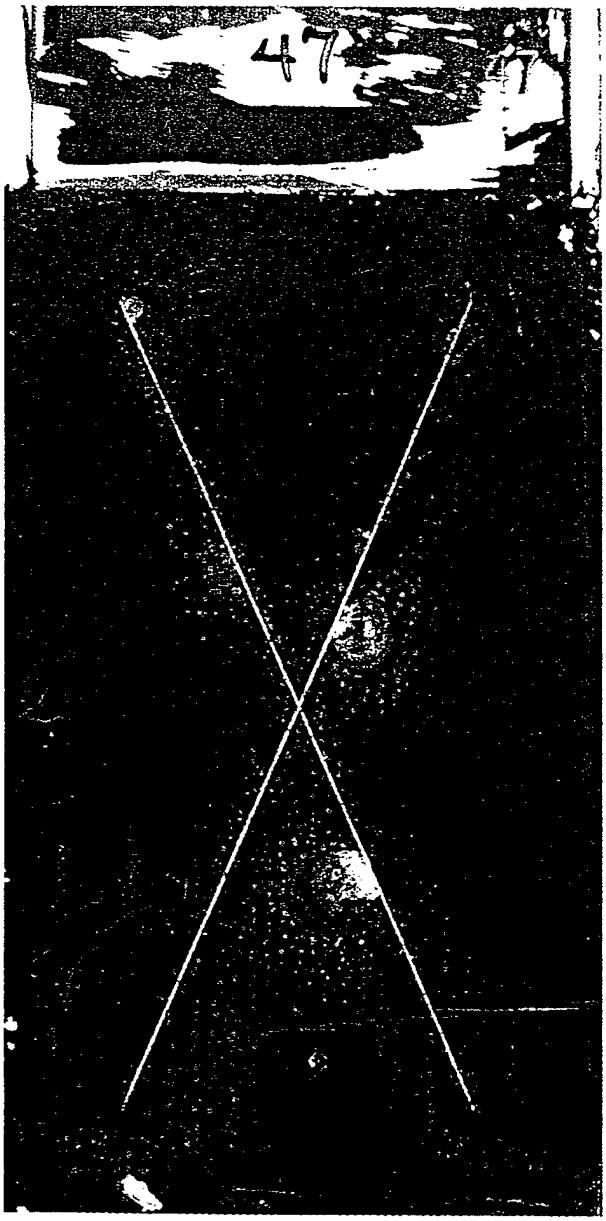
DEFT 44-W-28



Chromate Conversion Coated

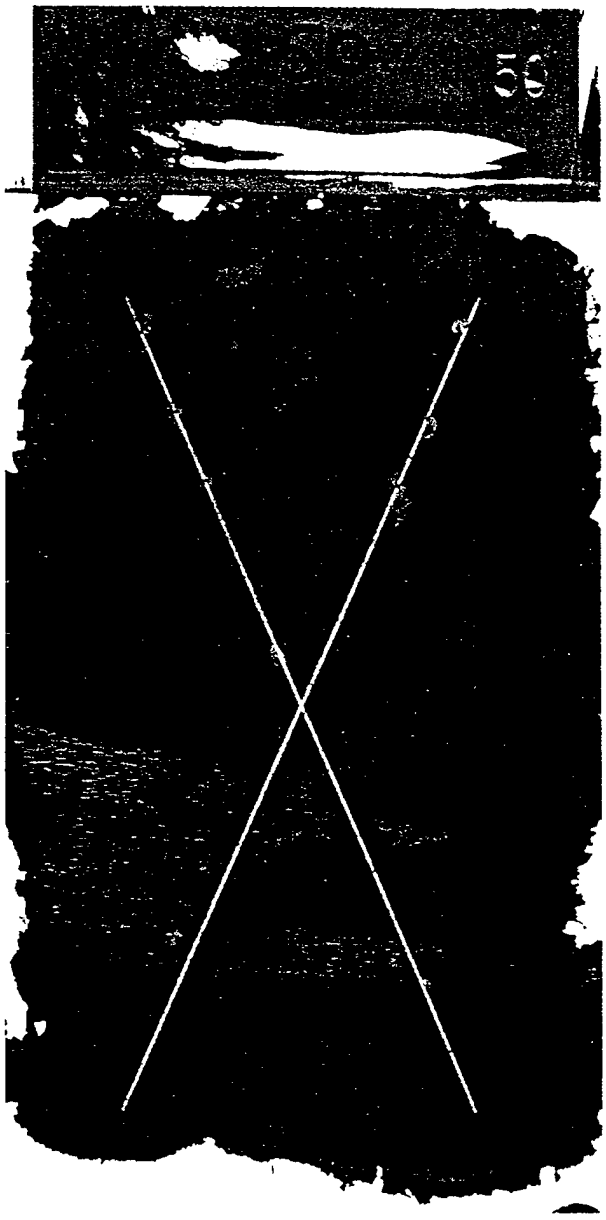
Figure B4 – Photographs of 7075-T6 Panels Exposed to 5% Salt Spray for 3000 Hours, Then Stripped.

DEFT 44-W-25



Cerium Conversion Coated

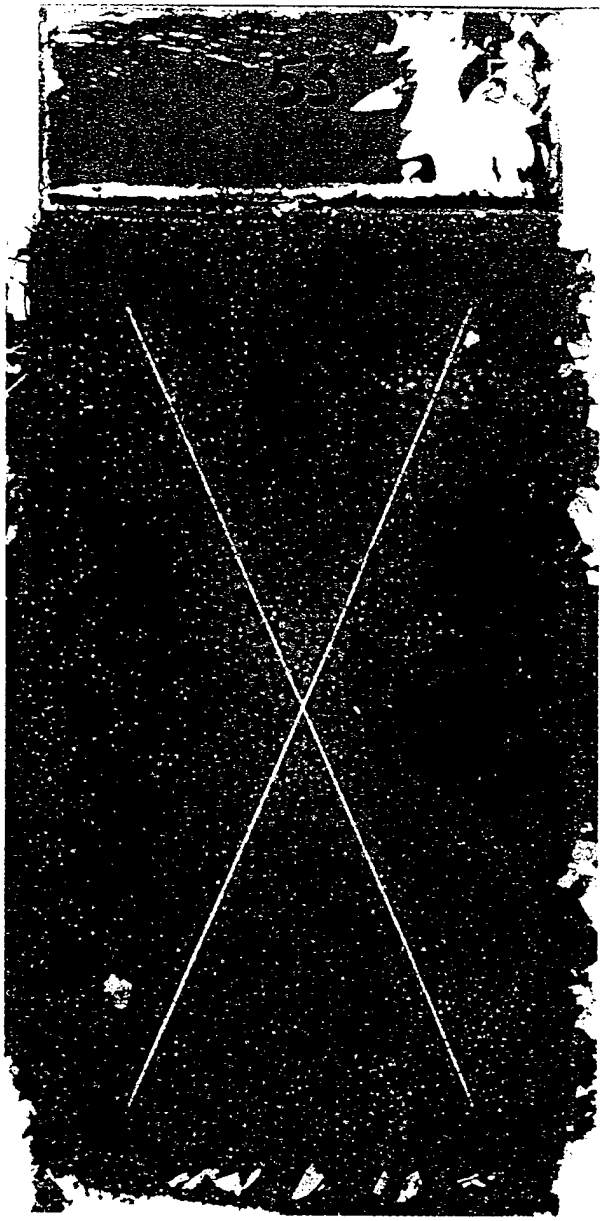
DEFT 44-W-27



Cerium Conversion Coated

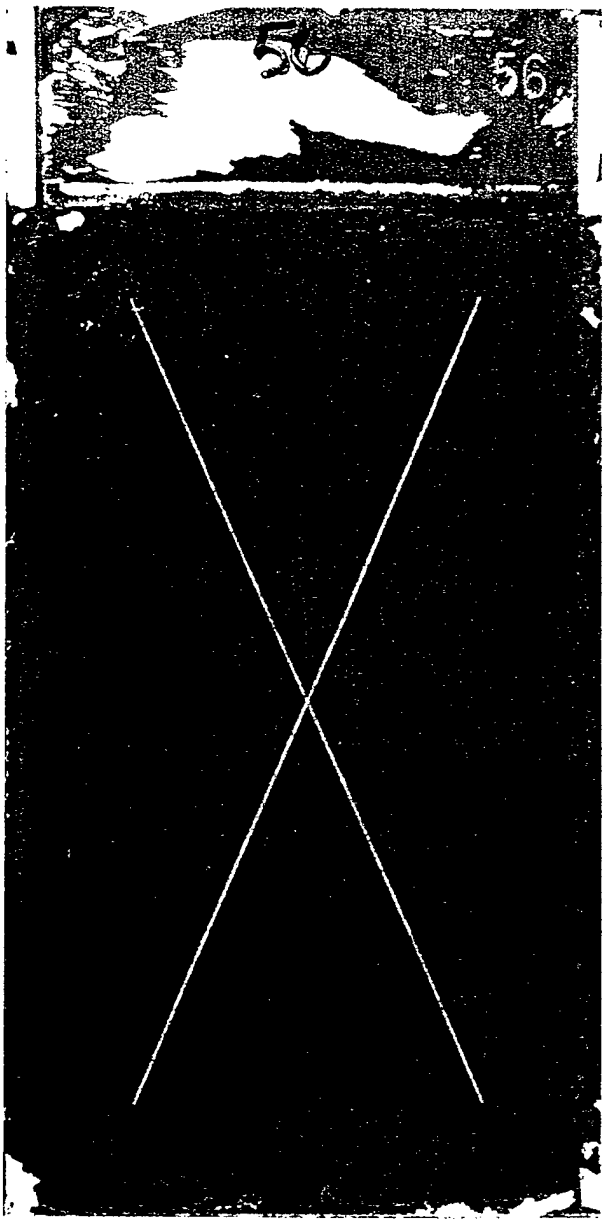
Figure B5 – Photographs of 7075-T6 Panels Exposed to 5% Salt Spray for 3000 Hours, Then Stripped.

DEFT 44-W-28



Cerium Conversion Coated

DEFT 44-GN-72



Cerium Conversion Coated

Figure B6 – Photographs of 7075-T6 Panels Exposed to 5% Salt Spray for 3000 Hours, Then Stripped.

APPENDIX C

SO_2 Salt Spray Corrosion Per ASTM G 85

Photographic Documentation of 2024-T3 Aluminum Panels Exposed to SO_2 Salt Spray for 2-Weeks.

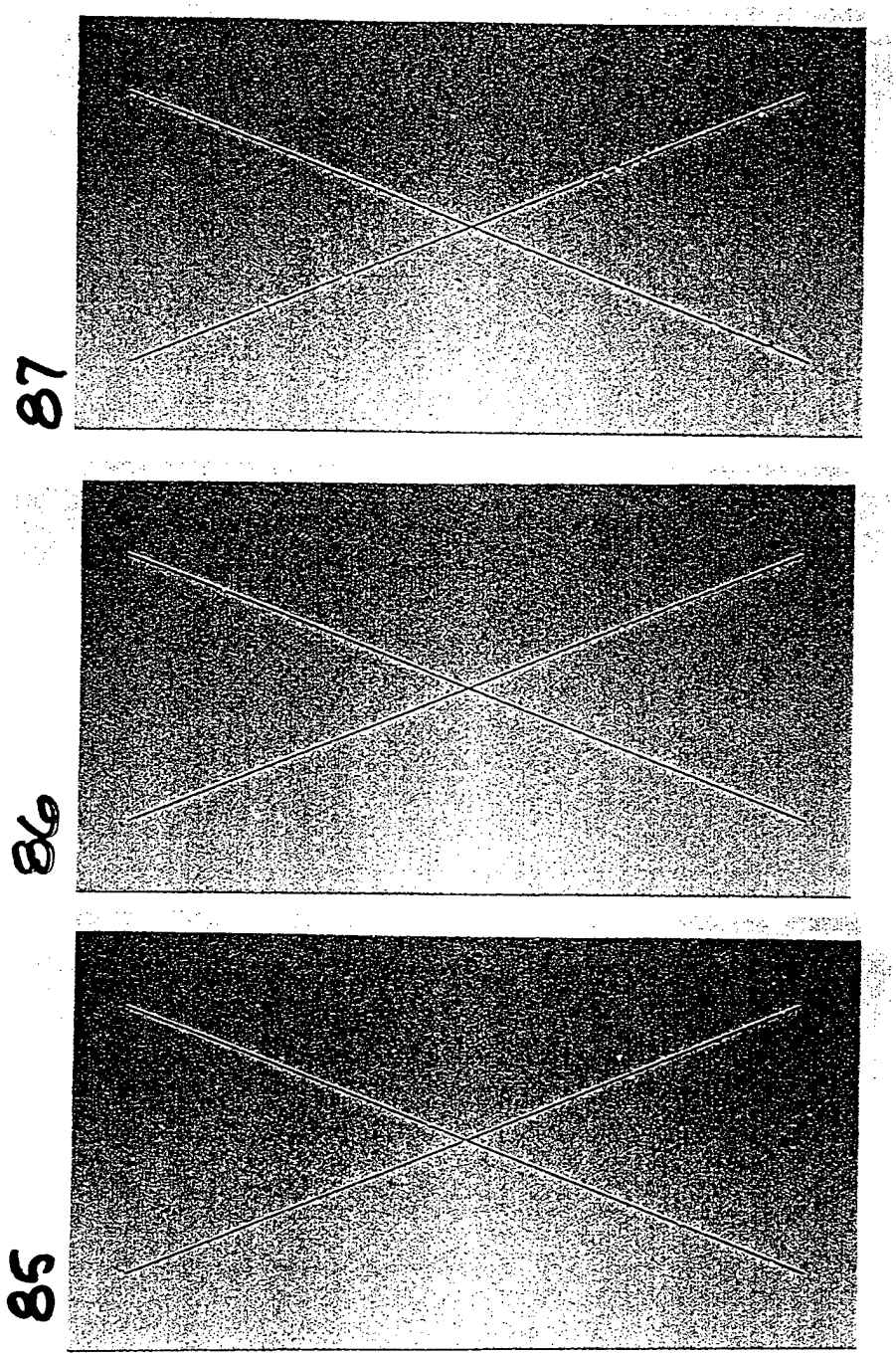


Figure C1 – Photographs of Chromate Conversion Coated 2024-T3 Aluminum Panels After Exposure to SO_2 Salt Spray for 2-Weeks.

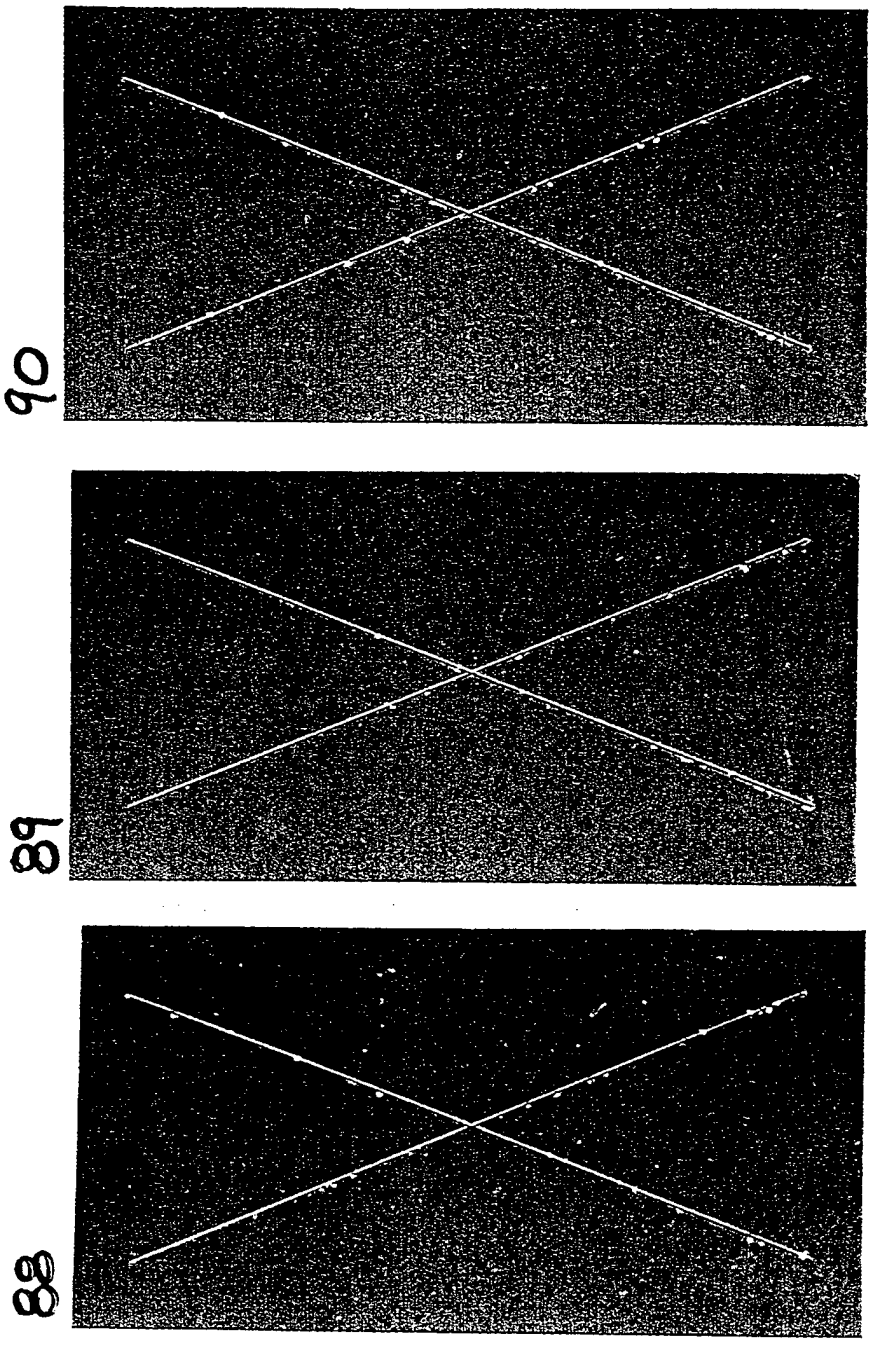


Figure C2 – Photographs of Chromate Conversion Coated 2024-T3 Aluminum Panels After Exposure to SO_2 Salt Spray for 2-Weeks.

DEXTER 10PW22-2

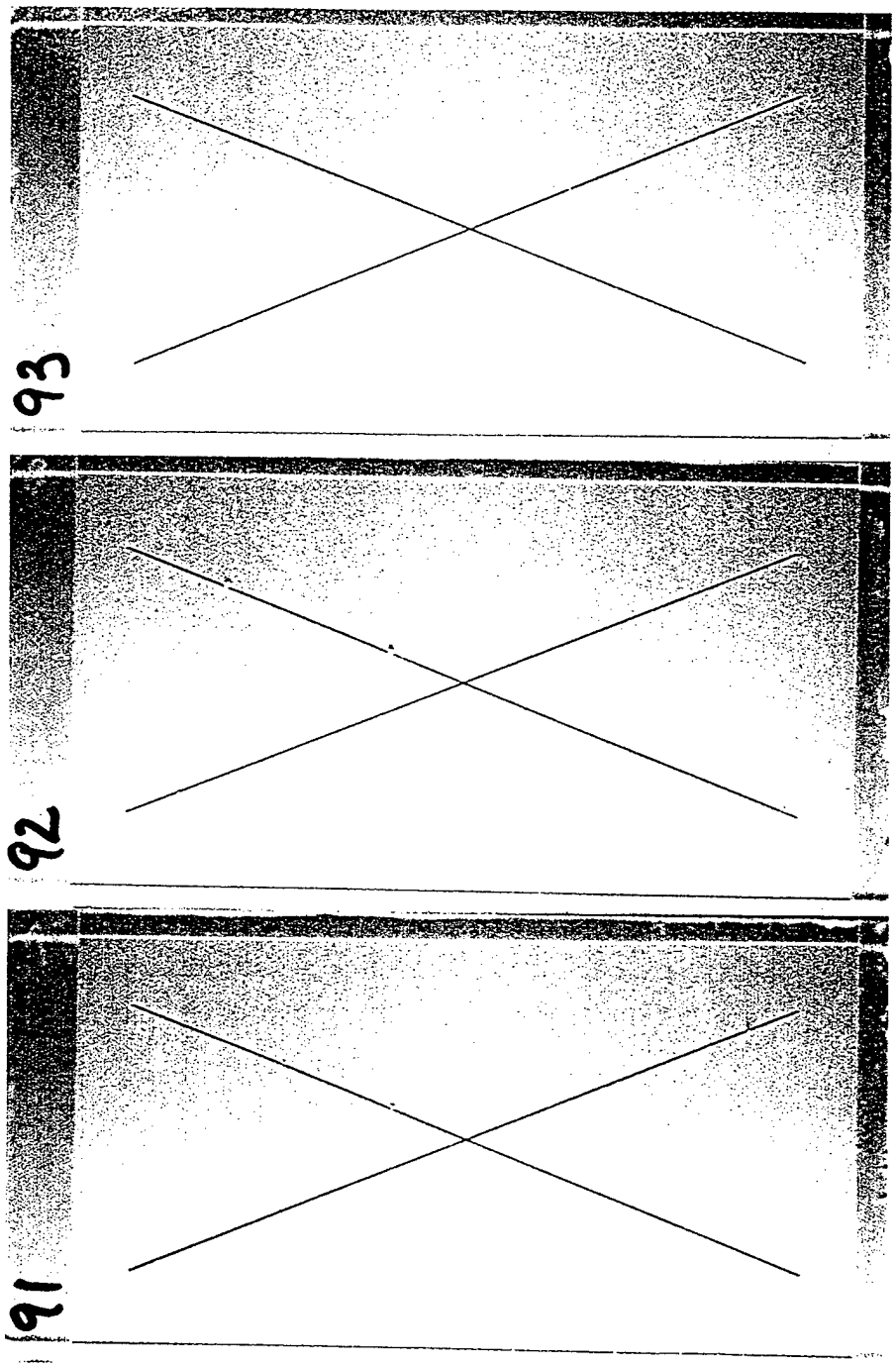


Figure C3 – Photographs of Chromate Conversion Coated 2024-T3 Aluminum Panels After Exposure to SO_2 Salt Spray for 2-Weeks.

PRC-DE SOTO EWAE118

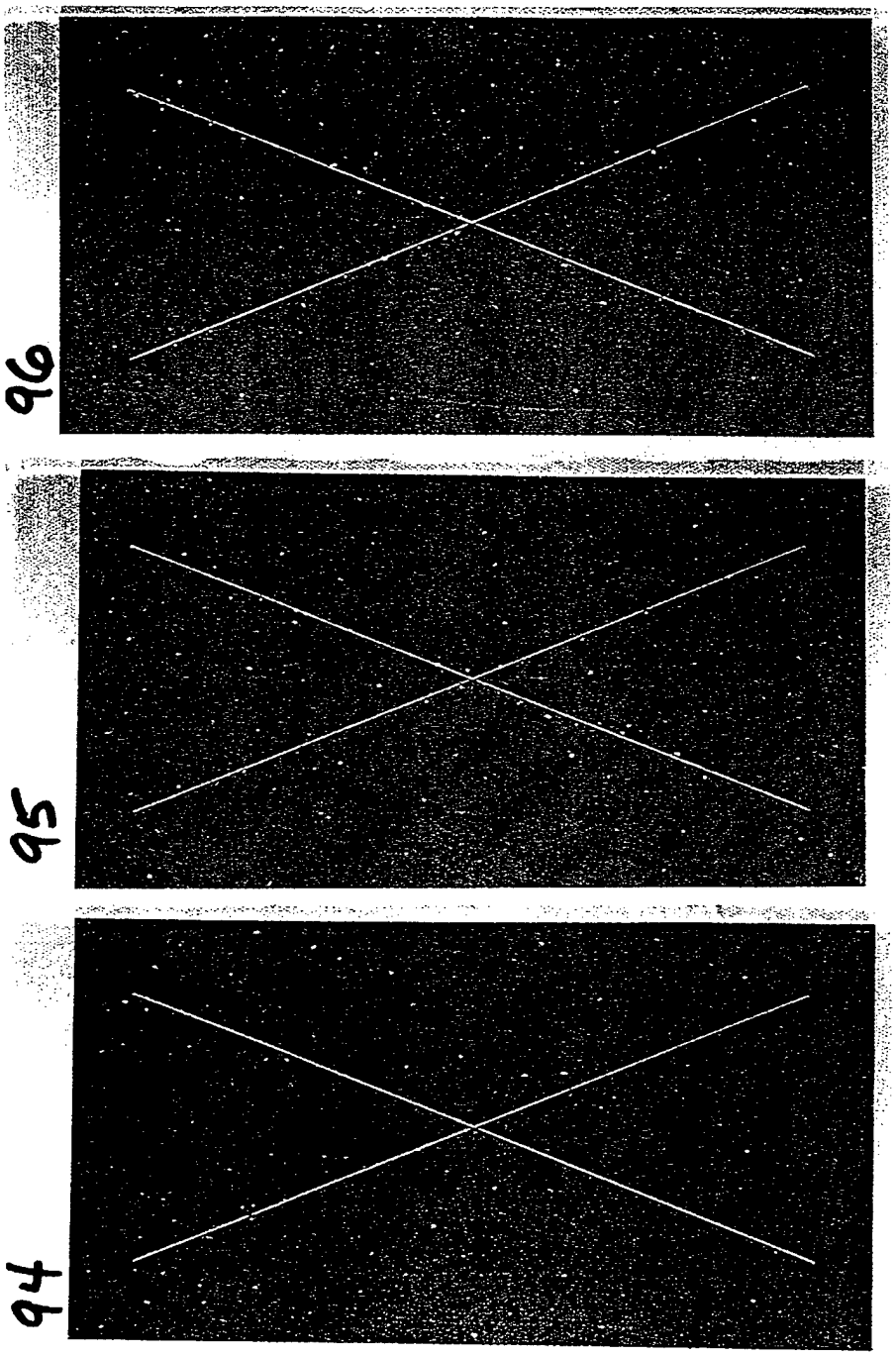


Figure C4 – Photographs of Chromate Conversion Coated 2024-T3 Aluminum Panels After Exposure to SO_2 Salt Spray for 2-Weeks.

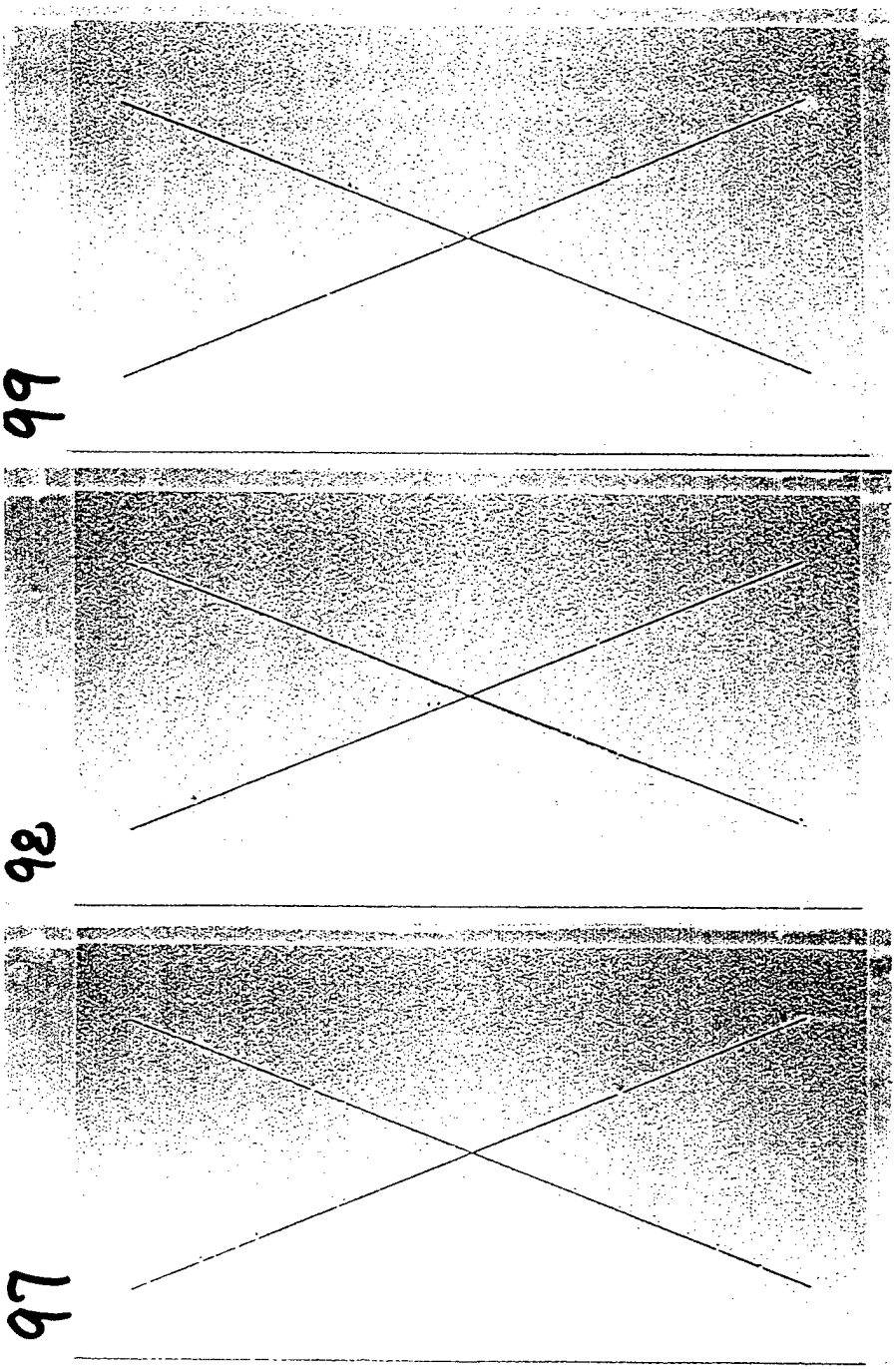


Figure C5 – Photographs of Chromate Conversion Coated 2024-T3 Aluminum Panels After Exposure to SO_2 Salt Spray for 2-Weeks.

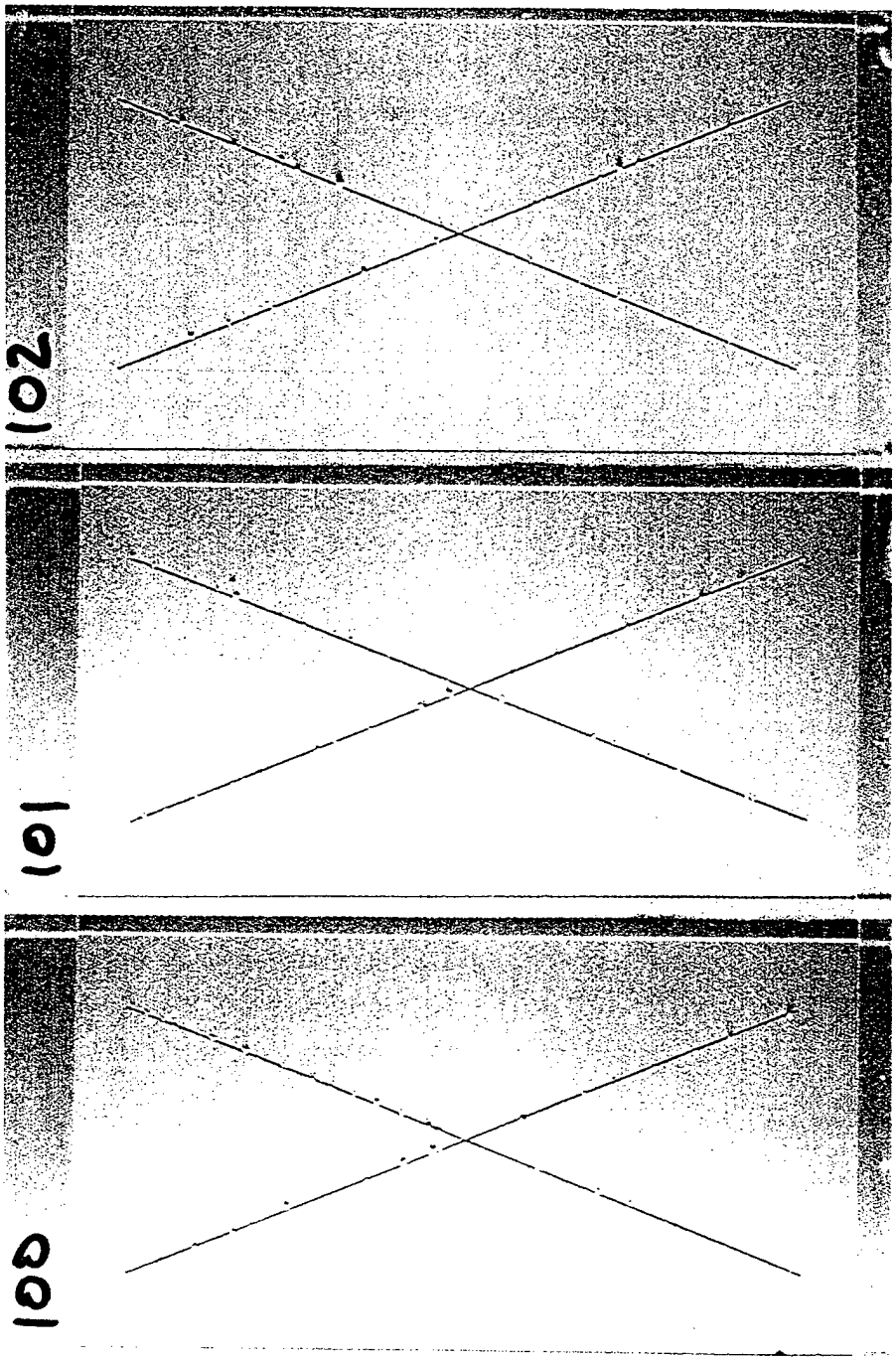


Figure C6 – Photographs of Chromate Conversion Coated 2024-T3 Aluminum Panels After Exposure to SO_2 Salt Spray for 2-Weeks.

DEFT 44-W-27

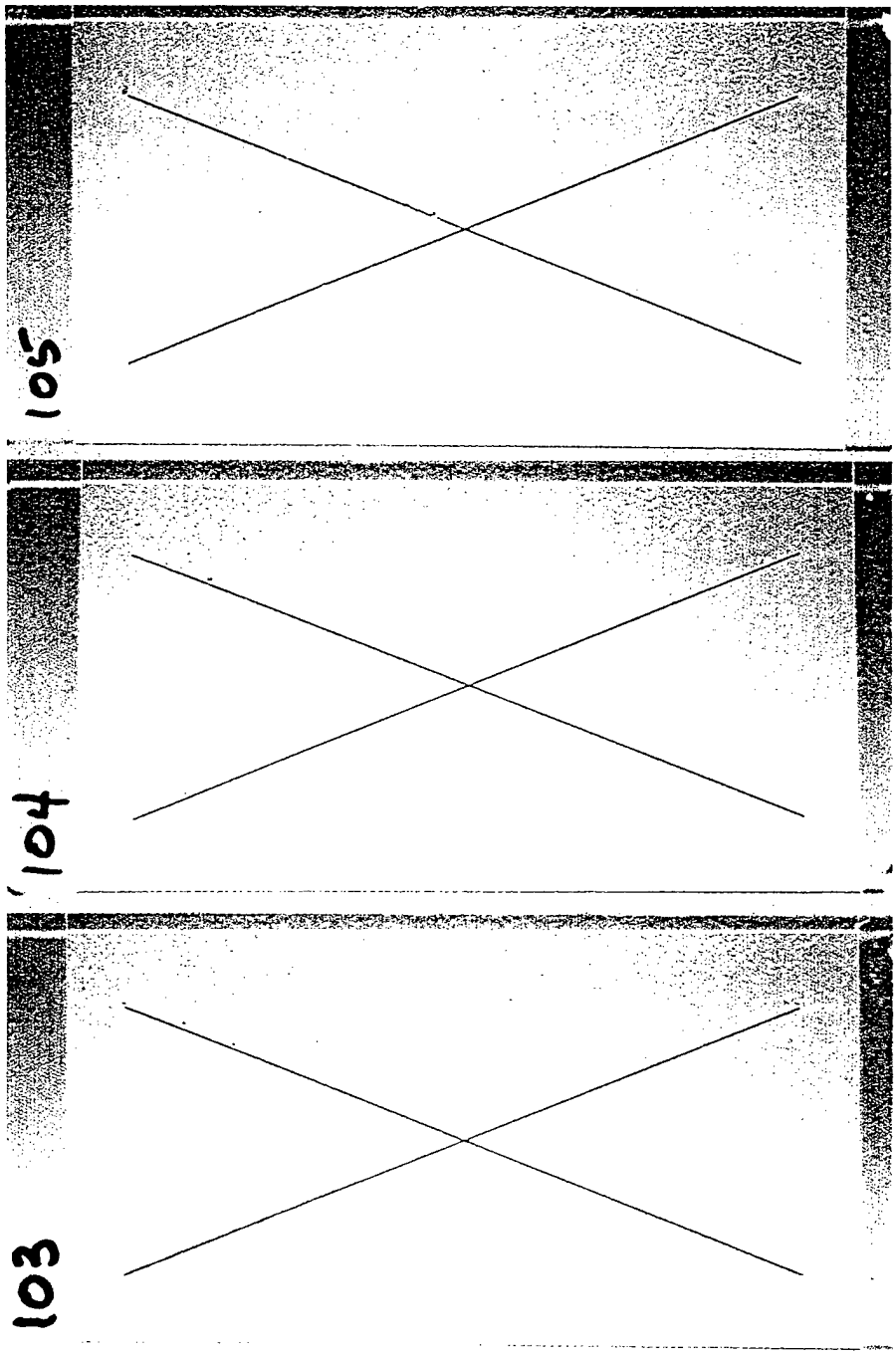


Figure C7 – Photographs of Chromate Conversion Coated 2024-T3 Aluminum Panels After Exposure to SO_2 Salt Spray for 2-Weeks.

APPENDIX D

SO_2 Salt Spray Corrosion Per ASTM G 85

Photographic Documentation of 2024-T3 Aluminum Panels Exposed to SO_2 Salt Spray for 2-Weeks, Then Stripped.

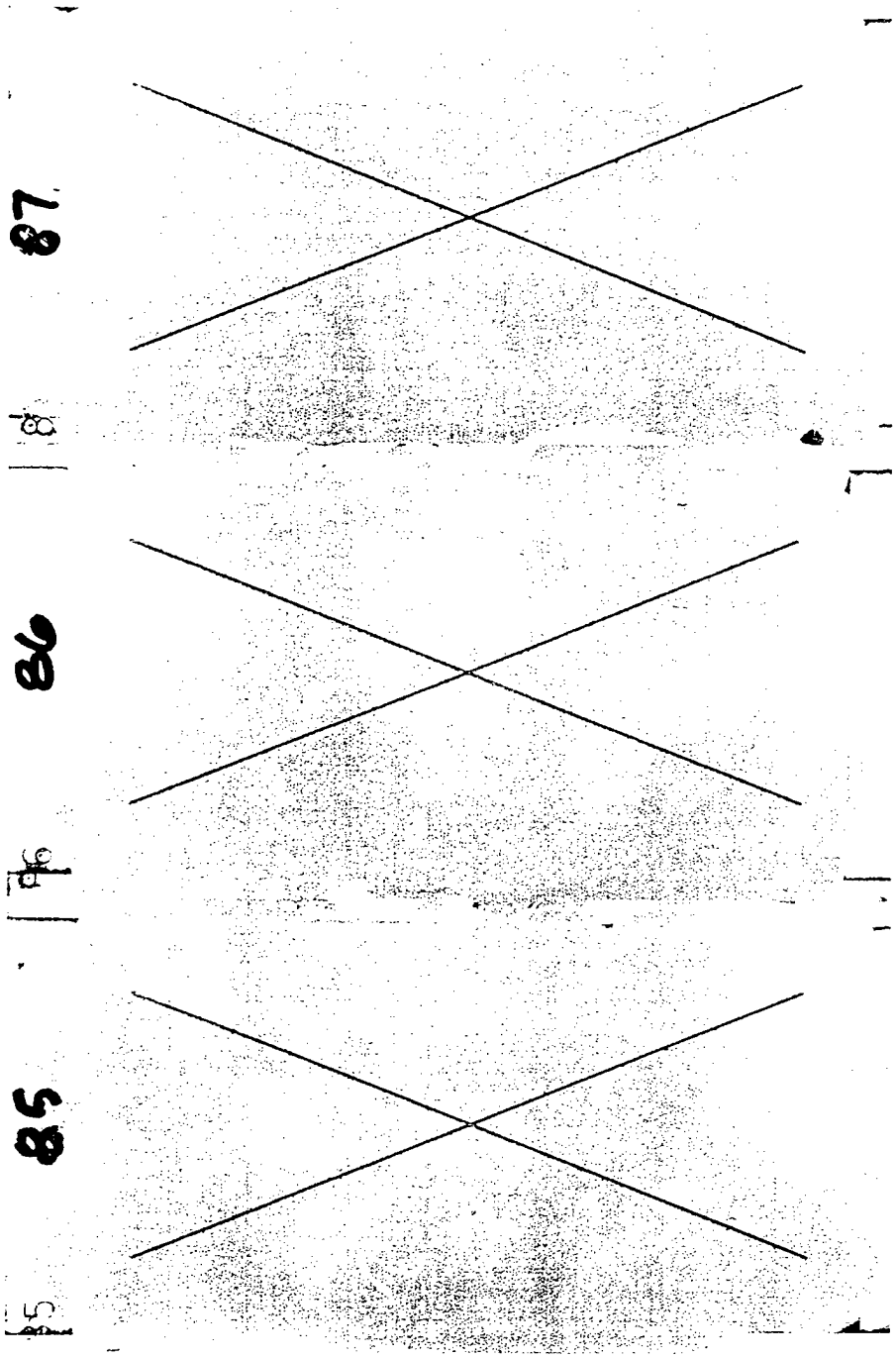


Figure D1 – Photographs of Chromate Conversion Coated 2024-T3 Aluminum Panels After Exposure to SO_2 Salt Spray for 2-Weeks, Then Stripped.

U.S. PAINT W4102

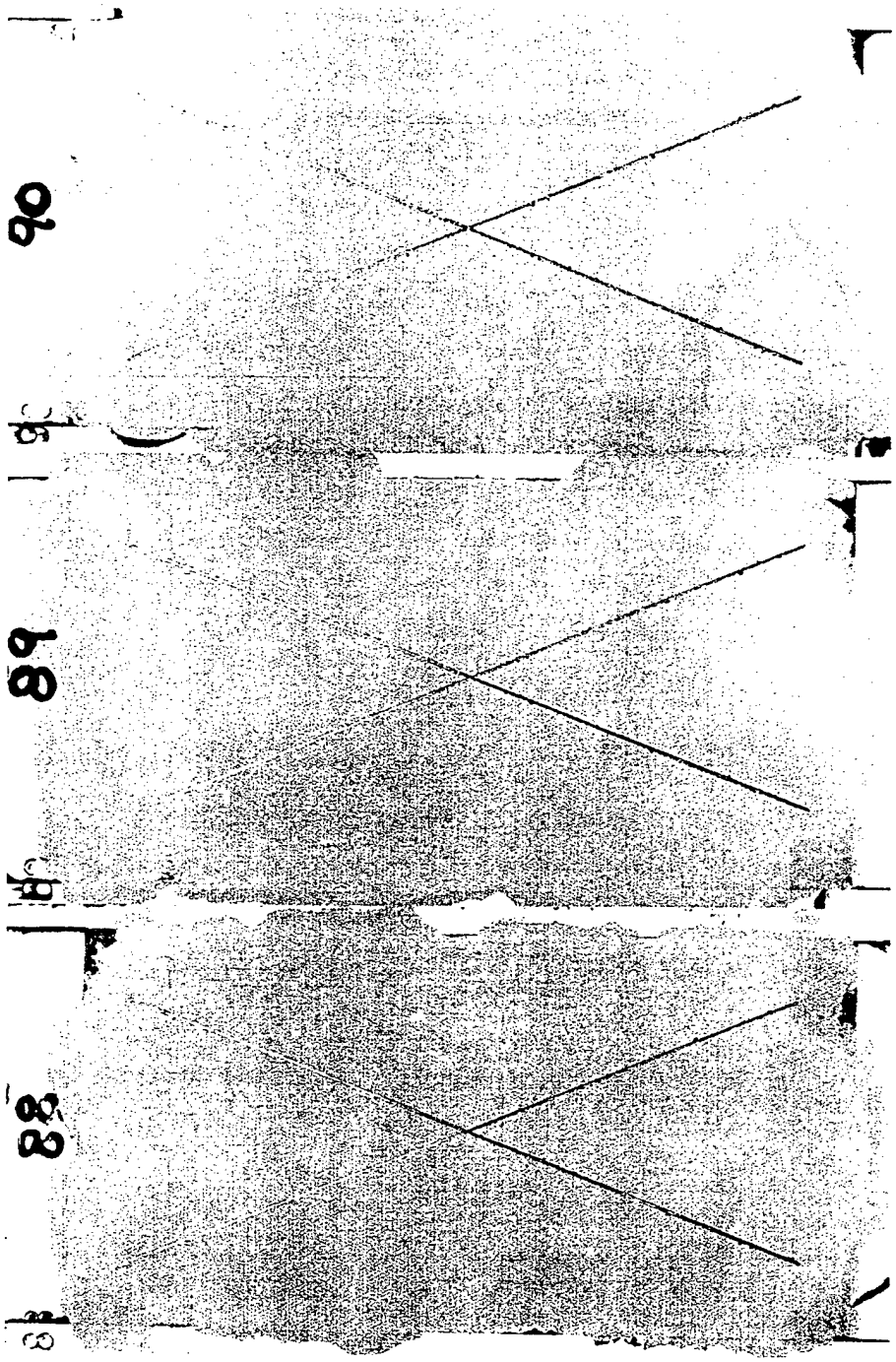


Figure D2 – Photographs of Chromate Conversion Coated 2024-T3 Aluminum Panels After Exposure to SO_2 Salt Spray for 2-Weeks, Then Stripped.

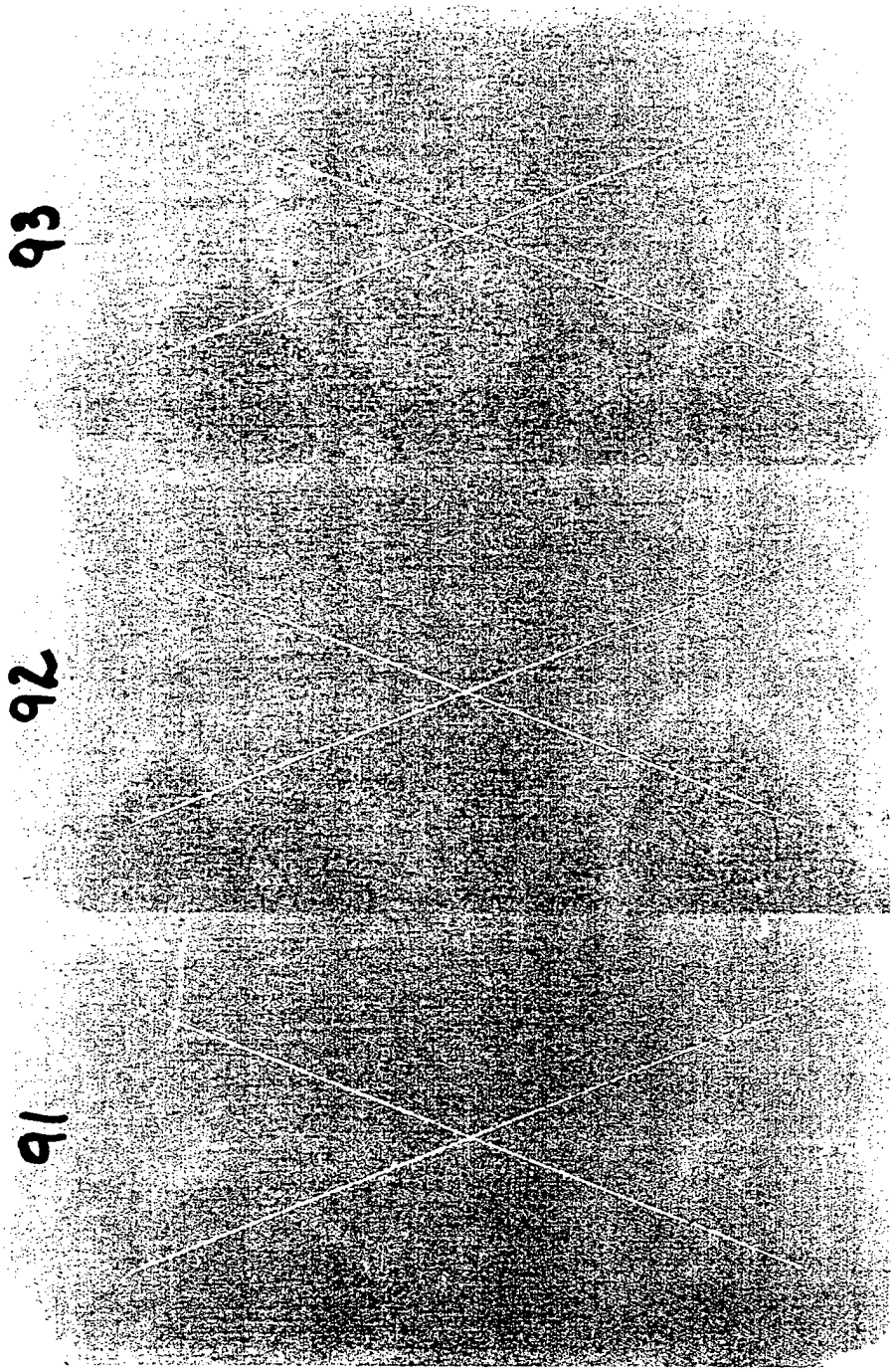


Figure D3 – Photographs of Chromate Conversion Coated 2024-T3 Aluminum Panels After Exposure to SO_2 Salt Spray for 2-Weeks, Then Stripped.

PRC-DE SOTO EWAE118

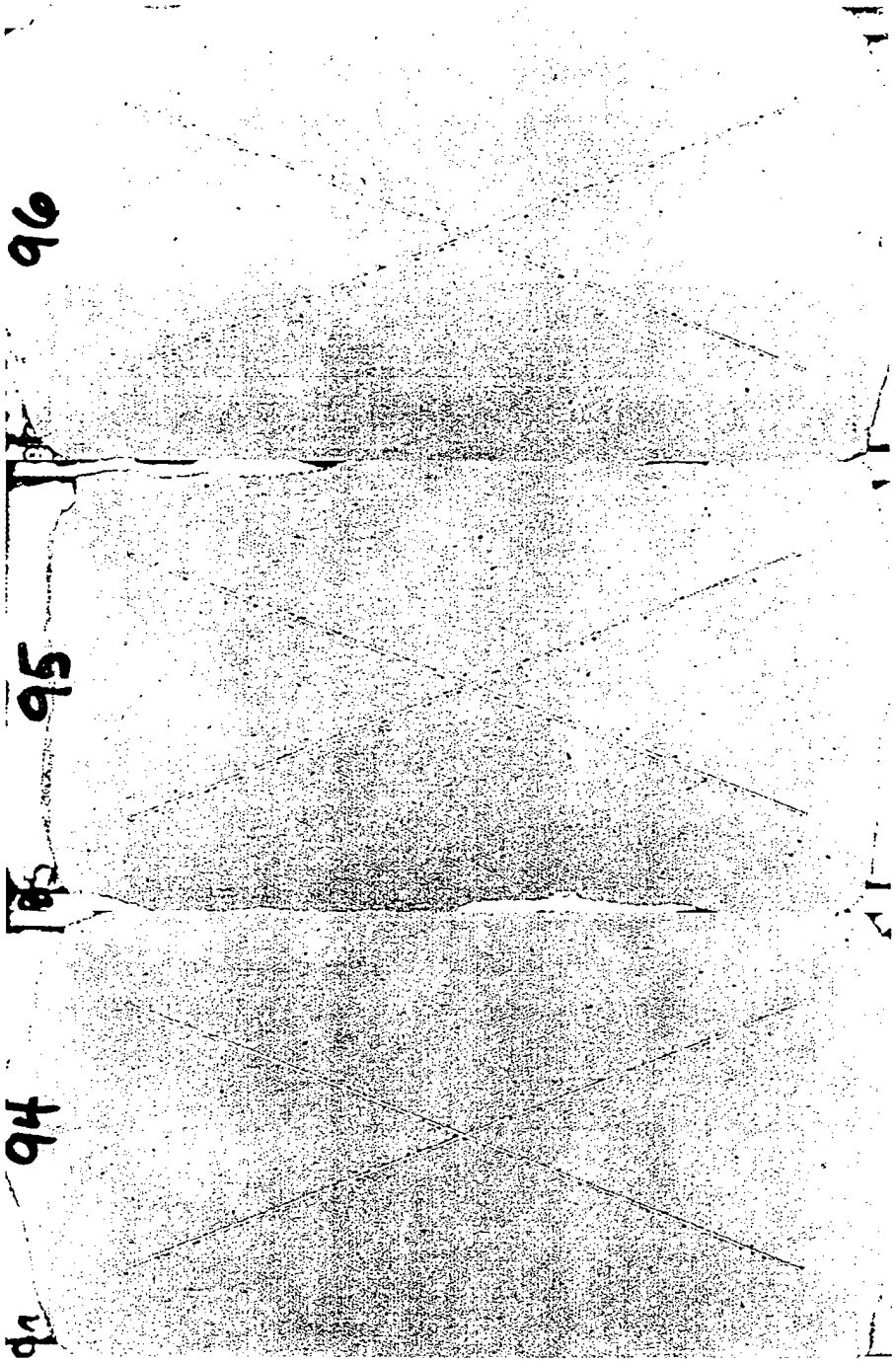


Figure D4 – Photographs of Chromate Conversion Coated 2024-T3 Aluminum Panels After Exposure to SO_2 Salt Spray for 2-Weeks, Then Stripped.

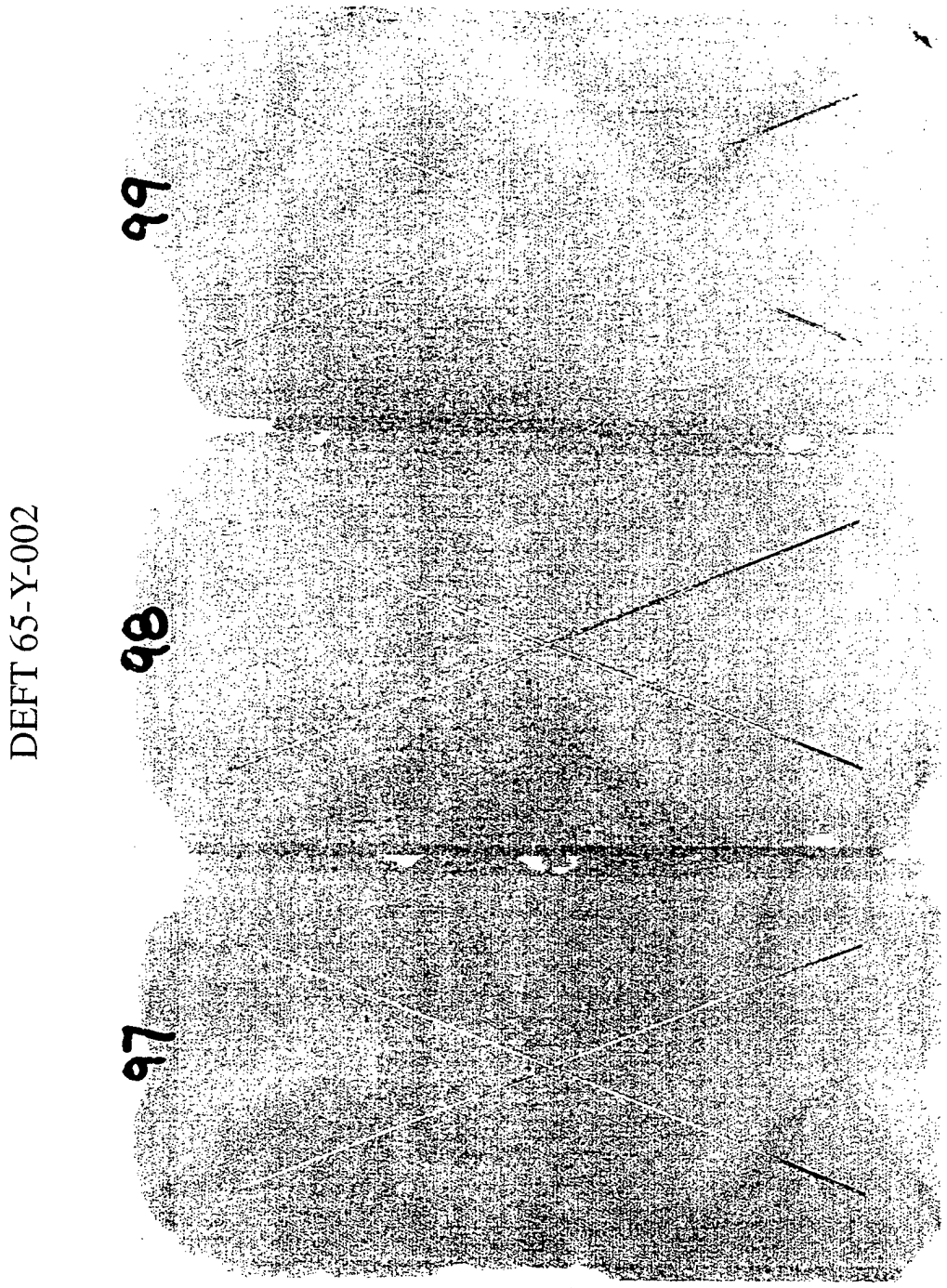


Figure D5 – Photographs of Chromate Conversion Coated 2024-T3 Aluminum Panels After Exposure to SO_2, Salt Spray for 2-Weeks, Then Stripped.

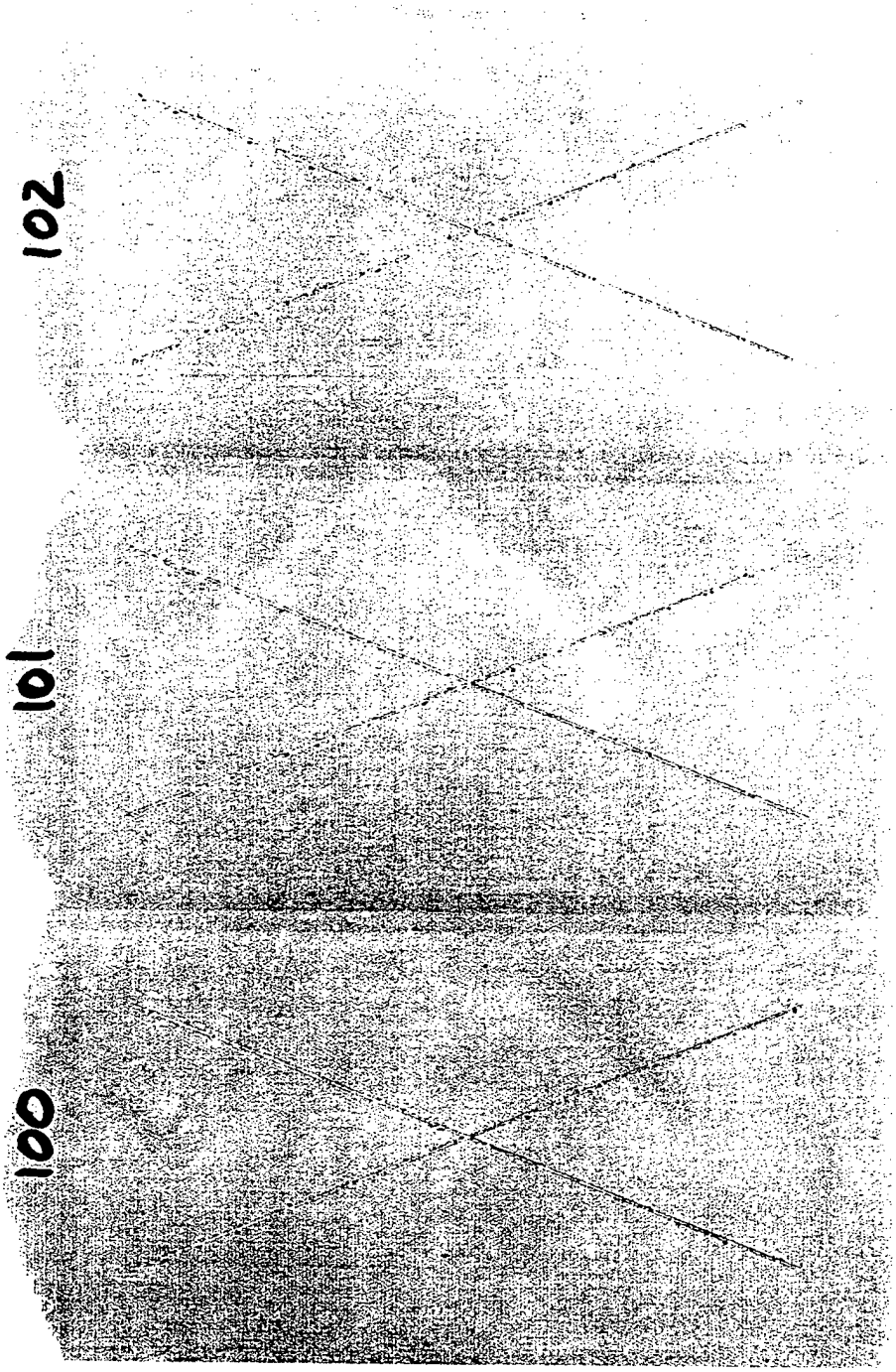


Figure D6 – Photographs of Chromate Conversion Coated 2024-T3 Aluminum Panels After Exposure to SO_2 Salt Spray for 2-Weeks, Then Stripped.

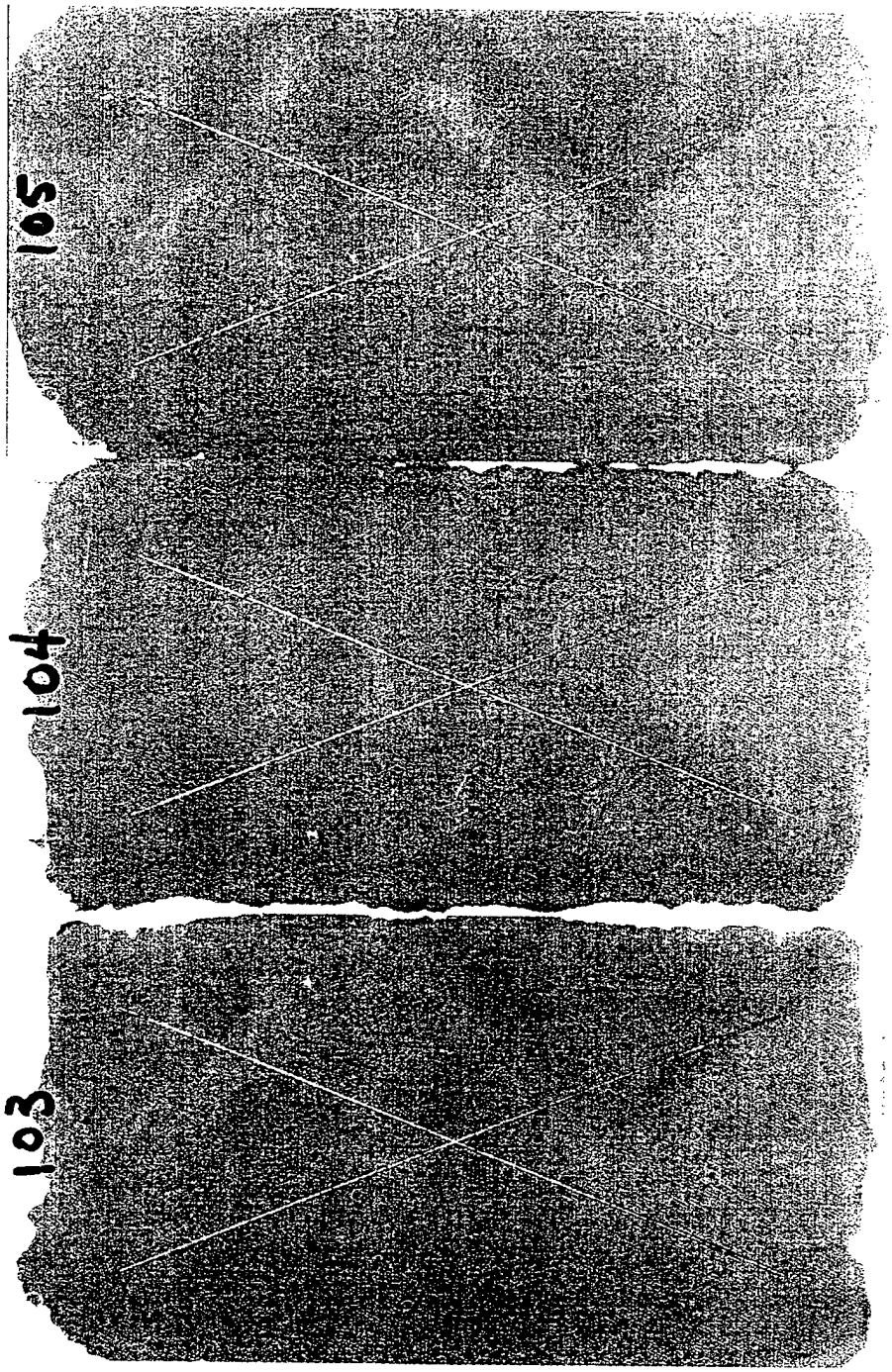


Figure D7 – Photographs of Chromate Conversion Coated 2024-T3 Aluminum Panels After Exposure to SO_2 Salt Spray for 2-Weeks, Then Stripped.

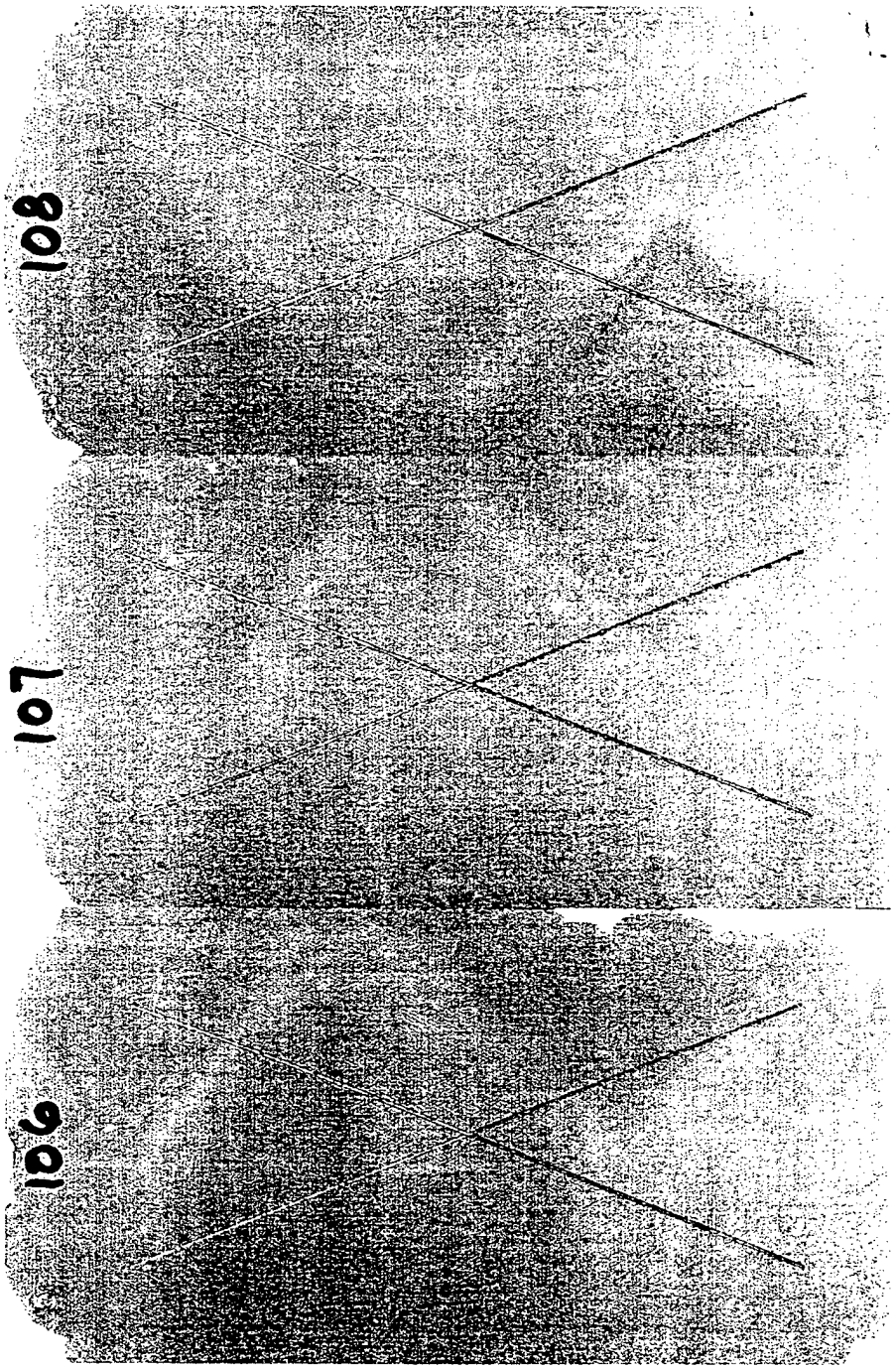


Figure D8 – Photographs of Chromate Conversion Coated 2024-T3 Aluminum Panels After Exposure to SO_2 Salt Spray for 2-Weeks, Then Stripped.

UNIVERSITY OF MISSOURI-ROLLA CERIUM INHIBITED PRIMER – 2nd ROUND

WR 515-896

FEBRUARY 2001

REPORT NUMBER 254.01.0006.01



TECHNICAL MEMORANDUM
ENGINEERING LABORATORIES

REPORT TYPE: FINAL

TECH MEMO: 254.01.0006.01
DATE: 06-FEB-01 REV:

TITLE: UNIVERSITY OF MISSOURI-ROLLA CERIUM INHIBITED PRIMER - SECOND ROUND

MODEL NO: MISC MODEL TYPE: MISC
REQ DOC: WR 515-896
TEST ART DELIVERY: N/A
CHARGE NO: HX2-H1-501
SET-UP START: N/A
CONTRACT NO: N/A
TEST START: 24-APR-00
REQUESTING DEPT: 679 TEST COMP.: 15-NOV-00
PART NUMBER: N/A
QUANTITY: 11 TEARDOWN COMP.: N/A

DISTRIBUTION

NAME	DEPT
M. R. PORTER	679
R.J. SARGENT *	254
L.K. TRIPLITT (3)	679
DEPT. FILES*	254
ENGR. SUPPORT*/**	348

* PAGE 1 ONLY
** ORIGINAL REPORT

TEST ARTICLE DESCRIPTION: Aluminum substrates, chromate and cerium conversion coat pretreatments with primer/topcoat systems.
MANUFACTURER: DEFT, PRC-DESOTO
TEST ARTICLE DISPOSITION: Returned to requester
TEST LOCATION/FACILITY NO.: CHEMICAL PROCESSES LAB, BLDG 102, ST. LOUIS
TEST CATEGORY: MATERIALS & PROCESSES
TUNNEL OCCUPANCY HOURS: N/A TEST RUNS/DATA POINTS: N/A
TYPE OF DATA ACQUIRED: CORROSION AND ADHESION
NO. OF DATA CHANNELS: N/A
TEST VARIABLES AND CONDITIONS: Corrosion environments

OTHER LAB REPORTS: N/A
SUPPLEMENTARY REPORTS: N/A

KEYWORDS:
1. MATERIALS
2. ADHESION
3. CERIUM CONVERSION COAT
4. CERIUM INHIBITED PRIMER
5. FILIFORM CORROSION
6. NEUTRAL SALT FOG
7. SO2/SALT SPRAY
8. TOPCOAT

1. TEST OBJECTIVE: The United States Air Force has issued University of Missouri-Rolla (UMR) a contract to develop cerium based conversion coating & primers. UMR has subcontracted some of this work to Boeing-STL. This is a second round of tests on cerium inhibited primer formulations. A cerium based conversion coat pretreatment will also be evaluated.

2. ABSTRACT OF RESULTS: Two chromated primers were tested with various cerium inhibited waterborne/high solids primers. The cerium inhibited primers did not perform as well as the chromated primers in corrosion tests. All cerium inhibited primers passed the wet tape adhesion test. The cerium inhibited pretreatment performed poorly in the corrosion test.

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RELEASED: N

3 Description of Test Articles

3.1 Metal Substrates

3.1.1 Boeing prepared one hundred sixty-five (165) aluminum test specimens for painting. An additional thirty-two (32) aluminum test specimens were pretreated by the University of Missouri-Rolla (UMR) coatings test group. Alloy types, specimen sizes, and surface pre-treatments are identified in Table 1.

3.2 Waterborne Epoxy Primers

3.2.1 Deft, MMS 423/425, MIL-PRF-85582, Type I, Class C2; 44-GN-72A/B, chromate control.

3.2.2 Deft, cerium phosphate inhibited primer, 44-W-31A/B.

3.2.3 Deft, barium metaborate inhibited primer, 44-W-30A/B.

3.2.4 Deft, cerium pentane dionate inhibited primer, 44-W-32A/B.

3.3 High Solids Epoxy Primers

3.3.1 Deft, MIL-PRF-23377G, Type I , Class C, 02-Y-040A/B, chromate control.

3.3.2 Deft, cerium phosphate inhibited primer, 44-W-047/02-Y-040CAT.

3.3.3 Deft, barium metaborate inhibited primer, 44-W-042/02-Y-040CAT.

3.3.4 Deft, barium metaborate/cerium nitrate inhibited primer, 44-W-045/02-Y-040CAT.

3.3.5 Deft, cerium pentane dionate inhibited primer, 44-W-046/02-Y-040CAT.

3.3.6 Deft, cerium nitrate inhibited primer, 44-W-044/02-Y-040CAT.

3.3.7 Deft, K-White primer, 44-W-043/02-Y-040CAT.

3.4 Test Topcoat

3.4.1 PRC DeSoto Desothane HS polyurethane topcoat, MIL-PRF-85285, Type I, CA8201/ F17925 / CA8000D.

4 Test Procedure

4.1 Substrate Pretreatment

4.1.1 Chromate Conversion Coat - One hundred and sixty-five aluminum specimens were conversion coated in building 598 production with Iridite 14-2 per P.S. 13209 in preparation for primer coating. Specimens were prepared twenty-four hours before primer applications and were protected with Kraft paper until primed.

4.1.2 UMR Cerium Conversion Coat - Thirty-two aluminum specimens were cerium conversion coated by UMR in preparation for primer coating. Specimens were delivered to the laboratory the morning of the primer applications.

4.1.3 Primer and Topcoat Applications - Primer applications were allowed to dry at room ambient temperature over night prior to the topcoat application. Primer dry film thickness values averaged between 0.001 and 0.0021 inches and the topcoat averaged 0.0026 inches. Application data and product manufacturing information are presented in Table 2. Dry film thickness values measured for each coating are shown in Table 3. All specimens were subjected to a fourteen-day room temperature air cure before testing.

4.2 Corrosion Resistance

4.2.1 Salt/SO_2 Fog Exposure - Specimens were scribed with a Hermes engraving machine, from corner to corner (forming an "X") through the coatings into bare metal, taped (edges and back) and exposed to salt/SO_2 fog per ASTM G 85 Annex A4 for 336 hours. After 168 hours, the specimens were removed from the salt fog chamber and examined for film failure or evidence of corrosion.

4.2.2 Neutral Salt Spray Exposure - Specimens were scribed with a Hermes engraving machine, from corner to corner (forming an "X") through the coatings into bare metal and taped (edges and back). The test groups were exposed to 5% salt spray per ASTM B 117 for 3000 hours. At 1000-hour intervals, the specimens were removed from the salt spray chamber and examined for film failure or evidence of corrosion.

4.2.3 Filiform Corrosion: Diagonal lines were scribed in each panel forming an "X" in the coating surface film exposing the metal substrate. Scribes were made with a Hermes engraving machine until the substrate surface had been penetrated. Each specimen edge and back surface was covered with a protective tape. The panels were placed vertically, with the long dimension horizontal, in a desiccator vessel containing 750ml of 12N hydrochloric acid (HCl). The panels were exposed for one hour at 77°F while being supported approximately two inches above the liquid level. Upon completion of the one hour HCl exposure, the specimens were immediately placed without rinsing in an environmental chamber maintained at 104±3°F and 80 ±5% RH for 1000 hours. Panels were held with the long

dimension at a 6° inclination from vertical and with the coated side facing upward. Visual observations were not made during the exposure. After a 1000-hour exposure, the specimens shall show no filaments extending ¼ inch beyond the scribe lines. A majority of filaments shall be less than $^1/_8$ inch in length.

4.3 Adhesion

4.3.1 Wet Tape Adhesion - After curing at room temperature for fourteen days , one half of each panel was immersed in tap water for 24 hours and a scribed wet tape test was performed per P.S. 21313. The panels were removed from the water, wiped dry with a cheesecloth and scribed with an X-Acto© knife. A pair of parallel lines was scribed one inch apart and an 'X' was scribed between the parallel scribe ends. 3M © brand 250 tape was placed over the scribe lines and pressed into place with a 4½ pound rubber coated roller (eight passes). The tape was removed with one quick motion and the area under the tape was examined for surface adhesion. The process to test a panel (removing from water to the completion of the tape test) was completed within three minutes.

5 Test Results

5.1 Corrosion Resistance

5.1.1 Salt/SO_2 Fog Exposure - Three high solids primers, cerium nitrate, cerium phosphate and cerium pentane dionate, performed the best during this test. Each exhibited corrosion extensions beyond the scribe lines up to 1/64 inch. The waterborne control and the barium metaborate high solids primers performed the worst, exhibiting darkening of the scribe lines and corrosion extensions from 1/32 to 1/16 inches beyond the scribe. The corrosion, when present, was located at isolated individual sites along the scribes. The number of sites had no correlation to the length of the corrosion extension. The ASTM D 1564 corrosion ratings are provided in Table 4 for each specimen. Photographic documentation of each specimen is provided in Appendix A. One specimen from each set of three is shown after stripping with Turco 5469. Observations recorded during the interim and final inspections are shown in Appendix F, Table 1.

5.1.2 Neutral Salt Spray Exposure

5.1.2.1 Chromate Conversion Coated Bare 7075-T6 Aluminum Substrates - The control primers exhibited no corrosion extending beyond the scribe lines and only slight corrosion within the scribe lines. The best cerium inhibited primer performance was exhibited by the cerium phosphate high solids primer, which had no corrosion extending beyond the scribe lines and some corrosion product build up in the lines. The remaining primers each had white corrosion products in much of the scribe line areas

with some corrosion extensions beyond the scribe line. The worst performance was exhibited by cerium nitrate high solids primer as one of the specimens developed a 1/8 inch blister along a scribe line. The ASTM D 1564 corrosion ratings are provided in Table 5 for each specimen. Photographic documentation was made at each thousand hour inspection interval of each specimen. One, two and three thousand hour photographs are provided in Appendixes B, C and D respectively. Observations recorded during the interim and final inspections are shown in Appendix F, Table 2.

5.1.2.2 Chromate Conversion Coated Bare 2024-T3 Aluminum Substrates - The chromated control primers perform well in this test with the high solids control exhibiting no corrosion in the scribe lines. Four of the cerium inhibited primers had corrosion products in the scribe lines with no corrosion extensions beyond the scribe. The worst performance was exhibited by cerium nitrate high solids primer specimens with two specimens developing blisters up to 1/4 inch along a scribe line and 1/32 inch blisters in areas away from the scribe lines. The ASTM D 1564 corrosion ratings are provided in Table 6 for each specimen. Photographic documentation was made at each thousand hour inspection interval of each specimen. One, two and three thousand hour photographs are provided in Appendixes B, C and D respectively. Observations recorded during the interim and final inspections are shown in Appendix F, Table 3.

5.1.2.3 UMR Cerium Conversion Coated Bare 7075-T6 Aluminum Substrates - None of the primers performed well on this substrate pretreatment. The best performance was exhibited by the waterborne chromated primer which exhibited corrosion extensions beyond the scribe lines after 1000 hours of exposure. Five of the cerium inhibited primers were removed from test after 1000 hours of exposure and three were removed after an additional 1000 hours of exposure. The best cerium inhibited primer performance was exhibited by waterborne cerium phosphate and cerium pentane dionate primers. Each had white corrosion products in much of the scribe line areas and developed blisters up to 3/16 inch along a scribe. The ASTM D 1564 corrosion ratings are provided in Table 7 for each specimen. Photographic documentation was made at each thousand hour inspection interval of each specimen. One, two and three thousand hour photographs are provided in Appendixes B, C and D respectively. Observations recorded during the interim and final inspections are shown in Appendix F, Table 4.

5.1.3 Filiform Corrosion - All primers passed the filiform corrosion test with no filament extensions greater than 1/4 inch and with the majority of all filaments less than 1/8 inch in length. The best performance was exhibited by the high solids barium metaborate and barium metaborate / cerium nitrate primers. The test results are shown in Table 8 and photographic documentation of each specimen is shown in Appendix E.

5.2 Adhesion

5.2.1 Wet Tape Adhesion - All primers passed this test. The cerium pentane dionate waterborne primer performed the best, with all three specimens exhibiting no primer removal whatsoever. All other primers exhibited some trace peeling along the scribe. Most primers exhibited trace peeling on all three specimens. The ASTM D 3359 ratings are shown in Table 9.

6 Summary

The cerium inhibited pretreated specimens performed poorly in the neutral salt spray corrosion test with all primer coatings failing the corrosion criteria. None of the cerium inhibited primers performed as well as the chromated control primers on chromate conversion coated substrates in the 3000-hour neutral salt spray test. However, several of the cerium inhibited primers did perform better than either of chromated control primers during the 500-hour SO_2/salt spray test. All primers performed relatively well in the wet tape adhesion tests. A summary of the test results is shown in Table 10 and a ranking of each primer in each individual test is shown in Table 11.

Table 1. Stamping Plan

SUBSTRATE TYPE	SPECIMEN SIZE (inch)	PRETREATMENT TYPE	TOPCOAT TYPE	PANEL ID	TEST
Bare 7075-T6	0.032 x 3 x 6	Chromate Conversion Coat	None	1 - 33	Neutral Salt Corrosion
	0.032 x 1.5 x 3	UMR Cerium Conversion Coat		34 - 66	
Bare 2024-T3	0.032 x 3 x 6	Chromate Conversion Coat		100 - 132	
	0.032 x 3 x 6			232 - 264	SO_2/Salt Spray Corrosion
Alclad 2024-T3	0.032 x 3 x 6			265 - 297	Wet Tape Adhesion
	0.032 x 3 x 6		PRC-DeSoto CA 8201	199 - 231	Filiform Corrosion

Table 2. Primer and Topcoat Application Data

DEFT PRIMER TYPE / TOPCOAT TYPE	BASE			CATALYST			COATING APPLICATION		
	PART NUMBER	BATCH NUMBER	EXP DATE	PART NUMBER	BATCH NUMBER	EXP DATE	DATE	TIME (MIXING/INDUCT)	VISC[1,2] (sec)
Waterborne Chromate Control	44-GN-72A	33972	Jun-00	44-GN-72B	33973	Jun-00	27-Apr	11:30 AM	16
Cerium Phosphate Waterborne	44-W-31A	L-14071	Apr-01	44-W-31B	L-14072	Apr-01	27-Apr	11:55 AM	14
Barium Metaborate Waterborne	44-W-30A	L-14069	Apr-01	44-W-30B	L-14070	Apr-01	27-Apr	12:05 PM	16
K White 140 High Solids	02-W-043A	L-14015	Apr-01	02-Y-040CAT	41821	Mar-01	27-Apr	9:50 AM	22
Cerium Pentane Dionate Waterborne	44-W-32A	L-14073	Apr-01	44-W-32B	L-14074	Apr-01	27-Apr	12:10 PM	16
High Solids Chromate Control	02-Y-040A	42133	Apr-01	02-Y-040CAT	42134	Apr-01	27-Apr	10:15 AM	24
Cerium Phosphate High Solids	02-W-047A	L-14041	Apr-00	02-Y-040CAT	41821	Mar-01	27-Apr	8:15 AM	56
Barium Metaborate High Solids	02-W-042A	L-14014	Apr-00	02-Y-040CAT	41821	Mar-01	27-Apr	8:25 AM	22
Barium Metaborate/ Cerium Nitrate High Solids	02-W-045A	L-14034	Apr-00	02-Y-040CAT	41821	Mar-01	27-Apr	9:00 AM	23
Cerium Pentane Dionate High Solids	02-W-046A	L-14035	Apr-00	02-Y-040CAT	41821	Mar-01	27-Apr	9:25 AM	20
Cerium Nitrate High Solids	02-W-044A	L-14033	Apr-00	02-Y-040CAT	41821	Mar-01	27-Apr	9:35 AM	38
PRC-DeSoto Desothane	CA8201/ F17925	525510	Sep-00	CA 8000D	510582	Jul-00	28-Apr	8:50 AM	20

Note:

[1] Viscosity measurements were taken at room temperature with a #4 Ford cup.

[2] High solids test primers were mixed in a 3:1 ratio, base to catalyst. Waterborne primers were mixed as a kit.

Table 3. Dry Film Thickness Values

DEFT PRIMER TYPE / TOPCOAT TYPE	PRODUCT NUMBER	COATING APPLICATION DATE	THICKNESS VALUE			
			MEAN (mils)	STANDARD DEVIATION (mils)	LOW (mils)	HIGH (mils)
Waterborne Chromate Control	44-GN-72	27-Apr	1.34	0.11	1.12	1.62
Cerium Phosphate Waterborne	44-W-31	27-Apr	1.03	0.10	0.81	1.25
Barium Metaborate Waterborne	44-W-30	27-Apr	1.13	0.11	0.94	1.39
K White 140 High Solids	02-W-043	27-Apr	1.55	0.16	1.22	2.03
Cerium Pentane Dionate Waterborne	44-W-32	27-Apr	1.12	0.09	0.93	1.42
High Solids Chromate Control	02-Y-040	27-Apr	1.46	0.14	1.22	1.84
Cerium Phosphate High Solids	02-W-047	27-Apr	1.85	0.25	1.45	2.69
Barium Metaborate High Solids	02-W-042	27-Apr	2.09	0.17	1.67	2.36
Barium Metaborate/ Cerium Nitrate High Solids	02-W-045	27-Apr	1.78	0.23	1.35	2.39
Cerium Pentane Dionate High Solids	02-W-046	27-Apr	1.40	0.13	1.13	1.67
Cerium Nitrate High Solids	02-W-044	27-Apr	1.80	0.17	1.43	2.14
PRC-DeSoto Desothane	CA8201/F17925	28-Apr	2.60	0.31	2.05	3.83

Table 4. 336-Hour SO_2/Salt Spray Corrosion (ASTM G 85) Test Results

PRIMER TYPE	PANEL ID [1]	PRODUCT NUMBER	CORROSION [6]		RESULTS	
			SCRIBE LINE ASTM D 1654 CRITERIA [2]	SURFACE ASTM D 1654 CRITERIA [3]	MIL-PRF-85582 [4] (Pass / Fail)	MMS 423 [5] (Pass / Fail)
Waterborne						
	232	Deft 44-GN-72 (Chromated Control)	**7**	**10**	Fail	Fail
	233		7	10		
	234		7	10		
	235	Cerium Phosphate	**8**	**10**	Fail	Fail
	236		7	10		
	237		8	10		
	238	Barium Metaborate	**8**	**10**	Fail	Pass
	239		8	10		
	240		8	10		
	244	Cerium Pentane Dionate	**8**	**10**	Fail	Fail
	245		7	10		
	246		8	10		
High Solids						
	247	Deft 02-Y-040 (Chromated Control)	**8**	**10**	Fail	Pass
	248		8	10		
	249		8	10		
	241	K White 140	**9**	**10**	Fail	Pass
	242		9	10		
	243		8	10		
	250	Cerium Phosphate	**9**	**10**	Fail	Pass
	251		9	10		
	252		9	10		
	253	Barium Metaborate	**7**	**10**	Fail	Fail
	254		7	10		
	255		8	10		
	256	Barium Metaborate/Cerium Nitrate	**8**	**10**	Fail	Pass
	257		8	10		
	258		8	10		
	259	Cerium Pentane Dionate	**9**	**10**	Fail	Pass
	260		9	10		
	261		9	10		
	262	Cerium Nitrate	**9**	**10**	Fail	Pass
	263		9	10		
	264		9	10		

Notes:

[1] Specimens were 0.032 inch bare 2024-T3 aluminum chromate conversion coated per P.S. 13209.

[2] Ratings (10 to 0) are identified below, Scribe Line Numerical Ratings.

[3] Ratings (10 to 0) are identified below, Field Area Numerical Rating.

[4] The primer shall show no sign of blistering, softening, or lifting of the coating, or any corrosion in or beyond the scribe lines.

[5] The primer shall show no sign of blistering, softening or lifting of the coating, or any corrosion extending 1/32 inch beyond the scribe lines.

[6] Rating values in bold print are observations made on stripped specimens.

Scribe Line Numerical Rating per ASTM D 1654:

Representative Mean Creepage From Scribe:

Inches (Approximate)	Rating Number
0	10
0 to 1/64	9
1/64 to 1/32	8
1/32 to 1/16	7
1/16 to 1/8	6
1/8 to 3/16	5
3/16 to 1/4	4
1/4 to 3/8	3
3/8 to 1/2	2
1/2 to 5/8	1

Field Area Numerical Rating per ASTM D 1654:

Rating of Unscribed Area:

Area Failed, %	Rating Number
0 to 1	10
2 to 3	9
4 to 6	8
7 to 10	7
11 to 20	6
21 to 30	5
31 to 40	4
41 to 55	3
56 to 75	2
Over 75	1

Table 5. 3000-Hour Neutral Salt Spray Test Results on Bare 7075-T6 Conversion Coated Substrates

PRIMER TYPE	PANEL ID [1]	PRODUCT NUMBER	CORROSION [5]		RESULTS	
			SCRIBE LINE ASTM D 1654 CRITERIA [2]	SURFACE ASTM D 1654 CRITERIA [3]	MIL-PRF-85582 [4] (Pass / Fail)	MMS 423 [5] (Pass / Fail)
Waterborne						
	1	Deft 44-GN-72 (Chromated Control)	10	10	Fail	Pass
	2		10	10		
	3		10	10		
	4	Cerium Phosphate	9	10	Fail	Pass
	5		10	10		
	6		9	10		
	7	Barium Metaborate	8	10	Fail	Pass
	8		8	10		
	9		8	10		
	13	Cerium Pentane Dionate	9	10	Fail	Pass
	14		9	10		
	15		9	10		
High Solids						
	16	Deft 02-Y-040 (Chromated Control)	10	10	Fail	Pass
	17		10	10		
	18		10	10		
	10	K White 140	9	10	Fail	Pass
	11		8	10		
	12		8	10		
	19	Cerium Phosphate	10	10	Fail	Pass
	20		10	10		
	21		10	10		
	22	Barium Metaborate	8	10	Fail	Pass
	23		8	10		
	24		8	10		
	25	Barium Metaborate/Cerium Nitrate	9	10	Fail	Fail
	26		9	10		
	27		7	10		
	28	Cerium Pentane Dionate	8	10	Fail	Fail
	29		8	10		
	30		7	10		
	31	Cerium Nitrate	4	10	Fail	Fail
	32		9	10		
	33		8	10		

Notes:

[1] Specimens were 0.032 inch bare 7075-T6 aluminum chromate conversion coated per P.S. 13209.

[2] Ratings (10 to 0) are identified below, Scribe Line Numerical Ratings.

[3] Ratings (10 to 0) are identified below, Field Area Numerical Rating.

[4] The primer shall show no sign of blistering, softening or lifting of the coating, or any corrosion extending 1/32 inch beyond the scribe lines.

[5] Rating values in bold print are observations made on stripped specimens.

Scribe Line Numerical Rating per ASTM D 1654:

Representative Mean Creepage From Scribe:

Inches (Approximate)	Rating Number
0	10
0 to 1/64	9
1/64 to 1/32	8
1/32 to 1/16	7
1/16 to 1/8	6
1/8 to 3/16	5
3/16 to 1/4	4
1/4 to 3/8	3
3/8 to 1/2	2
1/2 to 5/8	1

Field Area Numerical Rating per ASTM D 1654:

Rating of Unscribed Area:

Area Failed, %	Rating Number
0 to 1	10
2 to 3	9
4 to 6	8
7 to 10	7
11 to 20	6
21 to 30	5
31 to 40	4
41 to 55	3
56 to 75	2
Over 75	1

Table 6. 3000-Hour Neutral Salt Spray Test Results on Bare 2024-T3 Conversion Coated Substrates

PRIMER TYPE	PANEL ID [1]	PRODUCT NUMBER	CORROSION [5]		RESULTS	
			SCRIBE LINE ASTM D 1654 CRITERIA [2]	SURFACE ASTM D 1654 CRITERIA [3]	MIL-PRF-85582 [4] (Pass / Fail)	MMS 423 [5] (Pass / Fail)
Waterborne						
	100	Deft 44-GN-72 (Chromated Control)	10	10	Fail	Pass
	101		10	10		
	102		10	10		
	103	Cerium Phosphate	10	10	Fail	Pass
	104		10	10		
	105		10	10		
	106	Barium Metaborate	3	10	Fail	Fail
	107		6	10		
	108		6	10		
	112	Cerium Pentane Dionate	10	10	Fail	Pass
	113		10	10		
	114		8	10		
High Solids						
	115	Deft 02-Y-040 (Chromated Control)	10	10	Pass	Pass
	116		10	10		
	117		10	10		
	109	K White 140	10	10	Fail	Pass
	110		10	10		
	111		10	10		
	118	Cerium Phosphate	10	10	Fail	Pass
	119		10	10		
	120		10	10		
	121	Barium Metaborate	9	10	Fail	Pass
	122		9	10		
	123		9	10		
	124	Barium Metaborate/Cerium Nitrate	10	10	Fail	Pass
	125		10	10		
	126		9	10		
	127	Cerium Pentane Dionate	10	10	Fail	Pass
	128		10	10		
	129		10	10		
	130	Cerium Nitrate	4	10	Fail	Fail
	131		4	10		
	132		5	10		

Notes:

[1] Specimens were 0.032 inch bare 2024-T3 aluminum chromate conversion coated per P.S. 13209.

[2] Ratings (10 to 0) are identified below, Scribe Line Numerical Ratings.

[3] Ratings (10 to 0) are identified below, Field Area Numerical Rating.

[4] The primer shall show no sign of blistering, softening or lifting of the coating, or any corrosion extending 1/32 inch beyond the scribe lines.

[5] Rating values in bold print are observations made on stripped specimens.

Scribe Line Numerical Rating per ASTM D 1654:

Representative Mean Creepage From Scribe:

Inches (Approximate)	Rating Number
0	10
0 to 1/64	9
1/64 to 1/32	8
1/32 to 1/16	7
1/16 to 1/8	6
1/8 to 3/16	5
3/16 to 1/4	4
1/4 to 3/8	3
3/8 to 1/2	2
1/2 to 5/8	1

Field Area Numerical Rating per ASTM D 1654:

Rating of Unscribed Area:

Area Failed, %	Rating Number
0 to 1	10
2 to 3	9
4 to 6	8
7 to 10	7
11 to 20	6
21 to 30	5
31 to 40	4
41 to 55	3
56 to 75	2
Over 75	1

Table 7. 3000-Hour Neutral Salt Spray Test Results on Bare 7075-T6 Cerium Conversion Coated Substrates

PRIMER TYPE	PANEL ID [1]	PRODUCT NUMBER	CORROSION [5]		RESULTS	
			SCRIBE LINE ASTM D 1654 CRITERIA [2]	SURFACE ASTM D 1654 CRITERIA [3]	MIL-PRF-85582 [4] (Pass / Fail)	MMS 423 [5] (Pass / Fail)
Waterborne						
	34	Deft 44-GN-72 (Chromated Control)	9	10	Fail	Pass
	35		8	10		
	36		8	10		
	38	Cerium Phosphate	5	10	Fail	Fail
	39		6	10		
	40	Barium Metaborate	Removed After 1000 Hours	10	Fail	Fail
	41			10		
	42			10		
	46	Cerium Pentane Dionate	5	10	Fail	Fail
	47		3	10		
	48		8	10		
High Solids						
	49	Deft 02-Y-040 (Chromated Control)	Removed After 2000 Hours	6	Fail	Fail
	50			1		
	51			1		
	43	K White 140	Removed After 1000 Hours	1	Fail	Fail
	44			1		
	45			1		
	52	Cerium Phosphate	Removed After 1000 Hours	1	Fail	Fail
	53			1		
	54			1		
	55	Barium Metaborate	Removed After 1000 Hours	1	Fail	Fail
	56			1		
	57			3		
	58	Barium Metaborate/Cerium Nitrate	Removed After 2000 Hours	4	Fail	Fail
	59			2		
	60			5		
	61	Cerium Pentane Dionate	Removed After 1000 Hours	1	Fail	Fail
	62			1		
	63			1		
	64	Cerium Nitrate	Removed After 2000 Hours	5	Fail	Fail
	65			1		
	66			1		

Notes:

[1] Specimens were 0.032 inch bare 7075-T6 aluminum UMR cerium conversion coated.

[2] Ratings (10 to 0) are identified below, Scribe Line Numerical Ratings.

[3] Ratings (10 to 0) are identified below, Field Area Numerical Rating.

[4] The primer shall show no sign of blistering, softening or lifting of the coating, or any corrosion extending 1/32 inch beyond the scribe lines.

[5] Rating values in bold print are observations made on stripped specimens.

Scribe Line Numerical Rating per ASTM D 1654:

Representative Mean Creepage From Scribe:

Inches (Approximate)	Rating Number
0	10
0 to 1/64	9
1/64 to 1/32	8
1/32 to 1/16	7
1/16 to 1/8	6
1/8 to 3/16	5
3/16 to 1/4	4
1/4 to 3/8	3
3/8 to 1/2	2
1/2 to 5/8	1

Field Area Numerical Rating per ASTM D 1654:

Rating of Unscribed Area:

Area Failed, %	Rating Number
0 to 1	10
2 to 3	9
4 to 6	8
7 to 10	7
11 to 20	6
21 to 30	5
31 to 40	4
41 to 55	3
56 to 75	2
Over 75	1

Table 8. 1000-Hour Filiform Corrosion Test Results on Alclad 2024-T3 Conversion Coated Substrates

PRIMER TYPE	PANEL ID [1]	PRODUCT NUMBER	NUMBER OF FILAMENTS > 1/4 INCH	MAJORITY OF FILAMENTS LESS THAN 1/8 INCH	MMS 423 RESULTS [2] (Pass / Fail)
Waterborne					
	199	Deft 44-GN-72 (Chromated Control)	0	Yes	Pass
	200		0	Yes	
	201		0	Yes	
	202	Cerium Phosphate	0	Yes	Pass
	203		0	Yes	
	204		0	Yes	
	205	Barium Metaborate	0	Yes	Pass
	206		0	Yes	
	207		0	Yes	
	211	Cerium Pentane Dionate	0	Yes	Pass
	212		0	Yes	
	213		0	Yes	
High Solids					
	214	Deft 02-Y-040 (Chromated Control)	0	Yes	Pass
	215		0	Yes	
	216		0	Yes	
	208	K White 140	0	Yes	Pass
	209		0	Yes	
	210		0	Yes	
	217	Cerium Phosphate	0	Yes	Pass
	218		0	Yes	
	219		0	Yes	
	220	Barium Metaborate	0	Yes	Pass
	221		0	Yes	
	222		0	Yes	
	223	Barium Metaborate/Cerium Nitrate	0	Yes	Pass
	224		0	Yes	
	225		0	Yes	
	226	Cerium Pentane Dionate	0	Yes	Pass
	227		0	Yes	
	228		0	Yes	
	229	Cerium Nitrate	0	Yes	Pass
	230		0	Yes	
	231		0	Yes	

Notes:

[1] Specimens were 0.032 inch alclad 2024-T3 aluminum chromate conversion coated per P.S. 13209.

[2] MMS 423A (Table 1, Test 19) corrosion failure criteria. The majority of filaments shall extend less than 0.125 inch from the scribe line and none may extend more than 0.250 inch from scribe line.

Table 9. Wet Tape Adhesion Test Results

PRIMER TYPE	PANEL ID [1]	PRODUCT NUMBER	PERCENTAGE OF PRIMER REMOVED % [2]	ASTM D3359 [3]	MMS 423B Results [4]
Waterborne					
	265	Deft 44-GN-72 (Chromated Control)	0	5A	Pass
	266		0	4A	
	267		0	4A	
	268	Cerium Phosphate	0	4A	Pass
	269		0	4A	
	270		0	4A	
	271	Barium Metaborate	0	4A	Pass
	272		0	5A	
	273		0	4A	
	277	Cerium Pentane Dionate	0	5A	Pass
	278		0	5A	
	279		0	5A	
High Solids					
	280	Deft 02-Y-040 (Chromated Control)	0	4A	Pass
	281		0	4A	
	282		0	4A	
	274	K White 140	0	4A	Pass
	275		0	4A	
	276		0	4A	
	283	Cerium Phosphate	0	4A	Pass
	284		0	4A	
	285		0	4A	
	286	Barium Metaborate	0	4A	Pass
	287		0	4A	
	288		0	4A	
	289	Barium Metaborate/Cerium Nitrate	0	4A	Pass
	290		0	4A	
	291		0	4A	
	292	Cerium Pentane Dionate	0	4A	Pass
	293		0	4A	
	294		0	4A	
	295	Cerium Nitrate	0	4A	Pass
	296		0	4A	
	297		0	4A	

Notes:

[1] Specimens were 0.020 inch alclad 2024-T3 aluminum chromate conversion coated per P.S. 13209.

[2] Specimens were examined for removal and uplifting of the primer coating.

[3] ASTM D 3359 Criteria

5A - No peeling or removal

4A - Trace peeling or removal along incisions

3A - Jagged removal along incisions up to 1/16 inch on either side

2A - Jagged removal along most of incisions up to 1/8 inch on either side

1A - Removal from most of the area of the "X" under the tape

0A - Removal beyond the area of the "X"

[4] The primer shall show no adhesion failure

Table 10. Summary of Test Results

TABLE	TEST TYPE / DURATION	METAL / TREATMENT [1]	TEST COATINGS										
			WATERBORNE PRIMERS				HIGH SOLIDS PRIMERS						
			Deft 44-GN-72 (Chromated Control)	Cerium Phosphate	Barium Metaborate	Cerium Pentane Dionate	Deft 02-Y-040 (Chromated Control)	K White 140	Cerium Phosphate	Barium Metaborate	Barium Metaborate/ Cerium Nitrate	Cerium Pentane Dionate	Cerium Nitrate
5	3000 Hr. Neutral Salt Spray	7075-T6 Bare - Chromate Conversion Coat	P	P	F	P	P	P	P	P	F	F	F
6	3000 Hr. Neutral Salt Spray	2024-T3 Bare - Chromate Conversion Coat	P	P	F	P	P	P	P	P	P	P	F
7	3000 Hr. Neutral Salt Spray	7075-T6 Bare - UMR Cerium Conversion Coat	P	F	F	F	F	F	F	F	F	F	F
4	500 Hr. SO_2/Salt Spray	2024-T3 Bare - Chromate Conversion Coat	F	F	P	F	P	P	P	F	P	P	P
8	1000 Hr. Filiform Corrosion	2024-T3 Alclad - Chromate Conversion Coat	P	P	P	P	P	P	P	P	P	P	P
9	Scribed Wet Tape Adhesion	2024-T3 Alclad - Chromate Conversion Coat	P	P	P	P	P	P	P	P	P	P	P

Note:

[1] Substrate pretreatments:

a) Chromate conversion coat per P.S. 13209

b) Cerium conversion coated by University of Missouri - Rolla.

Table 10. Summary of Test Results - Ranking (1 = Best)

TABLE	TEST TYPE / DURATION	METAL / TREATMENT [1]	TEST COATINGS										
			WATERBORNE PRIMERS				HIGH SOLIDS PRIMERS						
			Deft 44-GN-72 (Chromated Control)	Cerium Phosphate	Barium Metaborate	Cerium Pentane Dionate	Deft 02-Y-040 (Chromated Control)	K White 140	Cerium Phosphate	Barium Metaborate	Barium Metaborate/ Cerium Nitrate	Cerium Pentane Dionate	Cerium Nitrate
5	3000 Hr. Neutral Salt Spray	7075-T6 Bare - Chromate Conversion Coat	1	4	10	5	1	6	3	7	8	9	11
6	3000 Hr. Neutral Salt Spray	2024-T3 Bare - Chromate Conversion Coat	2	6	10	7	1	5	3	9	8	3	11
7	3000 Hr. Neutral Salt Spray	7075-T6 Bare - UMR Cerium Conversion Coat	1	3	7	2	4	9	9	8	5	9	6
4	500 Hr. SO_2/Salt Spray	2024-T3 Bare - Chromate Conversion Coat	11	9	7	8	5	4	1	10	6	1	1
8	1000 Hr. Filiform Corrosion	2024-T3 Alclad - Chromate Conversion Coat	4	8	4	10	2	4	7	1	2	10	8
9	Scribed Wet Tape Adhesion	2024-T3 Alclad - Chromate Conversion Coat	2	3	2	1	3	3	3	3	3	3	3

Pass	Marginal	Fail

Note:

[1] Substrate pretreatments:

a) Chromate conversion coat per P.S. 13209

b) Cerium conversion coated by University of Missouri - Rolla.

The data presented in this report, to the best of my knowledge and belief, is complete, accurate and complies with all test requirements of the requesting document.

APPENDIX A

SO_2 / Salt Spray Exposure Specimen

Photographic Documentation

ASTM G85

PRIMER PAGE

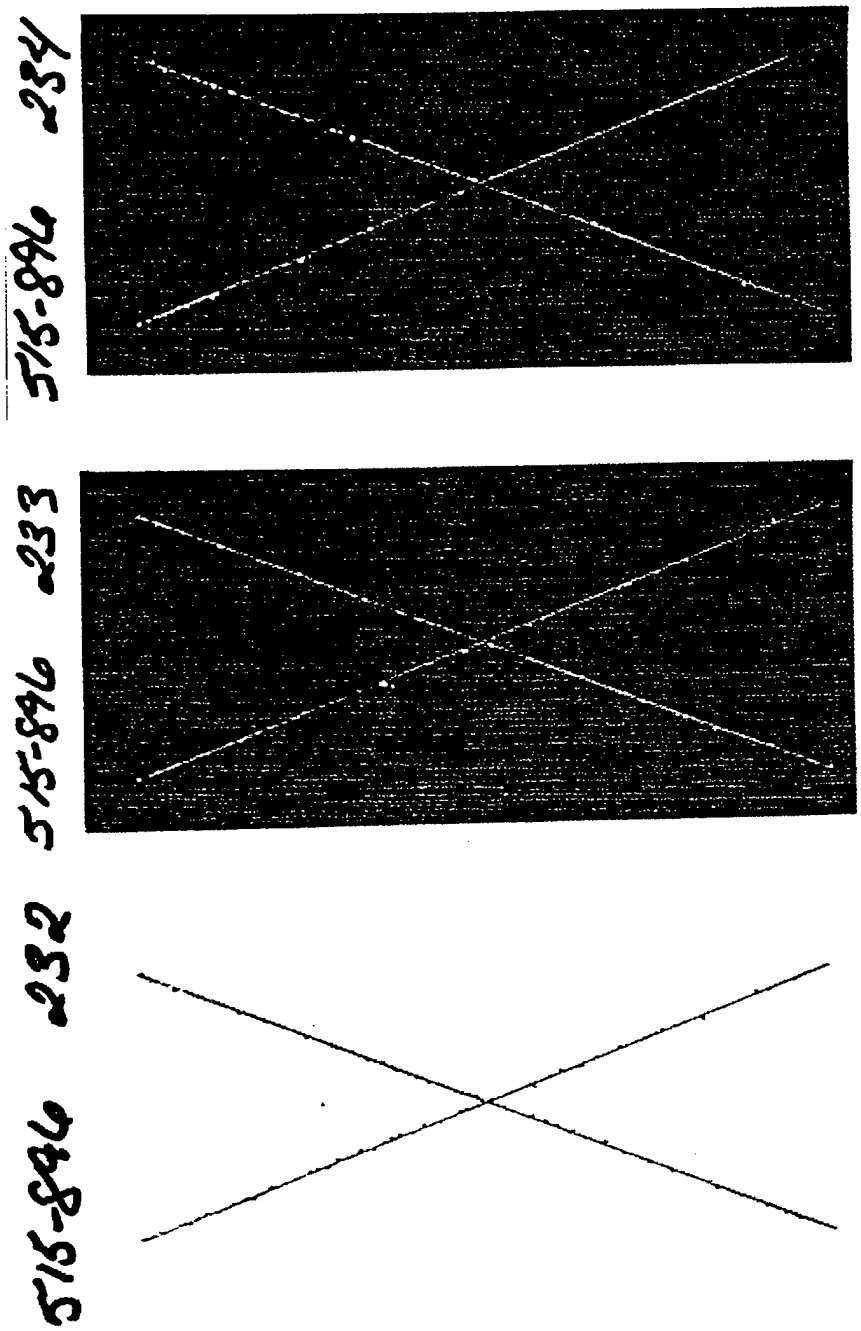
Scans of Specimens

Deft 44-GN-72, Waterborne Chromate Control.	A3
Deft 44-W-31, Cerium Phosphate, Waterborne	A4
Deft 44-W-30, Barium Metaborate, Waterborne	A5
Deft 02-W-043, K-White, High Solids	A6
Deft 44-W-32, Cerium Pentane Dionate, Waterborne	A7
Deft 02-Y-040, High Solids Chromate Control	A8
Deft 02-W-047, Cerium Phosphate, High Solids	A9
Deft 02-W-042, Barium Metaborate, High Solids	A10
Deft 02-W-045, Barium Metaborate / Cerium Nitrate, High Solids	A11
Deft 02-W-046, Cerium Pentane Dionate, High Solids	A12
Deft 02-W-044, Cerium Nitrate, High Solids	A13

Photographs of Specimens with Illumination from the Side

Deft 44-GN-72, Waterborne Chromate Control.	A14
Deft 44-W-31, Cerium Phosphate, Waterborne	A15
Deft 44-W-30, Barium Metaborate, Waterborne	A16
Deft 02-W-043, K-White, High Solids	A17
Deft 44-W-32, Cerium Pentane Dionate, Waterborne	A18
Deft 02-Y-040, High Solids Chromate Control	A19
Deft 02-W-047, Cerium Phosphate, High Solids	A20
Deft 02-W-042, Barium Metaborate, High Solids	A21
Deft 02-W-045, Barium Metaborate / Cerium Nitrate, High Solids	A22
Deft 02-W-046, Cerium Pentane Dionate, High Solids	A23
Deft 02-W-044, Cerium Nitrate, High Solids	A24

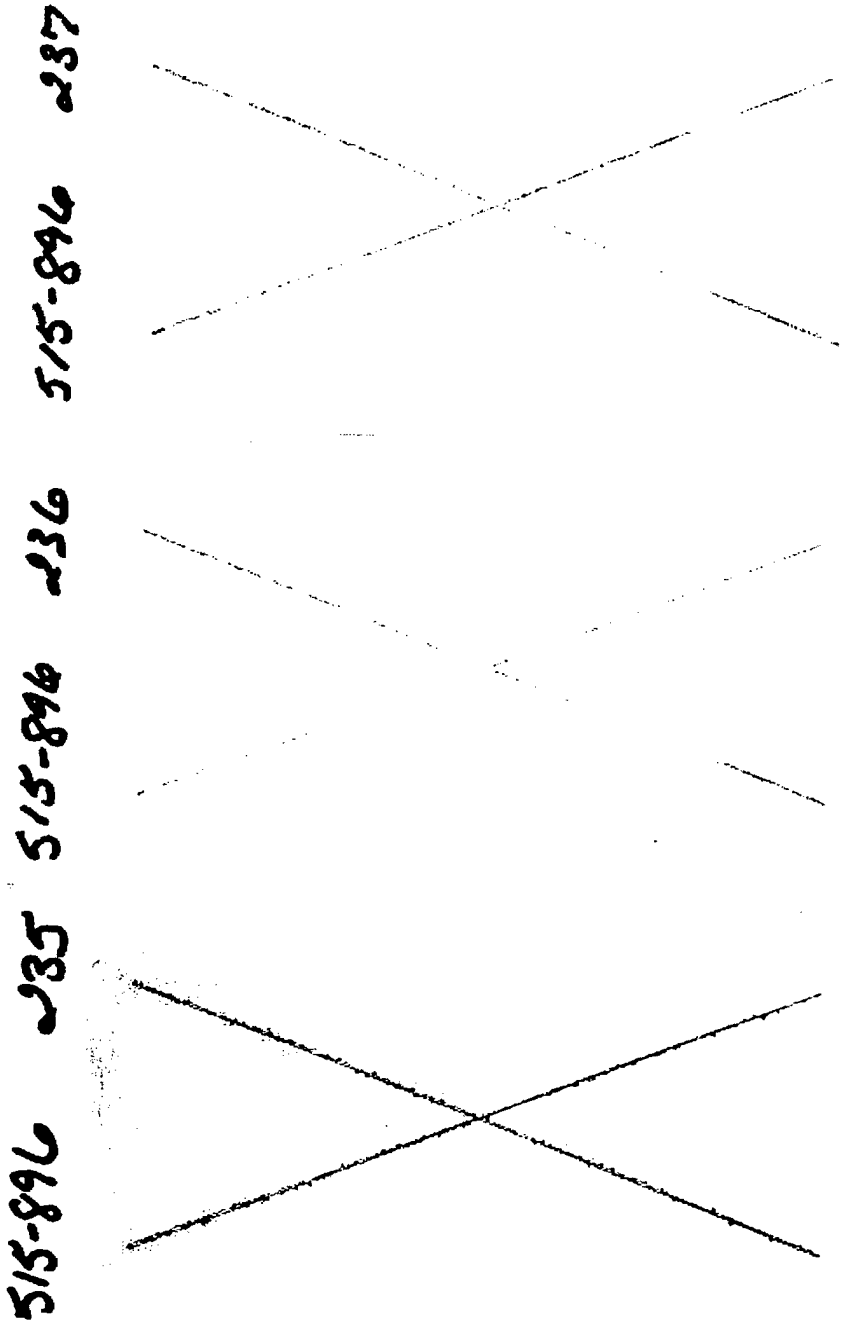
336 Hour SO_2 / Salt Spray Exposure Test Specimens



Bare 2024-T3 Chromate Conversion Coated Aluminum

Figure A1. Deft 44-GN-72, Waterborne Chromate Control.

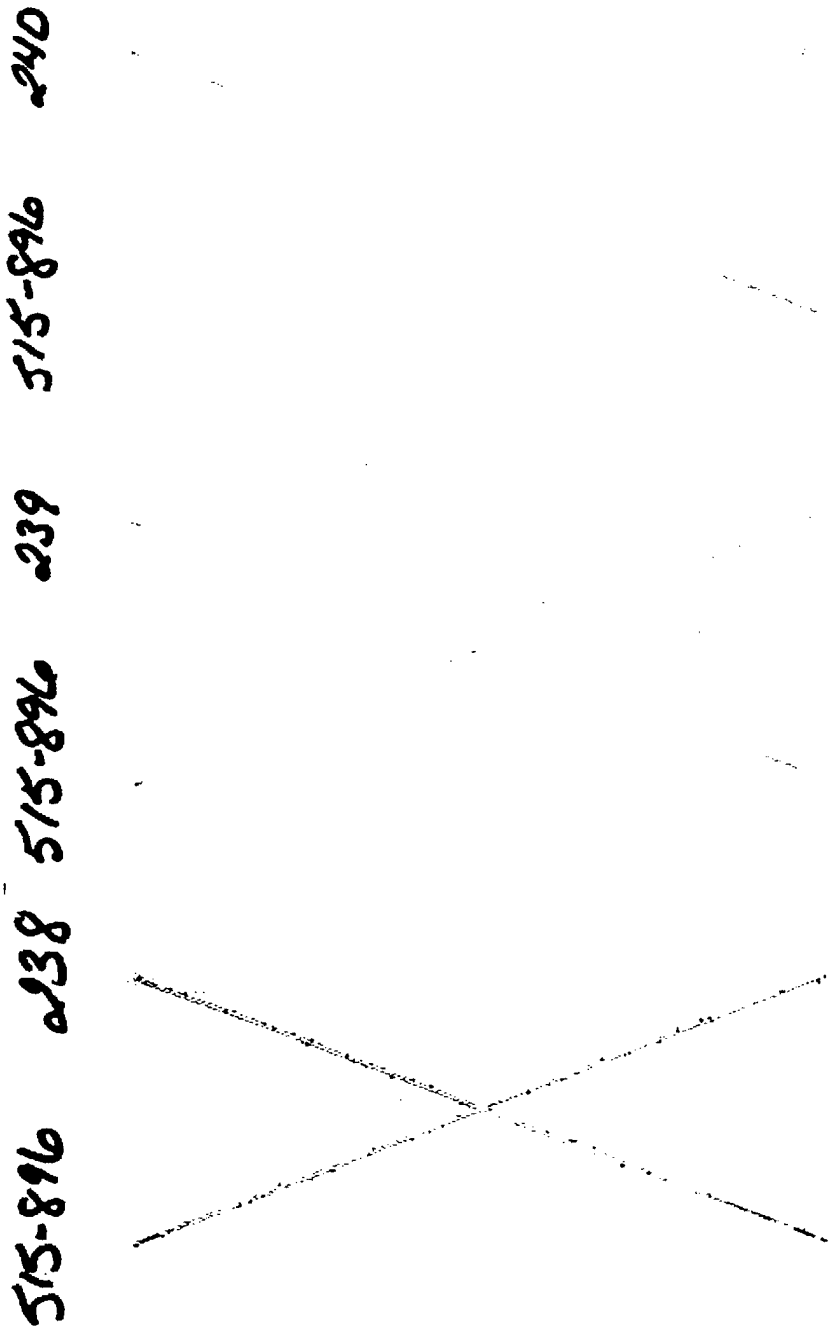
336 Hour SO_2 / Salt Spray Exposure Test Specimens



Bare 2024-T3 Chromate Conversion Coated Aluminum

Figure A2. Deft 44-W-31, Cerium Phosphate, Waterborne.

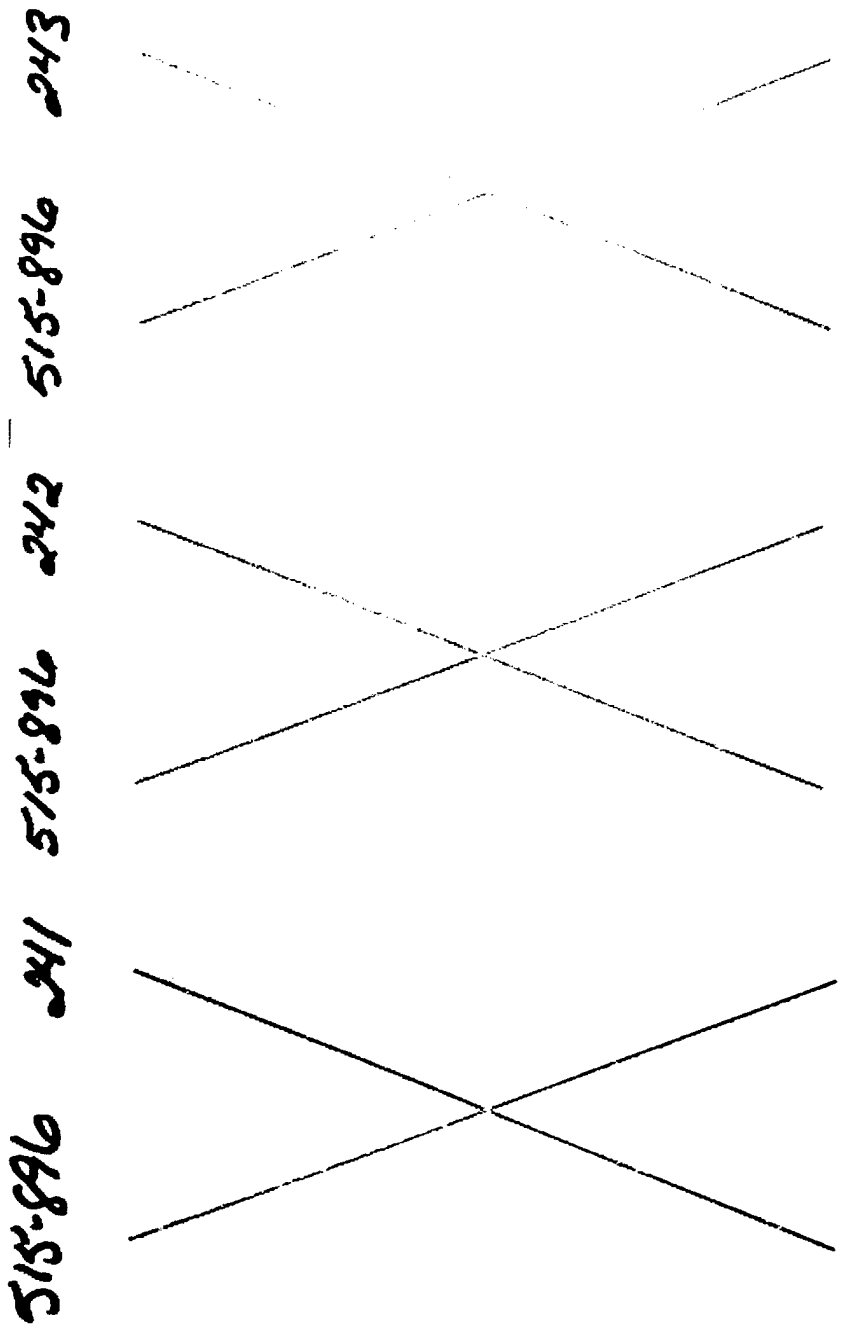
336 Hour SO_2 / Salt Spray Exposure Test Specimens



Bare 2024-T3 Chromate Conversion Coated Aluminum

Figure A3. Deft 44-W-30, Barium Metaborate, Waterborne.

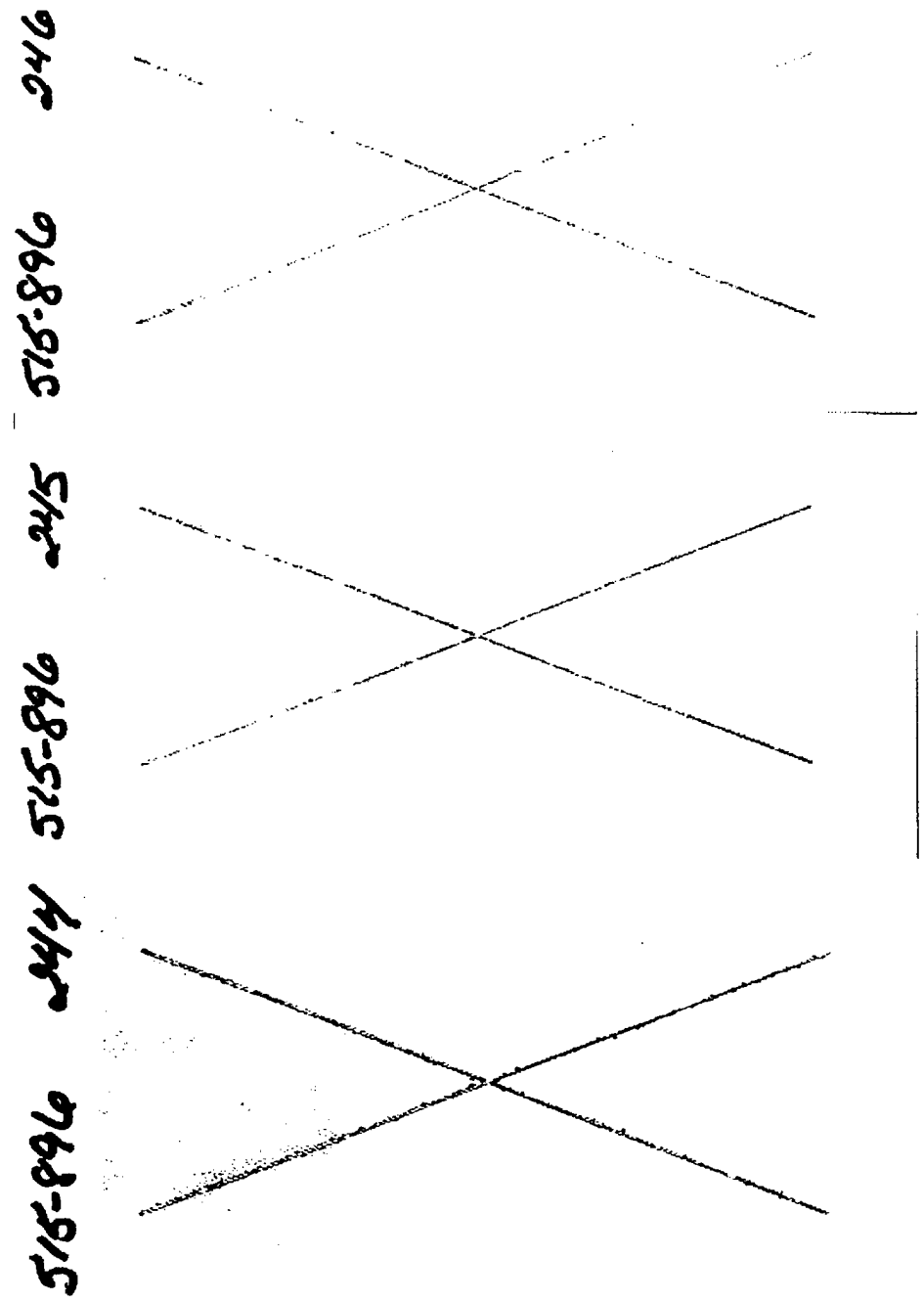
336 Hour SO_2 / Salt Spray Exposure Test Specimens



Bare 2024-T3 Chromate Conversion Coated Aluminum

Figure A4. Deft 02-W-043, K-White, High Solids.

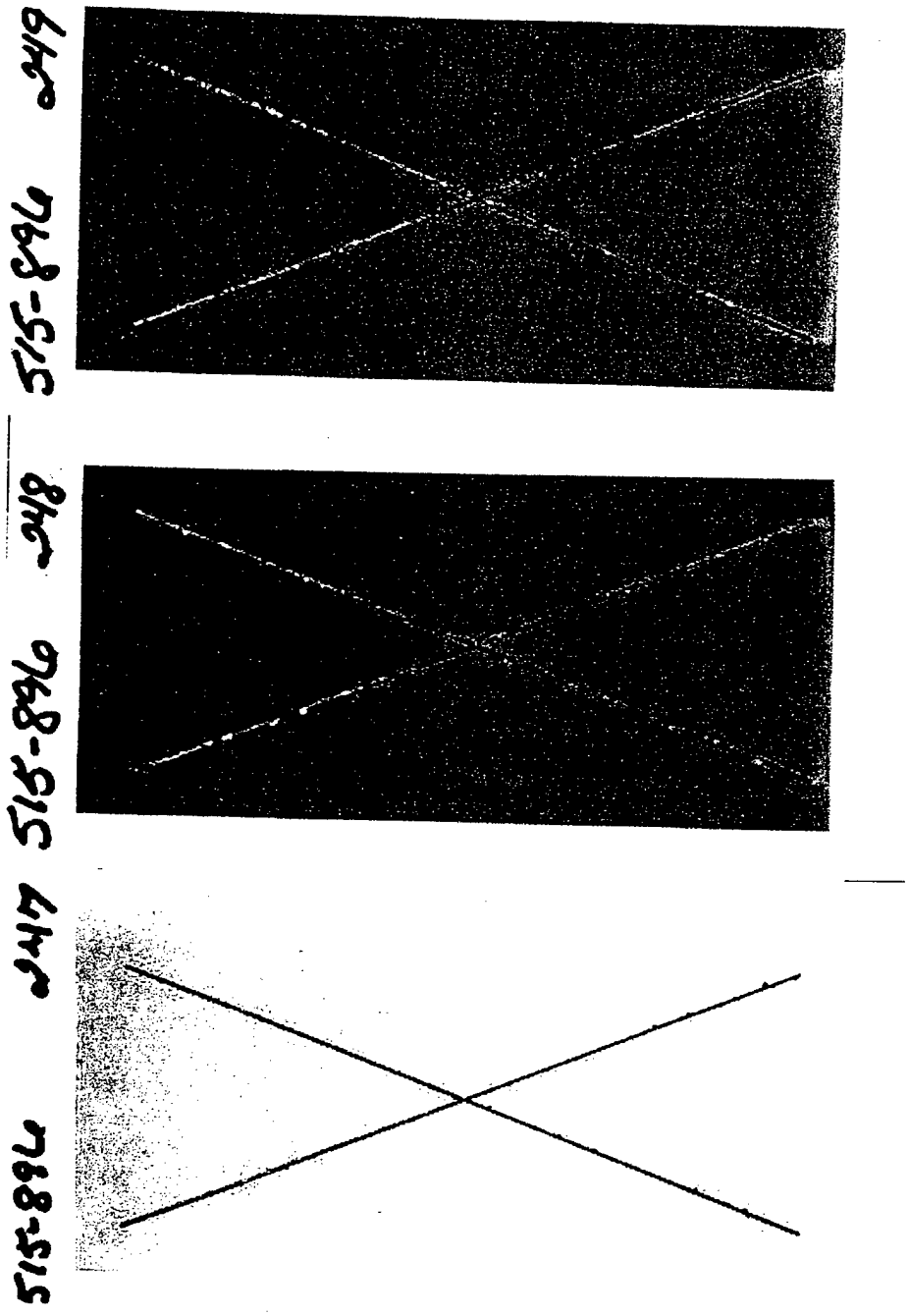
336 Hour SO_2 / Salt Spray Exposure Test Specimens



Bare 2024-T3 Chromate Conversion Coated Aluminum

Figure A5. Deft 44-W-32, Cerium Pentane Dionate, Waterborne.

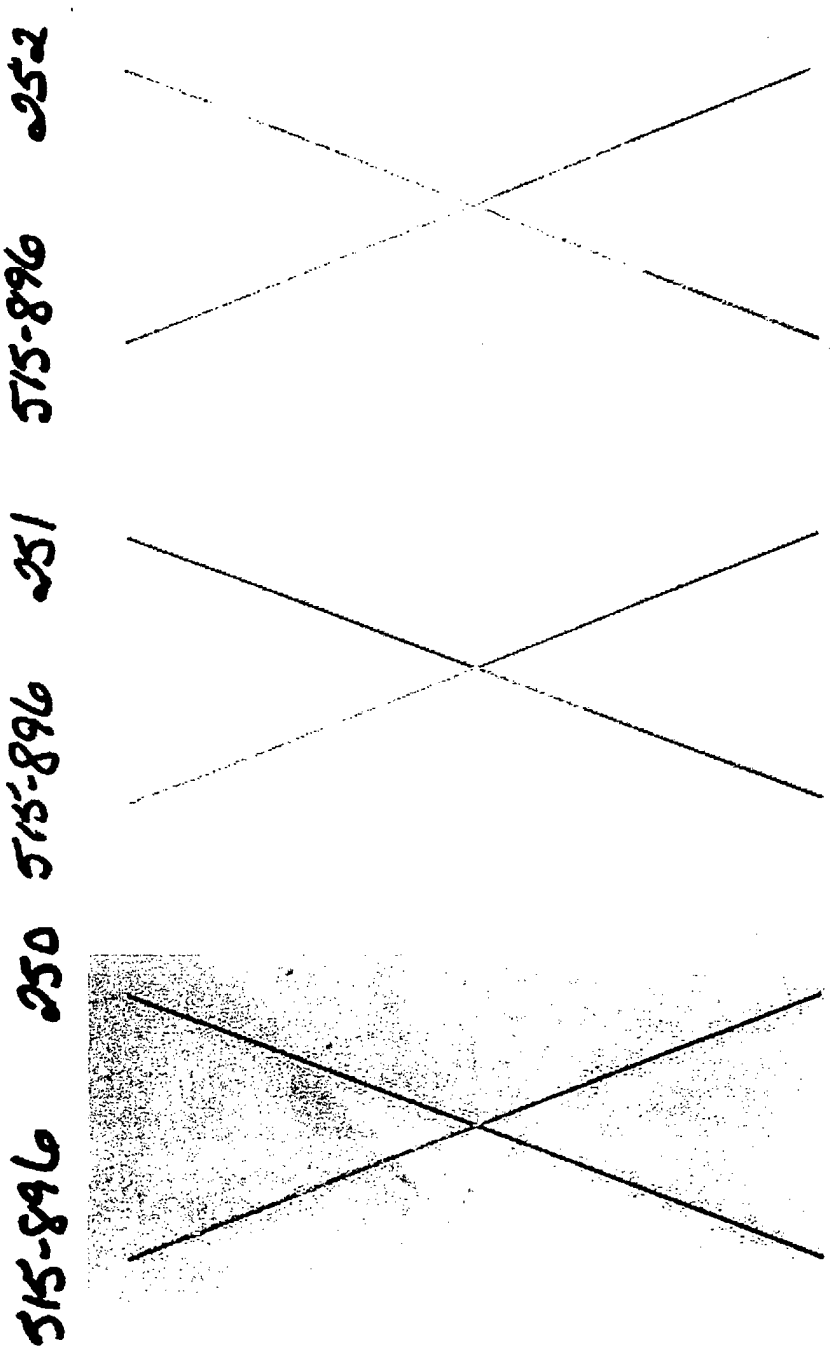
336 Hour SO_2 / Salt Spray Exposure Test Specimens



Bare 2024-T3 Chromate Conversion Coated Aluminum

Figure A6. Deft 02-Y-040, High Solids Chromate Control.

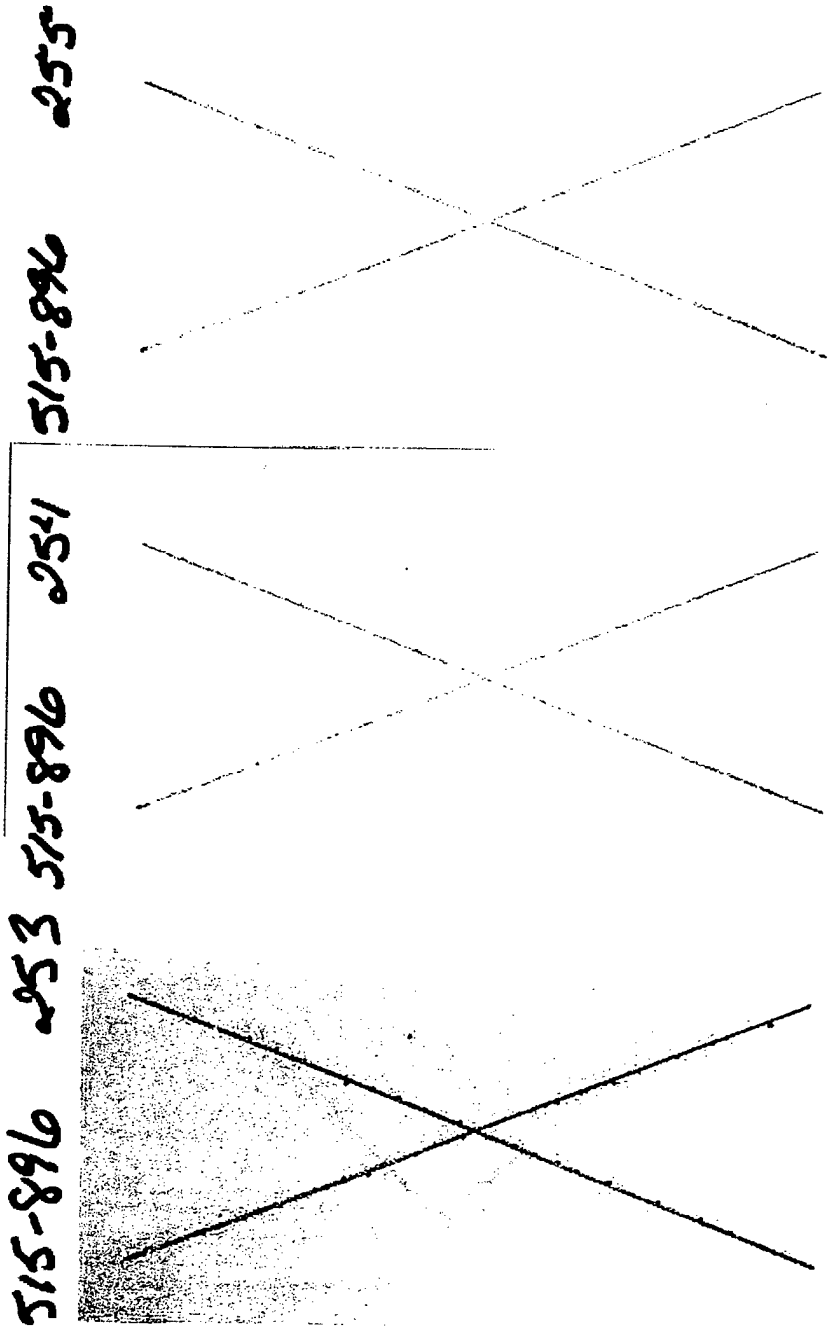
336 Hour SO_2 / Salt Spray Exposure Test Specimens



Bare 2024-T3 Chromate Conversion Coated Aluminum

Figure A7. Deft 02-W-047, Cerium Phosphate, High Solids.

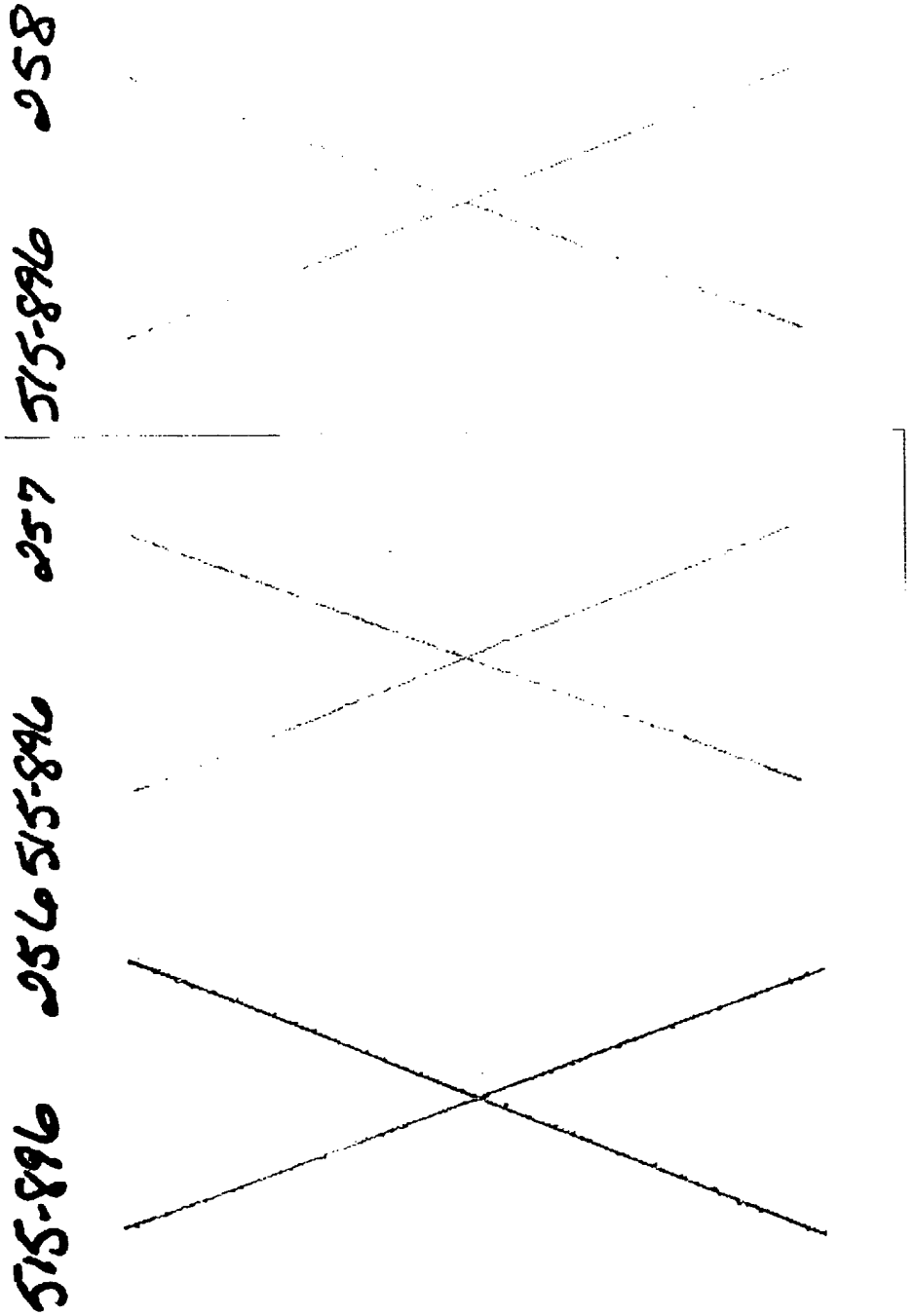
336 Hour SO_2 / Salt Spray Exposure Test Specimens



Bare 2024-T3 Chromate Conversion Coated Aluminum

Figure A8. Deft 02-W-042, Barium Metaborate, High Solids.

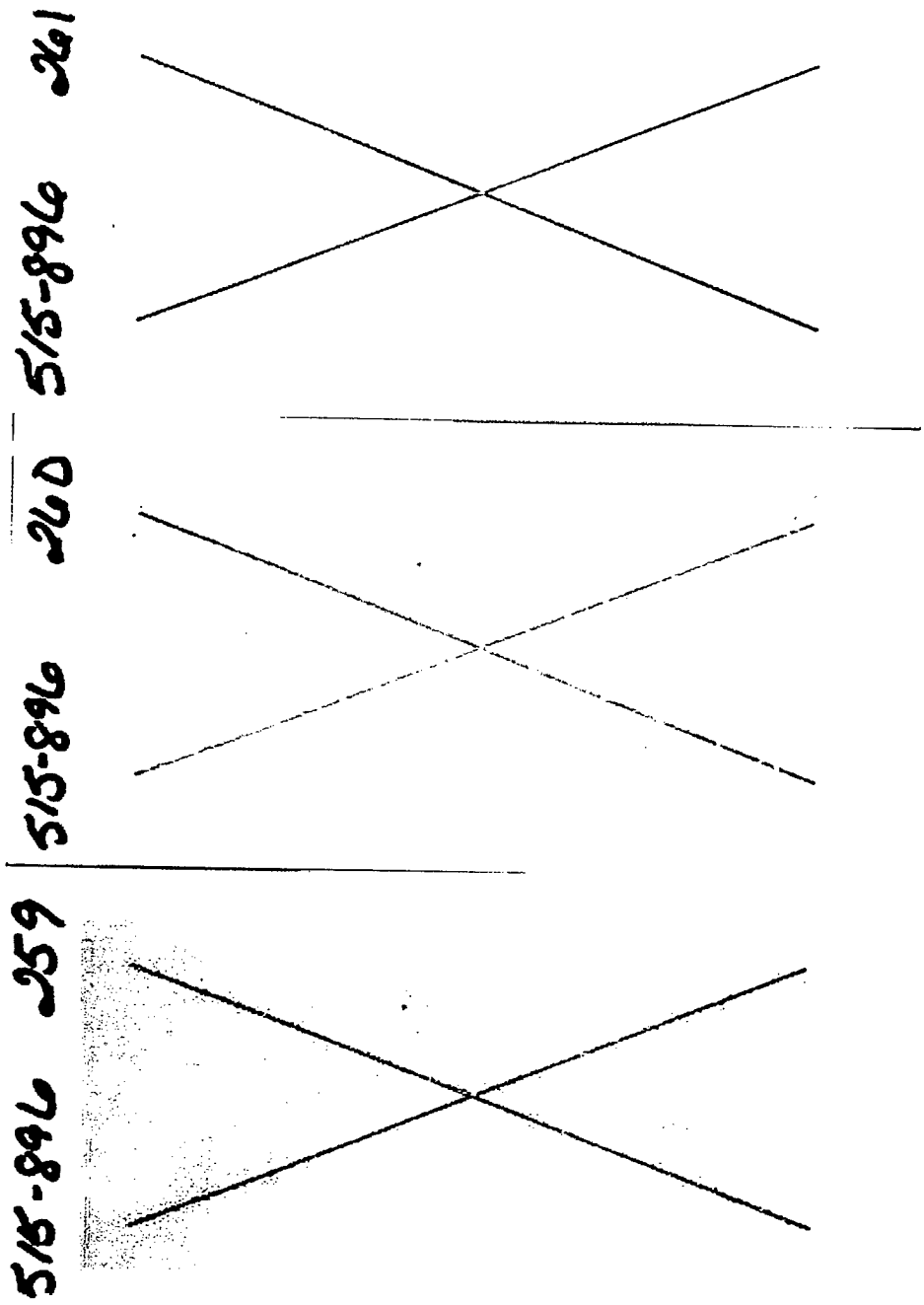
336 Hour SO_2 / Salt Spray Exposure Test Specimens



Bare 2024-T3 Chromate Conversion Coated Aluminum

Figure A9. Deft 02-W-045, Barium Metaborate / Cerium Nitrate, High Solids.

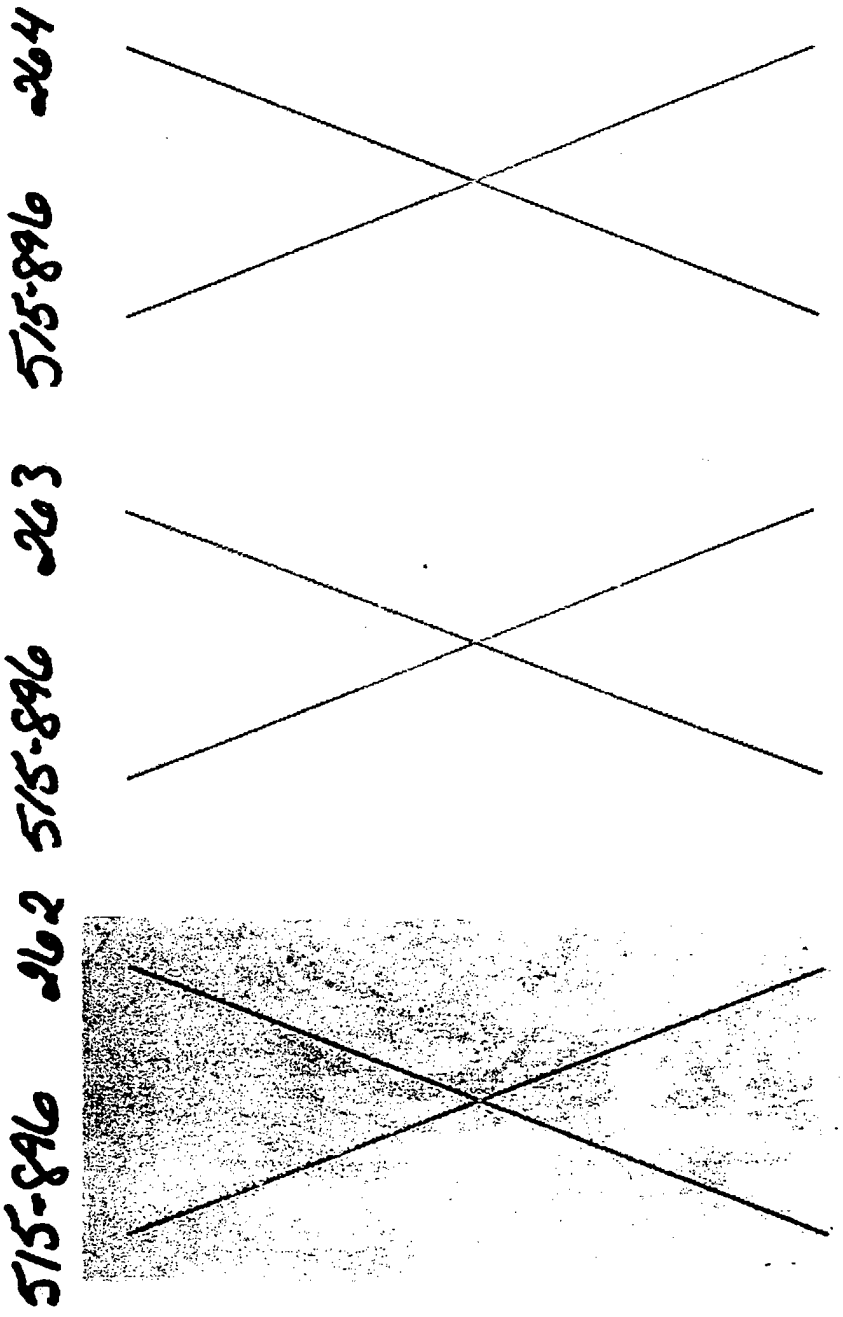
336 Hour SO_2 / Salt Spray Exposure Test Specimens



Bare 2024-T3 Chromate Conversion Coated Aluminum

Figure A10. Deft 02-W-046, Cerium Pentane Dionate, High Solids.

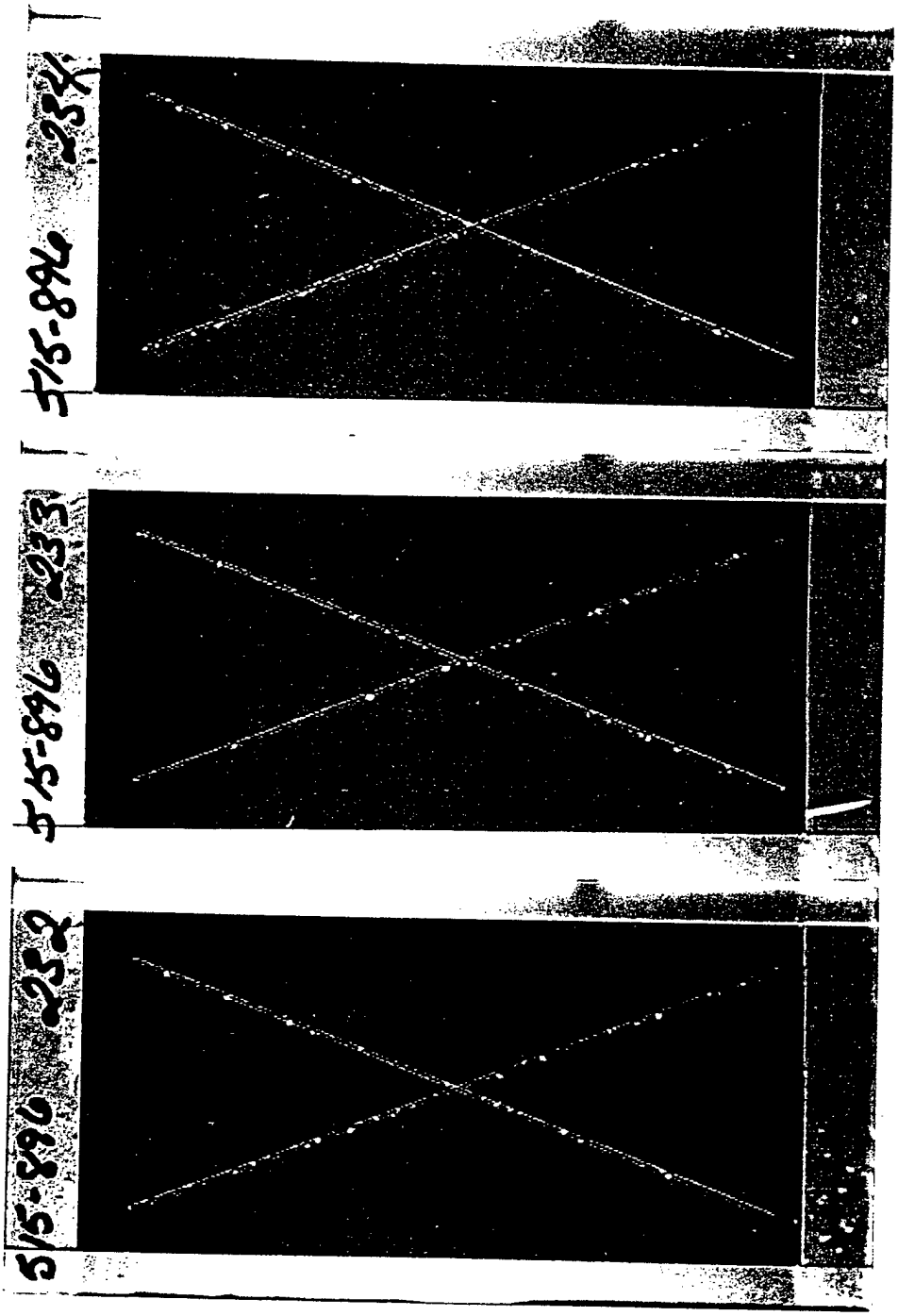
336 Hour SO_2 / Salt Spray Exposure Test Specimens



Bare 2024-T3 Chromate Conversion Coated Aluminum

Figure A11. Deft 02-W-044, Cerium Nitrate, High Solids.

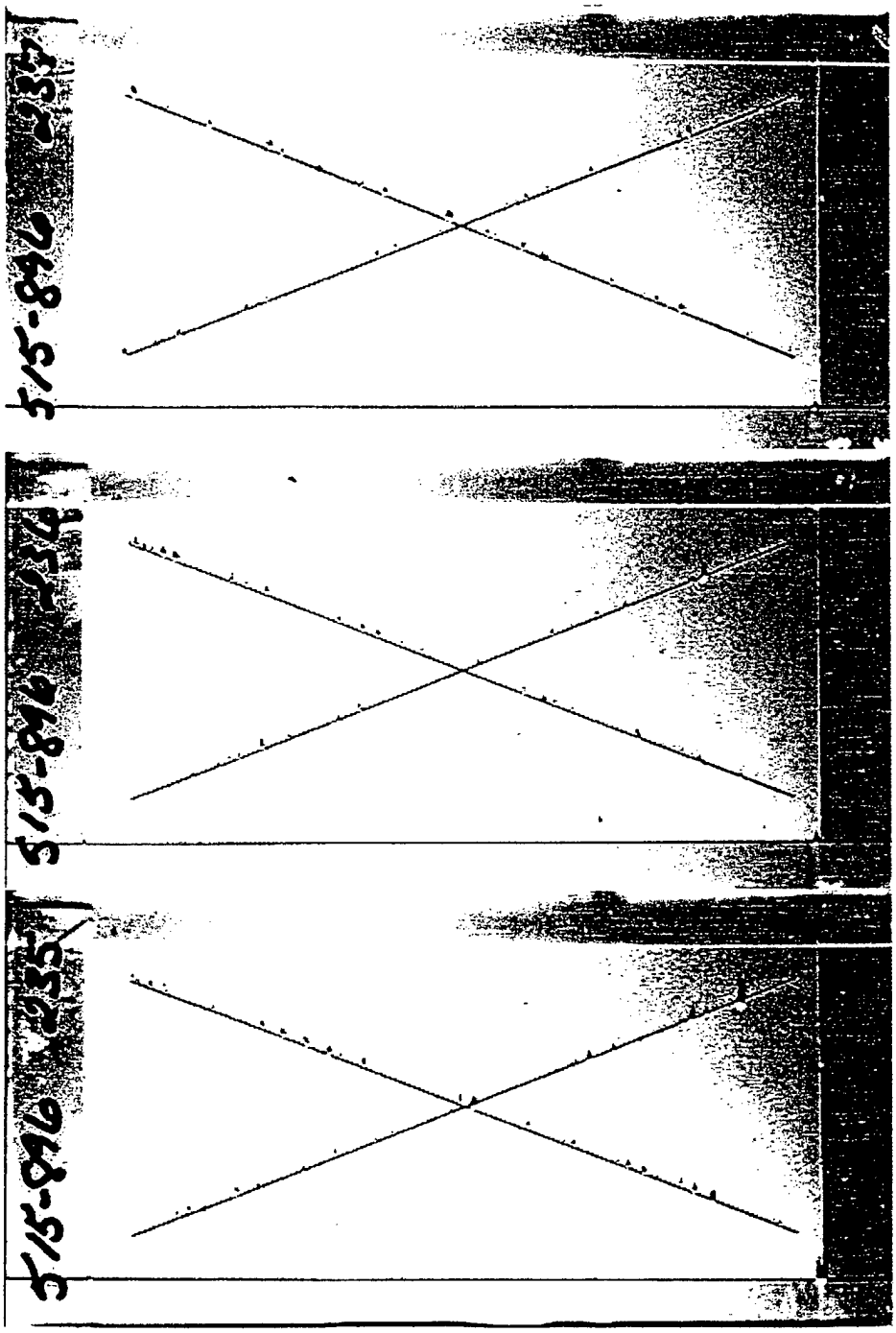
336 Hour SO_2 / Salt Spray Exposure Test Specimens



Bare 2024-T3 Chromate Conversion Coated Aluminum

Figure A12. Deft 44-GN-72, Waterborne Chromate Control.

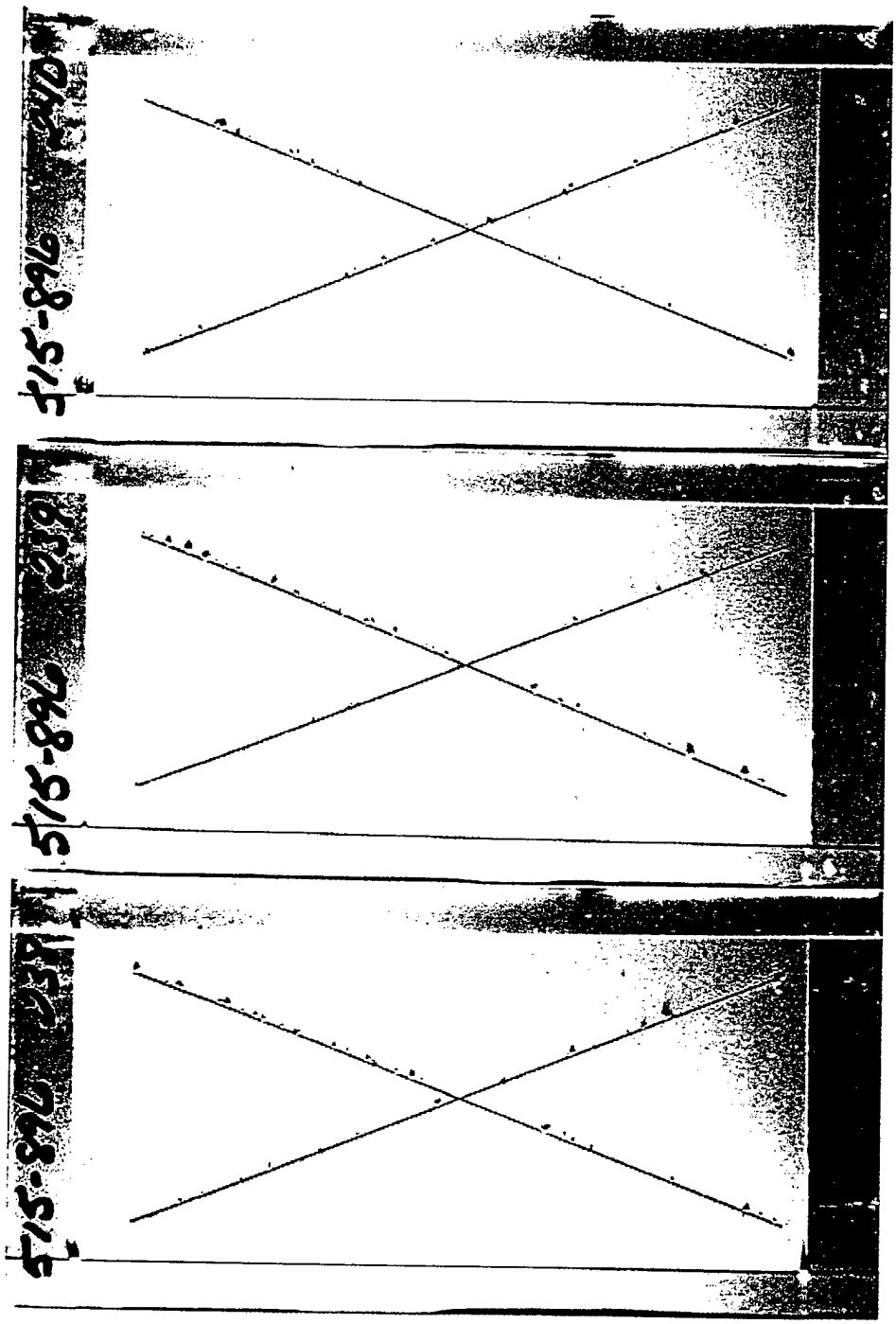
336 Hour SO_2 / Salt Spray Exposure Test Specimens



Bare 2024-T3 Chromate Conversion Coated Aluminum

Figure A13. Deft 44-W-31, Cerium Phosphate, Waterborne.

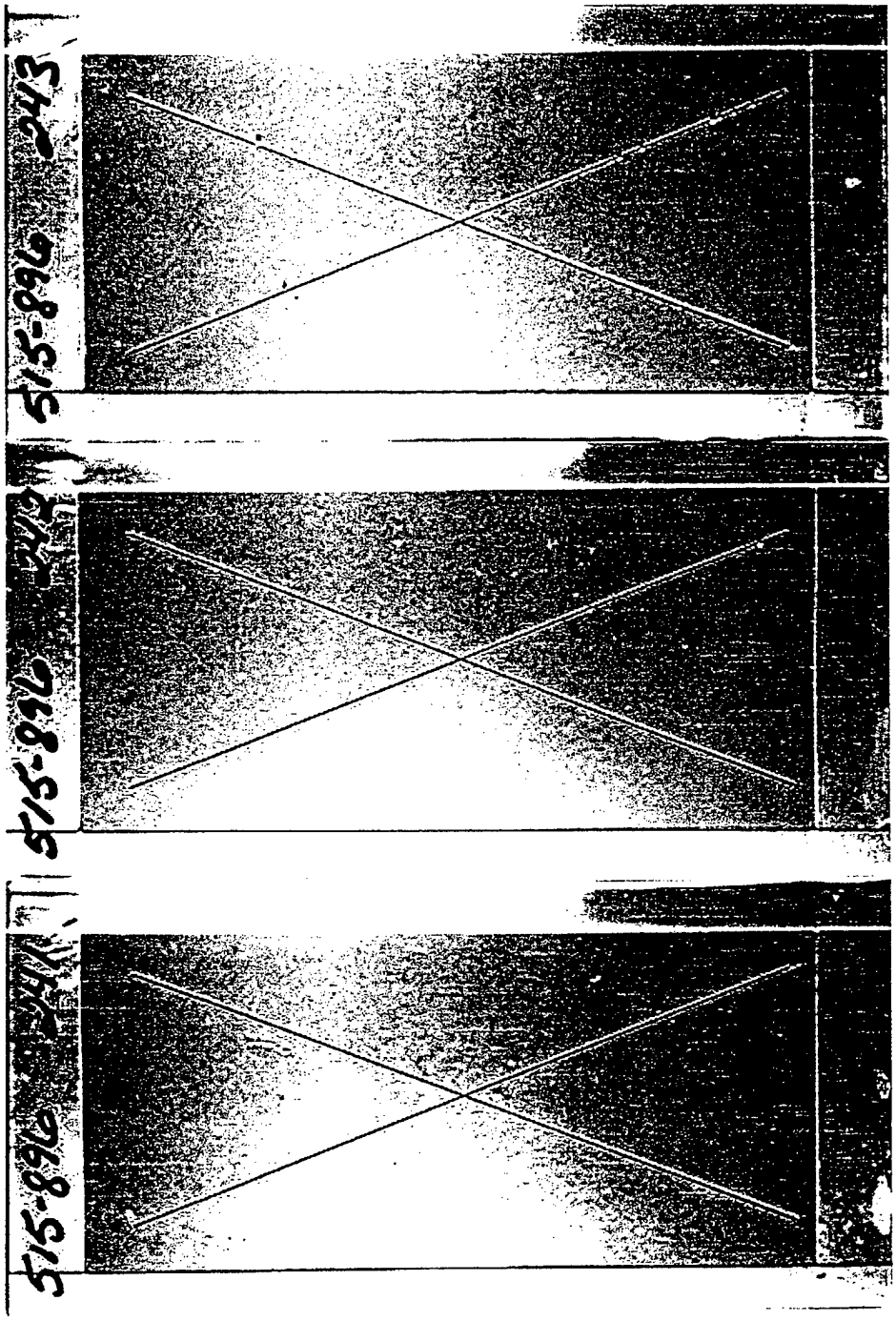
336 Hour SO_2 / Salt Spray Exposure Test Specimens



Bare 2024-T3 Chromate Conversion Coated Aluminum

Figure A14. Deft 44-W-30, Barium Metaborate, Waterborne.

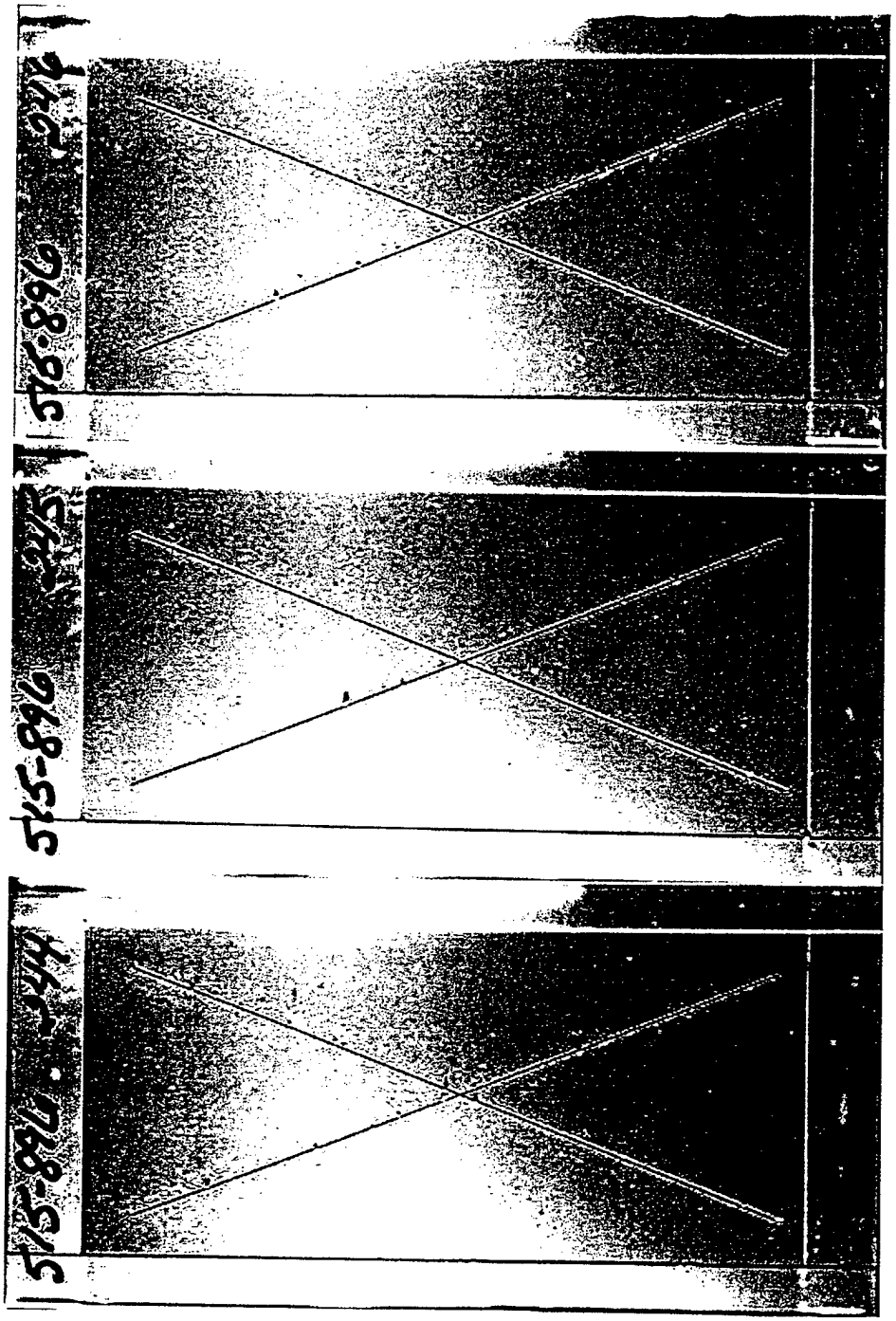
336 Hour SO_2 / Salt Spray Exposure Test Specimens



Bare 2024-T3 Chromate Conversion Coated Aluminum

Figure A15. Deft 02-W-043, K-White, High Solids.

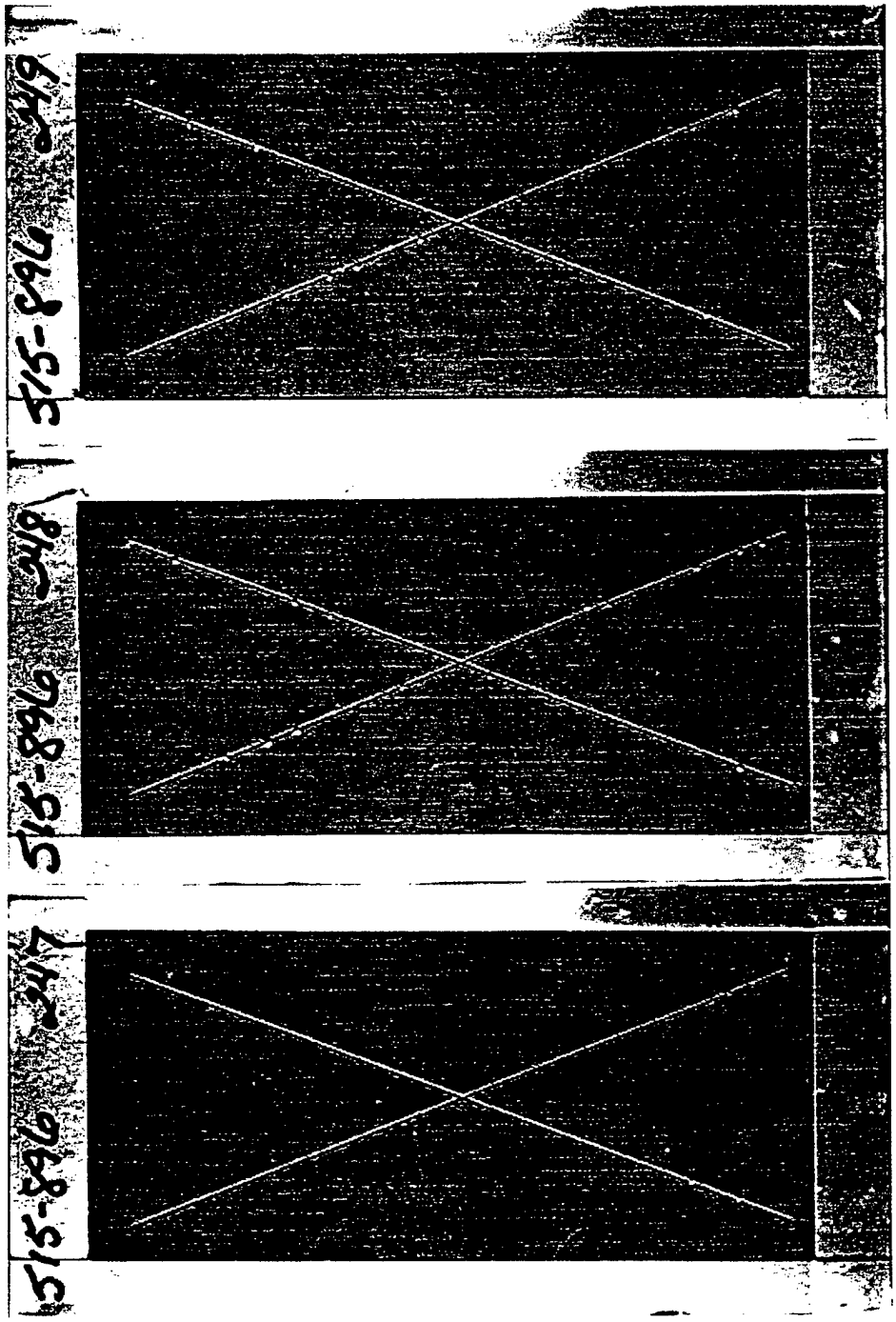
336 Hour SO_2 / Salt Spray Exposure Test Specimens



Bare 2024-T3 Chromate Conversion Coated Aluminum

Figure A16. Deft 44-W-32, Cerium Pentane Dionate, Waterborne.

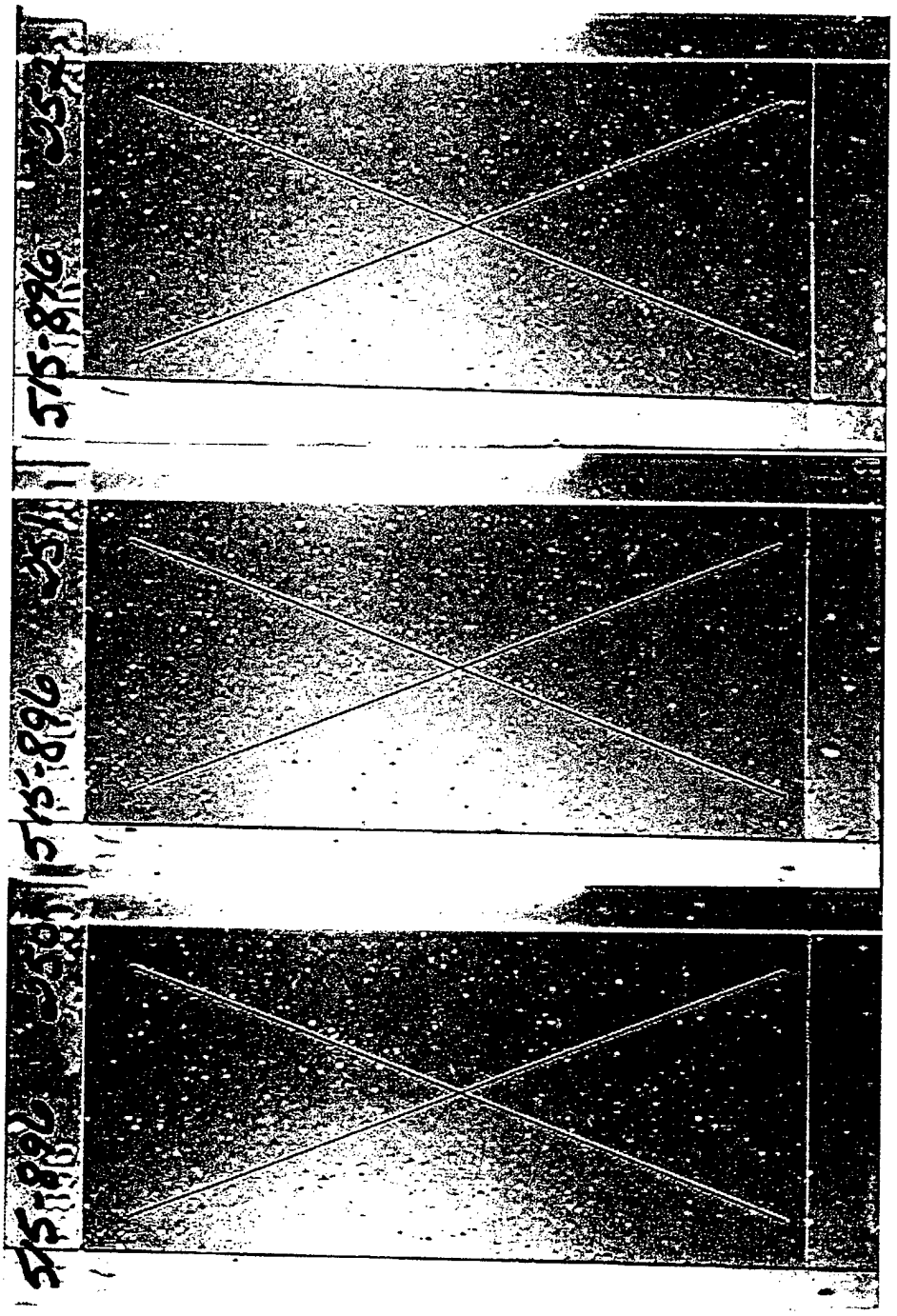
336 Hour SO_2 / Salt Spray Exposure Test Specimens



Bare 2024-T3 Chromate Conversion Coated Aluminum

Figure A17. Deft 02-Y-040, High Solids Chromate Control.

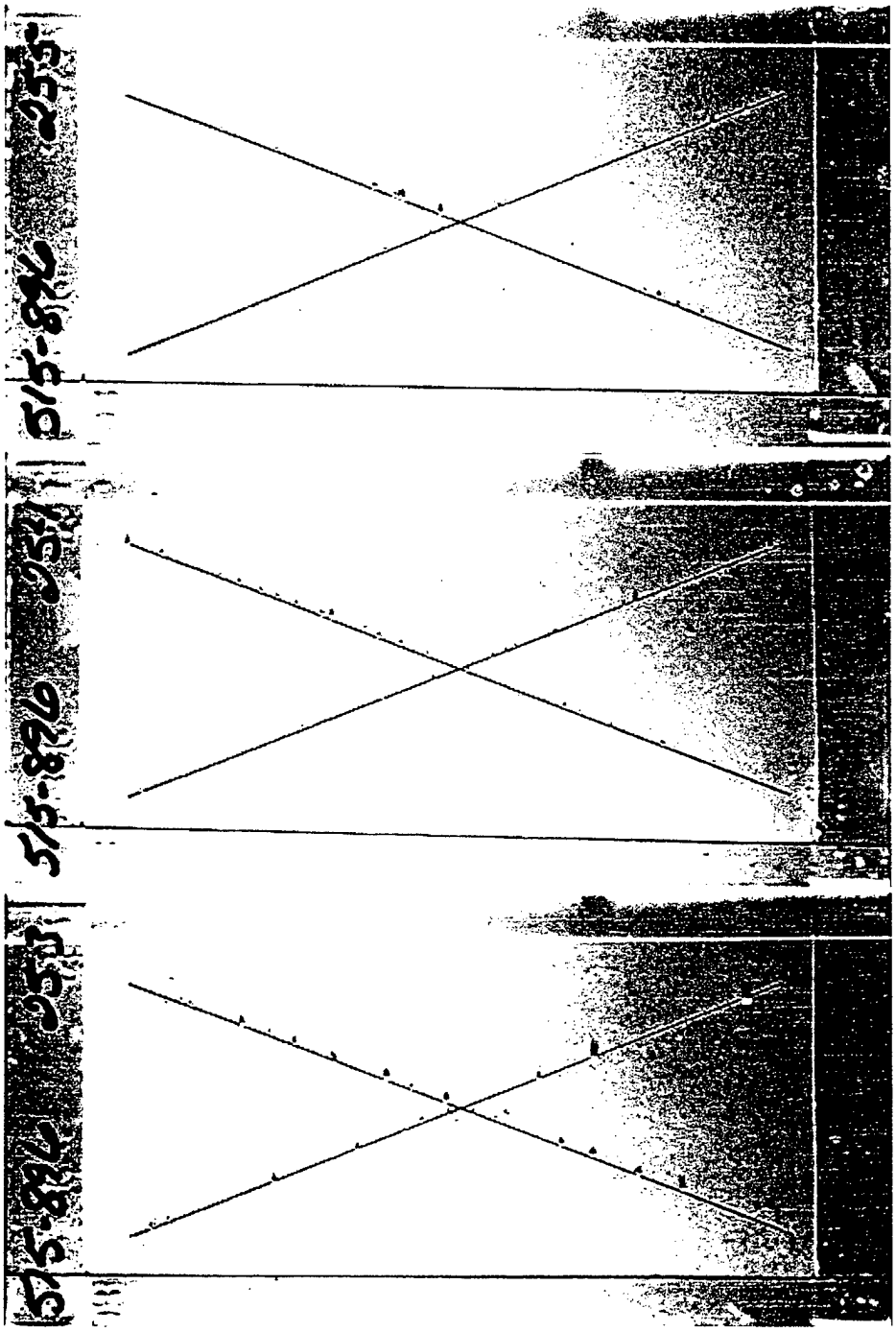
336 Hour SO_2 / Salt Spray Exposure Test Specimens



Bare 2024-T3 Chromate Conversion Coated Aluminum

Figure A18. Deft 02-W-047, Cerium Phosphate, High Solids.

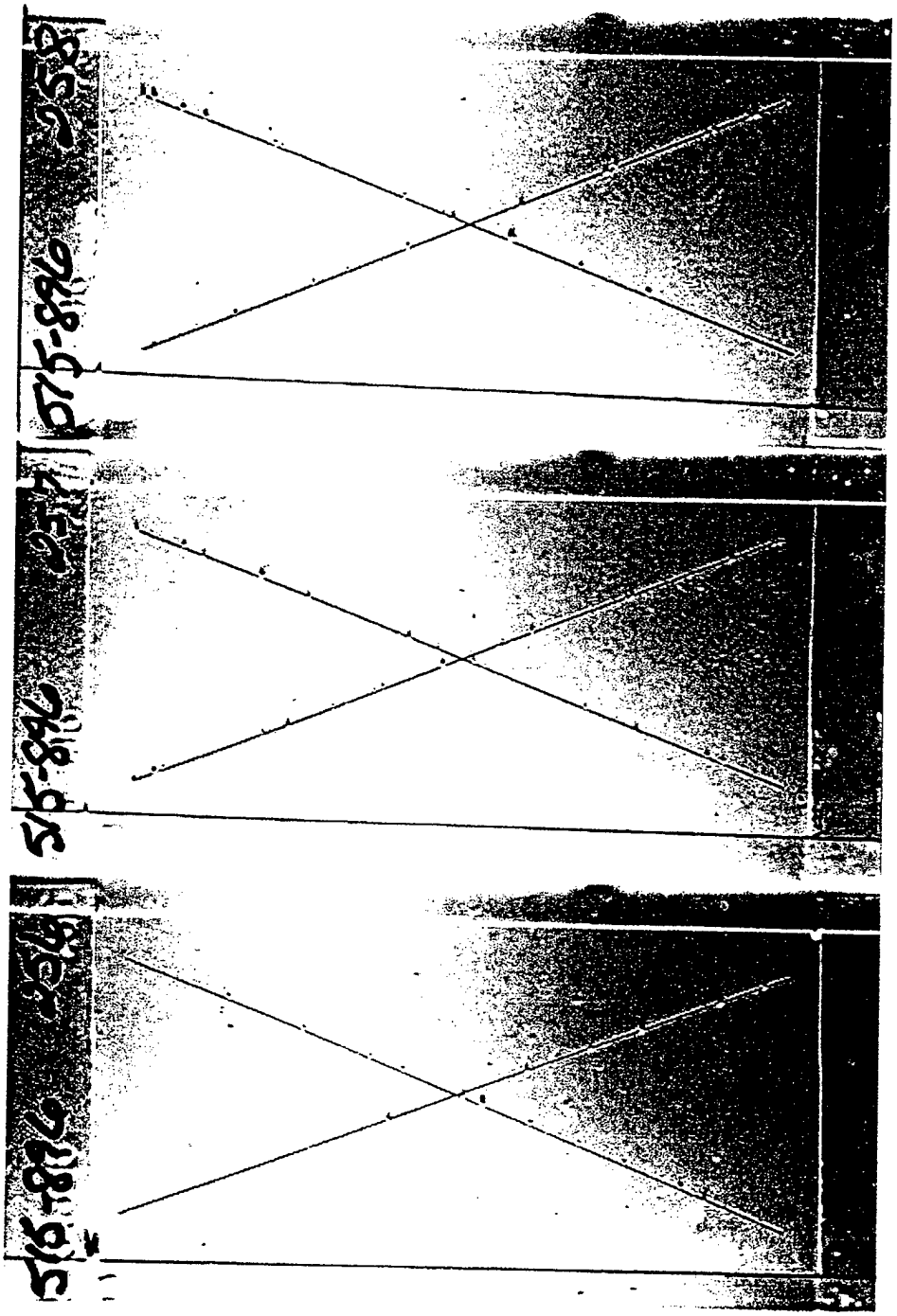
336 Hour SO_2 / Salt Spray Exposure Test Specimens



Bare 2024-T3 Chromate Conversion Coated Aluminum

Figure A19. Deft 02-W-042, Barium Metaborate, High Solids.

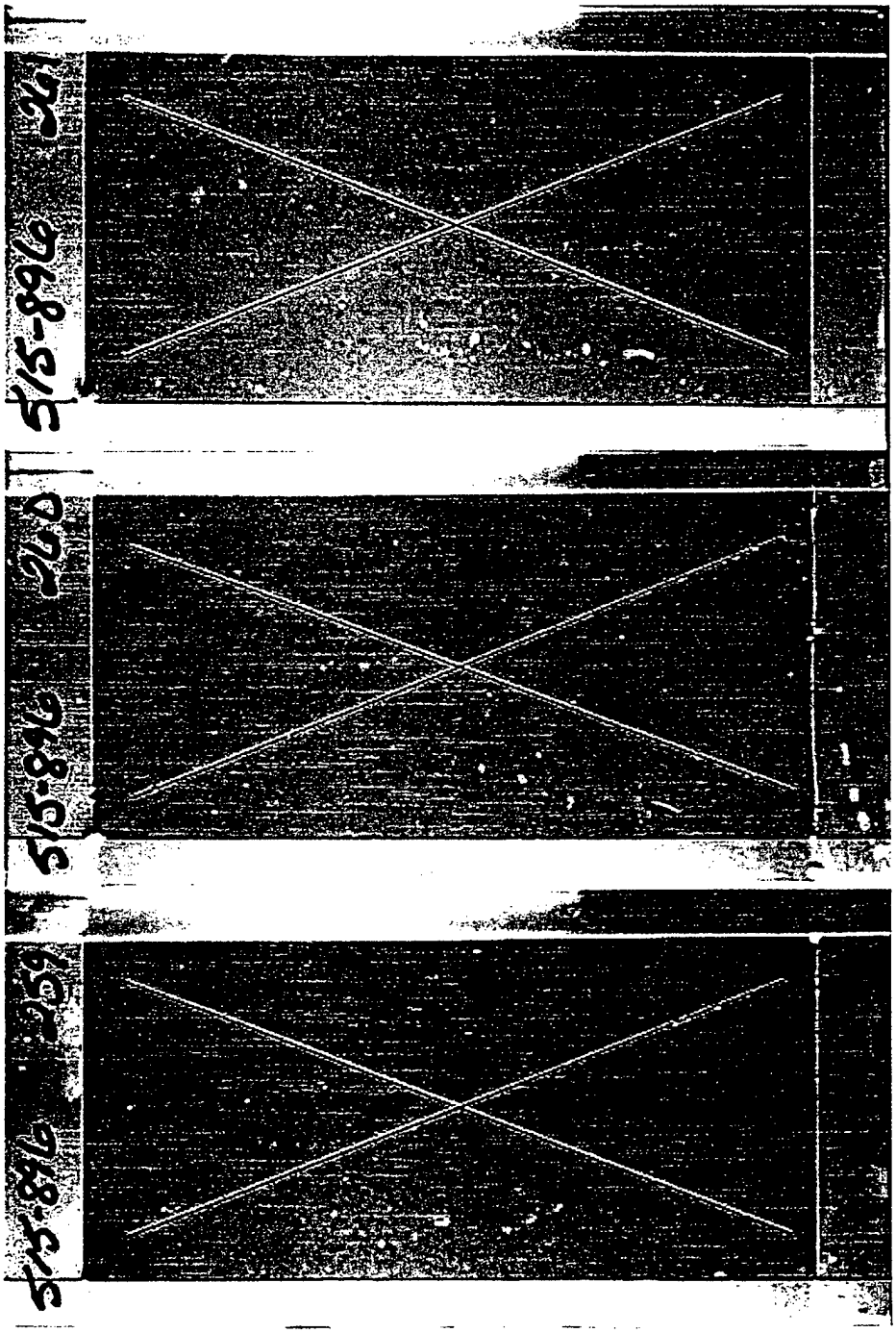
336 Hour SO_2 / Salt Spray Exposure Test Specimens



Bare 2024-T3 Chromate Conversion Coated Aluminum

Figure A20. Deft 02-W-045, Barium Metaborate / Cerium Nitrate, High Solids.

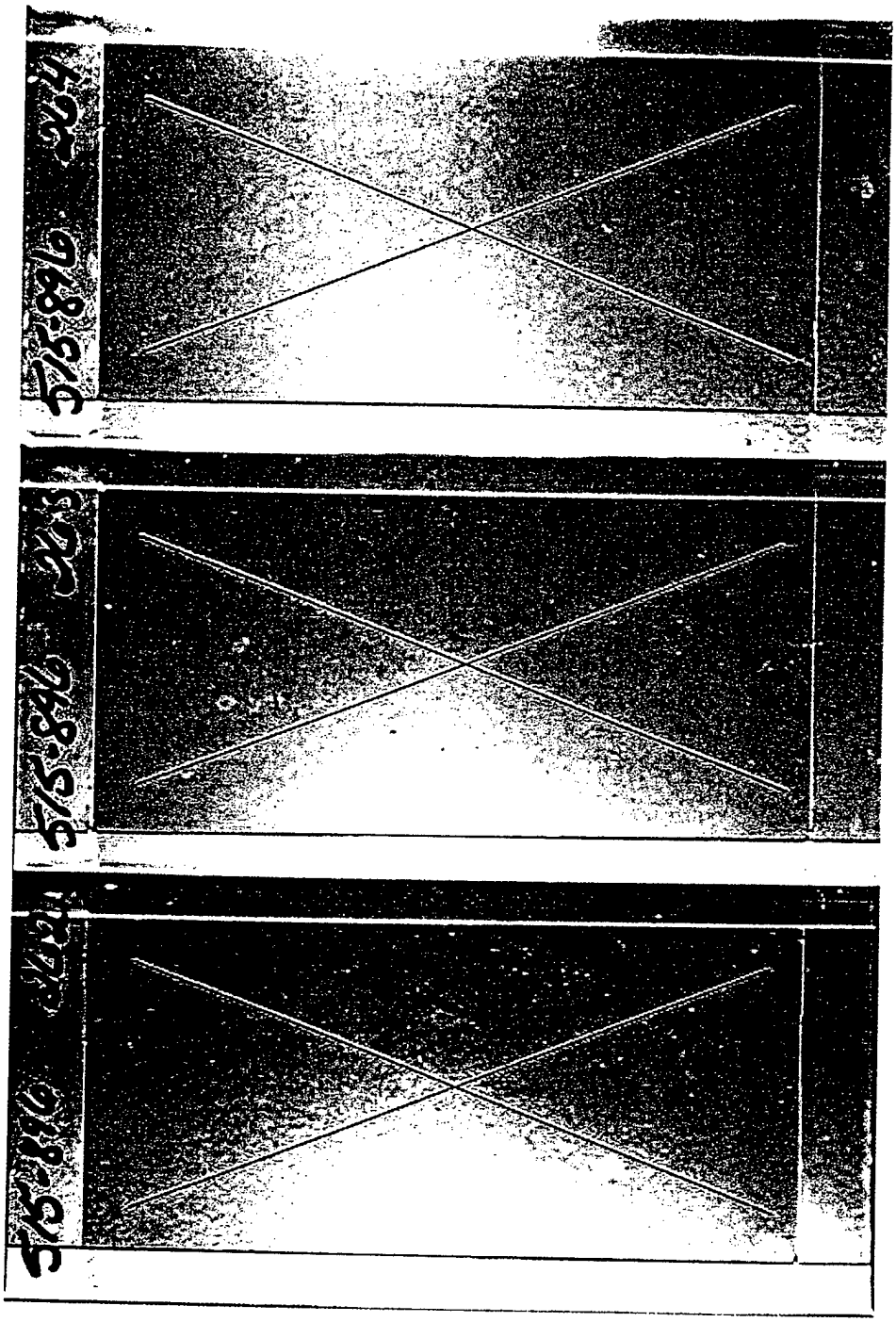
336 Hour SO_2 / Salt Spray Exposure Test Specimens



Bare 2024-T3 Chromate Conversion Coated Aluminum

Figure A21. Deft 02-W-046, Cerium Pentane Dionate, High Solids.

336 Hour SO_2 / Salt Spray Exposure Test Specimens



Bare 2024-T3 Chromate Conversion Coated Aluminum

Figure A22. Deft 02-W-044, Cerium Nitrate, High Solids.

The data presented in this report, to the best of my knowledge and belief, is complete, accurate and complies with all test requirements of the requesting document.

APPENDIX B

1000 Hour Neutral Salt Spray Specimens

Photographic Documentation

ASTM B117

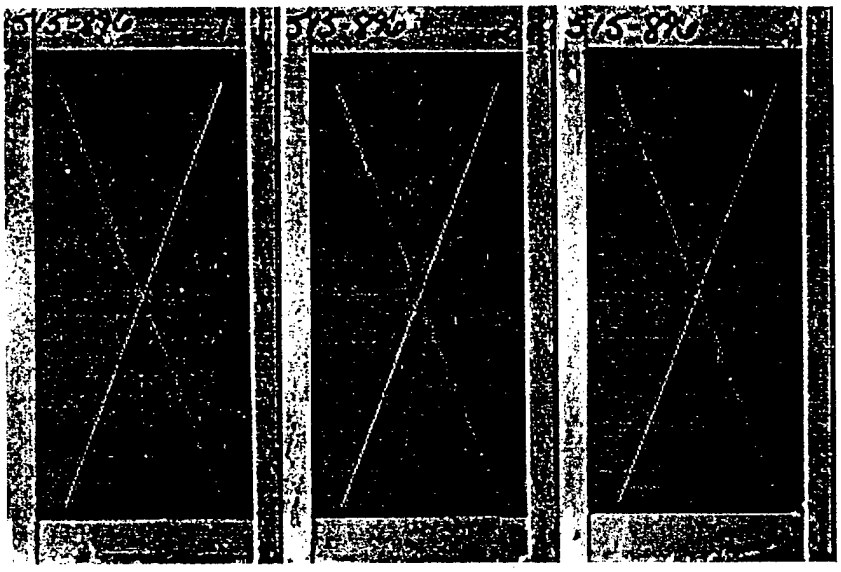
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Photographs of Specimens with Illumination from the Side

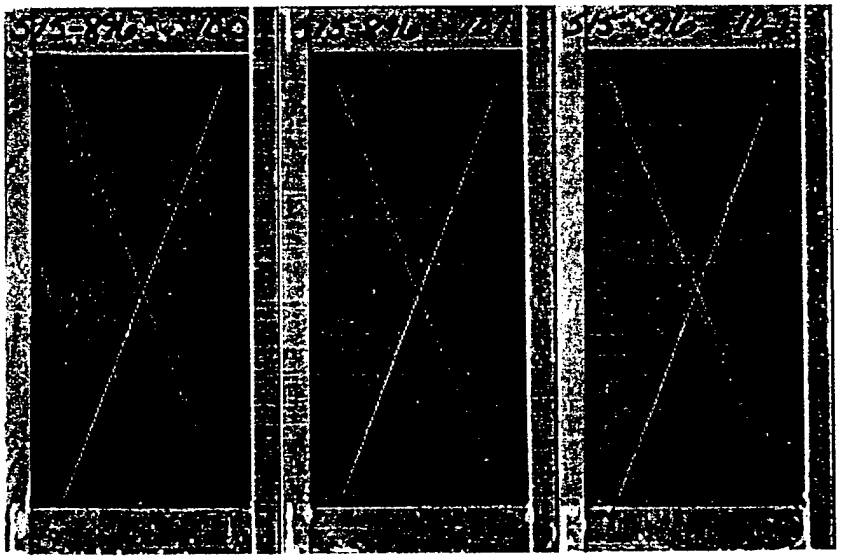
Deft 44-GN-72, Waterborne Chromated Control.	B3
Deft 44-W-31, Cerium phosphate, Waterborne	B4
Deft 44-W-30, Barium Metaborate, Waterborne	B5
Deft 02-W-043, K-White, High Solids	B6
Deft 44-W-32, Cerium Pentane Dionate, Waterborne	B7
Deft 02-Y-040, High Solids Chromated Control	B8
Deft 02-W-047, Cerium phosphate, High Solids	B9
Deft 02-W-042, Barium Metaborate, High Solids	B10
Deft 02-W-045, Barium Metaborate / cerium Nitrate, High Solids	B11
Deft 02-W-046, Cerium Pentane Dionate, High Solids	B12
Deft 02-W-044, Cerium Nitrate, High Solids	B13

1000-HOUR NEUTRAL SALT SPRAY SPECIMENS

Chromate Conversion
Coated Bare 7075-T6
Aluminum Substrates



Chromate Conversion
Coated Bare 2024-T3
Aluminum Substrates



UMR Cerium Conversion
Coated Bare 7075-T6
Aluminum Substrates

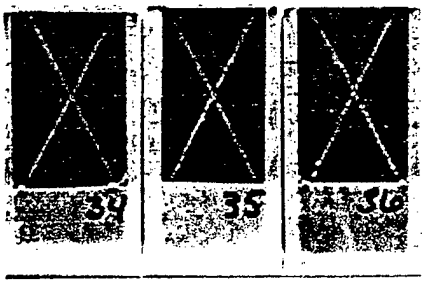
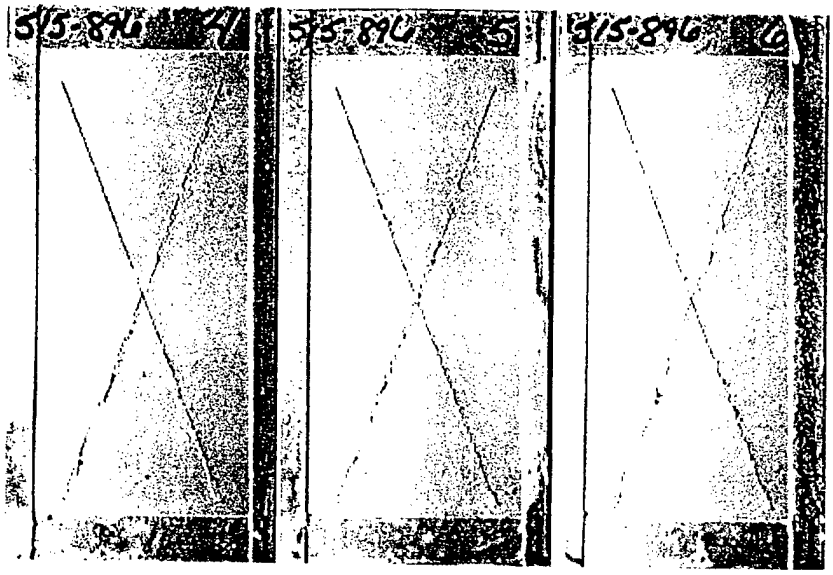


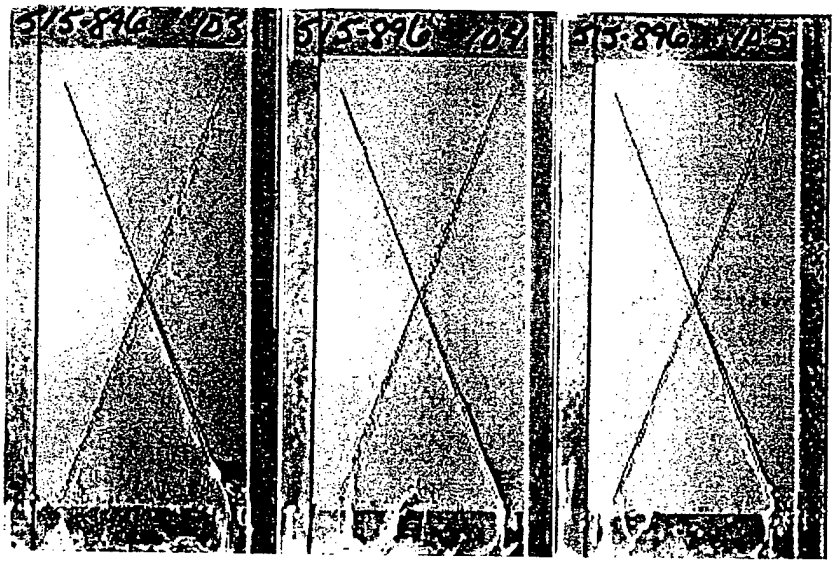
Figure B1. Deft 44-GN-72, Waterborne Chromate Control.

1000-HOUR NEUTRAL SALT SPRAY SPECIMENS

Chromate Conversion
Coated Bare 7075-T6
Aluminum Substrates



Chromate Conversion
Coated Bare 2024-T3
Aluminum Substrates



UMR Cerium Conversion
Coated Bare 7075-T6
Aluminum Substrates

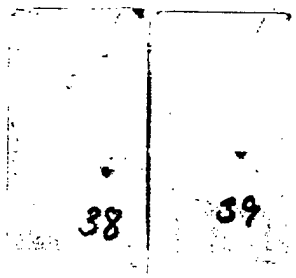
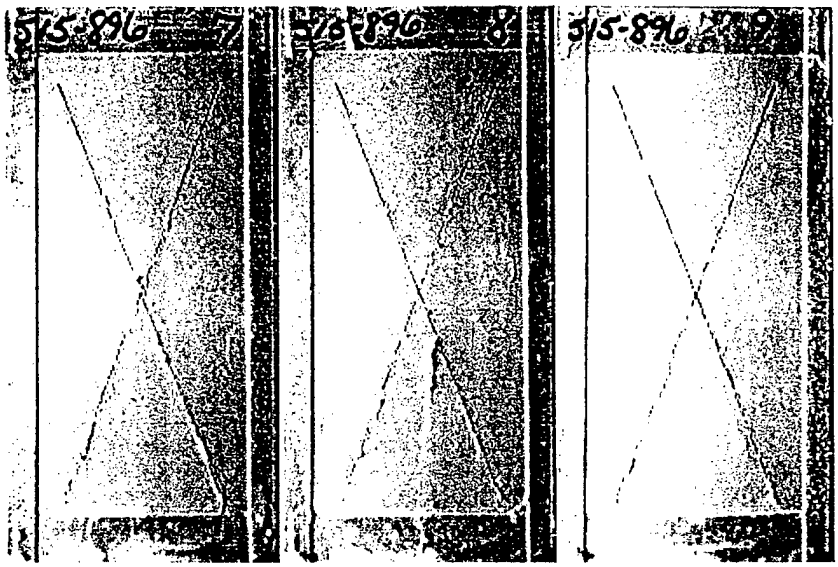


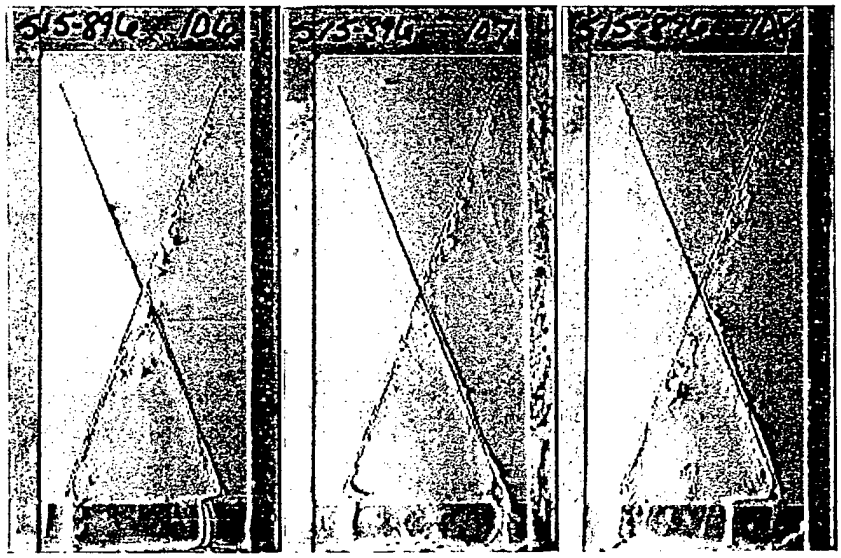
Figure B2. Deft 44-W-31, Cerium Phosphate, Waterborne.

1000-HOUR NEUTRAL SALT SPRAY SPECIMENS

Chromate Conversion
Coated Bare 7075-T6
Aluminum Substrates



Chromate Conversion
Coated Bare 2024-T3
Aluminum Substrates



UMR Cerium Conversion
Coated Bare 7075-T6
Aluminum Substrates

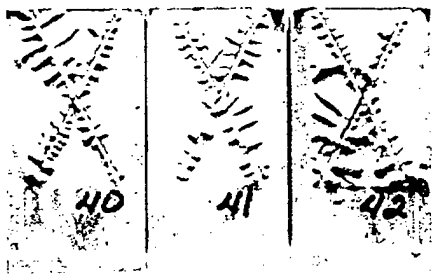
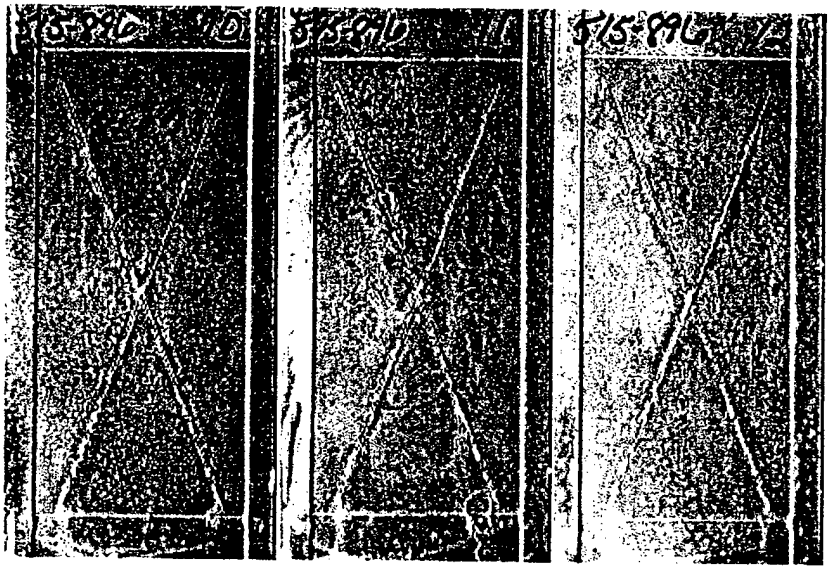


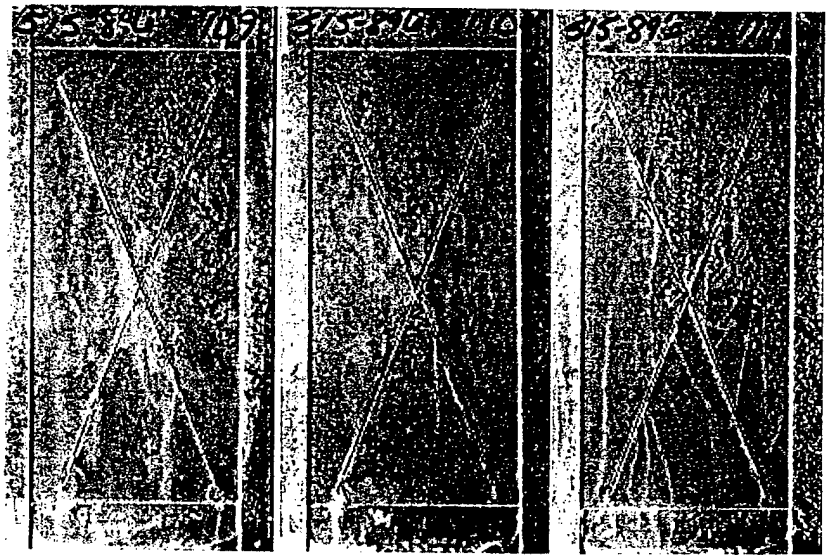
Figure B3. Deft 44-W-30, Barium Metaborate, Waterborne.

1000-HOUR NEUTRAL SALT SPRAY SPECIMENS

Chromate Conversion
Coated Bare 7075-T6
Aluminum Substrates



Chromate Conversion
Coated Bare 2024-T3
Aluminum Substrates



UMR Cerium Conversion
Coated Bare 7075-T6
Aluminum Substrates

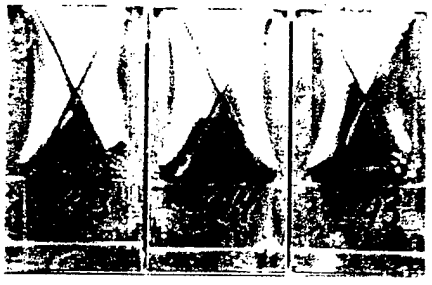
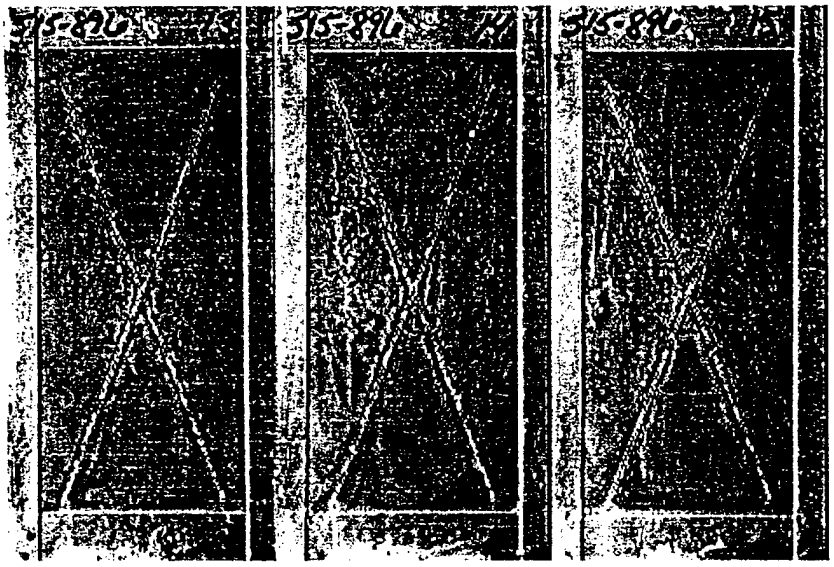


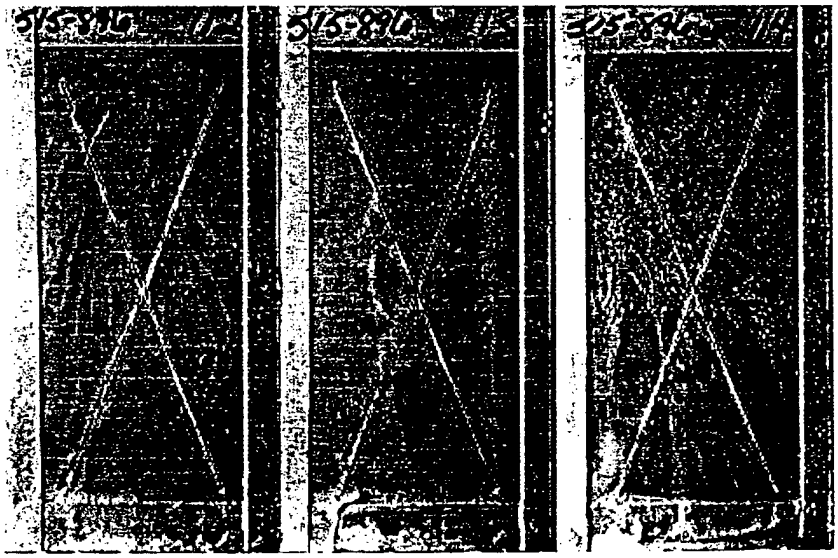
Figure B4. Deft 02-W-043, K-White, High Solids.

1000-HOUR NEUTRAL SALT SPRAY SPECIMENS

Chromate Conversion
Coated Bare 7075-T6
Aluminum Substrates



Chromate Conversion
Coated Bare 2024-T3
Aluminum Substrates



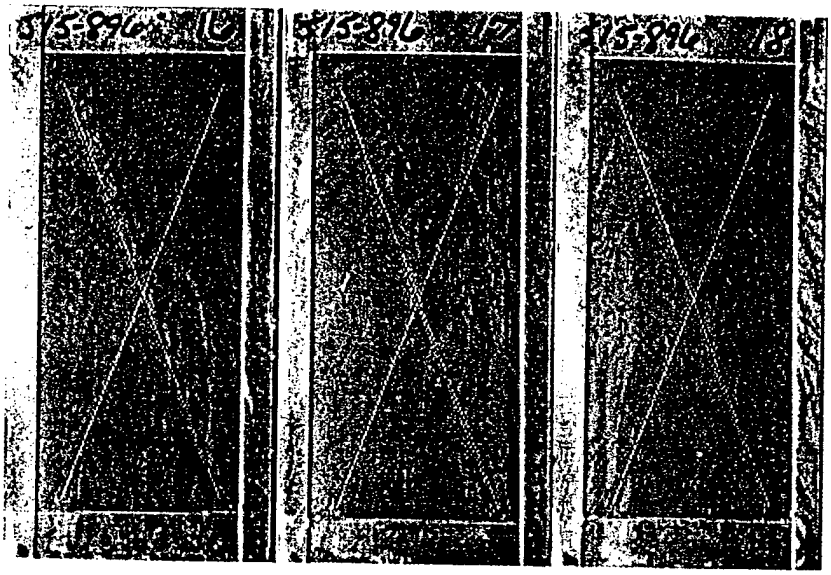
UMR Cerium Conversion
Coated Bare 7075-T6
Aluminum Substrates



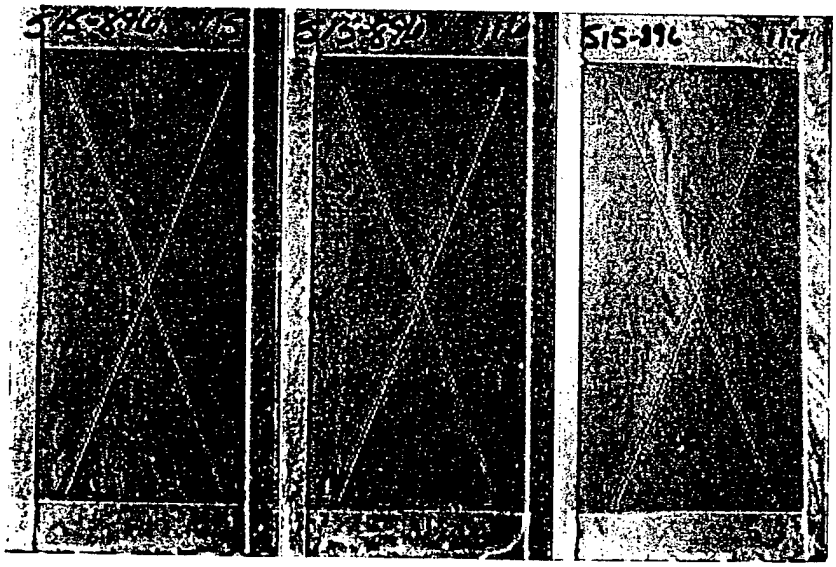
Figure B5. Deft 44-W-32, Cerium Pentane Dionate, Waterborne.

1000-HOUR NEUTRAL SALT SPRAY SPECIMENS

Chromate Conversion
Coated Bare 7075-T6
Aluminum Substrates



Chromate Conversion
Coated Bare 2024-T3
Aluminum Substrates



UMR Cerium Conversion
Coated Bare 7075-T6
Aluminum Substrates

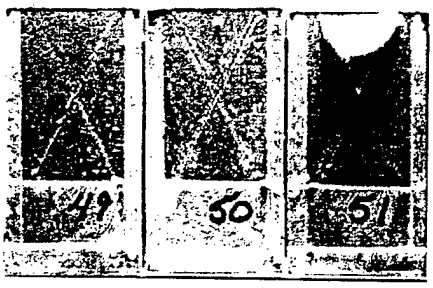
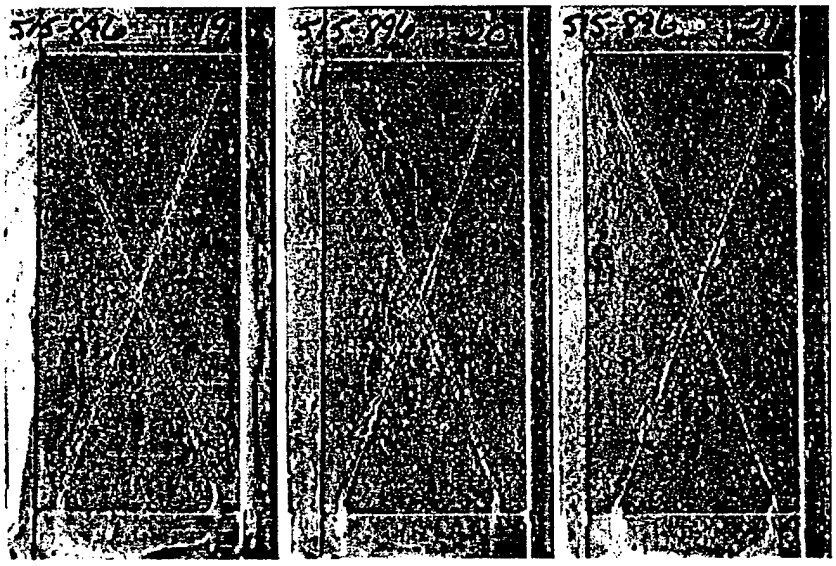


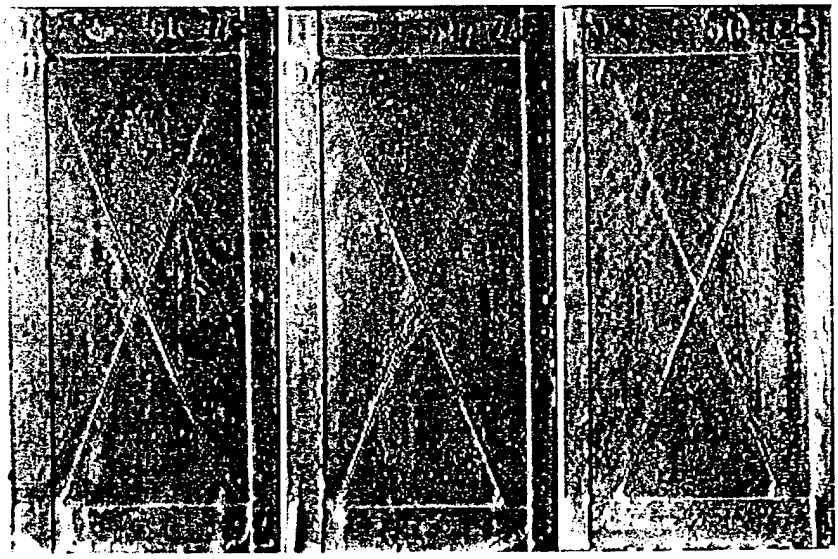
Figure B6. Deft 02-Y-040, High Solids Chromate Control.

1000-HOUR NEUTRAL SALT SPRAY SPECIMENS

Chromate Conversion
Coated Bare 7075-T6
Aluminum Substrates



Chromate Conversion
Coated Bare 2024-T3
Aluminum Substrates



UMR Cerium Conversion
Coated Bare 7075-T6
Aluminum Substrates

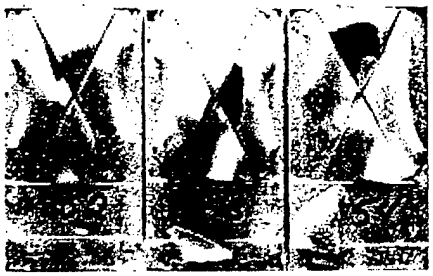
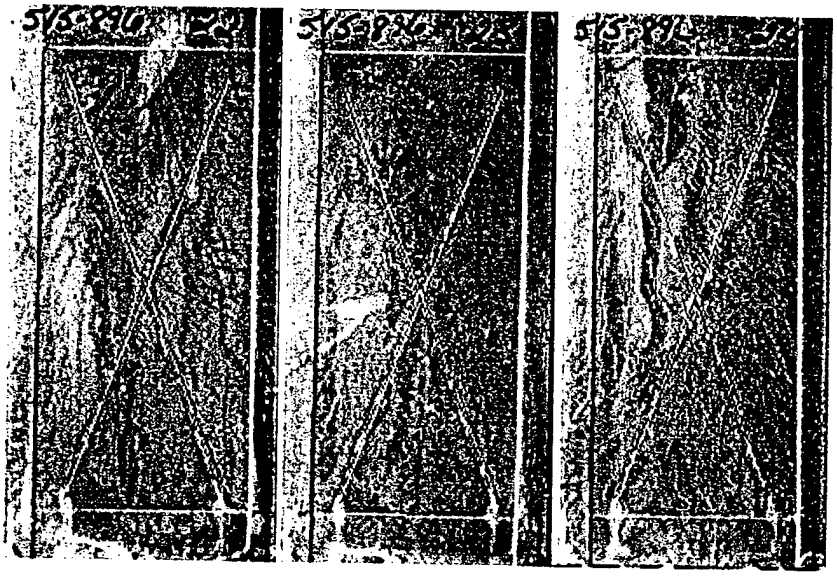


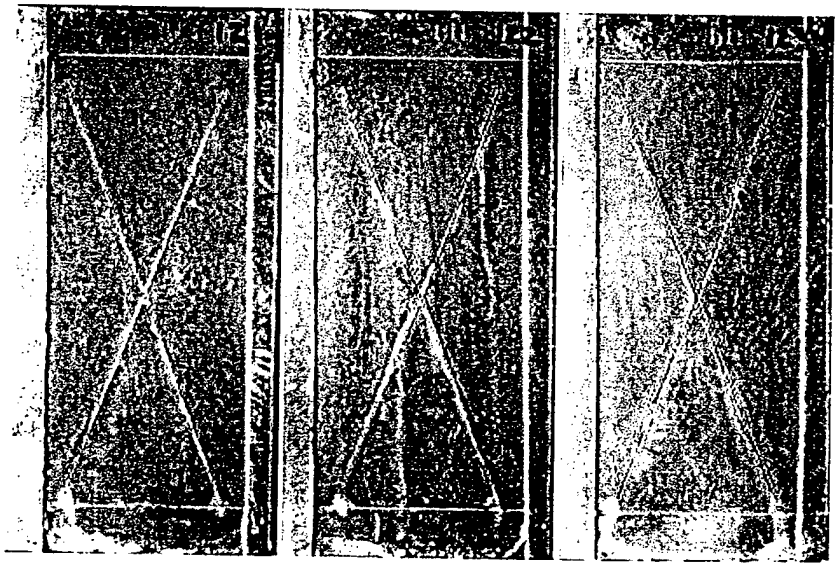
Figure B7. Deft 02-W-047, Cerium Phosphate, High Solids.

1000-HOUR NEUTRAL SALT SPRAY SPECIMENS

Chromate Conversion
Coated Bare 7075-T6
Aluminum Substrates



Chromate Conversion
Coated Bare 2024-T3
Aluminum Substrates



UMR Cerium Conversion
Coated Bare 7075-T6
Aluminum Substrates

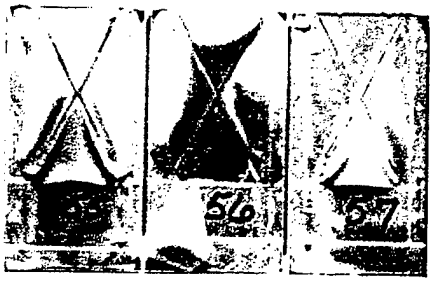
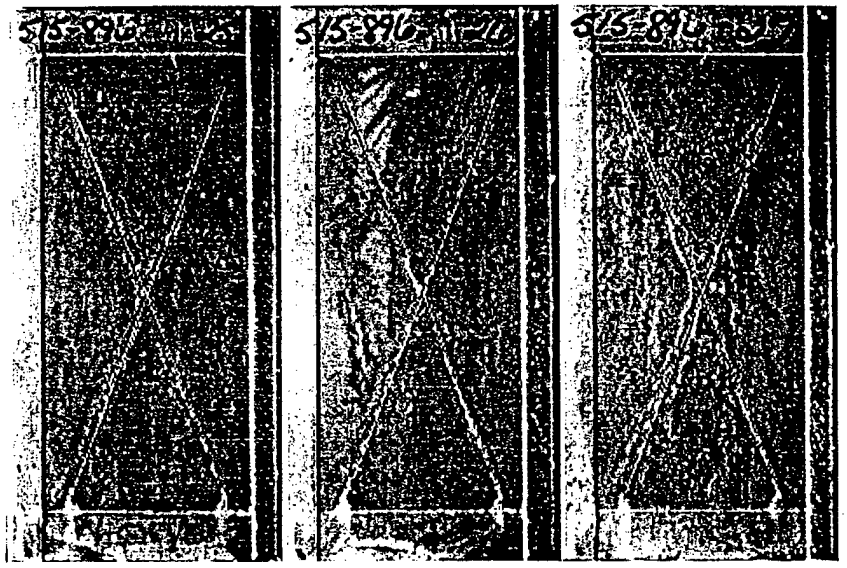


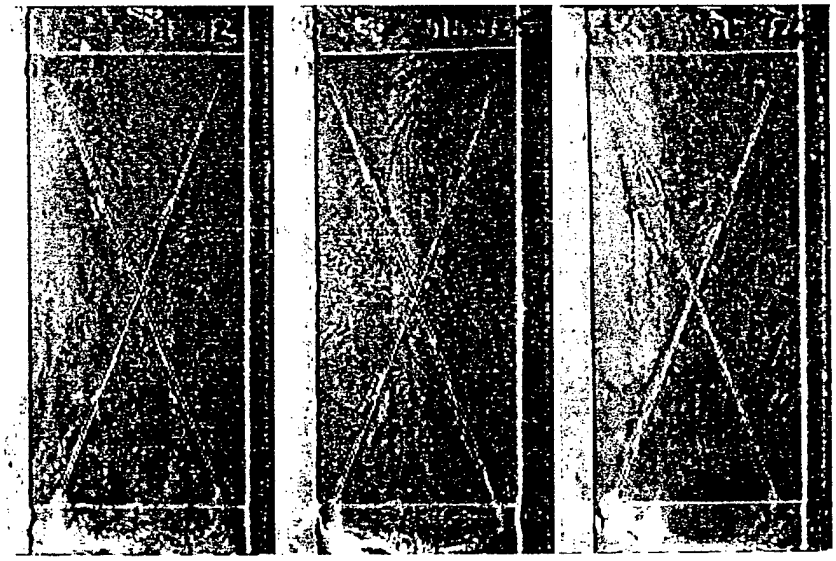
Figure B8. Deft 02-W-042, Barium Metaborate, High Solids

1000-HOUR NEUTRAL SALT SPRAY SPECIMENS

Chromate Conversion
Coated Bare 7075-T6
Aluminum Substrates



Chromate Conversion
Coated Bare 2024-T3
Aluminum Substrates



UMR Cerium Conversion
Coated Bare 7075-T6
Aluminum Substrates

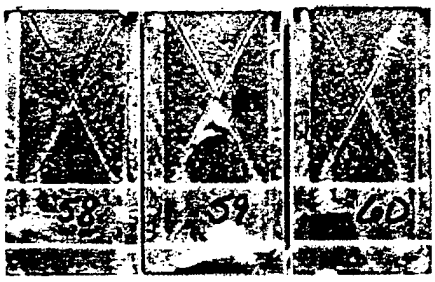
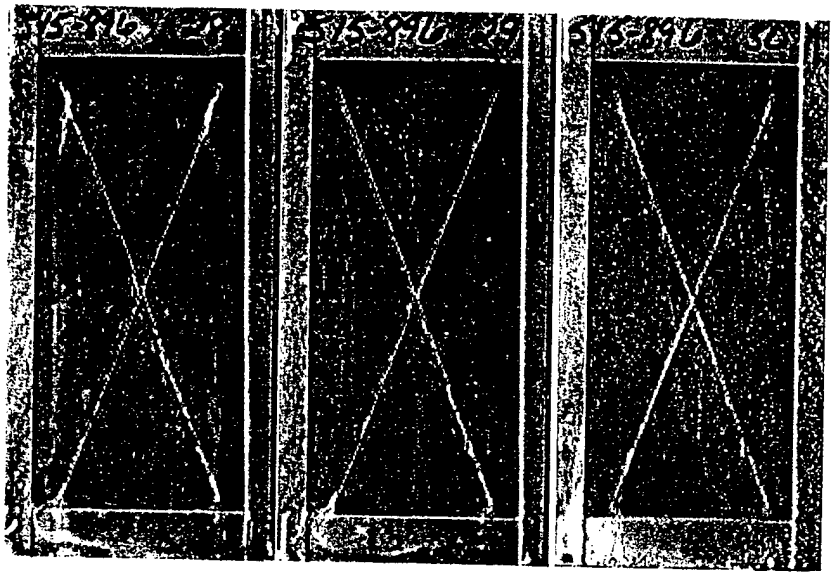


Figure B9. Deft 02-W-045, Barium Metaborate / Cerium Nitrate, High Solids.

1000-HOUR NEUTRAL SALT SPRAY SPECIMENS

Chromate Conversion
Coated Bare 7075-T6
Aluminum Substrates



Chromate Conversion
Coated Bare 2024-T3
Aluminum Substrates



UMR Cerium Conversion
Coated Bare 7075-T6
Aluminum Substrates

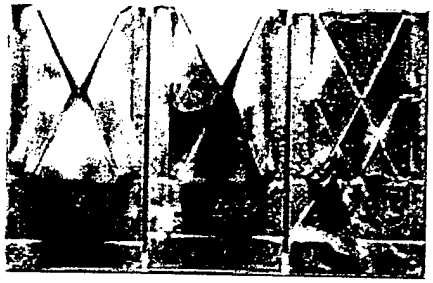
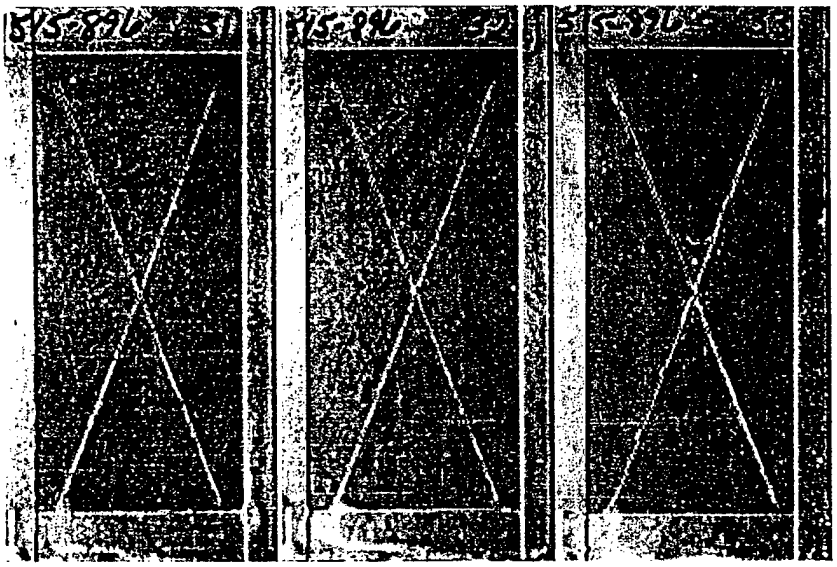


Figure B10. Deft 02-W-046, Cerium Pentane Dionate, High Solids.

1000-HOUR NEUTRAL SALT SPRAY SPECIMENS

Chromate Conversion
Coated Bare 7075-T6
Aluminum Substrates



Chromate Conversion
Coated Bare 2024-T3
Aluminum Substrates



UMR Cerium Conversion
Coated Bare 7075-T6
Aluminum Substrates

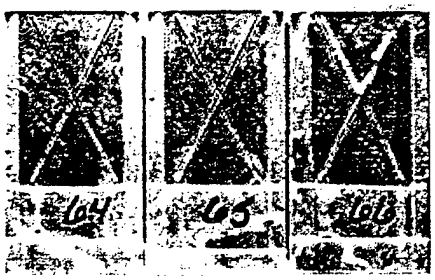


Figure B11. Deft 02-W-044, Cerium Nitrate, High Solids.

The data presented in this report, to the best of my knowledge and belief, is complete, accurate and complies with all test requirements of the requesting document.

APPENDIX C

2000 Hour Neutral Salt Spray Specimens

Photographic Documentation

ASTM B117

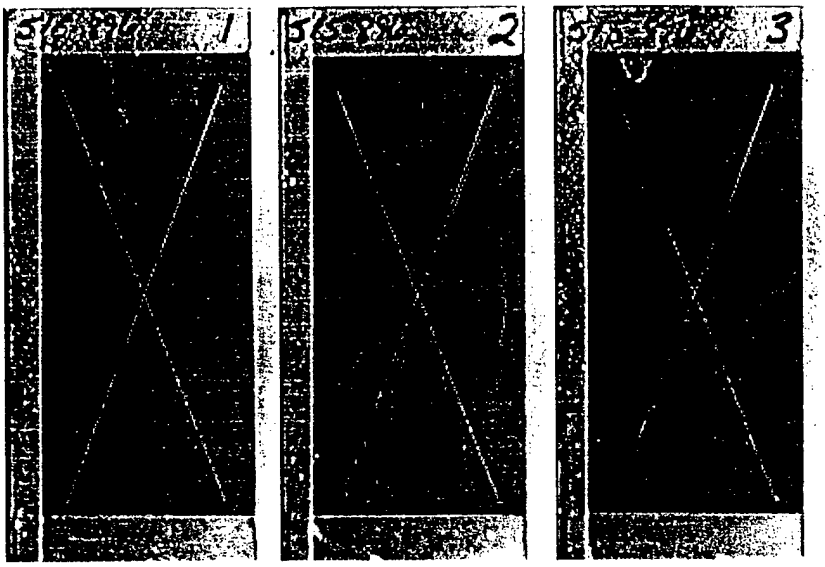
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Photographs of Specimens with Illumination from the Side

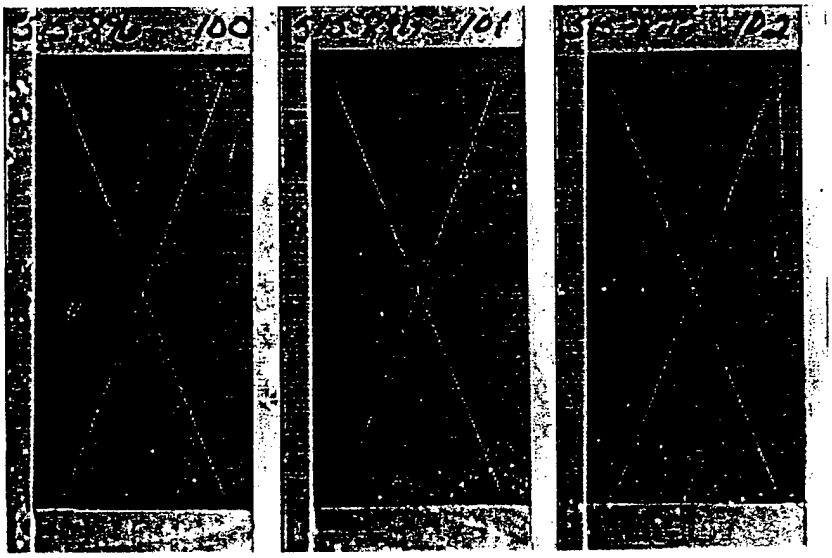
Deft 44-GN-72, Waterborne Chromated Control.	C3
Deft 44-W-31, Cerium phosphate, Waterborne	C4
Deft 44-W-30, Barium Metaborate, Waterborne	C5
Deft 02-W-043, K-White, High Solids	C6
Deft 44-W-32, Cerium Pentane Dionate, Waterborne	C7
Deft 02-Y-040, High Solids Chromated Control	C8
Deft 02-W-047, Cerium phosphate, High Solids	C9
Deft 02-W-042, Barium Metaborate, High Solids	C10
Deft 02-W-045, Barium Metaborate / cerium Nitrate, High Solids	C11
Deft 02-W-046, Cerium Pentane Dionate, High Solids	C12
Deft 02-W-044, Cerium Nitrate, High Solids	C13

2000-HOUR NEUTRAL SALT SPRAY SPECIMENS

Chromate Conversion
Coated Bare 7075-T6
Aluminum Substrates



Chromate Conversion
Coated Bare 2024-T3
Aluminum Substrates



UMR Cerium Conversion
Coated Bare 7075-T6
Aluminum Substrates

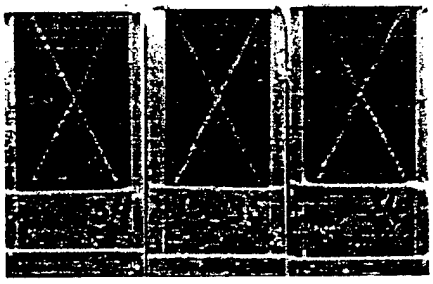
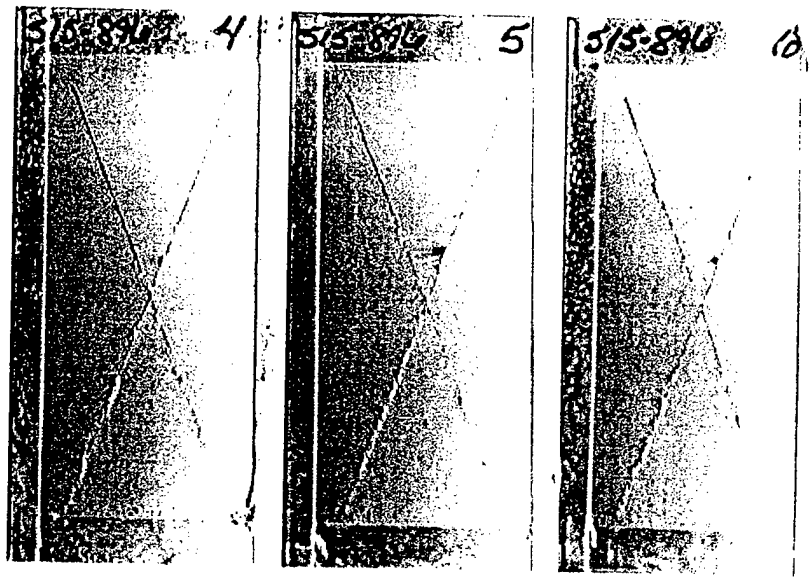
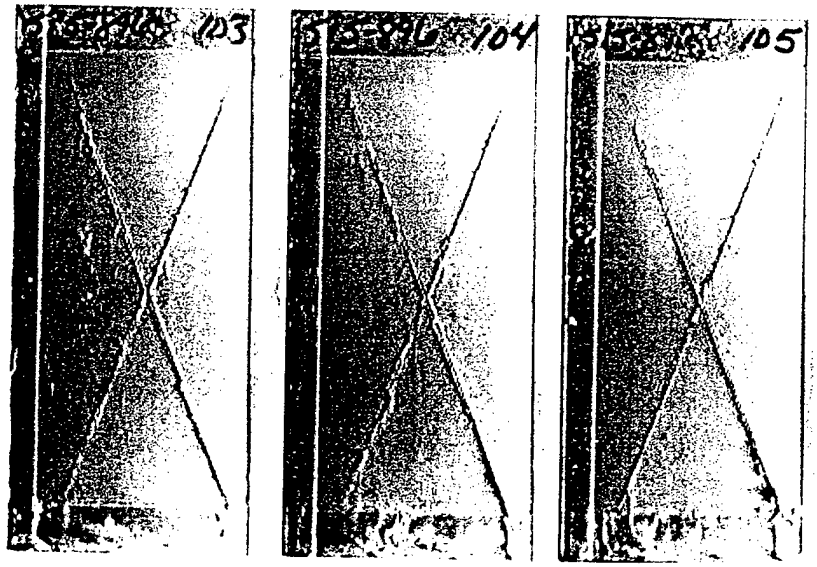


Figure C1. Deft 44-GN-72, Waterborne Chromate Control.

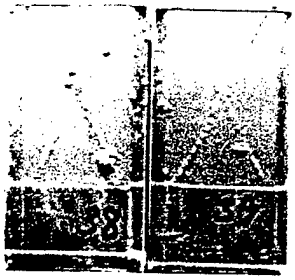
2000-HOUR NEUTRAL SALT SPRAY SPECIMENS



Chromate Conversion
Coated Bare 7075-T6
Aluminum Substrates



Chromate Conversion
Coated Bare 2024-T3
Aluminum Substrates

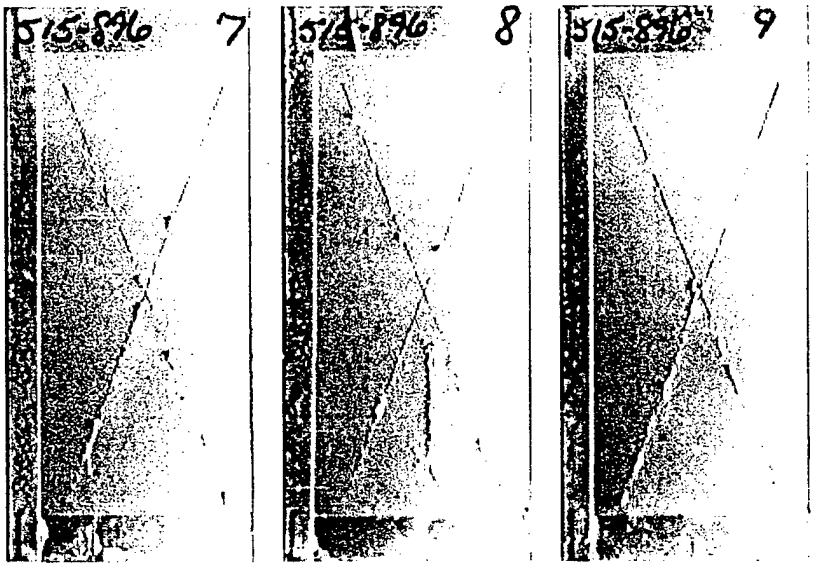


UMR Cerium Conversion
Coated Bare 7075-T6
Aluminum Substrates

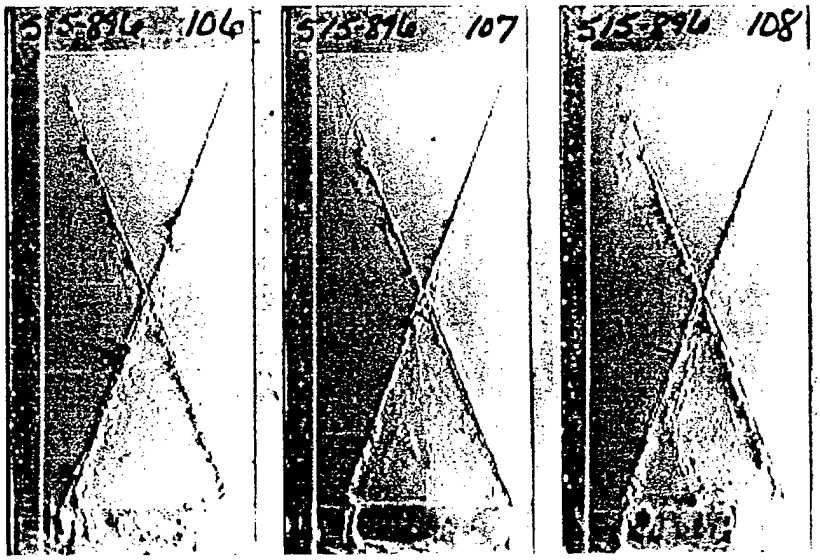
Figure C2. Deft 44-W-31, Cerium Phosphate, Waterborne.

2000-HOUR NEUTRAL SALT SPRAY SPECIMENS

Chromate Conversion
Coated Bare 7075-T6
Aluminum Substrates



Chromate Conversion
Coated Bare 2024-T3
Aluminum Substrates



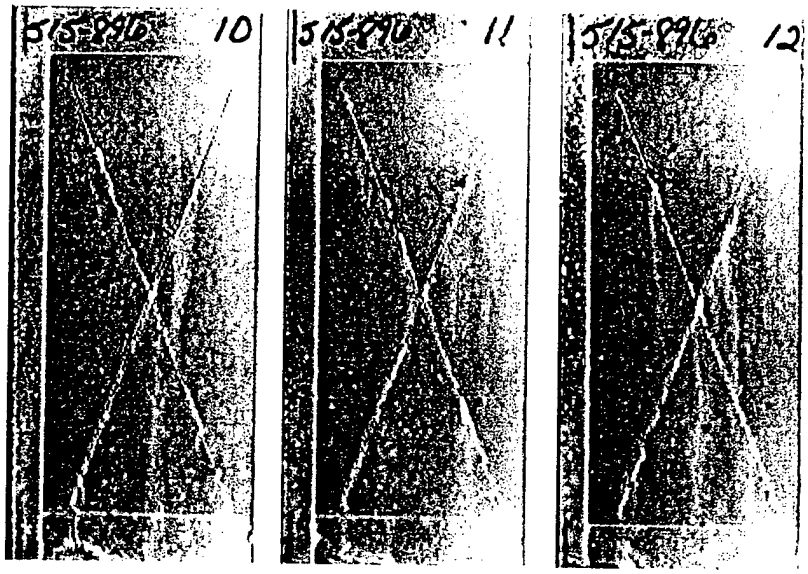
UMR Cerium Conversion
Coated Bare 7075-T6
Aluminum Substrates

Specimens Removed From Test After
1000 Hours

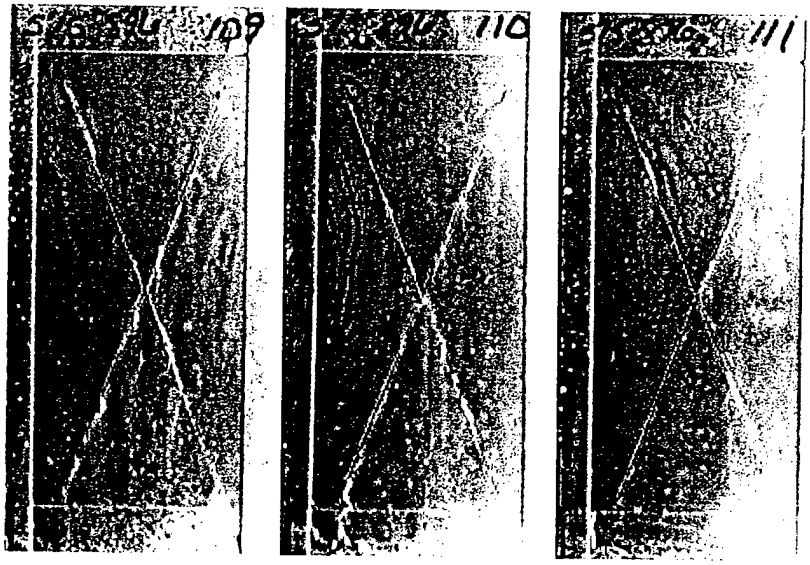
Figure C3. Deft 44-W-30, Barium Metaborate, Waterborne.

2000-HOUR NEUTRAL SALT SPRAY SPECIMENS

Chromate Conversion
Coated Bare 7075-T6
Aluminum Substrates



Chromate Conversion
Coated Bare 2024-T3
Aluminum Substrates



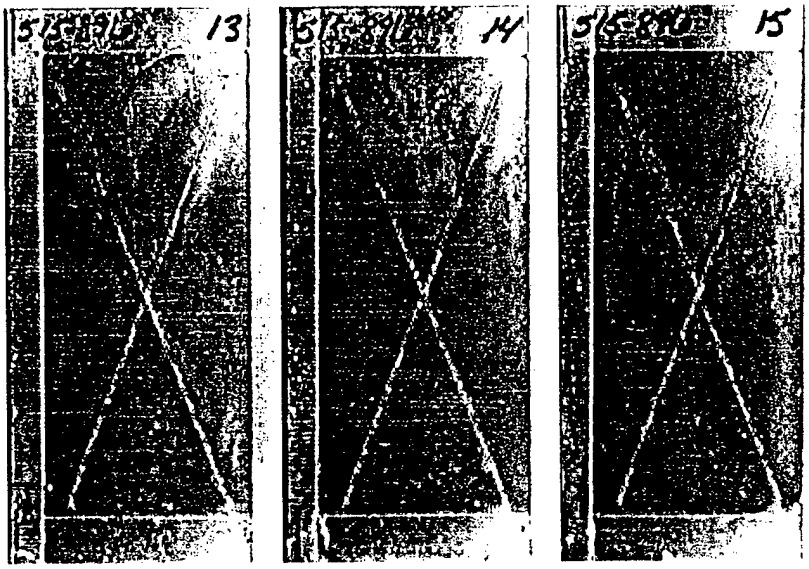
UMR Cerium Conversion
Coated Bare 7075-T6
Aluminum Substrates

Specimens Removed From Test After
1000 Hours

Figure C4. Deft 02-W-043, K-White, High Solids.

2000-HOUR NEUTRAL SALT SPRAY SPECIMENS

Chromate Conversion
Coated Bare 7075-T6
Aluminum Substrates



Chromate Conversion
Coated Bare 2024-T3
Aluminum Substrates



UMR Cerium Conversion
Coated Bare 7075-T6
Aluminum Substrates

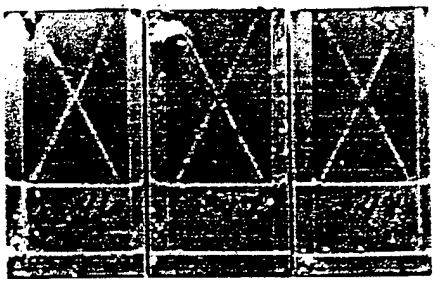
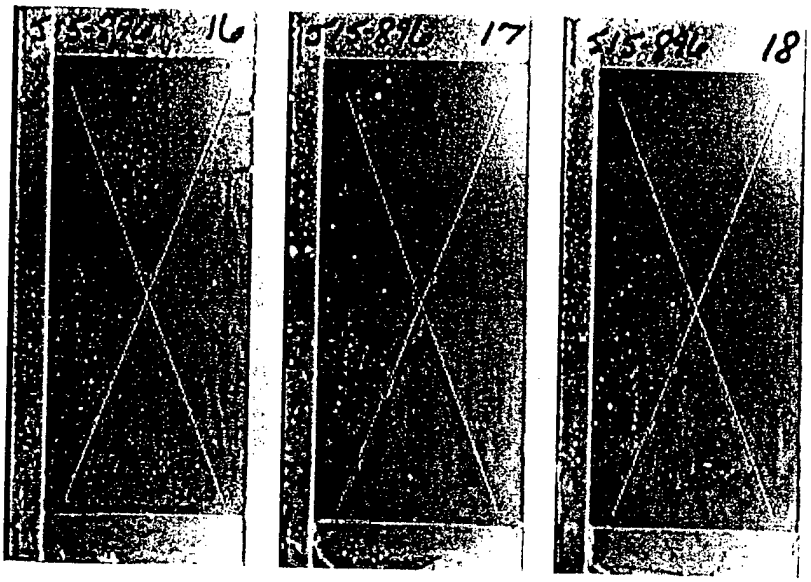


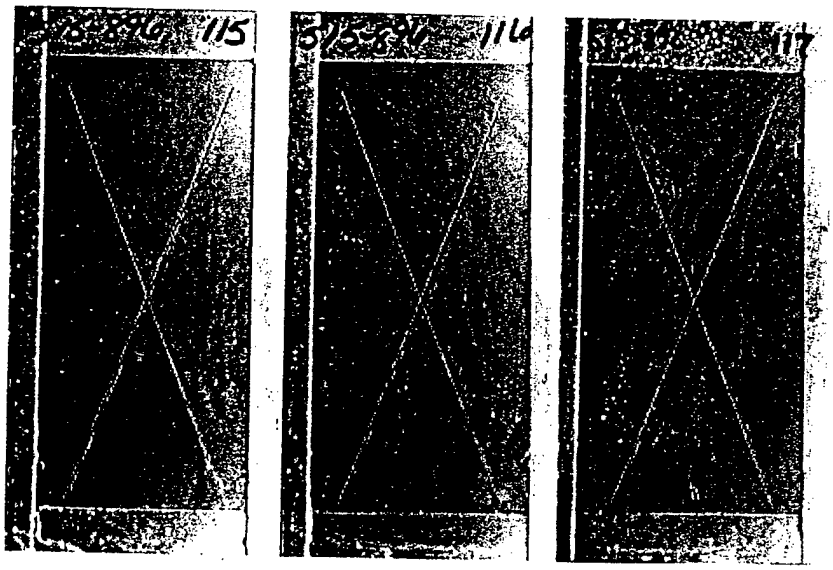
Figure C5. Deft 44-W-32, Cerium Pentane Dionate, Waterborne.

2000-HOUR NEUTRAL SALT SPRAY SPECIMENS

Chromate Conversion
Coated Bare 7075-T6
Aluminum Substrates



Chromate Conversion
Coated Bare 2024-T3
Aluminum Substrates



UMR Cerium Conversion
Coated Bare 7075-T6
Aluminum Substrates

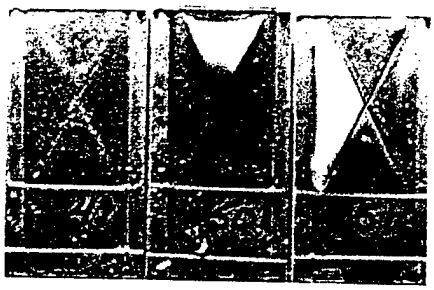
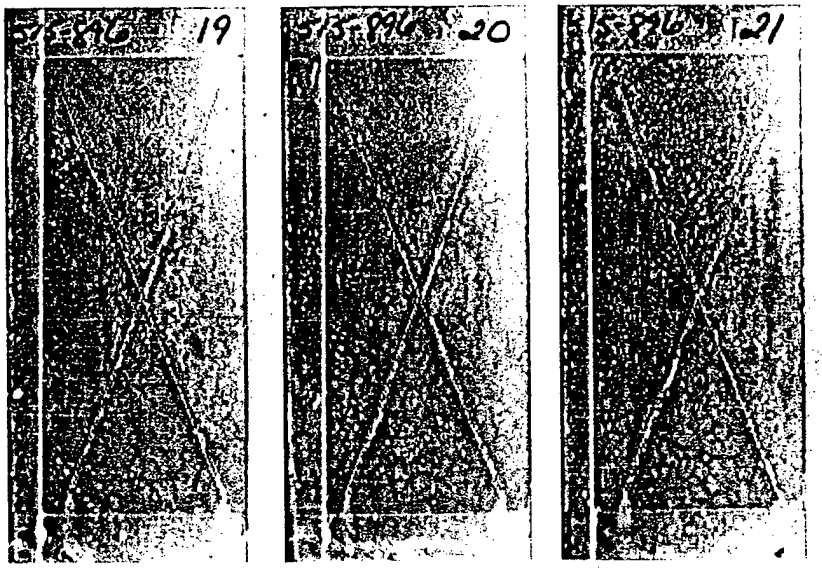


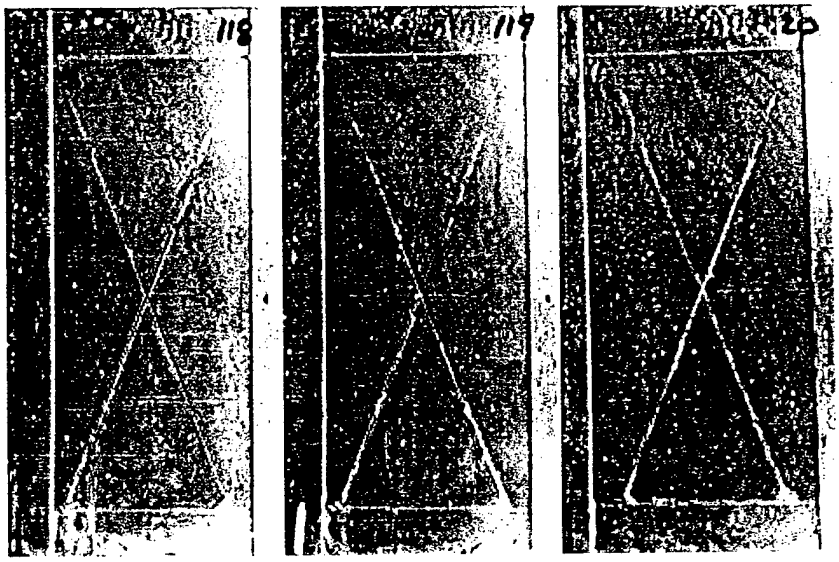
Figure C6. Deft 02-Y-040, High Solids Chromate Control.

2000-HOUR NEUTRAL SALT SPRAY SPECIMENS

Chromate Conversion
Coated Bare 7075-T6
Aluminum Substrates



Chromate Conversion
Coated Bare 2024-T3
Aluminum Substrates



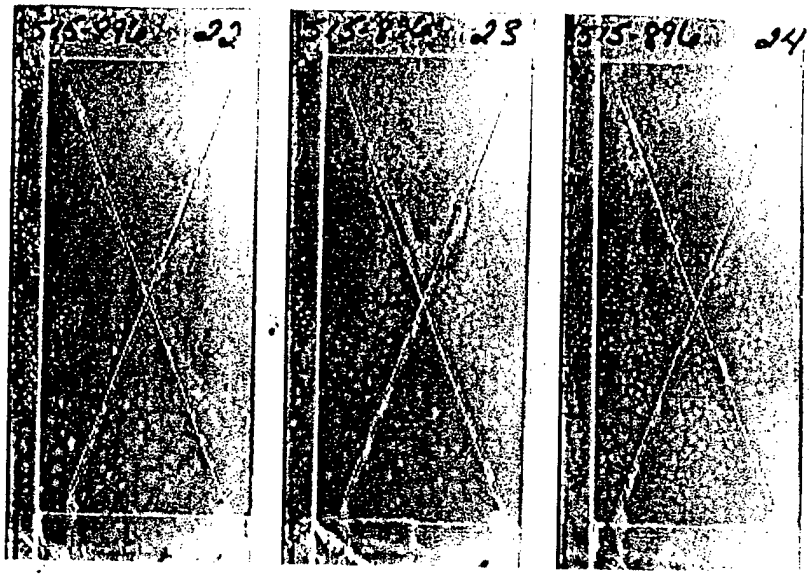
UMR Cerium Conversion
Coated Bare 7075-T6
Aluminum Substrates

Specimens Removed From Test After
1000 Hours

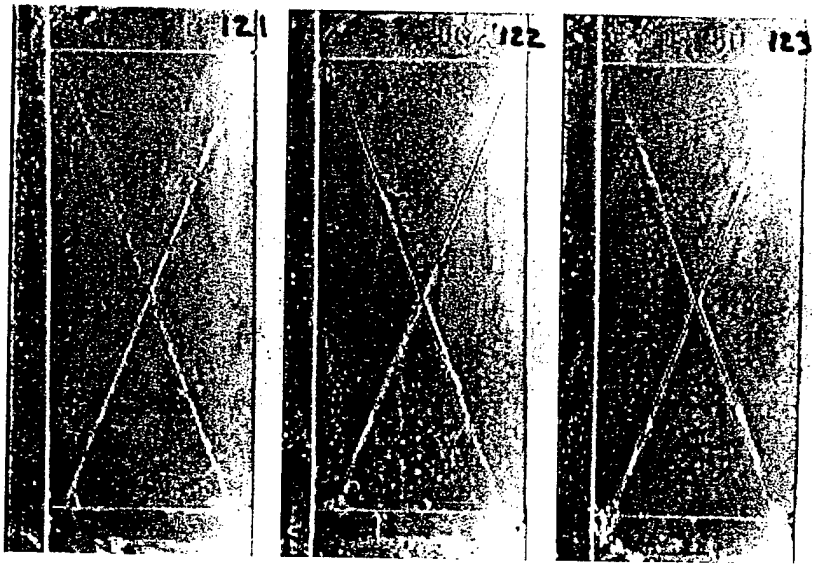
Figure C7. Deft 02-W-047, Cerium Phosphate, High Solids.

2000-HOUR NEUTRAL SALT SPRAY SPECIMENS

Chromate Conversion
Coated Bare 7075-T6
Aluminum Substrates



Chromate Conversion
Coated Bare 2024-T3
Aluminum Substrates



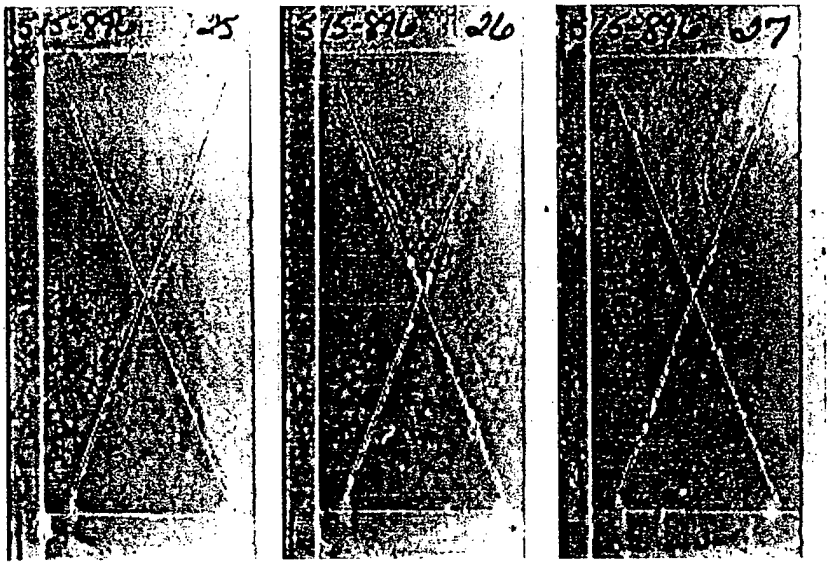
UMR Cerium Conversion
Coated Bare 7075-T6
Aluminum Substrates

Specimens Removed From Test After
1000 Hours

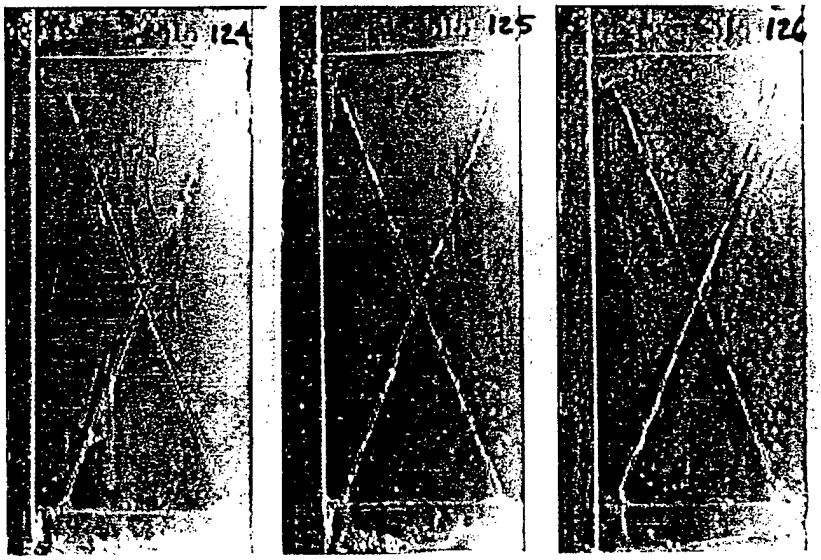
Figure C8. Deft 02-W-042, Barium Metaborate, High Solids

2000-HOUR NEUTRAL SALT SPRAY SPECIMENS

Chromate Conversion
Coated Bare 7075-T6
Aluminum Substrates



Chromate Conversion
Coated Bare 2024-T3
Aluminum Substrates



UMR Cerium Conversion
Coated Bare 7075-T6
Aluminum Substrates

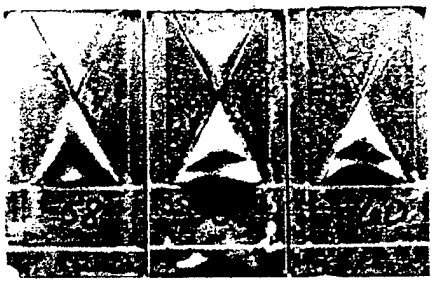
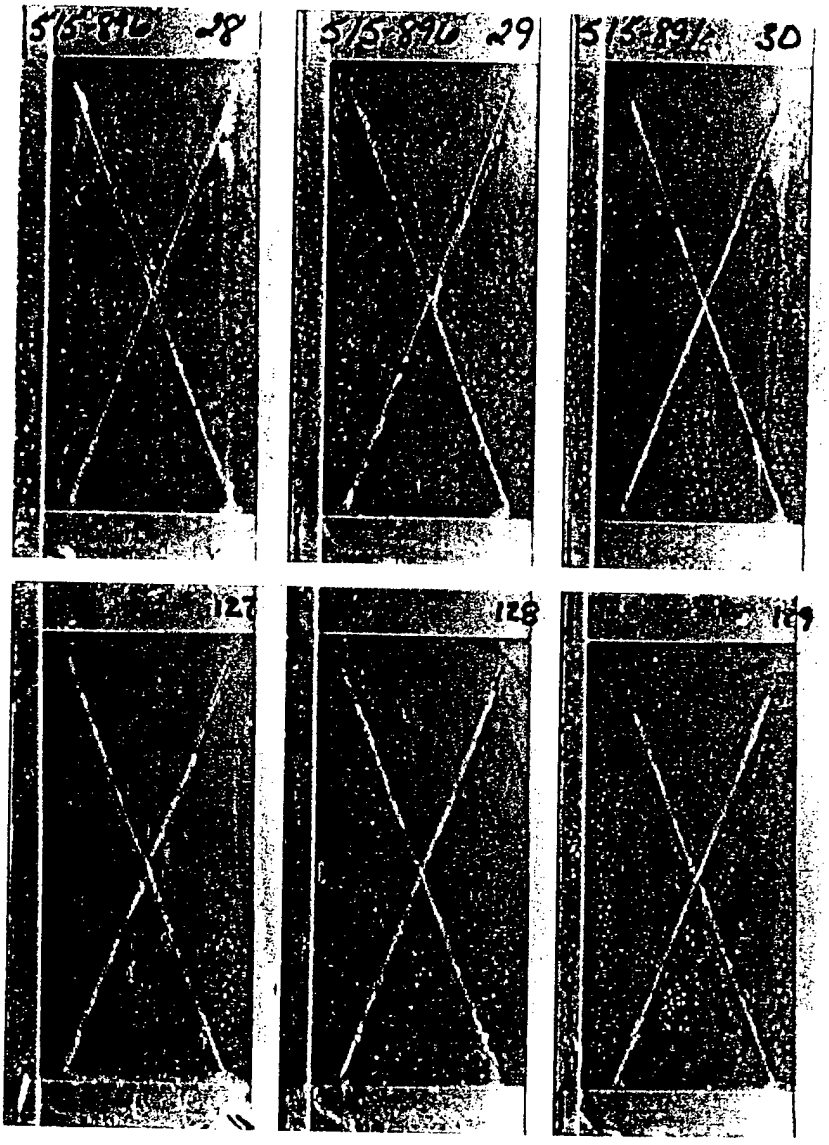


Figure C9. Deft 02-W-045, Barium Metaborate / Cerium Nitrate, High Solids.

2000-HOUR NEUTRAL SALT SPRAY SPECIMENS



Chromate Conversion Coated Bare 7075-T6 Aluminum Substrates

Chromate Conversion Coated Bare 2024-T3 Aluminum Substrates

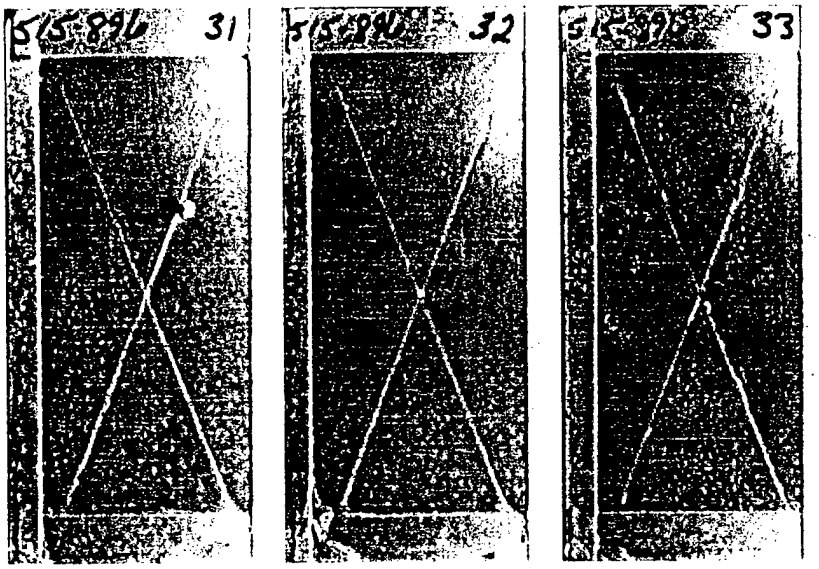
UMR Cerium Conversion Coated Bare 7075-T6 Aluminum Substrates

Specimens Removed From Test After 1000 Hours

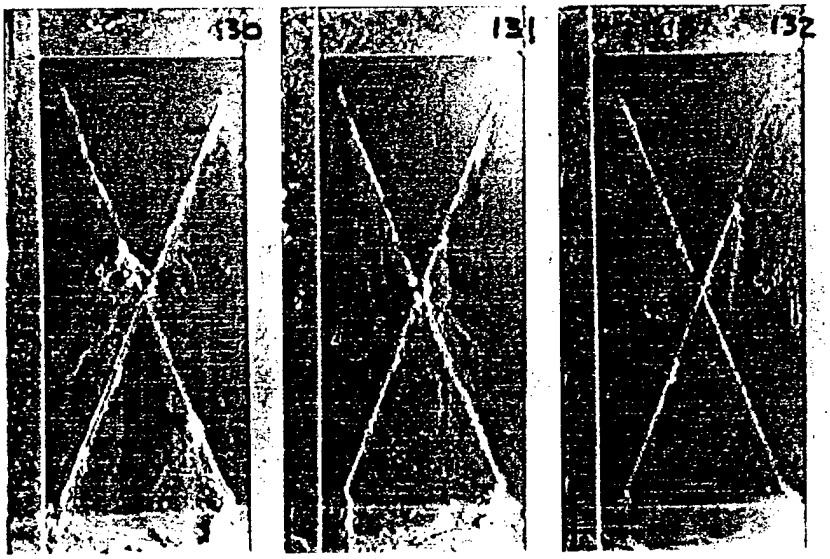
Figure C10. Deft 02-W-046, Cerium Pentane Dionate, High Solids.

2000-HOUR NEUTRAL SALT SPRAY SPECIMENS

Chromate Conversion
Coated Bare 7075-T6
Aluminum Substrates



Chromate Conversion
Coated Bare 2024-T3
Aluminum Substrates



UMR Cerium Conversion
Coated Bare 7075-T6
Aluminum Substrates



Figure C11. Deft 02-W-044, Cerium Nitrate, High Solids.

The data presented in this report, to the best of my knowledge and belief, is complete, accurate and complies with all test requirements of the requesting document.

APPENDIX D

3000 Hour Neutral Salt Spray Specimens

Photographic Documentation

ASTM B117

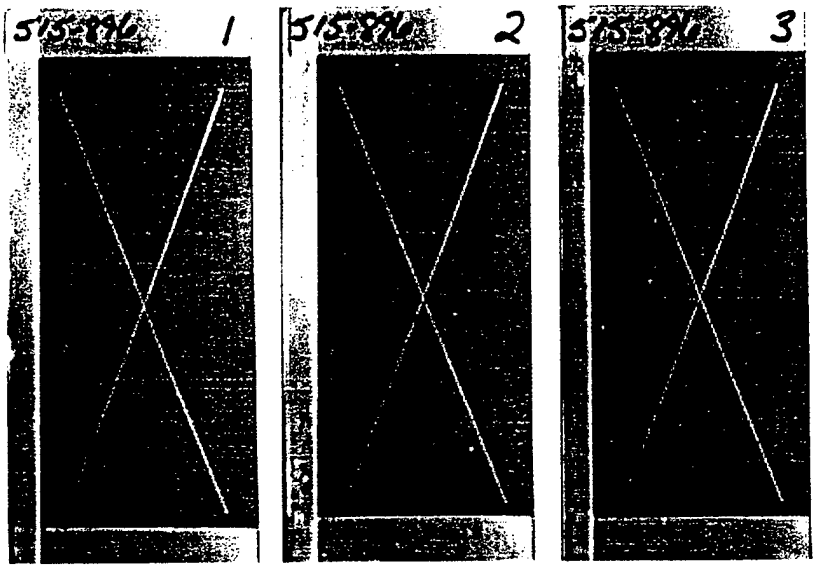
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Photographs of Specimens with Illumination from the Side

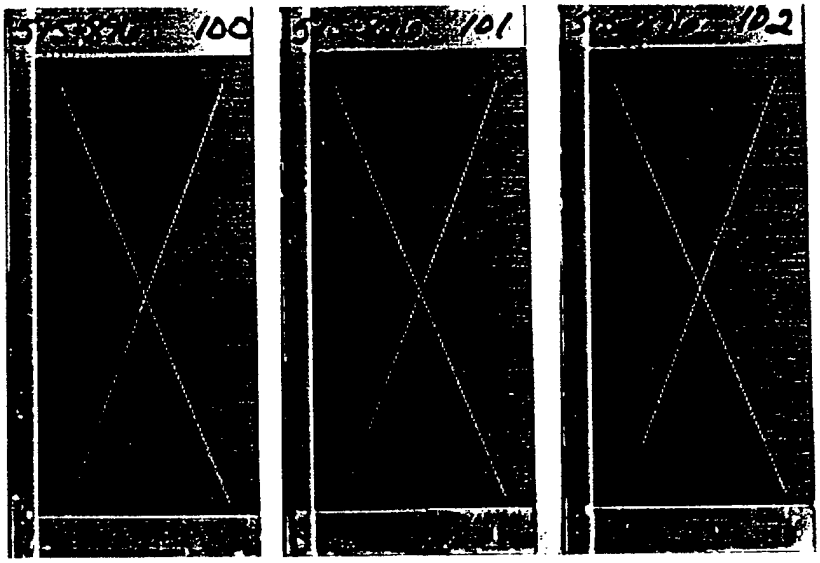
Deft 44-GN-72, Waterborne Chromated Control.	D3
Deft 44-W-31, Cerium phosphate, Waterborne	D4
Deft 44-W-30, Barium Metaborate, Waterborne	D5
Deft 02-W-043, K-White, High Solids	D6
Deft 44-W-32, Cerium Pentane Dionate, Waterborne	D7
Deft 02-Y-040, High Solids Chromated Control	D8
Deft 02-W-047, Cerium phosphate, High Solids	D9
Deft 02-W-042, Barium Metaborate, High Solids	D10
Deft 02-W-045, Barium Metaborate / cerium Nitrate, High Solids	D11
Deft 02-W-046, Cerium Pentane Dionate, High Solids	D12
Deft 02-W-044, Cerium Nitrate, High Solids	D13

3000-HOUR NEUTRAL SALT SPRAY SPECIMENS

Chromate Conversion
Coated Bare 7075-T6
Aluminum Substrates



Chromate Conversion
Coated Bare 2024-T3
Aluminum Substrates



UMR Cerium Conversion
Coated Bare 7075-T6
Aluminum Substrates

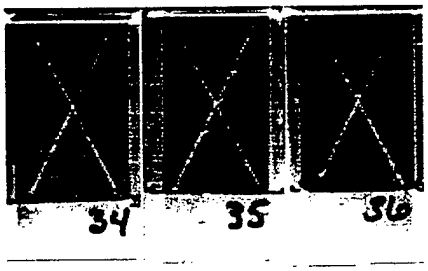
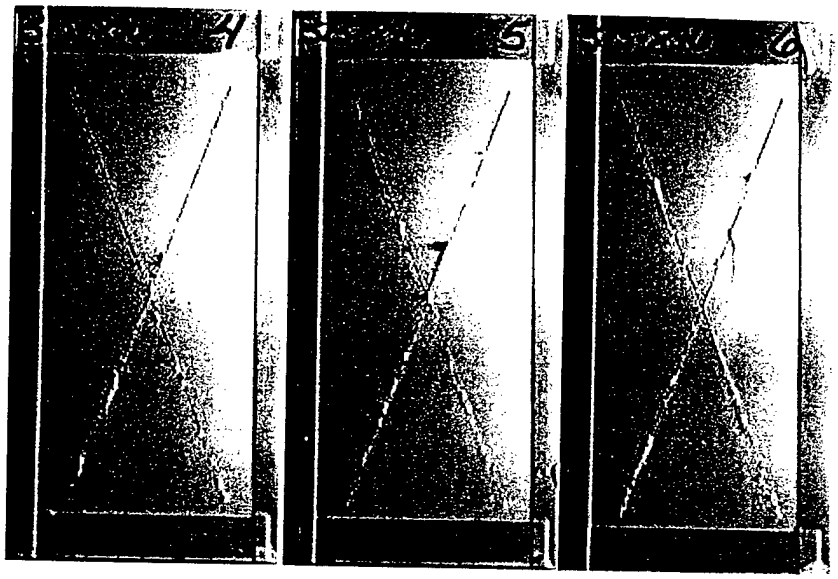


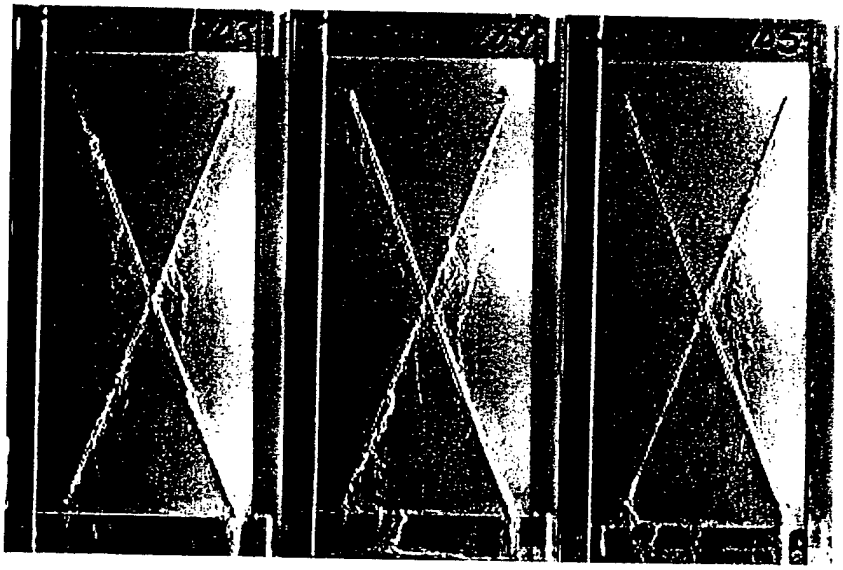
Figure D1. Deft 44-GN-72, Waterborne Chromate Control.

3000-HOUR NEUTRAL SALT SPRAY SPECIMENS

Chromate Conversion
Coated Bare 7075-T6
Aluminum Substrates



Chromate Conversion
Coated Bare 2024-T3
Aluminum Substrates



UMR Cerium Conversion
Coated Bare 7075-T6
Aluminum Substrates

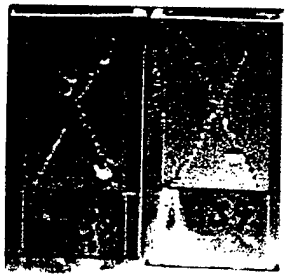
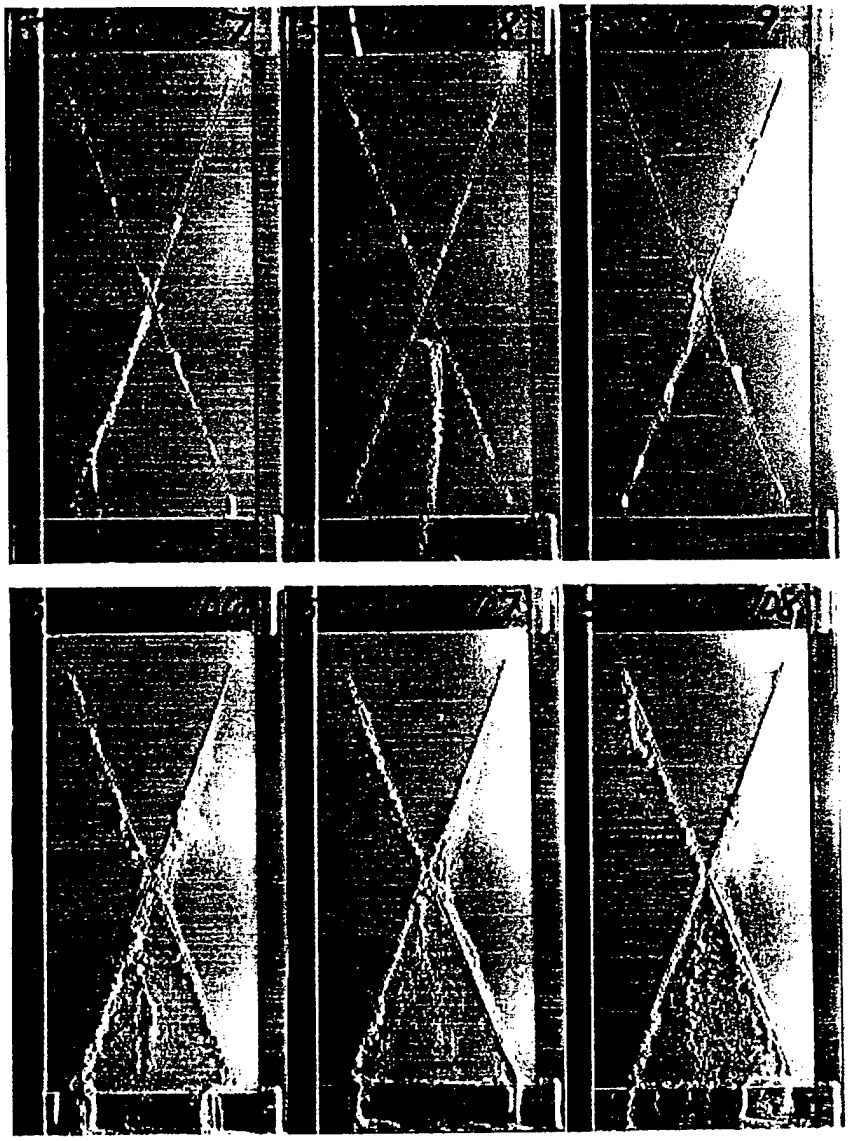


Figure D2. Deft 44-W-31, Cerium Phosphate, Waterborne.

3000-HOUR NEUTRAL SALT SPRAY SPECIMENS



Chromate Conversion
Coated Bare 7075-T6
Aluminum Substrates

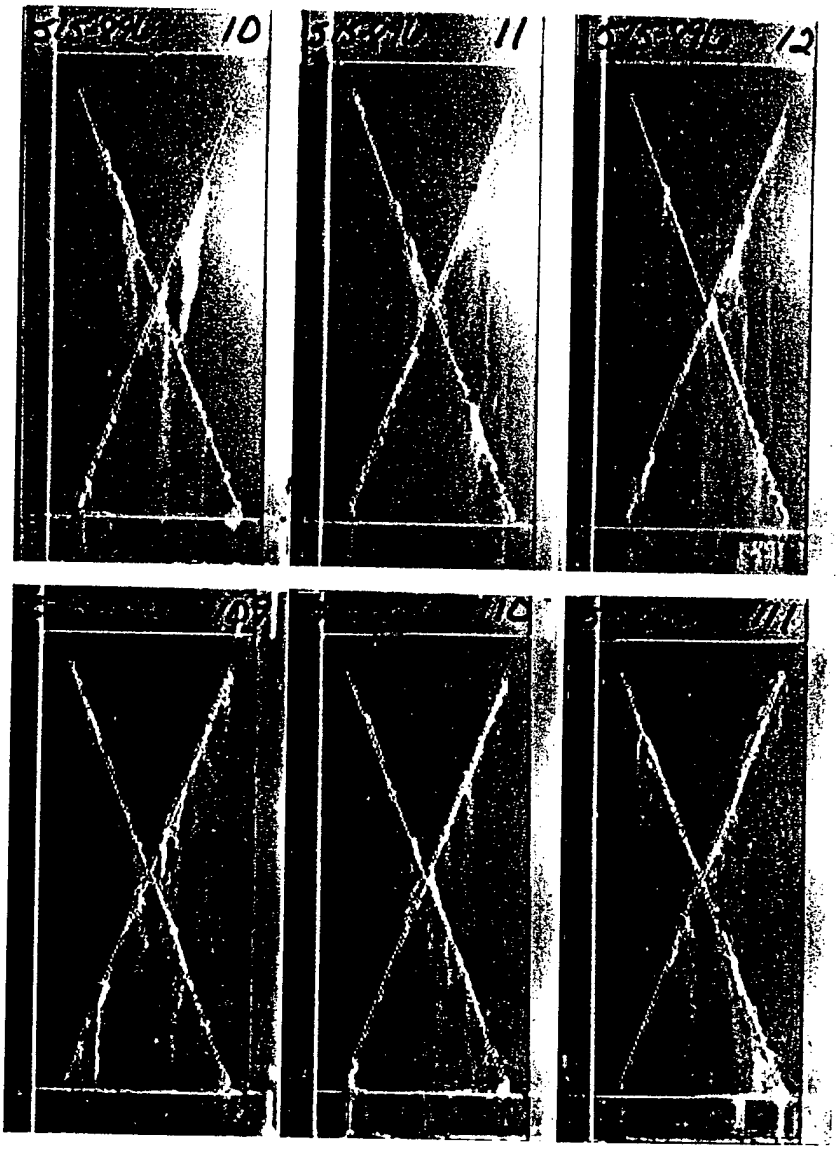
Chromate Conversion
Coated Bare 2024-T3
Aluminum Substrates

UMR Cerium Conversion
Coated Bare 7075-T6
Aluminum Substrates

Specimens Removed From Test After
1000 Hours

Figure D3. Deft 44-W-30, Barium Metaborate, Waterborne.

3000-HOUR NEUTRAL SALT SPRAY SPECIMENS



Chromate Conversion Coated Bare 7075-T6 Aluminum Substrates

Chromate Conversion Coated Bare 2024-T3 Aluminum Substrates

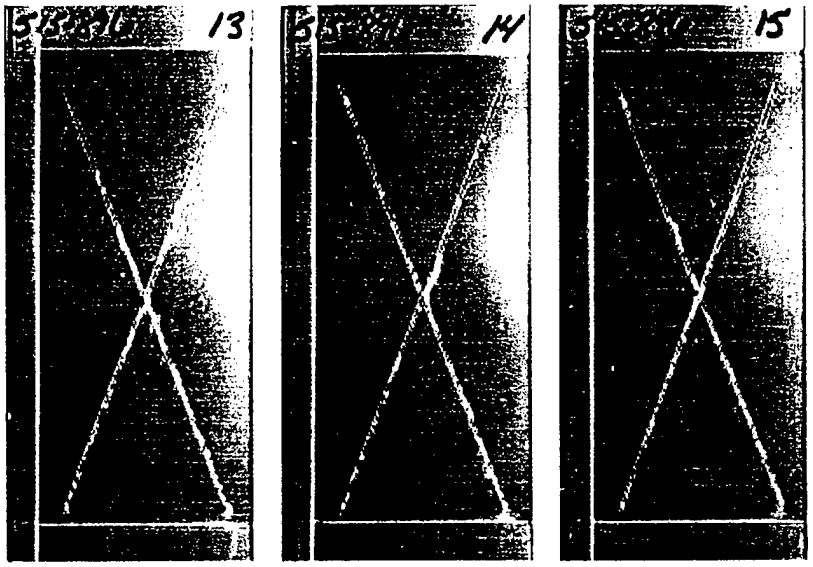
UMR Cerium Conversion Coated Bare 7075-T6 Aluminum Substrates

Specimens Removed From Test After 1000 Hours

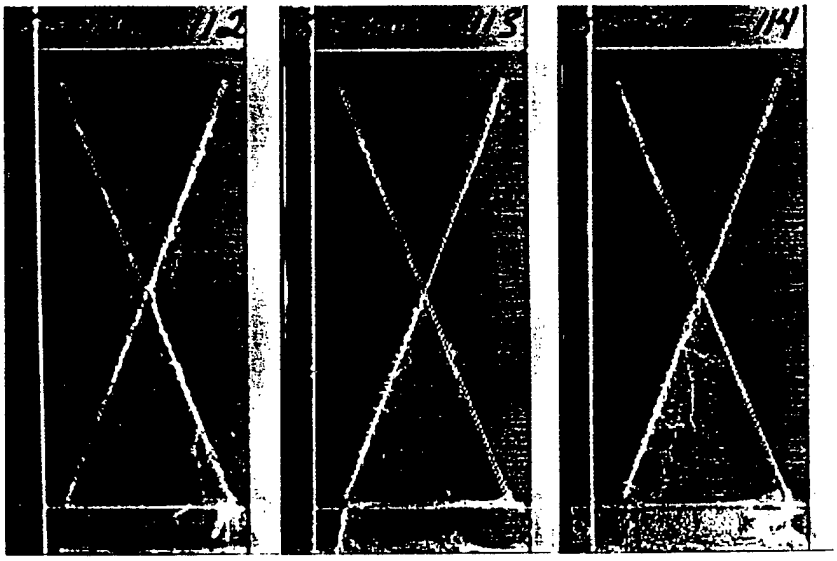
Figure D4. Deft 02-W-043, K-White, High Solids.

3000-HOUR NEUTRAL SALT SPRAY SPECIMENS

Chromate Conversion
Coated Bare 7075-T6
Aluminum Substrates



Chromate Conversion
Coated Bare 2024-T3
Aluminum Substrates



UMR Cerium Conversion
Coated Bare 7075-T6
Aluminum Substrates

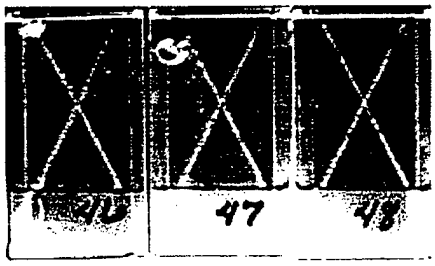
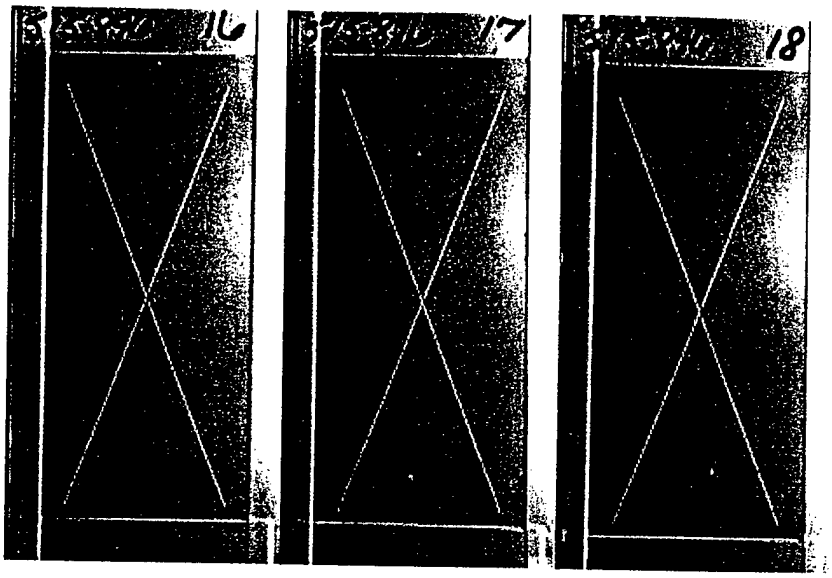


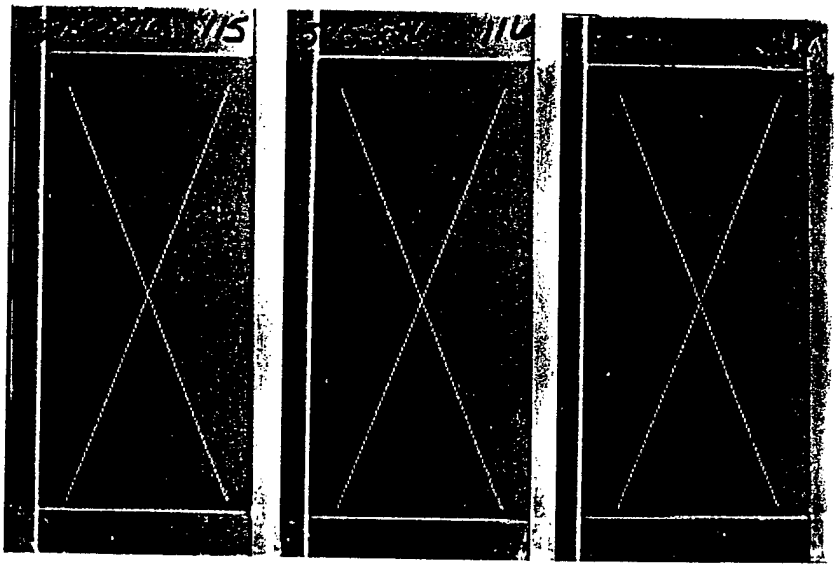
Figure D5. Deft 44-W-32, Cerium Pentane Dionate, Waterborne.

3000-HOUR NEUTRAL SALT SPRAY SPECIMENS

Chromate Conversion
Coated Bare 7075-T6
Aluminum Substrates



Chromate Conversion
Coated Bare 2024-T3
Aluminum Substrates



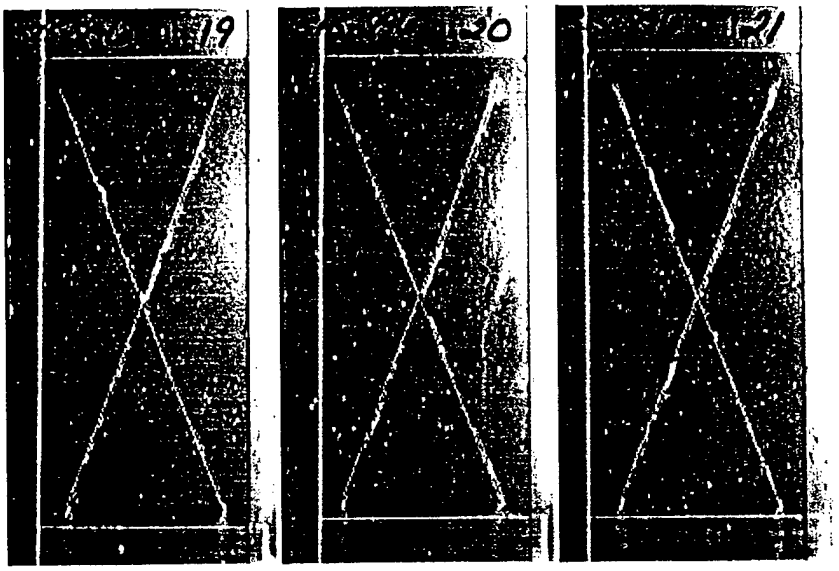
UMR Cerium Conversion
Coated Bare 7075-T6
Aluminum Substrates

Specimens Removed From Test After
2000 Hours

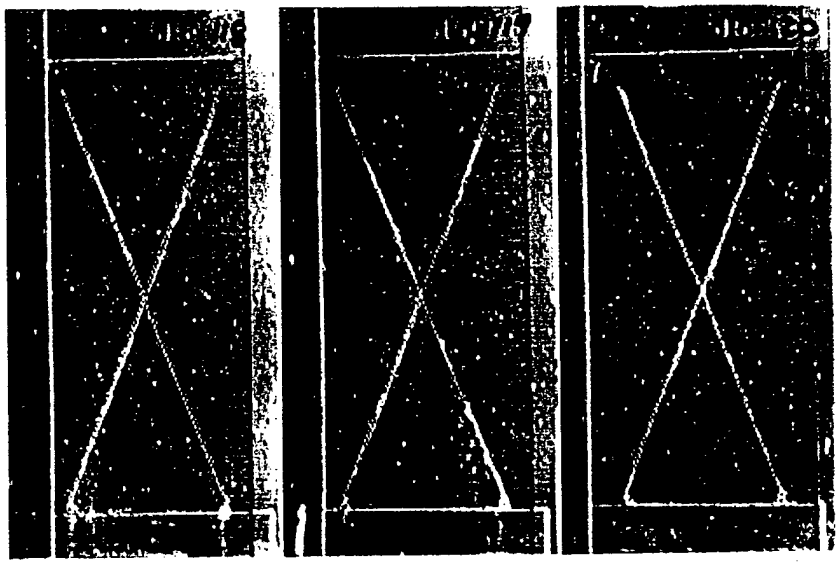
Figure D6. Deft 02-Y-040, High Solids Chromate Control.

3000-HOUR NEUTRAL SALT SPRAY SPECIMENS

Chromate Conversion
Coated Bare 7075-T6
Aluminum Substrates



Chromate Conversion
Coated Bare 2024-T3
Aluminum Substrates



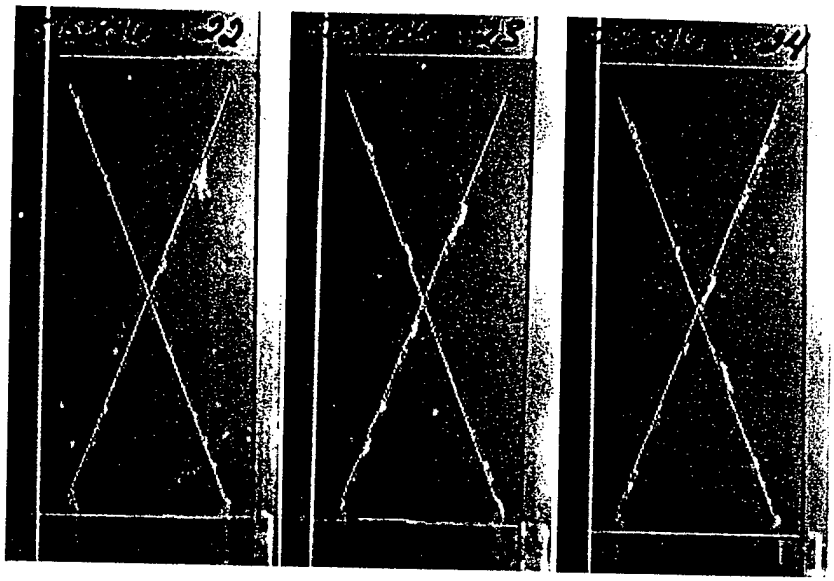
UMR Cerium Conversion
Coated Bare 7075-T6
Aluminum Substrates

Specimens Removed From Test After
1000 Hours

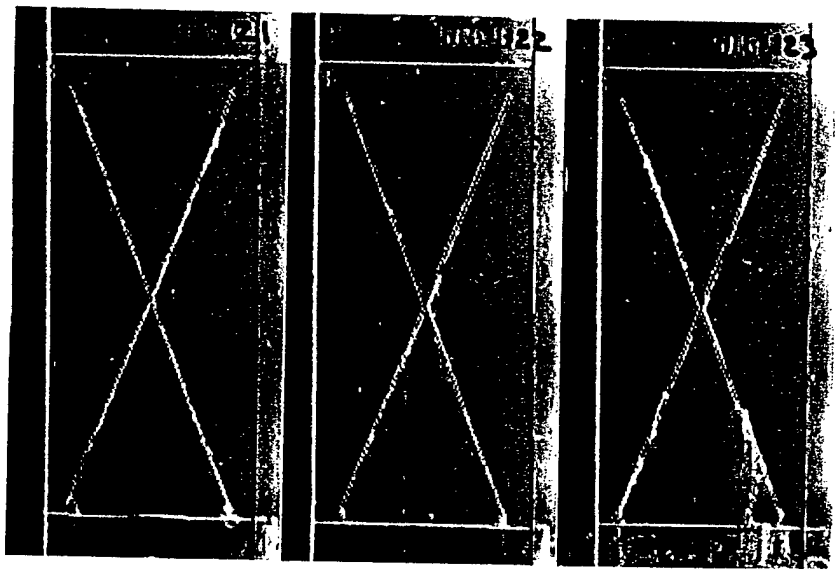
Figure D7. Deft 02-W-047, Cerium Phosphate, High Solids.

3000-HOUR NEUTRAL SALT SPRAY SPECIMENS

Chromate Conversion
Coated Bare 7075-T6
Aluminum Substrates



Chromate Conversion
Coated Bare 2024-T3
Aluminum Substrates



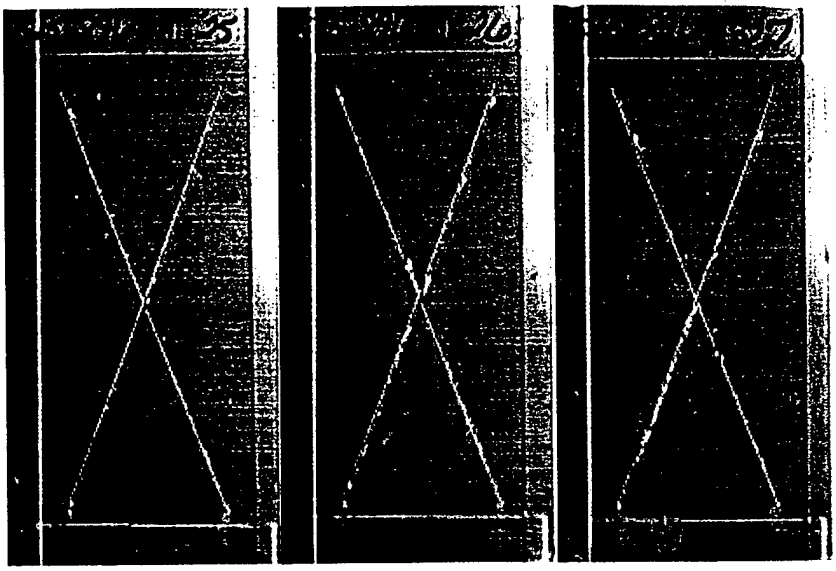
UMR Cerium Conversion
Coated Bare 7075-T6
Aluminum Substrates

Specimens Removed From Test After
1000 Hours

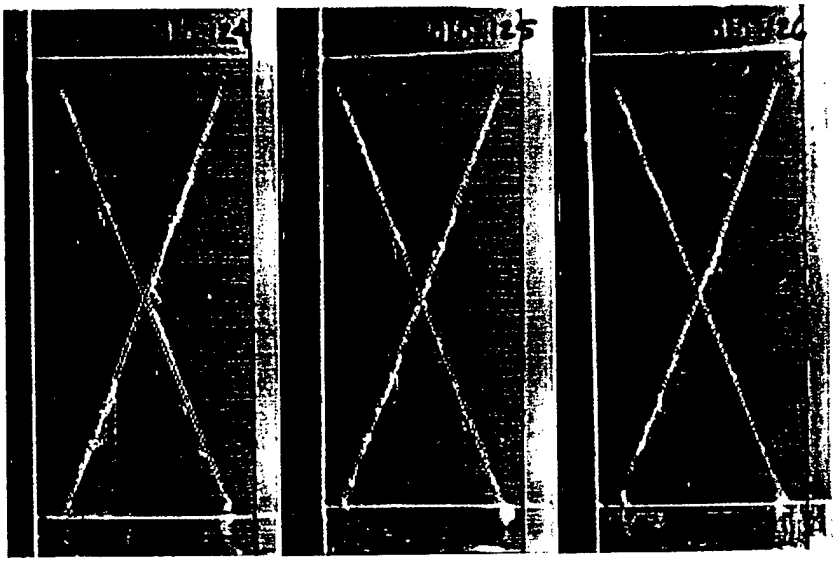
Figure D8. Deft 02-W-042, Barium Metaborate, High Solids.

3000-HOUR NEUTRAL SALT SPRAY SPECIMENS

Chromate Conversion
Coated Bare 7075-T6
Aluminum Substrates



Chromate Conversion
Coated Bare 2024-T3
Aluminum Substrates

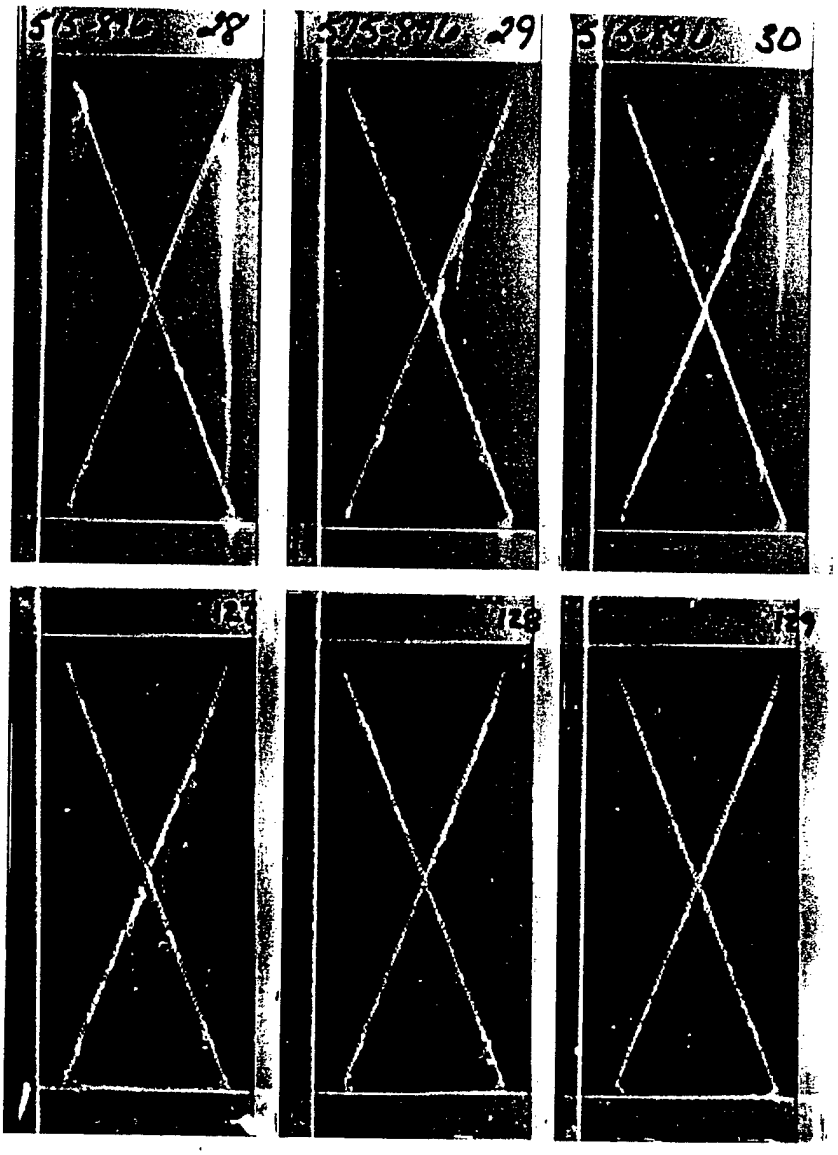


UMR Cerium Conversion
Coated Bare 7075-T6
Aluminum Substrates

Specimens Removed From Test After
2000 Hours

Figure D9. Deft 02-W-045, Barium Metaborate / Cerium Nitrate, High Solids.

3000-HOUR NEUTRAL SALT SPRAY SPECIMENS



Chromate Conversion
Coated Bare 7075-T6
Aluminum Substrates

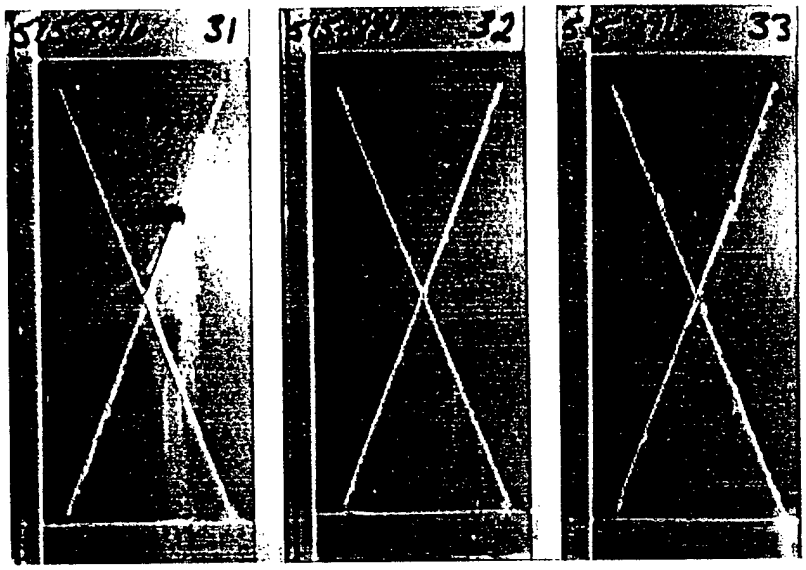
Chromate Conversion
Coated Bare 2024-T3
Aluminum Substrates

UMR Cerium Conversion
Coated Bare 7075-T6
Aluminum Substrates

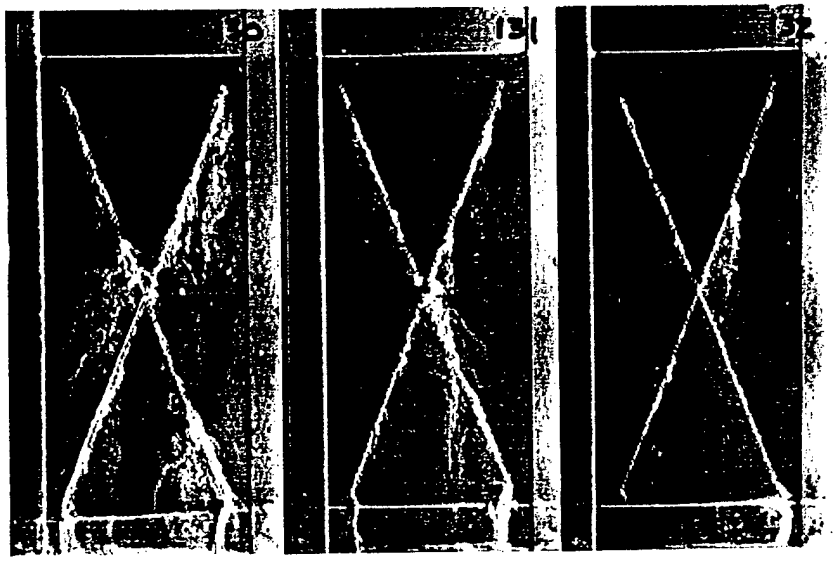
Specimens Removed From Test After
1000 Hours

Figure D10. Deft 02-W-046, Cerium Pentane Dionate, High Solids.

3000-HOUR NEUTRAL SALT SPRAY SPECIMENS



Chromate Conversion
Coated Bare 7075-T6
Aluminum Substrates



Chromate Conversion
Coated Bare 2024-T3
Aluminum Substrates

UMR Cerium Conversion
Coated Bare 7075-T6
Aluminum Substrates

Specimens Removed From Test After
2000 Hours

Figure D11. Deft 02-W-044, Cerium Nitrate, High Solids.

The data presented in this report, to the best of my knowledge and belief, is complete, accurate and complies with all test requirements of the requesting document.

APPENDIX E

Filiform Corrosion Specimen

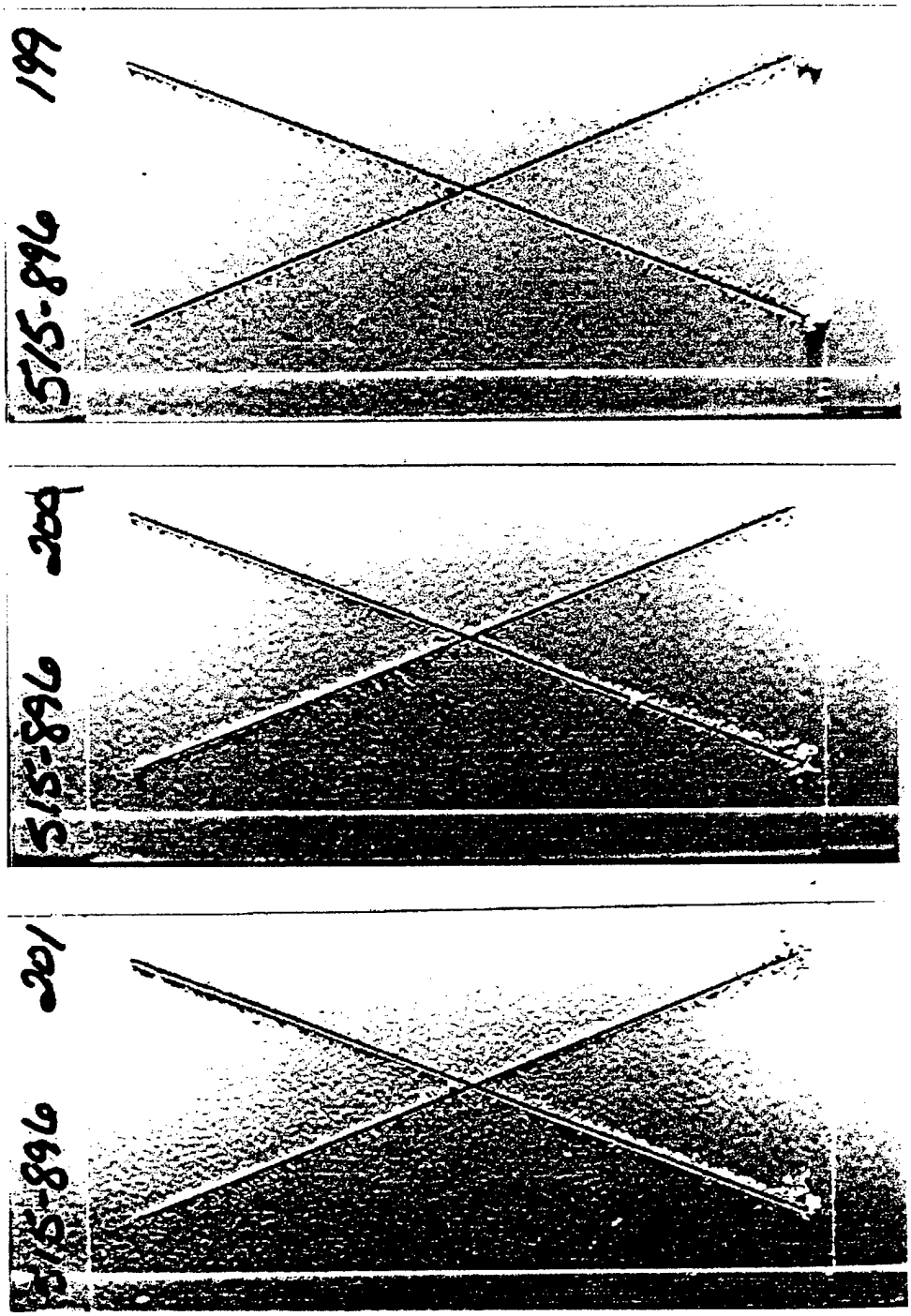
Photographic Documentation

PRIMER PAGE

Photographs of Specimens with Illumination from the Side

Deft 44-GN-72, Waterborne Chromated Control.	E3
Deft 44-W-31, Cerium phosphate, Waterborne	E4
Deft 44-W-30, Barium Metaborate, Waterborne	E5
Deft 02-W-043, K-White, High Solids	E6
Deft 44-W-32, Cerium Pentane Dionate, Waterborne	E7
Deft 02-Y-040, High Solids Chromated Control	E8
Deft 02-W-047, Cerium phosphate, High Solids	E9
Deft 02-W-042, Barium Metaborate, High Solids	E10
Deft 02-W-045, Barium Metaborate / cerium Nitrate, High Solids	E11
Deft 02-W-046, Cerium Pentane Dionate, High Solids	E12
Deft 02-W-044, Cerium Nitrate, High Solids	E13

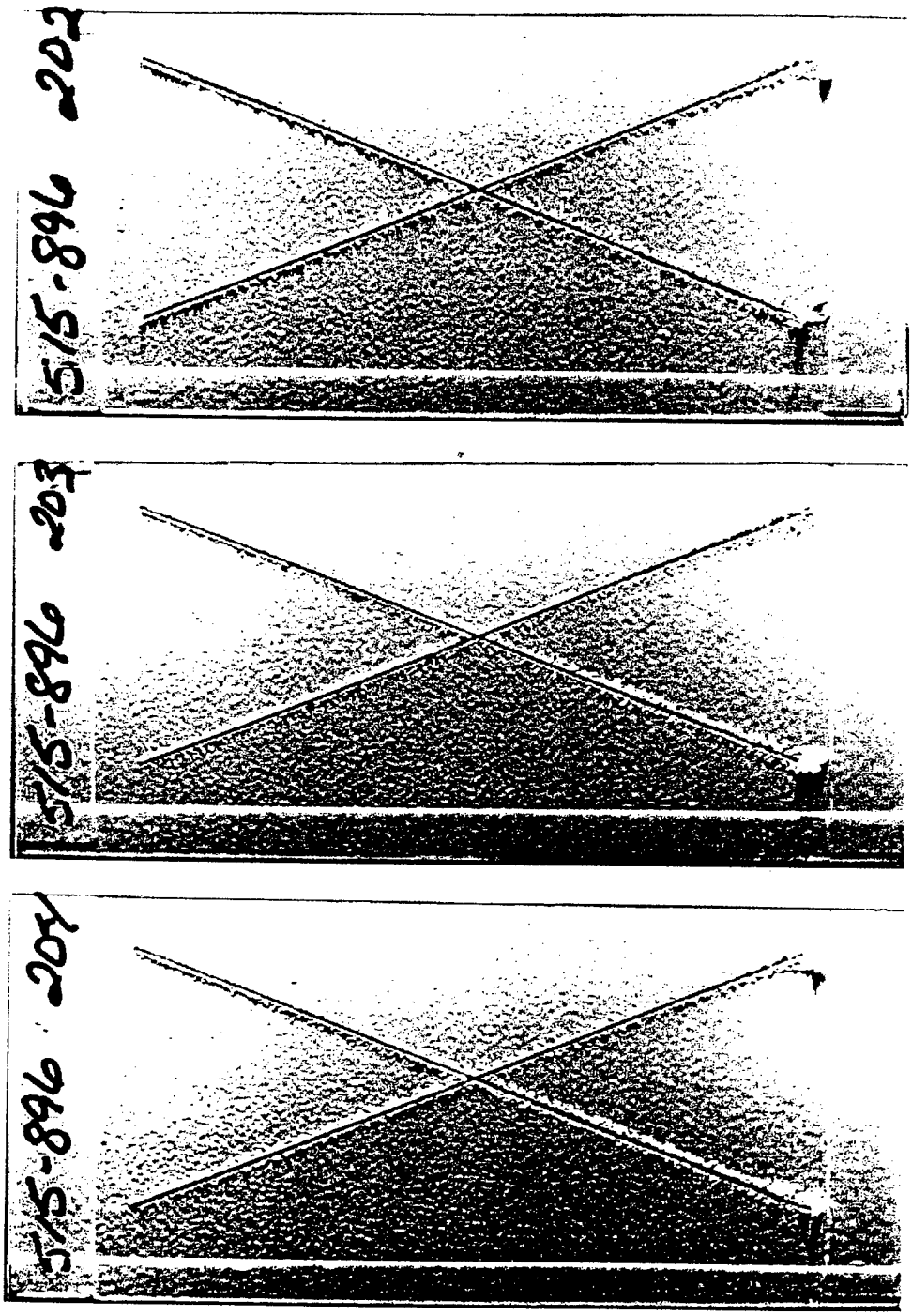
1000-HOUR FILIFORM CORROSION SPECIMENS



Conversion Coated Alclad 2024-T3 Substrates / PRC-DeSoto CA 8201/F17925 Gloss White Topcoat

Figure E1. Deft 44-GN-72, Waterborne Chromate Control.

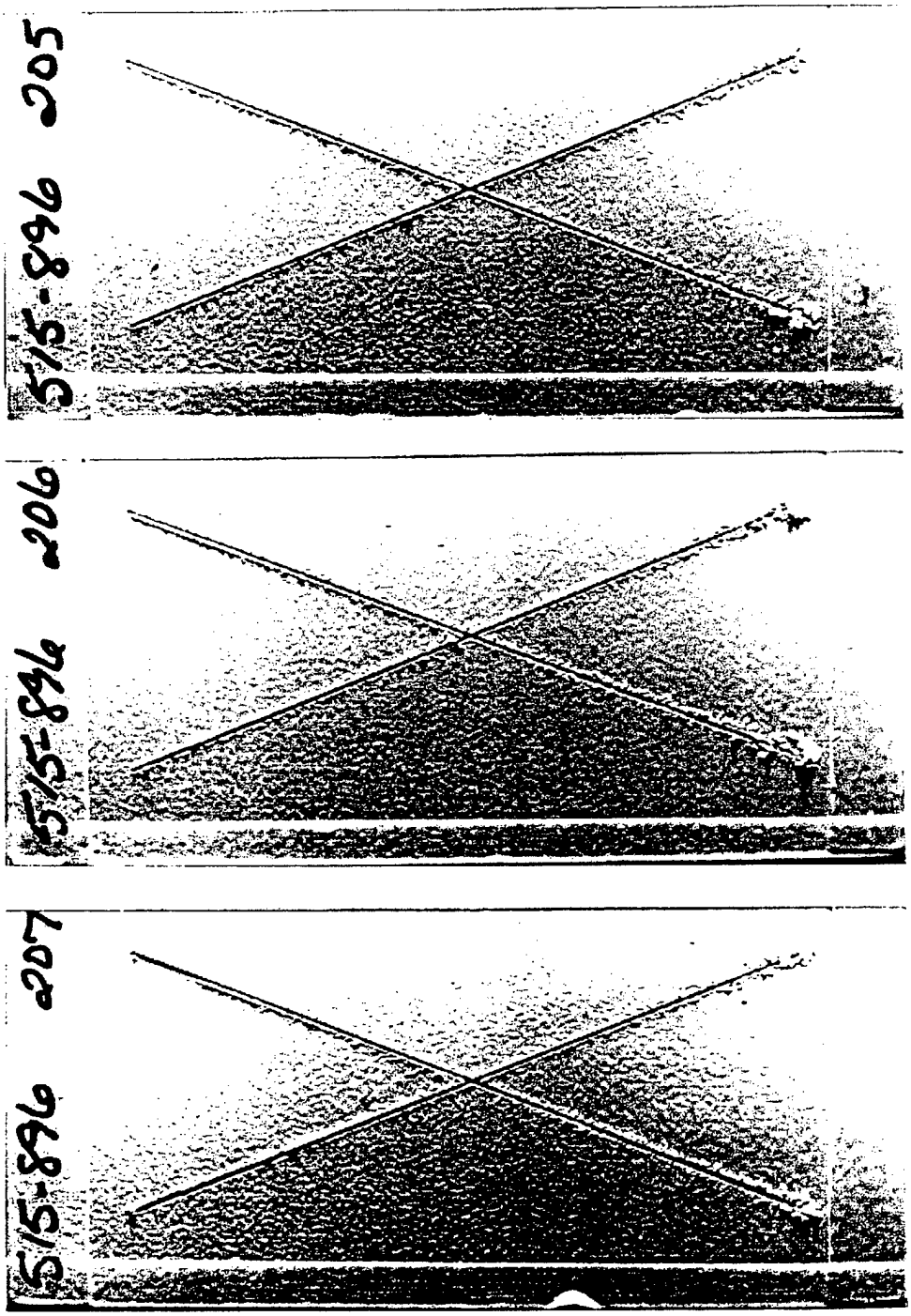
1000-HOUR FILIFORM CORROSION SPECIMENS



Conversion Coated Alclad 2024-T3 Substrates / PRC-DeSoto CA 8201/F17925 Gloss White Topcoat

Figure E2. Deft 44-W-31, Cerium Phosphate, Waterborne.

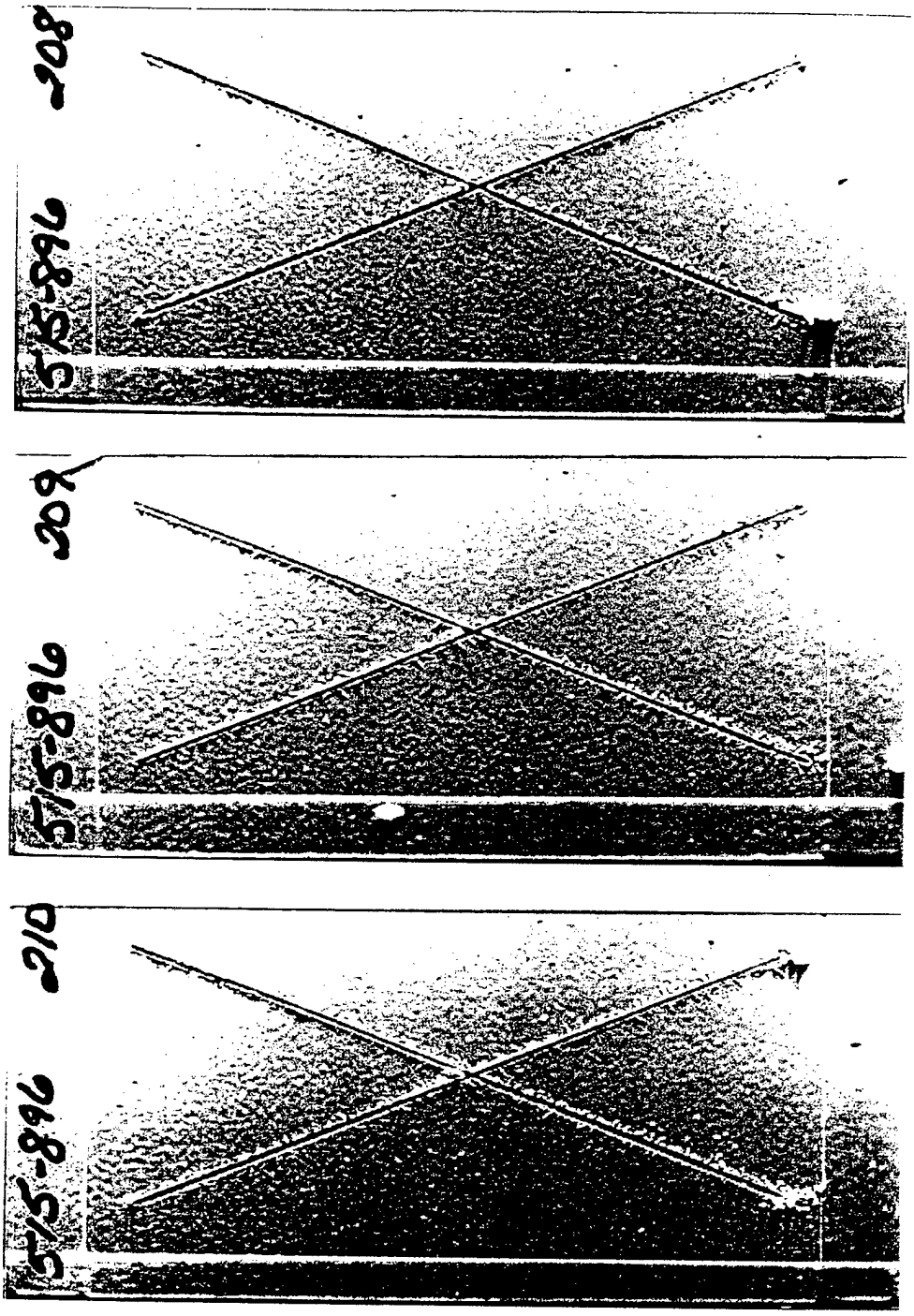
1000-HOUR FILIFORM CORROSION SPECIMENS



Conversion Coated Alclad 2024-T3 Substrates / PRC-DeSoto CA 8201/F17925 Gloss White Topcoat

Figure E3. Deft 44-W-30, Barium Metaborate, Waterborne.

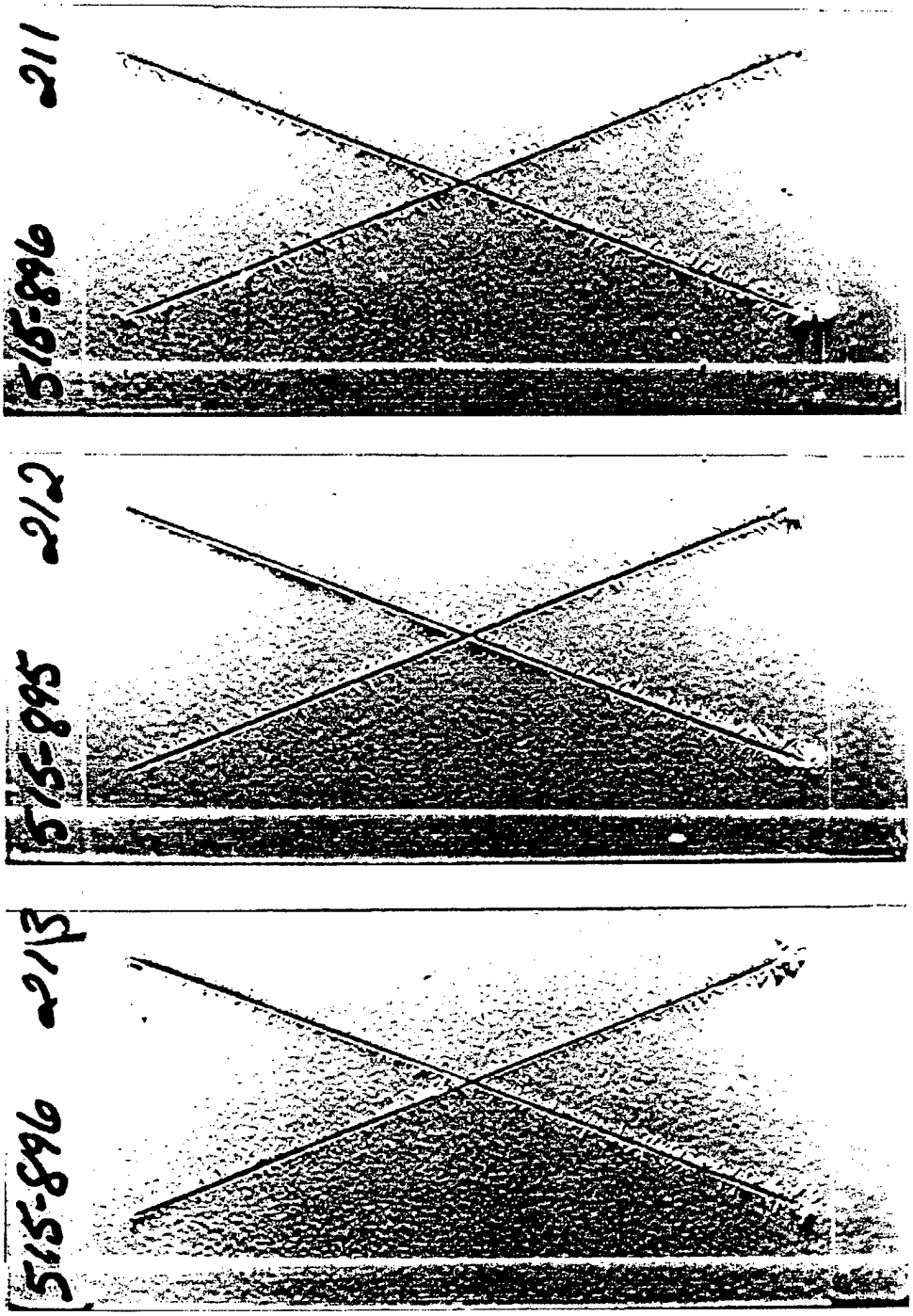
1000-HOUR FILIFORM CORROSION SPECIMENS



Conversion Coated Alclad 2024-T3 Substrates / PRC-DeSoto CA 8201/F17925 Gloss White Topcoat

Figure E4. Deft 02-W-043, K-White, High Solids.

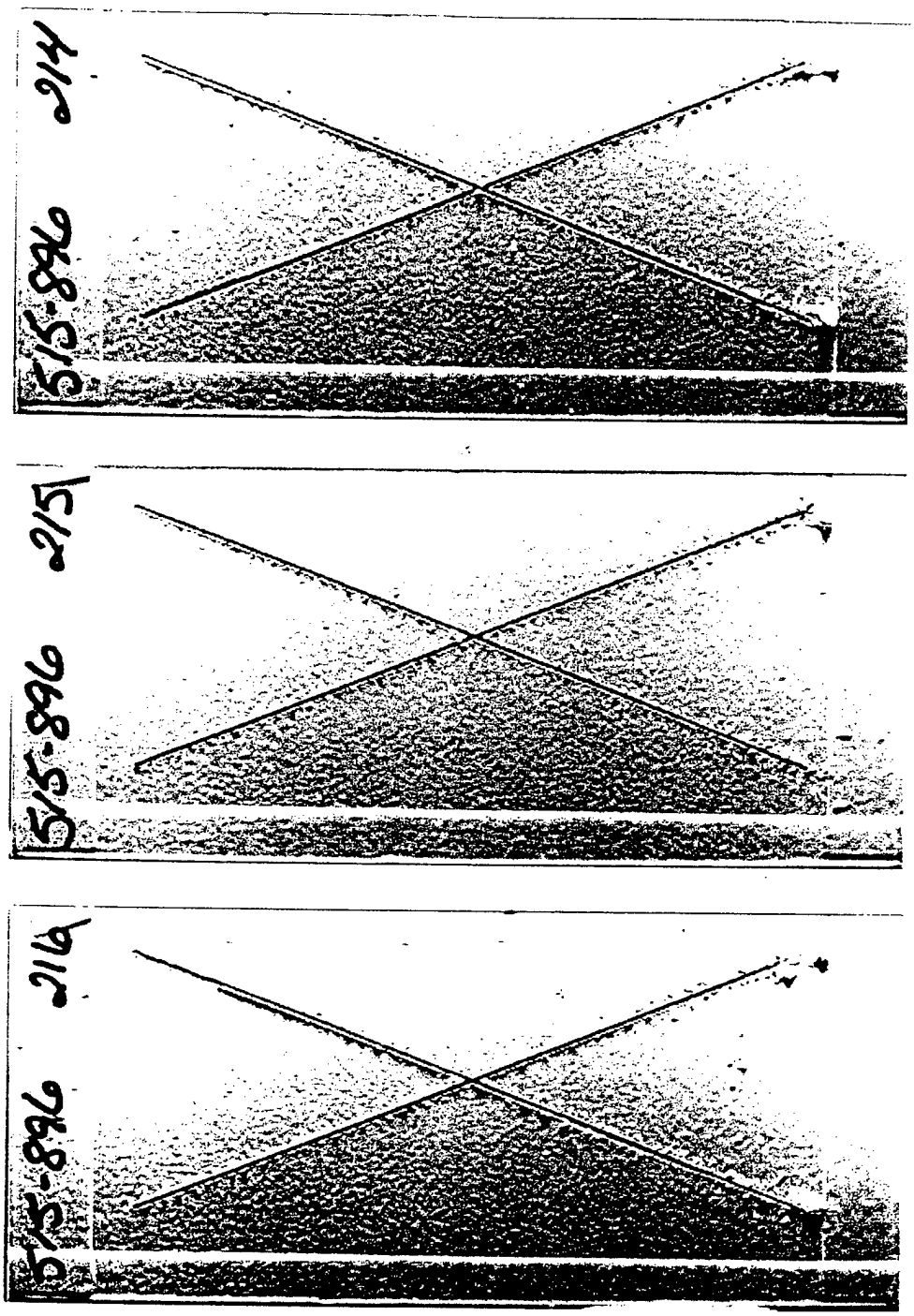
1000-HOUR FILIFORM CORROSION SPECIMENS



Conversion Coated Alclad 2024-T3 Substrates / PRC-DeSoto CA 8201/F17925 Gloss White Topcoat

Figure E5. Deft 44-W-32, Cerium Pentane Dionate, Waterborne.

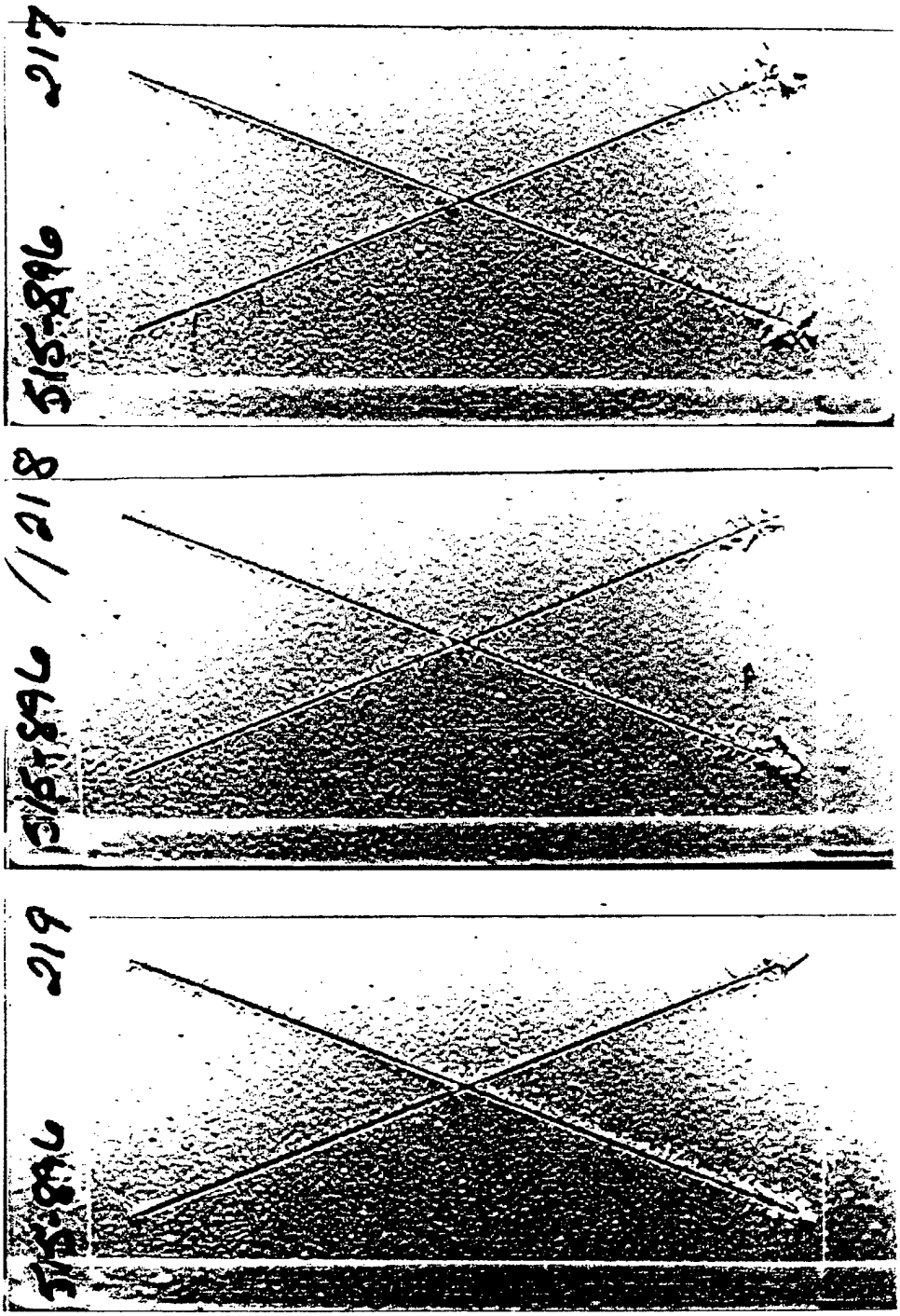
1000-HOUR FILIFORM CORROSION SPECIMENS



Conversion Coated Alclad 2024-T3 Substrates / PRC-DeSoto CA 8201/F17925 Gloss White Topcoat

Figure E6. Deft 02-Y-040, High Solids Chromate Control.

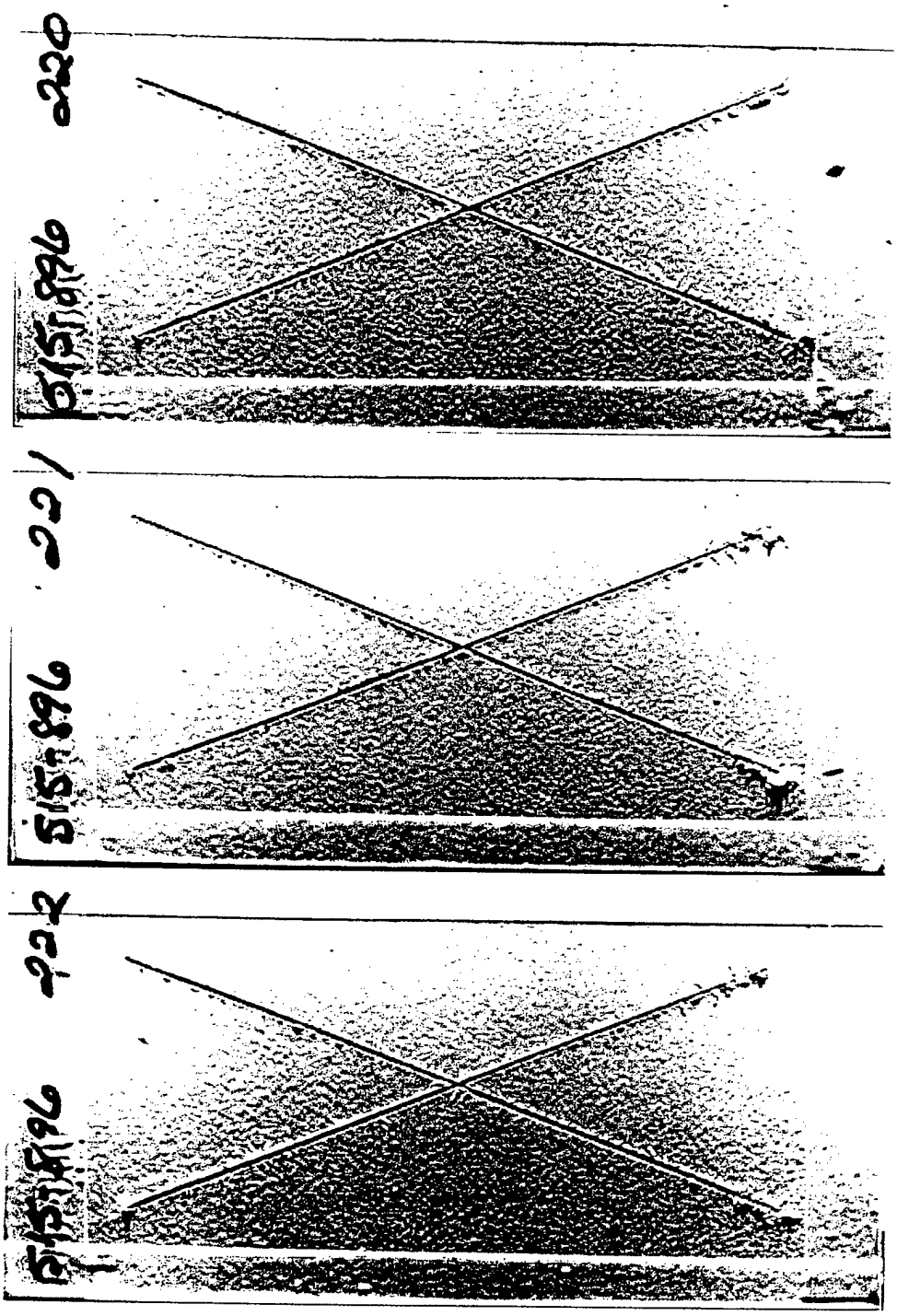
1000-HOUR FILIFORM CORROSION SPECIMENS



Conversion Coated Alclad 2024-T3 Substrates / PRC-DeSoto CA 8201/F17925 Gloss White Topcoat

Figure E7. Deft 02-W-047, Cerium Phosphate, High Solids.

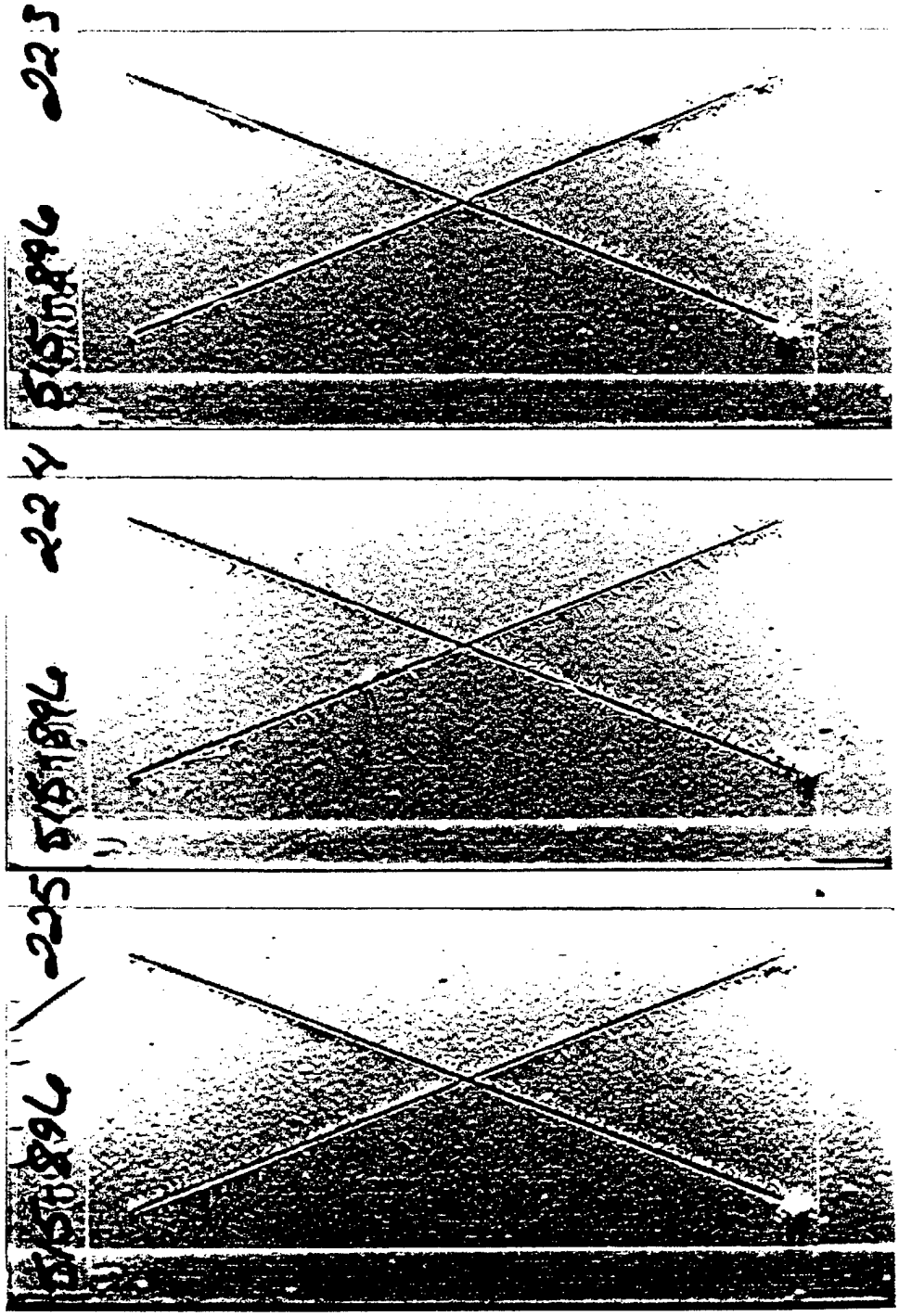
1000-HOUR FILIFORM CORROSION SPECIMENS



Conversion Coated Alclad 2024-T3 Substrates / PRC-DeSoto CA 8201/F17925 Gloss White Topcoat

Figure E8. Deft 02-W-042, Barium Metaborate, High Solids.

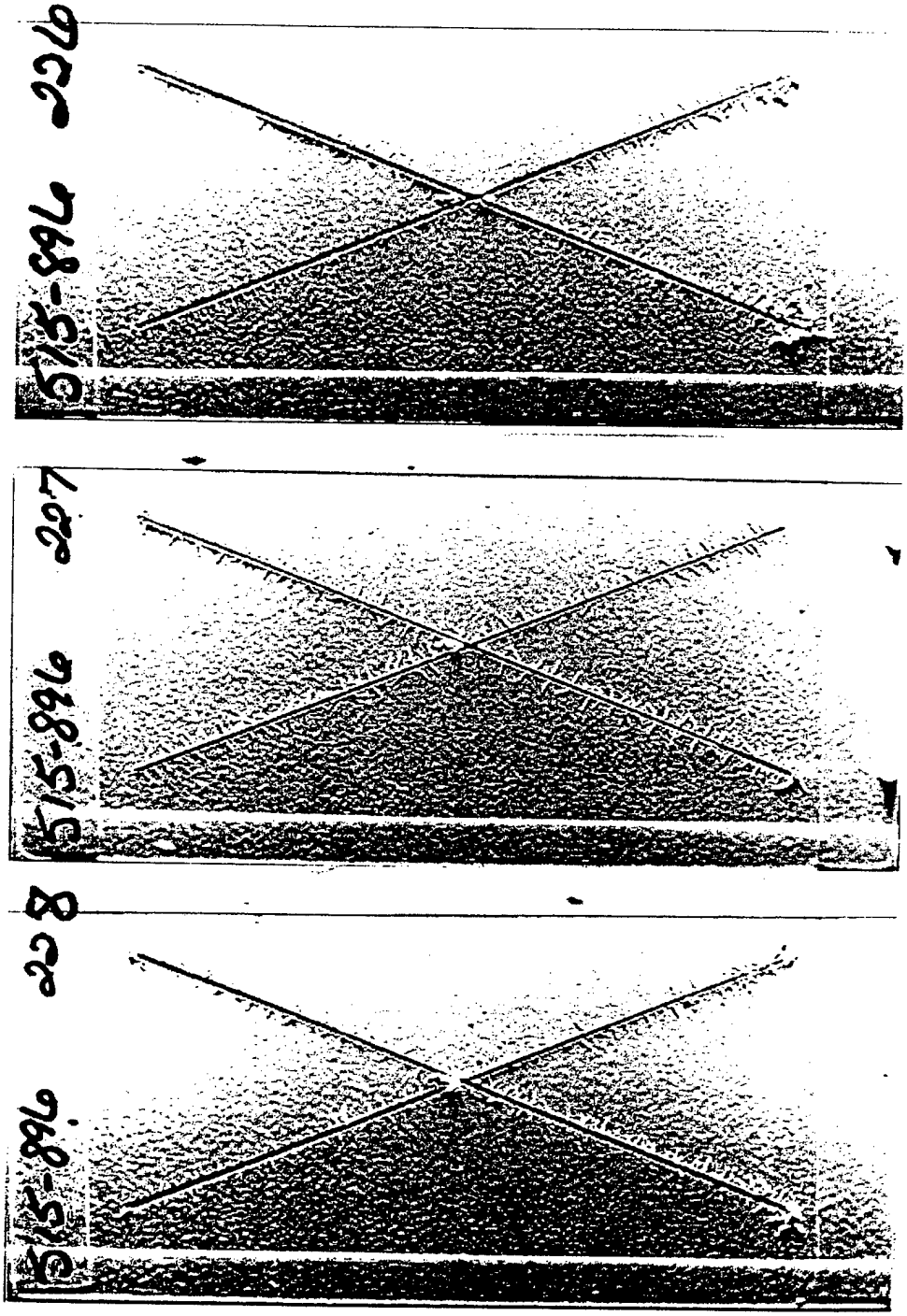
1000-HOUR FILIFORM CORROSION SPECIMENS



Conversion Coated Alclad 2024-T3 Substrates / PRC-DeSoto CA 8201/F17925 Gloss White Topcoat

Figure E9. Deft 02-W-045, Barium Metaborate / Cerium Nitrate, High Solids.

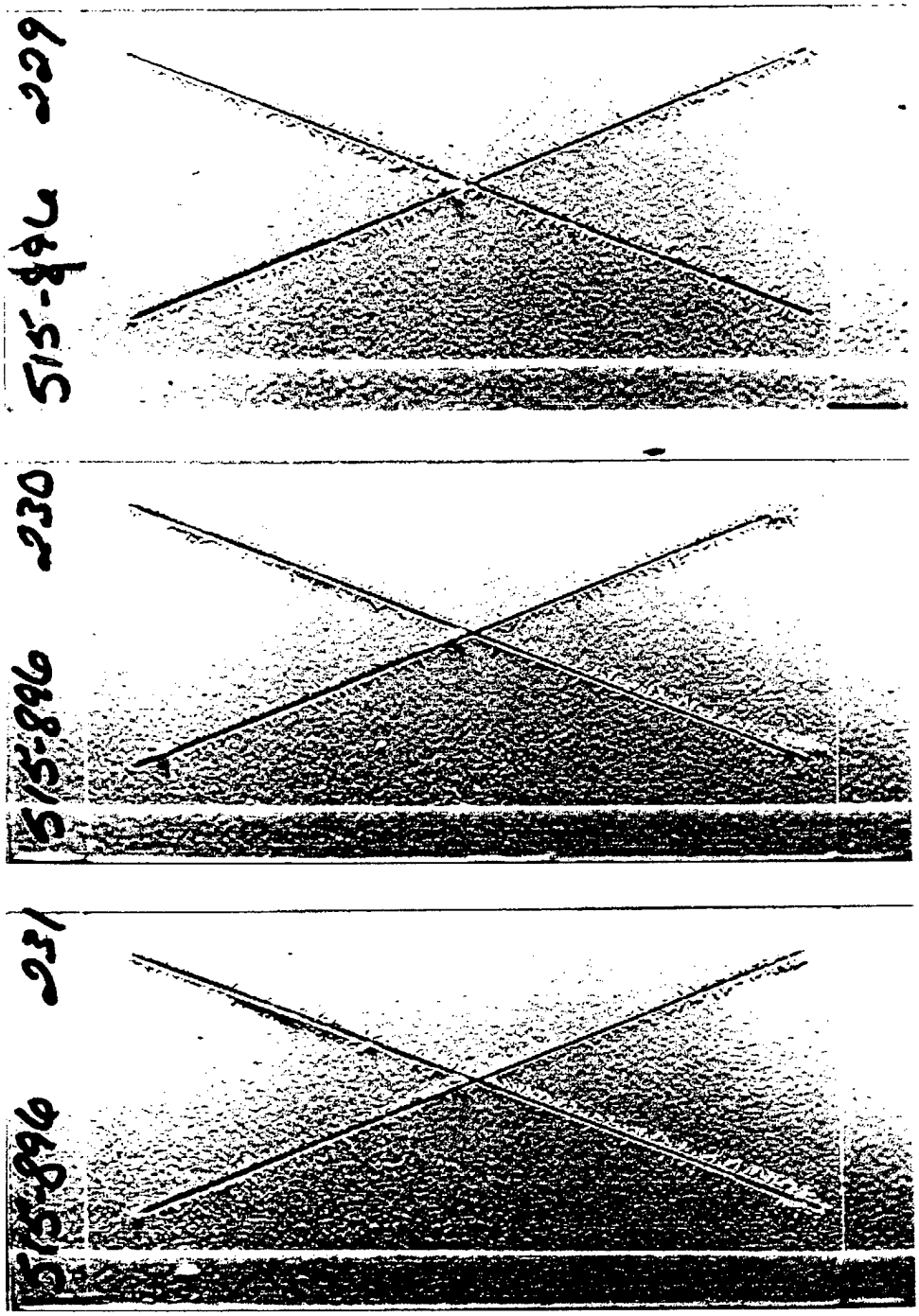
1000-HOUR FILIFORM CORROSION SPECIMENS



Conversion Coated Alclad 2024-T3 Substrates / PRC-DeSoto CA 8201/F17925 Gloss White Topcoat

Figure E10. Deft 02-W-046, Cerium Pentane Dionate, High Solids.

1000-HOUR FILIFORM CORROSION SPECIMENS



Conversion Coated Alclad 2024-T3 Substrates / PRC-DeSoto CA 8201/F17925 Gloss White Topcoat

Figure E11. Deft 02-W-044, Cerium Nitrate, High Solids.

The data presented in this report, to the best of my knowledge and belief, is complete, accurate and complies with all test requirements of the requesting document.

APPENDIX F

Corrosion Inspection Data

TEST TYPE **PAGE**

Table 1. ASTM G 85 Accelerated Corrosion (SO_2/Salt Spray)
Chromate Conversion Coated 2024-T3 Bare Aluminum Substrates F3

Table 2. ASTM B 117 5% Salt Spray
Chromate Conversion Coated 7075-T6 Bare Aluminum Substrates F5

Table 3. ASTM B 117 5% Salt Spray
Chromate Conversion Coated 2024-T3 Bare Aluminum Substrates F9

Table 4. ASTM B 117 5% Salt Spray
Cerium Conversion Coated 7075-T6 Bare Aluminum Substrates F13

Table 5. Corrosion Inspection Code Definitions F16

Table 1. SO_2 Corrosion Test Results

ALLOY	PRIMER	PANEL ID	HRS	CORROSION CODES [1]	BLISTER COUNT / COMMENTS
2024-T3 Bare Aluminum Conversion Coated Per P.S. 13209					
	Deft 44-GN-72 Water-Reducible Control	232	168		
			336		
		233	168		
			336		
		234	168		
			336		
	Cerium Phosphate Water-Reducible	235	168		
			336		
		236	168		
			336		
		237	168		
			336		
	Barium Metaborate Water-Reducible	238	168		
			336		
		239	168		
			336		
		240	168		
			336		
	K-White High Solids	241	168		
			336		
		242	168		
			336		
		243	168		
			336		
	Cerium Pentane Dionate Water-Reducible	244	168		
			336		
		245	168		
			336		
		246	168		
			336		
	Deft 02-Y-040 High Solids Control	247	168		
			336		
		248	168		
			336		
		249	168		
			336		

Chromate Conversion Coated Bare 2024-T3.

Table 1 (cont.).

Table 1. SO_2 Corrosion Test Results

ALLOY	PRIMER	PANEL ID	HRS	CORROSION CODES [1]	BLISTER COUNT / COMMENTS
2024-T3 Bare Aluminum Conversion Coated Per P.S. 13209					
	Cerium Phosphate High Solids	250	168		
			336		
		251	168		
			336		
		252	168		
			336		
	Barium Metaborate High Solids	253	168		
			336		
		254	168		
			336		
		255	168		
			336		
	Barium Metaborate / Cerium Nitrate High Solids	256	168		
			336		
		257	168		
			336		
		258	168		
			336		
	Cerium Pentane Dionate High Solids	259	168		
			336		
		260	168		
			336		
		261	168		
			336		
	Cerium Nitrate High Solids	262	168		
			336		
		263	168		
			336		
		264	168		
			336		

Note:
1 Corrosion code definitions are shown in Table 5.

Chromate Conversion Coated Bare 2024-T3.

Table 1.

Table 2. Neutral Salt Fog Corrosion Test Observations

ALLOY	PANEL ID	PRIMER TYPE	HRS	CORROSION CODES [1]	COMMENTS
7075-T6 Bare Aluminum Conversion Coated Per P.S. 13209	1	Deft 44GN72 (Waterborne Control)	1000	2 3 4 5 6 7 8 9 10 11 12 13 14 15 / B C D E F G H	
			1500		
			2000		
			2500		
			3000		
	2		1000	2 3 4 5 6 7 8 9 10 11 12 13 14 15 / B C D E F G H	
			1500		
			2000		
			2500		
			3000		
	3		1000	2 3 4 5 6 7 8 9 10 11 12 13 14 15 / B C D E F G H	
			1500		
			2000		
			2500		
			3000		
	4	Cerium Phosphate	1000	1 2 4 5 7 8 9 10 11 12 13 14 15 / B C D E F G H	
			1500		
			2000		
			2500		
			3000		
	5		1000	1 2 4 5 7 8 9 10 11 12 13 14 15 / B C D E F G H	
			1500		
			2000		
			2500		
			3000		
	6		1000	1 2 4 5 7 8 9 10 11 12 13 14 15 / B C D E F G H	
			1500		
			2000		
			2500		
			3000		
	7	Barium Metaborate	1000	1 2 4 5 7 8 9 10 11 12 13 14 15 / B C D E F G H	
			1500		
			2000		
			2500		
			3000		Many small blisters parellel to 1/4 section of lower scribe line
	8		1000	1 2 4 5 7 8 9 10 11 12 13 14 15 / B C D E F G H	
			1500		
			2000		
			2500		
			3000		Many small blisters below a scratch in center of panel (2 inch long trail of blisters)
	9		1000	1 2 4 5 7 8 9 10 11 12 13 14 15 / B C D E F G H	
			1500		
			2000		
			2500		
			3000		Many small blisters parellel to 1/4 section of lower scribe line

Chromate Conversion Coated Bare 7075-T6.

Table 2 (cont.).

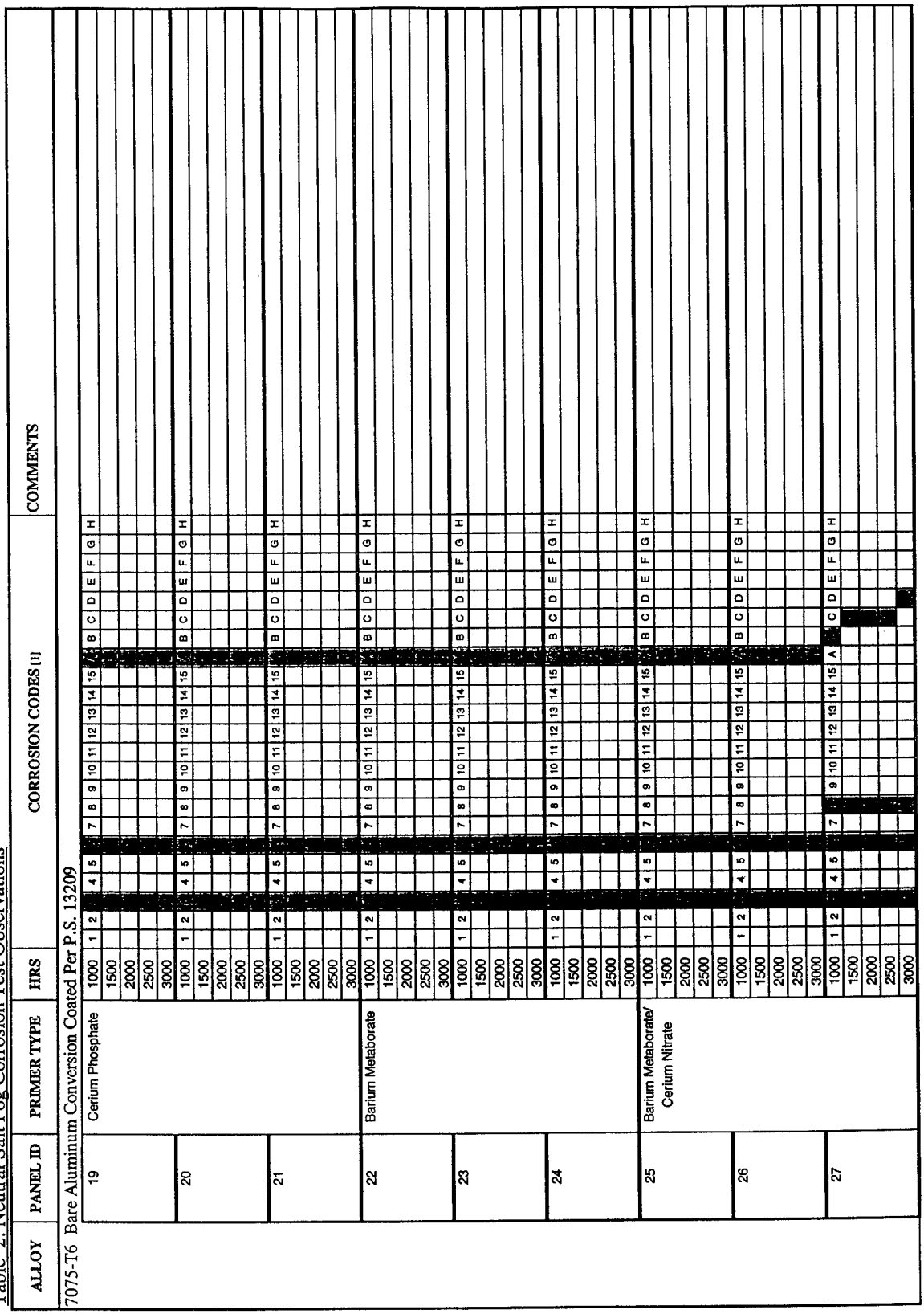
Table 2. Neutral Salt Fog Corrosion Test Observations

ALLOY	PANEL ID	PRIMER TYPE	HRS	CORROSION CODES [1]	COMMENTS
7075-T6 Bare Aluminum Conversion Coated Per P.S. 13209	10	K White 140	1000	1 2 4 5 7 8 9 10 11 12 13 14 15 B C D E F G H	
			1500		
			2000		
			2500		
			3000		
	11		1000	1 2 4 5 7 8 9 10 11 12 13 14 15 B C D E F G H	
			1500		
			2000		
			2500		
			3000		
	12		1000	1 2 4 5 7 8 9 10 11 12 13 14 15 B C D E F G H	
			1500		
			2000		
			2500		
			3000		
	13	Cerium Pentane Dionate	1000	1 2 4 5 7 8 9 10 11 12 13 14 15 B C D E F G H	
			1500		
			2000		
			2500		
			3000		
	14		1000	1 2 4 5 7 8 9 10 11 12 13 14 15 B C D E F G H	
			1500		
			2000		
			2500		
			3000		
	15		1000	1 2 4 5 7 8 9 10 11 12 13 14 15 B C D E F G H	
			1500		
			2000		
			2500		
			3000		
	16	Deft 02Y040 (High Solids Control)	1000	2 3 4 5 6 7 8 9 10 11 12 13 14 15 B C D E F G H	
			1500		
			2000		
			2500		
			3000		
	17		1000	2 3 4 5 6 7 8 9 10 11 12 13 14 15 B C D E F G H	
			1500		
			2000		
			2500		
			3000		
	18		1000	2 3 4 5 6 7 8 9 10 11 12 13 14 15 B C D E F G H	
			1500		
			2000		
			2500		
			3000		

Chromate Conversion Coated Bare 7075-T6.

Table 2 (cont.).

Table 2. Neutral Salt Fog Corrosion Test Observations



ALLOY	PANEL ID	PRIMER TYPE	HRS	CORROSION CODES [1]	COMMENTS
7075-T6 Bare Aluminum Conversion Coated Per P.S. 13209	19	Cerium Phosphate	1000	4 5 / 7 8 9 10 11 12 13 14 15 / B C D E F G H	
			1500		
			2000		
			2500		
			3000		
	20		1000	1 2 / 4 5 / 7 8 9 10 11 12 13 14 15 / B C D E F G H	
			1500		
			2000		
			2500		
			3000		
	21		1000	1 2 / 4 5 / 7 8 9 10 11 12 13 14 15 / B C D E F G H	
			1500		
			2000		
			2500		
			3000		
	22	Barium Metaborate	1000	1 2 / 4 5 / 7 8 9 10 11 12 13 14 15 / B C D E F G H	
			1500		
			2000		
			2500		
			3000		
	23		1000	1 2 / 4 5 / 7 8 9 10 11 12 13 14 15 / B C D E F G H	
			1500		
			2000		
			2500		
			3000		
	24		1000	1 2 / 4 5 / 7 8 9 10 11 12 13 14 15 / B C D E F G H	
			1500		
			2000		
			2500		
			3000		
	25	Barium Metaborate/ Cerium Nitrate	1000	1 2 / 4 5 / 7 8 9 10 11 12 13 14 15 / B C D E F G H	
			1500		
			2000		
			2500		
			3000		
	26		1000	1 2 / 4 5 / 7 8 9 10 11 12 13 14 15 / B C D E F G H	
			1500		
			2000		
			2500		
			3000		
	27		1000	1 2 / 4 5 / 7 9 10 11 12 13 14 15 A / C D E F G H	
			1500		
			2000		
			2500		
			3000		

Chromate Conversion Coated Bare 7075-T6.

Table 2 (cont.).

Table 2. Neutral Salt Fog Corrosion Test Observations

ALLOY	PANEL ID	PRIMER TYPE	HRS	CORROSION CODES [1]	COMMENTS
7075-T6 Bare Aluminum Conversion Coated Per P.S. 13209	28	Cerium Pentane Dionate	1000	10	
			1500	10	
			2000	10	
			2500	10	
			3000	10	
	29		1000	10	
			1500	10	
			2000	10	
			2500	10	
			3000	10	
	30		1000	10	
			1500	10	
			2000	10	
			2500	10	
			3000	10	
	31	Cerium Nitrate	1000	9 A B C E	
			1500	9	
			2000	9	
			2500	9	
			3000	9	One blister along scribe line
	32		1000	9	
			1500	9	
			2000	9	
			2500	9	
			3000	9	
	33		1000	9	
			1500	9	
			2000	9	
			2500	9	
			3000	9	

Note:
1 Corrosion code definitions are shown in Table 5.

Chromate Conversion Coated Bare 7075-T6.

Table 2.

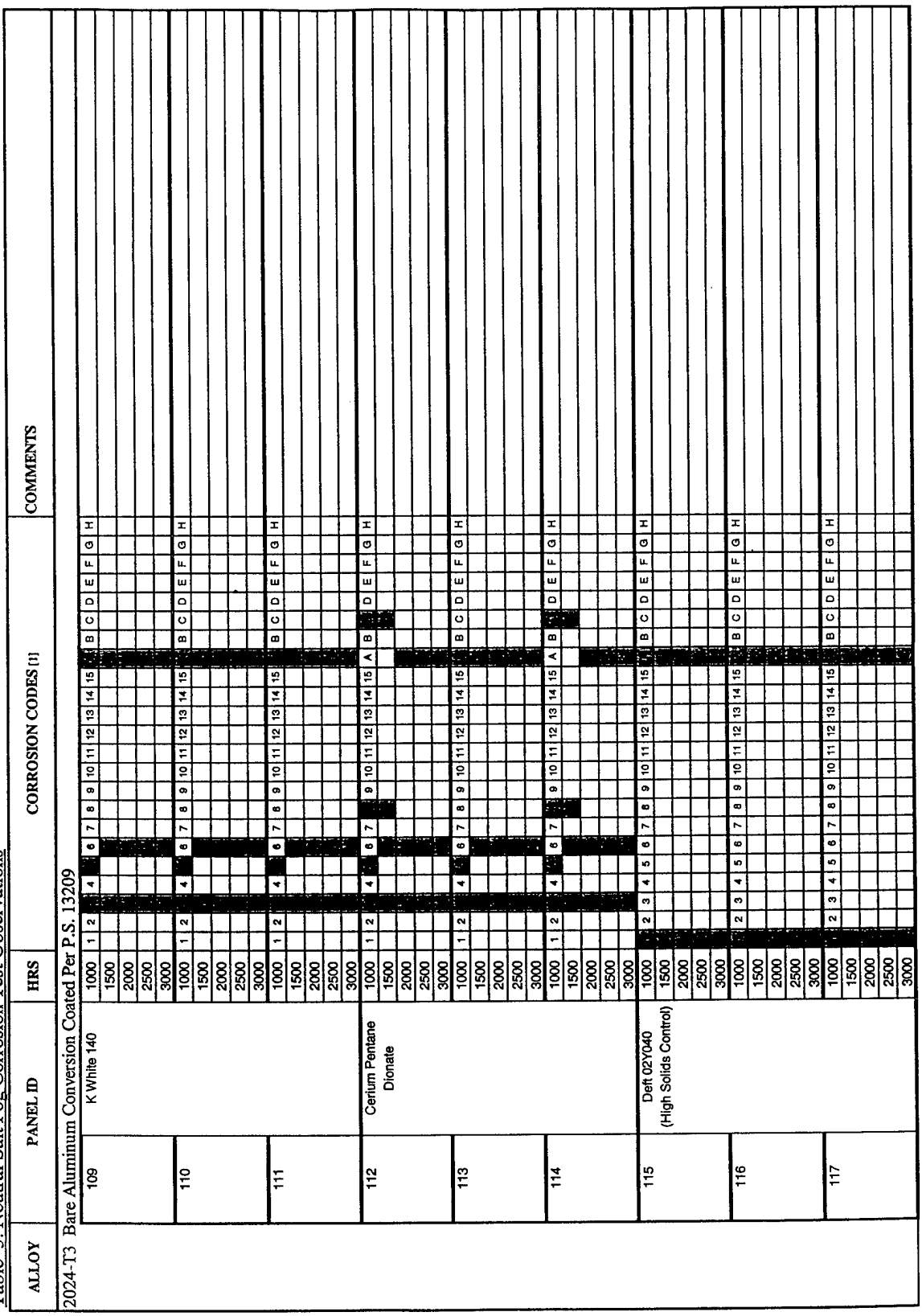
Table 3. Neutral Salt Fog Corrosion Test Observations

ALLOY	PANEL ID	HRS	CORROSION CODES [1]	COMMENTS
2024-T3 Bare Aluminum Conversion Coated Per P.S. 13209	100 Deft 44GN72 (Waterborne Control)	1000	4 6 7 8 9 10 11 12 13 14 15 B C D E F G H	
		1500		
		2000		
		2500		
		3000		
	101	1000	2 3 4 5 6 7 8 9 10 11 12 13 14 15 B C D E F G H	
		1500		
		2000		
		2500		
		3000		
	102	1000	2 3 4 5 6 7 8 9 10 11 12 13 14 15 B C D E F G H	
		1500		
		2000		
		2500		
		3000		
	103 Cerium Phosphate	1000	1 2 4 6 7 8 9 10 11 12 13 14 15 B C D E F G H	
		1500		
		2000		
		2500		
		3000		A few 1/32 inch dia blisters in the field area near scribe lines
	104	1000	1 2 4 6 7 8 9 10 11 12 13 14 15 B C D E F G H	
		1500		
		2000		
		2500		
		3000		A few 1/32 inch dia blisters in the field area near scribe lines
	105	1000	1 2 4 6 7 8 9 10 11 12 13 14 15 B C D E F G H	
		1500		
		2000		
		2500		
		3000		A few 1/32 inch dia blisters in the field area near scribe lines
	106 Barium Metaborate	1000	1 2 4 6 7 8 9 10 11 12 13 14 15 B C D E F G H	
		1500		
		2000		
		2500		
		3000		Many blisters up to 1/8 inch dia in the field area near scribe lines
	107	1000	1 2 4 6 7 8 9 10 11 12 13 14 15 B C D E F G H	
		1500		
		2000		
		2500		
		3000		Many blisters up to 1/8 inch dia in the field area near scribe lines
	108	1000	1 2 4 6 7 8 9 10 11 12 13 14 15 B C D E F G H	
		1500		
		2000		
		2500		
		3000		Many blisters up to 1/8 inch dia in the field area near scribe lines

Chromate Conversion Coated Bare 2024-T3.

Table 3 (cont.).

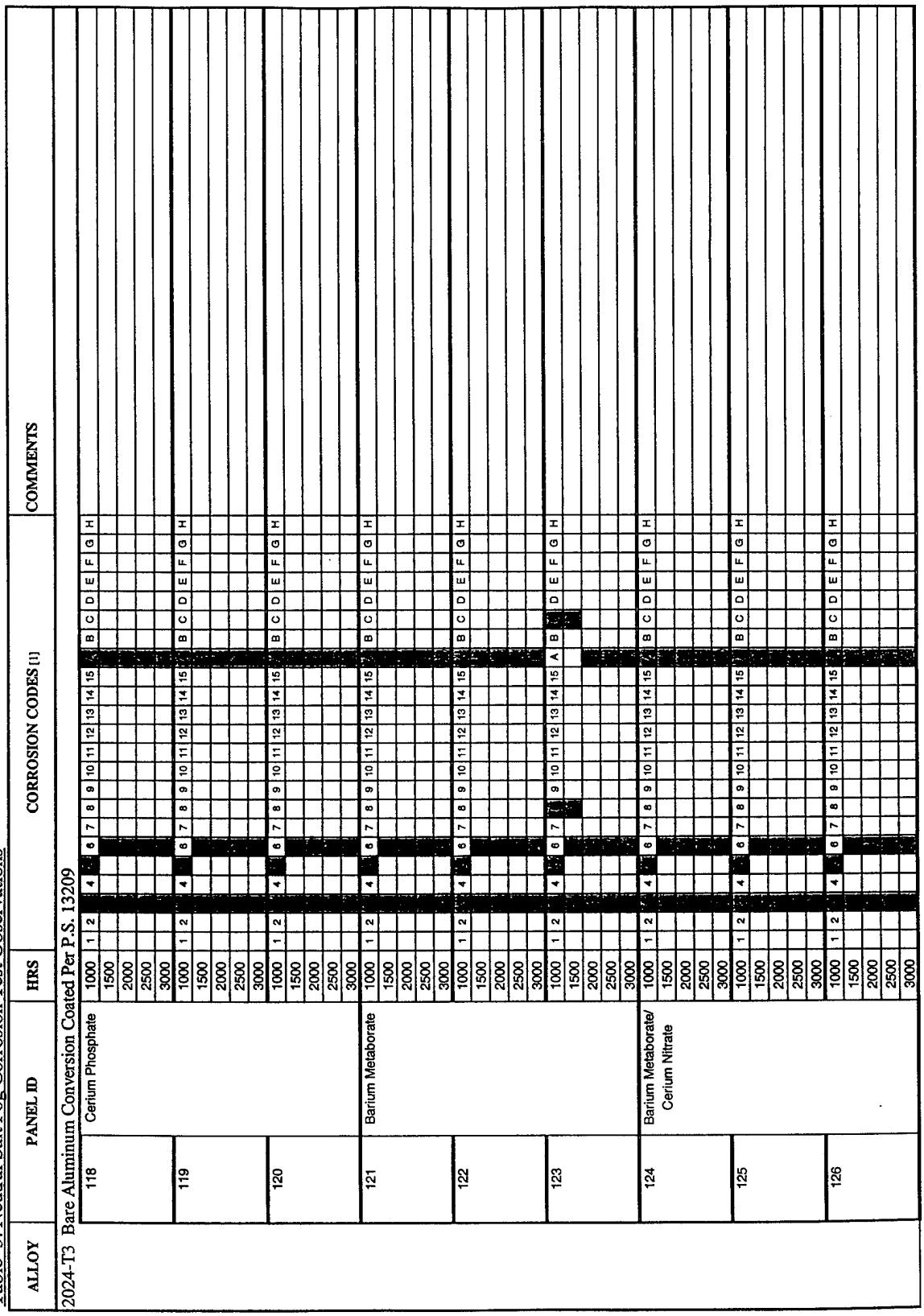
Table 3. Neutral Salt Fog Corrosion Test Observations



Chromate Conversion Coated Bare 2024-T3.

Table 3 (cont.).

Table 3. Neutral Salt Fog Corrosion Test Observations



Chromate Conversion Coated Bare 2024-T3.

Table 3 (cont.).

Table 3. Neutral Salt Fog Corrosion Test Observations

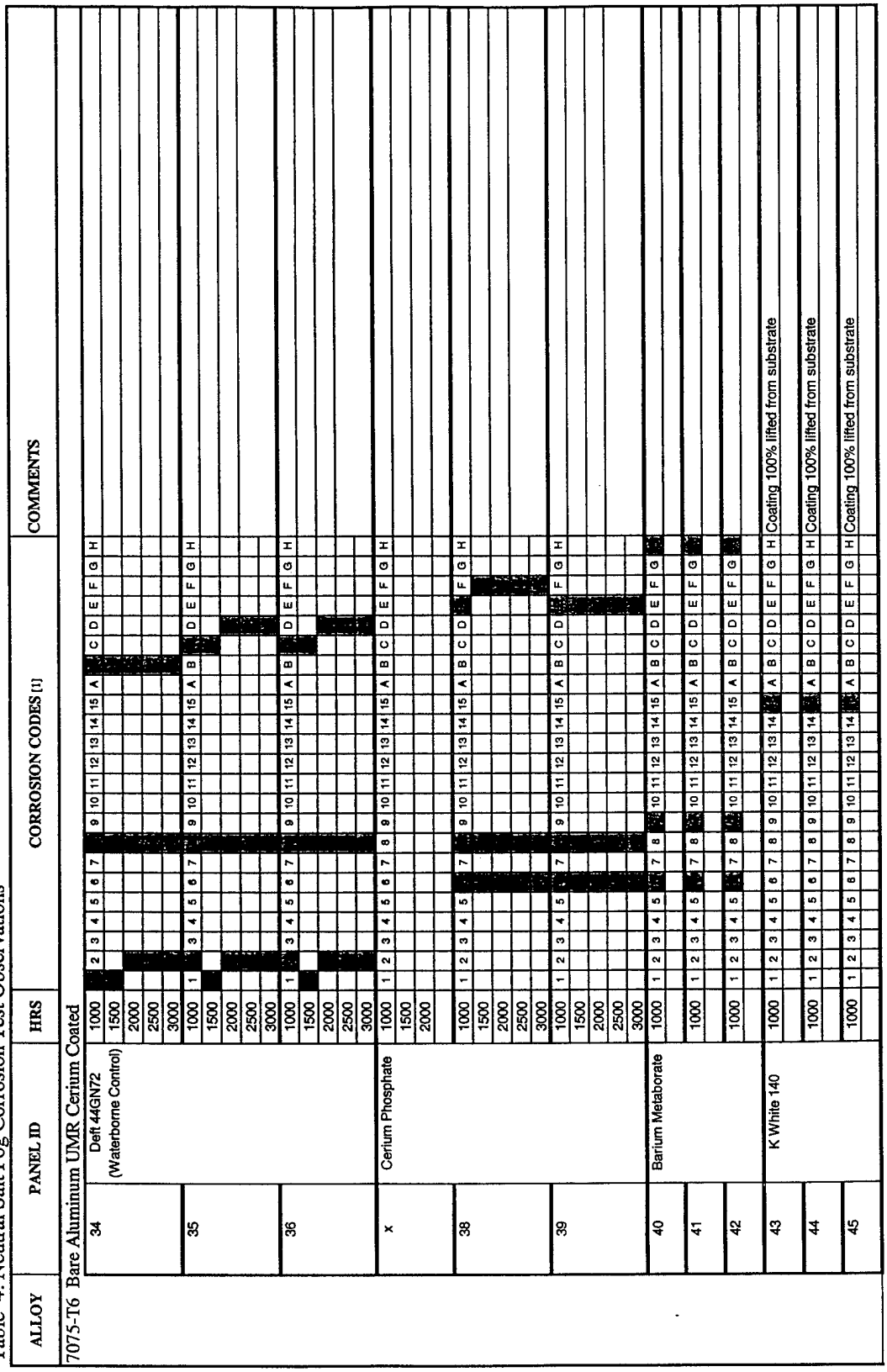
ALLOY	PANEL ID	HRS	CORROSION CODES [1]	COMMENTS
2024-T3 Bare Aluminum Conversion Coated Per P.S. 13209				
	127	Cerium Pentane Dionate	1000 1 2 4 6 7 9 10 11 12 13 14 15 A C D E F G H	
			1500	
			2000	
			2500	
			3000	
	128		1000 1 2 4 6 7 8 9 10 11 12 13 14 15 B C D E F G H	
			1500	
			2000	
			2500	
			3000	
	129		1000 1 2 4 6 7 8 9 10 11 12 13 14 15 B C D E F G H	
			1500	
			2000	
			2500	
			3000	
	130	Cerium Nitrate	1000 1 2 4 5 7 8 9 10 11 12 13 14 15 B C D E F G H	
			1500	
			2000	
			2500	
			3000	A few blisters up to 1/16 inch dia near scribe lines
	131		1000 1 2 4 6 7 9 10 11 12 13 14 15 A B C E F G H	
			1500	
			2000	
			2500	
			3000	A few blisters up to 1/32 inch dia near scribe lines
	132		1000 1 2 4 6 7 9 10 11 12 13 14 15 A B C E F G H	
			1500	
			2000	
			2500	
			3000	A few blisters up to 1/32 inch dia near scribe lines

Note:
1 Corrosion code definitions are shown in Table 5.

Chromate Conversion Coated Bare 2024-T3.

Table 3.

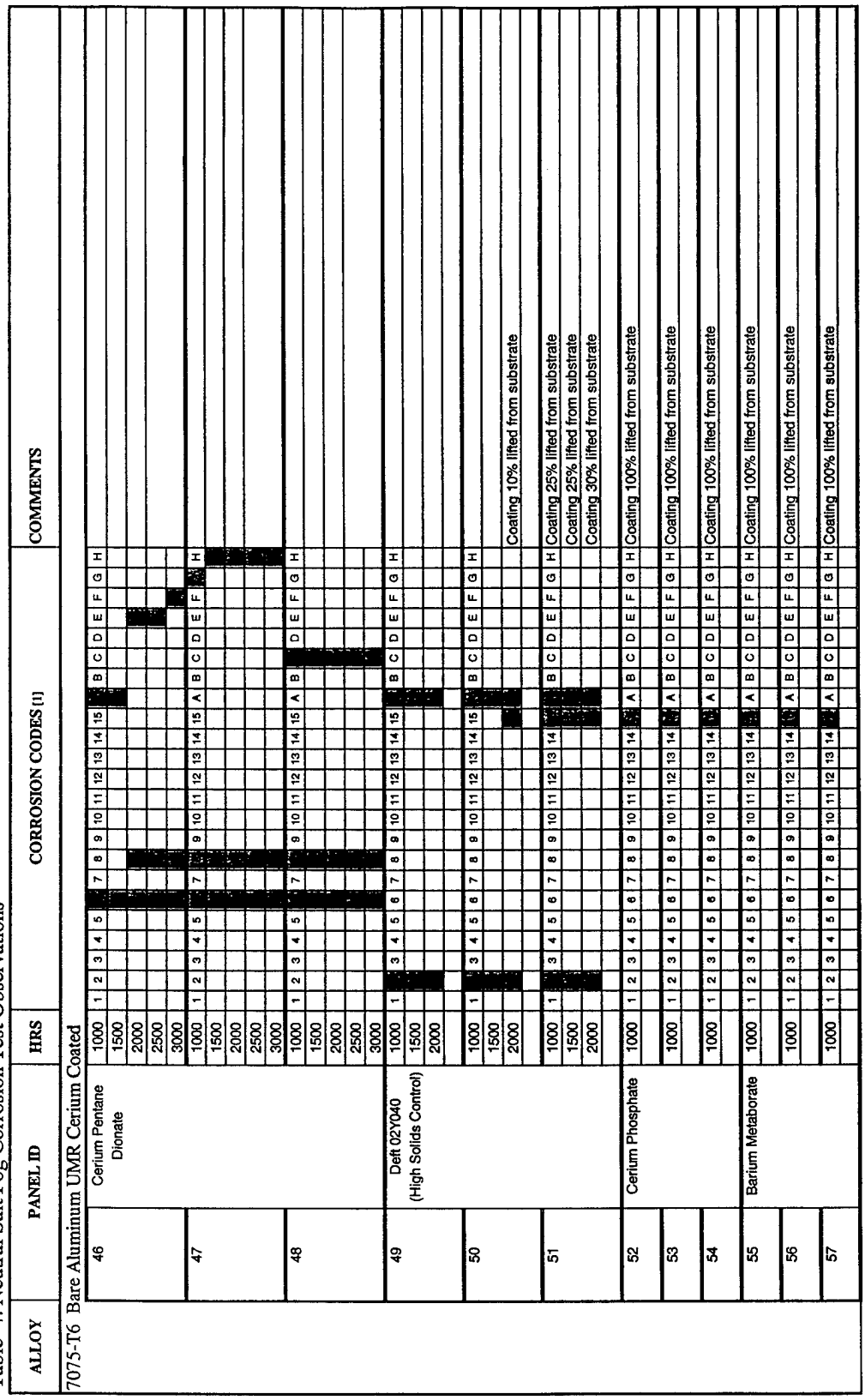
Table 4. Neutral Salt Fog Corrosion Test Observations



Cerium Conversion Coated Bare 7075-T6.

Table 4 (cont.).

Table 4. Neutral Salt Fog Corrosion Test Observations



ALLOY	PANEL ID	HRS	CORROSION CODES [1]	COMMENTS
7075-T6 Bare Aluminum UMR Cerium Coated				
46	Cerium Pentane Dionate	1000		
		1500		
		2000		
		2500		
		3000		
47		1000		
		1500		
		2000		
		2500		
		3000		
48		1000		
		1500		
		2000		
		2500		
		3000		
49	Deft 02Y040 (High Solids Control)	1000		
		1500		
		2000		
50		1000		Coating 10% lifted from substrate
		1500		
		2000		
51		1000		Coating 25% lifted from substrate
		1500		Coating 25% lifted from substrate
		2000		Coating 30% lifted from substrate
52	Cerium Phosphate	1000		Coating 100% lifted from substrate
53		1000		Coating 100% lifted from substrate
54		1000		Coating 100% lifted from substrate
55	Barium Metaborate	1000		Coating 100% lifted from substrate
56		1000		Coating 100% lifted from substrate
57		1000		Coating 100% lifted from substrate

Cerium Conversion Coated Bare 7075-T6.

Table 4 (cont.).

Table 4. Neutral Salt Fog Corrosion Test Observations

ALLOY	PANEL ID	HRS	CORROSION CODES [1]	COMMENTS
7075-T6 Bare Aluminum UMR Cerium Coated				
58	Barium Metaborate/ Cerium Nitrate	1000		Coating 5% lifted from substrate
		1500		Coating 10% lifted from substrate
		2000		Coating 30% lifted from substrate
59		1000		Coating 12% lifted from substrate
		1500		Coating 20% lifted from substrate
		2000		Coating 30% lifted from substrate
60		1000		
		1500		
		2000		Coating 20% lifted from substrate
61	Cerium Pentane	1000		Coating 100% lifted from substrate
62		1000		Coating 100% lifted from substrate
63		1000		Coating 100% lifted from substrate
64	Cerium Nitrate	1000		
		1500		
		2000		
65		1000		Coating 90% lifted from substrate
		1500		
		2000		Coating 95% lifted from substrate
66		1000		
		1500		Coating 35% lifted from substrate
		2000		Coating 85% lifted from substrate

Note:
1 Corrosion code definitions are shown in Table 5.

Cerium Conversion Coated Bare 7075-T6.

Table 4.

Table 5. Corrosion Test Finding Codes

1	Scribe line beginning to darken or shiny scribe.
2	Scribe lines > 50% darkened.
3	Scribe line dark or darkening.
4	Several localized sites of white salt in scribe lines.
5	Many localized sites of white salt in scribe lines.
6	White salt filling scribe lines.
7	Dark corrosion sites in scribe lines.
8	Few blisters under primer along scribe line. (<12)
9	Many blisters under primer along scribe line.
10	Slight lift along scribe lines.
11	Coating curling up along scribe.
12	Pin point sites/pits of corrosion on organic coating surface (1/16" to 1/8" dia.).
13	One or more blisters on surface away from scribe.
14	Many blisters under primer away from scribe.
15	Starting to blister over surface
	Scribe line ratings
A.	No creepage
B.	0 to 1/64 inch of corrosion creepage beyond the scribe
C.	1/64 to 1/32 inch of corrosion creepage beyond the scribe
D	1/32 to 1/16 inch of corrosion creepage beyond the scribe
E.	1/16 to 1/8 inch of corrosion creepage beyond the scribe
F.	1/8 to 3/16 inch of corrosion creepage beyond the scribe
G.	3/16 to 1/4 inch of corrosion creepage beyond the scribe
H.	1/4 to 3/8 inch of corrosion creepage beyond the scribe

The data presented in this report, to the best of my knowledge and belief, is complete, accurate and complies with all test requirements of the requesting document.