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Active metal-based corrosion protective coating systems for aircraft requiring no-chromate pretreatment☆

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ABSTRACT

There has been much R&D effort expended to develop pretreatments and coatings that allow the replacement of toxic, carcinogenic, mutagenic, environmentally hazardous chromates used as pretreatments and pigments in aircraft coating systems. There have been many claims for chromate replacement in primer and pretreatment systems for aircraft, but no systems presently are in use that can function and meet specifications without some form of chromate used in the pretreatment and/or primer. The Mg-rich primer technology developed at North Dakota State University and now in final commercial development at AKZO Nobel Aerospace Coatings shows that finally aerospace Al alloys can be protected against corrosion. With simple cleaning only or a non-chromate pretreatment, the Mg-rich primer (MgRP) + aerospace topcoat provides an aircraft protection system that gives corrosion protection that equals or exceeds any system using chromate in any form. About 18 peer reviewed papers have been published and at least twice that many presentations at technical meetings describing this new aircraft primer technology. There are an extensive number of samples in outdoor exposure, and in exposure on small parts of aircraft like port-hole covers and doors, and the coating system has been in accelerated exposure cabinets of all sorts. In the first versions of the magnesium primer premature blistering was noted during immersion or B117 continuous salt spray testing which may be due to hydrogen generation from water contact at a particle. Efforts to control the level of activity of the magnesium have been successfully accomplished since the testing reported in this paper which controls this phenomenon. Current formulations meet and exceed the ASTM B117 test results of full chromate primer systems. Open circuit potential (OCP) measurements indicate an extended period of cathodic protection of the Al aircraft alloys such as AA 2024 T-3 and AA 7075 T-6. After this stage of protection, a combination of Mg oxide, hydroxide and carbonate compounds seem to give protection to the system, as we have seen corrosion protection given to samples for greater than 10,000 h of cyclic exposure for Mg-rich primers with good aerospace topcoats. Preliminary data are presented for other Mg alloys as pigments in metal-rich coating systems. All data indicate that the Mg-rich (or Mg-alloy pigment-rich) primer + aircraft topcoat system gives excellent corrosion

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Abbreviations: ANAC, AKZO Nobel Aerospace Coatings; AFOSR, Air Force Office of Scientific Research (USA); ASTM, American Society for Testing and Materials; B117 NSS, ASTM Test Method B117 Neutral Salt Spray; HAZMAT, Hazardous Material; SERDP, Strategic Environmental R&D Program (USA); ESTCP, Environmental Security Technology Certification Program (USA); AFRL, Air Force Research Laboratory (USA); WPAFB, Wright-Patterson Air Force Base, Ohio (USA), home of materials research for the US Air Force; NDSU, North Dakota State University; DIN, Deutsches Institut für Normung; DOD, Department of Defense (USA); DOE, Department of Energy (USA); EPA, Environmental Protection (USA); EDX, energy dispersive X-ray analysis; SAS, simulated aircraft structures; OCP, open circuit potential; EIS, electrochemical impedance spectroscopy; ENM, electrochemical noise methods; XRD, X-ray diffraction; XPS, X-ray photoelectron spectroscopy; SEM, scanning electron microscopy; SVET, scanning vibrating electrode technique; SECM, scanning electrochemical microscopy; MgRP, Mg-rich primer; KC-135, identifier for primary US Air Force tanker aircraft that requires much chromate to repair; AA 2024 T-3, aluminum alloy 2024 T-3: commonly used aerospace alloy formed from 1.5% Mg, 4.4% Cu + small amounts of other metals + the remaining as Al and heat treated to a T-3 specification; AA 7075 T-6, aluminum alloy 7075-76: commonly used aerospace alloy used largely for naval aircraft whose composition is 1.6% Cu, 2.5% Mg, 5.6% Zn + small amounts of other metals + the remaining as Al and heat treated to a T-6 specification; AM60 Mg alloy, magnesium alloy used in aerospace and automotive areas 5% Al + 95% Mg; AZ91B Mg alloy, magnesium alloy used in aerospace and automotive areas 9.5% Al + 90.5% Mg; DHS, dilute Harrison's solution.

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protection by mechanisms entirely different from the modes of protection for aircraft alloys given by the toxic, carcinogenic chromate compounds now in use in all corrosion protection systems for aircraft. In most cases thus far examined, the protection, especially in cyclic exposure, exceeds the present chromate-based systems.

1. Introduction

1.1. The need for chromate replacement in aircraft coatings

Why was the Mg-rich primer technology developed? The initial and primary reason for its development was to provide a chromate-free corrosion protection system for aerospace Al alloys. The present use of chromates as pigments in the primers currently used from corrosion protection [1] (largely $SrCrO_4$ pigments [2]) as well as the chromates used in the Al-alloy pretreatment for painting is the major environmental hazard of aircraft production, maintenance and repair [3]. Lest we forget, chromates are among the most severe toxic and carcinogenic hazards that mankind has produced and introduced into the natural environment. It has long been acknowledged that the only allowable reason for their use is when no other scientifically verifiable replacement can be found in a safety related function. The total replacement of chromates has been identified as one of the major targets of DOD environmental R&D programs for almost 20 years. The handling and disposal of chromates in paint application and paint removal waste as a HAZMAT is further one of the major environmental costs of the DOD. Full details of the chromate hazards of present aerospace coatings systems are detailed at the DOD Strategic Environmental Research and Development Program (SERDP) website at http://www.serdp.org (e.g., SERDP Fact Sheet 1119: *Critical Factors for the Transition from Chromate to Chromate-Free Corrosion Protection*). Chromate replacement in aircraft coatings is such a very technical problem for two major reasons. The first is the unique material properties of the high strength Al alloys involved in aircraft [4], and the second the uniqueness of chromates as corrosion inhibiting materials for these alloys [5,6]. Aircraft alloys are specially designed alloys that impart high strength and light weight to aircraft, but are often susceptible to corrosion, especially the two most commonly used Al alloys AA 2024 T-3 and AA 7075 T-6 [7–9]. These are phase separated alloys that are in themselves highly complex metal-in-metal composites, but tend to have weakness towards local galvanic corrosion because of this structure.

Chromate pigments have a set of unique material properties, among the most important of which are a low, but significant, water solubility, the ability to act as both cathodic and anodic inhibitors, and a very complex oxidation/reduction chemistry. Details of these properties and their importance are discussed from the point of view of a pigment scientist in Ref. [5], and from the point of view of corrosion science in Ref. [6]. For further details on the unique, difficult to replace, corrosion control properties of chromates, one should see also the work of Frankel and McCreery [10]. The richness of properties detailed in these and many related studies [1] indicate that it is very difficult to replace, the present robust system based on chromate pigments and chromate pretreatments for Al.

As NDSU became involved in the study of aircraft coatings, initially in the testing mode, it became apparent that multiple methods of testing were going to be needed to understand all of the nuances of performance and interactions that were taking place in the very complex aircraft coating systems. A schematic of the system is given in Fig. 1, and shows that one is considering a multi-layer coating system, primer and topcoat, that also includes a pretreatment layer at the primer/Al-alloy substrate interface. Many candidate systems have been examined for Cr replacement in aircraft coatings. For replacing chromate-based pretreatments, these have included sol–gel pretreatment systems, cold-cathode plasma-polymerized pretreatment layers as well as the presently used chromate-based pretreatment baths. Many new pigments and composite pigmentary structures have been studied to replace the $SrCrO_4$ pigments now in use. Many other types of systems have also been examined as Cr replacements in coatings or pretreatments. Some coatings are chrome free, but require a chromate pretreatment to provide even marginal replacement for present systems. Some Cr-free pretreatment systems have been developed, but they do not function satisfactorily without the use of primers based on chromate pigments. No total aircraft coating system (pretreatment, primer and topcoat) currently available provides the extended corrosion lifetimes of the presently used systems without chromates in the primer, pretreatment or both. Some authors have gone so far as to describe their candidate materials for Cr replacement "SuperPrimer," [11] but alas, this material also provides insufficient corrosion protection by itself without chromates of some sort present.

Thus, there has existed a severe need for coatings that provide the excellent corrosion protection that chromate in pretreatment and primer provides. A true replacement system has not yet been found, as all of the widely touted systems for Cr replacement seem to give marginal corrosion protection when examined carefully in full qualification testing and outdoor exposure.

2. Alternates previously considered for chromates

Almost everything including the veritable "kitchen sink" has been tried for chromate replacement in coatings systems. (See http://www.corrdefense.org/ReferenceLibrary.aspx and http://www.serdp.org/ websites for further details as to the many studies on different methods and materials for chromate replacement that have been funded by the US DOD, DOE and EPA.) Also pertinent is an interesting analysis by Sinko [5] of all of the organic and inorganic inhibitors examined for Cr replacement. Kendig and Buchcheit [6] give a review of the many failed studies attempts at true chromate replacement in protecting aerospace alloys. Frankel and co-workers have done an extensive study of why chromates succeed so well at the corrosion protection of Al alloys, and have concluded that they function uniquely as anodic and cathodic inhibitors at very low concentrations in electrolyte solutions, especially those with Cl^- ions that cause so many problems for Al substrates. So, before the introduction of MgRP technology described below, many chromate replacement materials have been

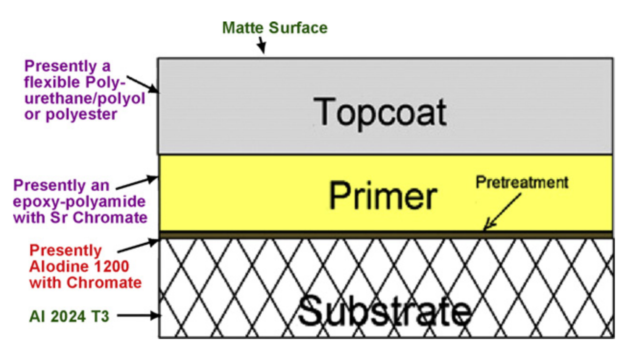

Fig. 1. Schematic of current aerospace coating system.