

REPORT DOCUMENTATION PAGE			Form Approved OMB No. 0704-0188		
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1. REPORT DATE		2. REPORT TYPE Professional Paper		3. DATES COVERED	
4. TITLE AND SUBTITLE Finishing Systems for Naval Aircraft Applications: Current Schemes and Future Trends		5a. CONTRACT NUMBER			
		5b. GRANT NUMBER			
		5c. PROGRAM ELEMENT NUMBER			
6. AUTHOR(S) Kevin Kovaleski Michael Kane		5d. PROJECT NUMBER			
		5e. TASK NUMBER			
		5f. WORK UNIT NUMBER			
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Naval Air Warfare Center Aircraft Division 22347 Cedar Point Road, Unit #6 Patuxent River, Maryland 20670-1161		8. PERFORMING ORGANIZATION REPORT NUMBER			
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) Naval Air Systems Command 47123 Buse Road Unit IPT Patuxent River, Maryland 20670-1547		10. SPONSOR/MONITOR'S ACRONYM(S)			
		11. SPONSOR/MONITOR'S REPORT NUMBER(S)			
12. DISTRIBUTION/AVAILABILITY STATEMENT Approved for public release; distribution is unlimited.					
13. SUPPLEMENTARY NOTES					
14. ABSTRACT Coating systems on Navy aircraft perform a variety of functions, but clearly the most critical of these is the protection of aircraft structures from environmental degradation. Protective coatings serve as the primary defense against corrosion of aircraft metallic alloys, as well as degradation of other materials such as polymeric composites. Traditional coatings for aircraft include inorganic pretreatments, epoxy primers, and polyurethane topcoats. Pretreatments provide some corrosion protection and prepare the surface for subsequent organic coatings. Primers normally contain high concentrations of corrosion inhibitors, such as chromates, and are designed to provide superior adhesion and corrosion protection. Polyurethane topcoats are formulated to enhance protection and durability; they also provide desired optical effects including aesthetics and camouflage. More recently, alternative coatings have been developed, such as nonhexavalent chromate pretreatments and primers, self-priming topcoats, flexible primers, low volatile organic compounds (VOC) content coatings, temporary and multifunctional coatings. These new developments reflect trends in protective coatings technology, changes in aircraft operational requirements/capabilities, and most dramatically, concerns over environmental protection and worker safety. These environmental issues have created a drive toward coatings protection and worker safety. These environmental issues have created a drive toward coatings with ultra low/zero concentrations of VOC and nontoxic corrosion inhibitors. In turn, these changes have led to concerns over long-term performance, especially protection against corrosion. This report reviews current protective coatings technology for Navy aircraft structures and discusses future needs and trends based on advancing technology, environmental concerns, and operational requirements. This report also summarizes the work performed under the Strategic Environmental Research and Development Program (SERDP) Task PP-65: Organic Protective Coatings and Application Technology and Task PP-66: Aircraft Maintenance Chromium Replacement that addresses these future needs and trends.					
15. SUBJECT TERMS					
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
a. REPORT	b. ABSTRACT	c. THIS PAGE			Kevin Kovaleski / Michael Kane
Unclassified	Unclassified	Unclassified			19b. TELEPHONE NUMBER (include area code)
			Unclassified	35	(301) 342-8049 / 342-0986

2006407 124

FINISHING SYSTEMS FOR NAVAL AIRCRAFT APPLICATIONS: CURRENT SCHEMES AND FUTURE TRENDS

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Coating systems on Navy aircraft perform a variety of functions, but clearly the most critical of these is the protection of aircraft structures from environmental degradation. Protective coatings serve as the primary defense against corrosion of aircraft metallic alloys, as well as degradation of other materials such as polymeric composites. Traditional coatings for aircraft include inorganic pretreatments, epoxy primers and polyurethane topcoats. Pretreatments provide some corrosion protection and prepare the surface for subsequent organic coatings. Primers normally contain high concentrations of corrosion inhibitors, such as chromates, and they are designed to provide superior adhesion and corrosion protection. Polyurethane topcoats are formulated to enhance protection and durability; they also provide desired optical effects including aesthetics and camouflage. More recently, alternative coatings have been developed, such as non-hexavalent chromate pretreatments and primers, self-priming topcoats, flexible primers, low volatile organic compounds (VOC) content coatings, temporary and multi-functional coatings. These new developments reflect trends in protective coatings technology, changes in aircraft operational requirements/capabilities, and, most dramatically, concerns over environmental protection and worker safety. These environmental issues have created a drive toward coatings with ultra low/zero concentrations of VOC and non-toxic corrosion inhibitors. In turn, these changes have led to concerns over long-term performance, especially protection against corrosion. This report reviews current protective coatings technology for Navy aircraft structures and discusses future needs and trends based on advancing technology, environmental concerns, and operational requirements. This report also summarizes the work performed under the Strategic Environmental Research and Development Program (SERDP) Task PP-65: Organic Protective Coatings and Application Technology and Task PP-66: Aircraft Maintenance Chromium Replacement that addresses these future needs and trends.

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1. INTRODUCTION

Coating systems on Navy aircraft perform a wide variety of functions. They provide desired optical effects (i.e., aesthetics, camouflage), corrosion prevention, erosion control, markings, electrical grounding, electromagnetic shielding, as well as other specialized properties. Clearly, their most critical contribution is the protection of materials and structures from corrosion and other forms of environmental degradation. An Air Force study (1) concluded that, "The rate controlling parameter for the corrosion of aircraft alloys, excluding the mechanical damage factor, is the degradation time of the protective coating system." These coatings protect not only metallic alloys from corrosion, but also plastics and polymeric composites from various degradation mechanisms (2). Specifically, Navy aircraft are deployed at coastal land bases or onboard aircraft carriers. The continuous proximity to salt water and high humidity combined with atmospheric impurities cause one of the most corrosive natural environments. In addition, many operational and maintenance chemicals commonly used or found on aircraft, such as paint strippers, battery acid, de-icing fluids, and cleaners, are corrosive. These effects are exaggerated even more so with aging fleet aircraft that have flown many flights over long periods of time, adding fatigue as another factor. Considering the high cost of these aircraft, in addition to fewer numbers of new aircraft programs, aircraft materials protection is of the utmost importance.

The most common organic coating system applied to the exterior surfaces of Navy aircraft consists of an inorganic pretreatment, an epoxy primer, and a polyurethane topcoat. In addition to this primer and topcoat paint system, other technologies have been introduced such as flexible primers and self-priming topcoats. These coating systems have protected aircraft structures from the frequently harsh operational environment due to their exceptional corrosion inhibition, adhesion, and durability characteristics.

Unfortunately, these coating systems have been identified as a major contributor to the generation of hazardous materials and hazardous waste for the Navy (3). Recently, changes in coating composition and application procedures have occurred because of these concerns for environmental protection and worker safety. Many of these coatings have contained high levels of volatile organic compounds (VOC) as solvents and plasticizers, and heavy metal compounds as corrosion inhibitors and colorants. These ingredients are being severely regulated and coating formulations are being drastically changed accordingly. These environmental issues have created a drive toward coatings with ultra low (possibly zero) concentrations of VOC and non-toxic corrosion inhibitors.

Nonetheless, corrosion protection remains a primary requirement and therefore these changes have led to concerns over long term performance. The practical lifetime of these coatings is 4 to 8 years, after which the coating system is removed. The aircraft surface is then cleaned, pretreated, and repainted. References (4-8) provide more information about general aircraft finishing systems. The following is a description of the specific finishing systems being used on Navy aircraft and future trends in these materials.

2. STANDARD FINISHING SYSTEMS

2.1 Surface Pretreatments The primary goal of surface preparation and pretreatment processes is the enhancement of the corrosion resistance and adhesion properties of subsequent organic coatings. Proper surface preparation is an important step in the protective treatment of aluminum, and is accomplished by using materials such as alkaline cleaners, etchants, and deoxidizers. These materials remove organic contamination along with the existing surface oxide layer of the aluminum to prepare it for subsequent chemical pretreatments. These pretreatments are used because of their enhancement of the overall protective finishing system. MIL-S-5002 "Surface Treatments and Inorganic Coatings for Metal Surfaces of Weapon Systems" is the military specification for surface preparation and pretreating of virtually every Navy aircraft and weapon system. The two primary surface pretreatments for aircraft are chromate conversion coatings and anodic films. Chromate conversion coatings (CCC) are excellent surface pretreatments for aluminum alloys. These materials chemically form a surface oxide film (typically 40-60 mg/ft²), which enhances the overall adhesion and corrosion prevention properties of the protective finishing system applied over them. Typical CCC film performance requirements are covered by MIL-C-5541, "Chemical Conversion Coatings on Aluminum and Aluminum Alloys" and CCC material properties are described in MIL-C-81706, "Chemical Conversion Materials for Coating Aluminum and Aluminum Alloys." Anodize processes form a thicker oxide film (200+ mg/ft²) by electrochemical means, which provides more protection against degradation than chemical conversion coatings. Anodize processes are performed in accordance with MIL-A-8625.

2.2 Primers Epoxy resins are commonly used as binders in high performance primers due to their exceptional adhesion and chemical resistance properties. The solventborne epoxy primer is manufactured and packaged as a two component epoxy/polyamide system. One component contains an epoxy resin that is the product of a condensation reaction between epichlorohydrin and bisphenol A. The second component is a solution of a multi-functional polyamide resin in a solvent blend. Upon mixing the two components, which is done just prior to application of the primer, reaction of epoxide and amide groups within the resins ensues according to Figure 1:

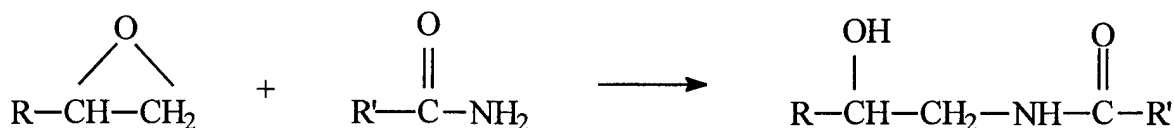


FIGURE 1. Chemical reaction for a typical two-part epoxy coating.

The product of this reaction is a highly crosslinked polymer which forms the matrix of the primer film. The chemical and mechanical properties of the epoxy matrix cause the primer to be adherent, chemically resistant, and durable. Hydroxyl groups on the solid epoxy are usually given

credit for the excellent adhesion of these coatings. References (9) and (10) provide detailed discussions of epoxy resin chemistry for coatings.

The epoxide component of the primer contains various pigments, including titanium dioxide, strontium chromate, and extender pigments. Strontium chromate is the most critical of these pigments since it is well known as an exceptional corrosion inhibitor, especially for aluminum. Titanium dioxide in the primer enhances durability, chemical resistance, and opacity of the applied coating. The extender pigments can be silicas, silicates, carbonates, or sulfates. The extenders are normally inexpensive and provide a cost-effective component that "fills" the coating and reduces gloss of the applied film. The surface irregularities that cause gloss reduction also act as anchors for a topcoat, thus enhancing inter-coat adhesion by improving the mechanical attachment. References (6) and (7) provide a comprehensive review of epoxy primer technology for aircraft applications.

Upon mixing the two components of the epoxy/polyamide primer, the curing reaction begins. After a dwell time of 30 minutes, the coating is suitable for spray application. The coating is applied to a dry film thickness of 15 to 24 micrometers (0.6 to 0.9 mils); the coating is tack free within 1 to 5 hours and dry hard within 6 to 8 hours. For corrosion-prone areas, the primer may be applied up to double this thickness. If a topcoat is to be applied, it is usually accomplished within the tack-free to dry-hard time period to ensure proper adhesion. The primer attains sufficient dry film properties within 7-14 days of application.

Since water is a primary factor in reducing adhesion of paint films and causing cathodic disbondment, adhesion is considered a critical paint performance property. Adhesion of the primer is characterized by a tape test after a 24-hour immersion exposure period in distilled water (11). The required performance is no coating removal from the substrate. Adhesion is also characterized by a method that quantifies the force required to scrape the primer from the substrate (12). Typically, scrape adhesion values of at least 3 kg are considered acceptable. Other adhesion tests employed in research and development laboratories are the tensile adhesion and Hesiometer knife-cutting adhesion tests (13). These sophisticated laboratory adhesion tests yield quantitative data but require more training and expertise to perform the tests and to analyze data compared to the tape and scrape adhesion tests.

Corrosion resistance is evaluated by applying the primer to chromate-conversion-coated aluminum substrates such as 2024 T3. After curing for 7-14 days, the primer is scribed with an "X" so that the substrate is exposed. Resistance to 5% NaCl salt fog exposure (ASTM B117) is required such that no substrate corrosion or coating defects are produced after 2000 hours of exposure. Resistance to filiform corrosion is evaluated on primed and top-coated test panels. After exposure to hydrochloric acid for one hour, the panels are exposed to high humidity for 1000 hours. Generally, specimens should not exhibit any filiform growth from the scribe greater than 6.35 mm (0.25 in) with the majority less than 3.175 mm (0.125 in). In addition to the salt fog and filiform tests, the Navy also requires the corrosion resistance of primed and then scribed aluminum/graphite epoxy specimens. This forms a galvanic couple which must withstand 5% NaCl salt fog exposure for 500 hours such that pitting greater than 1 mm (0.039 in) is not produced. SO₂/salt fog exposure (ASTM G85, Annex 4), cyclic wet/dry exposure, and electrochemical impedance spectroscopy have also been used to evaluate the corrosion resistance

properties of coating systems. The performance requirements of the standard solventborne epoxy primer are specified in MIL-PRF-23377, "Primer Coating: Epoxy Polyamide, Chemical and Solvent Resistant."

The high-performance waterborne epoxy primer that is currently used on exterior surfaces of many military aircraft was developed (14) and implemented in the Navy community in the late 1970's to mid 1980's. This primer is specified under MIL-PRF-85582, "Primer Coating: Epoxy, VOC Compliant, Chemical and Solvent Resistant." The primer is supplied as a two-component epoxy/amide or epoxy/amine system. The resin systems are water-reducible and film formation occurs via coalescence of resin particles and crosslinking of the epoxy/polyamide reactive groups. The pigments used are similar to those used in the solventborne primer system. For example, strontium chromate pigment is used as the primary active corrosion inhibitor in many waterborne primers. Organic co-solvents and surface active agents are also used to enhance formulation and processing properties such as water miscibility and dispersion stability, as well as film formation and quality.

The epoxy primer is brittle, especially at low temperatures (-51°C), which can potentially result in extensive cracking of the paint system in highly flexed areas of the aircraft. Sealants, which are sometimes spray-applied between the primer and topcoat in aircraft finishing systems to increase overall coating system flexibility, are soft, easily deformed, and difficult to apply and remove. An alternative is an organic coating that possesses the adhesion of a primer and the flexibility of a sealant, thus eliminating the logistical and application problems inherent in stocking and applying two materials instead of one. An elastomeric primer that provides these benefits has been characterized (15) and implemented on Navy aircraft. This technology conforms to TT-P-2760, "Primer Coating: Polyurethane, Elastomeric." This material is based on polyurethane resin technology, and a pigment system that contains strontium chromate for corrosion inhibition, and extender pigments for gloss control. Most of the requirements for this flexible primer are similar to those in the current epoxy primer specifications, with the exception of film flexibility. This requirement is significantly more stringent than those exhibited by the current epoxy primers: 80% versus 10% room temperature elongation, respectively. One of the major coating failure mechanisms on aircraft is cracking around fasteners, thus exposing bare metal. Application of this coating to numerous Navy and Air Force aircraft has resulted in less coating system failures due to cracking and chipping.

2.3 Topcoats A high-performance topcoat, conforming to MIL-PRF-85285, "Coating: Polyurethane, High Solids," is applied to Navy aircraft in order to enhance protection against the operational environment and to provide desired optical properties. Aliphatic polyurethane coatings are ideal for this application due to their superior weather and chemical resistance, durability, and flexibility. These urethanes are two-component reactive materials. One component of the coating is a polyisocyanate resin or an isocyanate-terminated prepolymer based on hexamethylene diisocyanate (HDI). The second component contains hydroxylated polyester. Upon mixing, the isocyanate groups react with the hydroxyl groups of the polyester as shown in Figure 2:

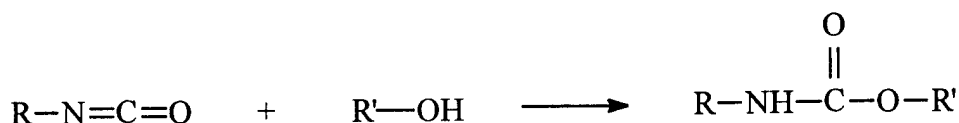


FIGURE 2. Chemical reaction for a typical two-part polyurethane coating.

The resulting polymer is flexible yet extremely durable and chemical resistant. Aliphatic isocyanates and polyesters are used in topcoats because they provide outstanding weather resistance compared to epoxies, whose aromatic groups degrade when exposed to ultraviolet light. References (16-19) provide more detailed discussions about polyurethane chemistry.

When the two components are combined and the polyurethane reaction begins, the coating is ready for application (i.e. no induction time is required). This coating is normally spray-applied to a dry film thickness of 50.8 ± 7.6 micrometers (2.0 ± 0.3 mils). The typical topcoat is set-to-touch and dry-hard (when cured at room temperature) within 2 and 8 hours, respectively. Although the painted surface can be handled after 6 hours without damage to the coating, full performance properties are normally not obtained until approximately 7-14 days.

The most critical performance requirements for topcoats are weather resistance, chemical resistance, and flexibility. Weather resistance is evaluated by laboratory exposure in an accelerated weathering chamber (20) for 500 hours according to ASTM G26. Exposure in this chamber consists of cycles of 102 minutes of high intensity ultraviolet light (xenon arc) followed by 18 minutes of combined ultraviolet light and water spray. Although studies have shown that there is no precise correlation with outdoor exposure (21-23), the accelerated exposure does indicate if the coating is susceptible to ultraviolet and/or water degradation. Both accelerated and real-time weathering conditions cause only minimal changes in the color, gloss, and flexibility of high performance aircraft topcoats.

Chemical stability is evaluated by exposure of the applied topcoats to various operational fluids such as lubricating oil, hydraulic fluid, and jet fuel at elevated temperatures and/or extended durations. Aerospace topcoats are also subjected to a dry heat of 121°C (250°F) for one hour. Suitable topcoats show no defects other than slight discoloration after exposure to these conditions.

Flexibility requirements for polyurethane topcoats include impact and mandrel bend tests. For high-gloss colors, a 40% elongation of the coating after impact at room temperature and a 180° bend around a 2.54 cm (1.0 in) cylindrical mandrel at -51°C (-60°F) are required without cracking of the film. Flexibility requirements for low-gloss colors are less stringent at low temperatures because it is difficult to formulate flexible low-gloss coatings due to high pigment concentrations. A high pigment concentration normally embrittles the film.

2.4 Self-Priming Topcoat The self-priming topcoat (SPT) is a VOC compliant, non-lead, non-chromated, high-solids polyurethane coating that was designed to replace the current primer and topcoat paint system used on aircraft (24). This technology conforms to TT-P-2756,

"Polyurethane Coating: Self-Priming Topcoat, Low Volatile Organic Compounds (VOC)." The SPT possesses the adhesion and corrosion inhibition properties of a primer as well as the durability and optical properties of a topcoat. The SPT effectively eliminates the need for a primer and thus eliminates the application manpower, time, and materials. In addition, the hazardous emissions and toxic wastes that are associated with current aerospace primers are eliminated. The specified thickness of this film is 50.8 to 66.0 micrometers (2.0 to 2.6 mils). SPT's have been successfully applied to a full variety of operational Navy aircraft (e.g., F-14, F-18, AV-8, H-3, H-46, P-3). These materials, however, are more sensitive to surface characteristics and have raised issues with regards to preparation and processing.

2.5 Specialty Coatings In addition to the current primers, topcoats, and self-priming topcoats used on the exterior surfaces of Navy aircraft, other specialized coatings are utilized to address specific concerns.

2.5.1 Sealants Although the current epoxy primers provide excellent adhesion and corrosion inhibition, they are brittle. This lack of ductility may result in cracking of the paint system on highly flexed areas of the aircraft. In order to improve the overall flexibility of the epoxy primer polyurethane topcoat coating system, sealants are frequently incorporated into aircraft finishing systems. These sprayable materials are applied between the primer and the topcoat at thicknesses up to 203 micrometers (8 mils) and are primarily formulated from polysulfide, polyurethane, and polythioether binders. Their elastic nature minimizes cracking of the paint system. Critical requirements in these specifications are low-temperature flexibility (mandrel bend tests), chemical resistance (fluid immersion at elevated temperatures), and corrosion resistance (5% NaCl salt spray tests). Although these sealants provide corrosion protection by the formation of a relatively impermeable barrier, some sealants also contain strontium chromate for chemical corrosion inhibition. A detailed discussion of this technology can be found in references (25) and (26).

2.5.2 Rain Erosion Coatings In addition to their harsh environment, aircraft must also endure seemingly harmless natural conditions that can deteriorate the performance of coatings and their underlying structures. One example of this phenomenon occurs when airborne debris, such as sand or rain droplets, impacts aircraft leading edges and radomes during flight. The force of impact from these particles can erode the coating system and adversely affect the underlying substrate. The current primer-topcoat and SPT paint systems do not provide adequate protection against this condition. Even when applied at two to three times its normal thickness, the coating system erodes prematurely.

The rain erosion-resistant coating used on Navy aircraft is a two component polyurethane material. One component consists of a pigmented, high molecular weight polyether-type polyurethane. The other component contains a clear ketimine (blocked diamine) resin that acts as both a crosslinking agent and a chain extender. When combined, the two components form an elastomeric coating which can absorb and dissipate the energy of impacting rain droplets, thus preventing failure. Flexibility is characterized by a 0.635 cm (0.25 in) mandrel bend at -51°C (-60°F) and tensile elongation of 450%, whereas the standard topcoat only requires a 2.54 cm

(1.0") or 5.08 cm (2.0") mandrel and elongation of 5 or 40 %. However, in order to exhibit this high elasticity, the polymer crosslink density is decreased causing reduced chemical resistance and weathering properties. In order to improve the finishing system durability, these materials are normally overcoated with the standard topcoat.

Although elastomeric coatings offer increased resistance to rain erosion, elastomeric tapes provide the optimum protection for Navy aircraft. These materials can be clear or pigmented polyurethane-based films and are supplied with or without an adhesive backing. Unlike coatings, these tapes are bonded to the surface and do not require a drying time. Early versions of these materials were clear aromatic type polyurethanes. Although durable, these aromatic materials had poor weatherability. The latest versions of these materials, however, are aliphatic. These new materials are extremely durable and have excellent weatherability.

2.5.3 High Temperature Resistant Coatings Various areas of Navy aircraft are routinely subjected to elevated temperatures during operation. The standard paint system was only designed to resist thermal exposures up to 176°C (350°F) for short durations. Therefore, two types of materials are employed for application in these areas: ceramic coatings and high temperature resistant silicone based coatings. Since ceramic coatings are beyond the scope of this review, they will not be discussed. Typical high temperature silicone based coatings use aluminum pigment and are designed to withstand temperatures up to 650°C (1200°F). They can be applied by conventional air spray and are cured by heating to 204°C (400°F) for 1 hour or upon elevated temperature exposure under component operation. During the curing period, the binder system for this coating will oxidize, leaving a barrier layer of silicone oxide/aluminum to protect the underlying substrate from adverse conditions. Although this material provides adequate barrier protection in the high temperature range, the performance diminishes dramatically in the mid-temperature range (260 to 370°C, 500 to 700°F) or when damaged.

2.5.4 Fuel Tank Coatings Certain internal areas of aircraft are exposed to selective environments that pose unique problems. One example is fuel tanks. Aviation fuels contain additives that may be corrosive. If left unprotected, fuel tanks would corrode and leak. In order to protect these areas, epoxy or polyurethane fuel tank coatings are used. These highly cross-linked, chemically resistant coatings are two component materials designed for application to non-ferrous surfaces. The fluid resistance requirements for this material are significantly more severe than those of the standard primer and topcoat. The conventional topcoat must withstand 24-hour immersion on unscribed panels without degradation, whereas the fuel tank coating specification requires 14 days immersion of specimens with scribes through the coating. This high degree of chemical resistance is necessary because the coating is not only subjected to the various chemicals contained in aviation fuels, but it is also exposed to aircraft operational chemicals, salt water and dilute acidic solutions (27).

3. COMPLIANT COATINGS ISSUES AND FUTURE TRENDS

3.1 Environmental Regulations And Hazardous Materials As the environmental consciousness of the world continues to increase, more efforts are being devoted to finding safe, compliant solutions to past, current, and future environmental problems. One major factor affecting the Naval Aviation in recent years, has been the Clean Air Act Amendment (CAAA) of 1990. This law significantly affects the type of materials and processes that will be approved for use in the future. In response to this situation, the Navy has expanded its efforts to reduce the amounts of hazardous materials generated from the cleaning, pretreating, plating, painting, and paint-removal processes used in both production and maintenance operations. The materials associated with these processes have been identified as major sources of hazardous waste by the EPA (28). Specifically, numerous research and development efforts have been established to address the environmental concerns with organic coatings. These environmental efforts can be described by two main thrusts: the development of low volatile organic compound (VOC) coatings and the development of non-toxic inhibited coatings. The efforts in low VOC are aimed at reducing the volatile organic compound content of aircraft coatings to meet environmental regulations, especially the state of California's Air Quality Management Districts (AQMD) rules and the CAAA Control Techniques Guideline (CTG) for the aerospace industry (one of 174 source categories). The development of non-toxic inhibited coatings is concerned with eliminating toxic heavy metal pigments, such as lead, chromates and cadmium, used in protective primers and topcoats.

Low VOC versions of the standard military aircraft primers and topcoats have already been developed to comply with the CAAA Aerospace CTG. These materials are based on waterborne and high solids. Projections based on new resin and additive chemistries bring VOC contents even lower as the twentieth century comes to a close. Figure 3 summarizes the VOC content of coatings for past, present, and future systems. Some solvents are legally designated by the Environmental Protection Agency (EPA) as neither VOCs nor HAPs; included here are such compounds as 1,1,1-trichloroethane and acetone. These "exempt" solvents, while solving a VOC problem in most cases, frequently create an ozone depleting chemical problem and are no longer perceived as a potential technology solution.

3.2 Non-Chromated Pretreatments One of the main environmental thrusts in the pretreatment area is the total elimination of hexavalent chromium. This toxic material has been used widely in the aforementioned processes because of its outstanding performance as a corrosion inhibitor for aluminum. This property is of particular importance to the Navy due to the extensive use of aluminum in aircraft and weapon systems. Chromium (VI) is a known carcinogen, and regulatory agencies have recently enacted rules that limit or prohibit the use of this material. This has resulted in a need for alternative materials to be developed.

Non-chromated alkaline cleaners and non-chromated deoxidizers have been identified as acceptable alternatives to the current chromated processes, and have been implemented by Naval facilities. These materials have provided satisfactory performance in these surface preparation

operations and in some cases they have been more cost effective than their chromated predecessors have.

Numerous non-chromated surface pretreatment materials have been investigated as replacements for the standard chromated conversion coating (CCC). A summary of one such investigation is

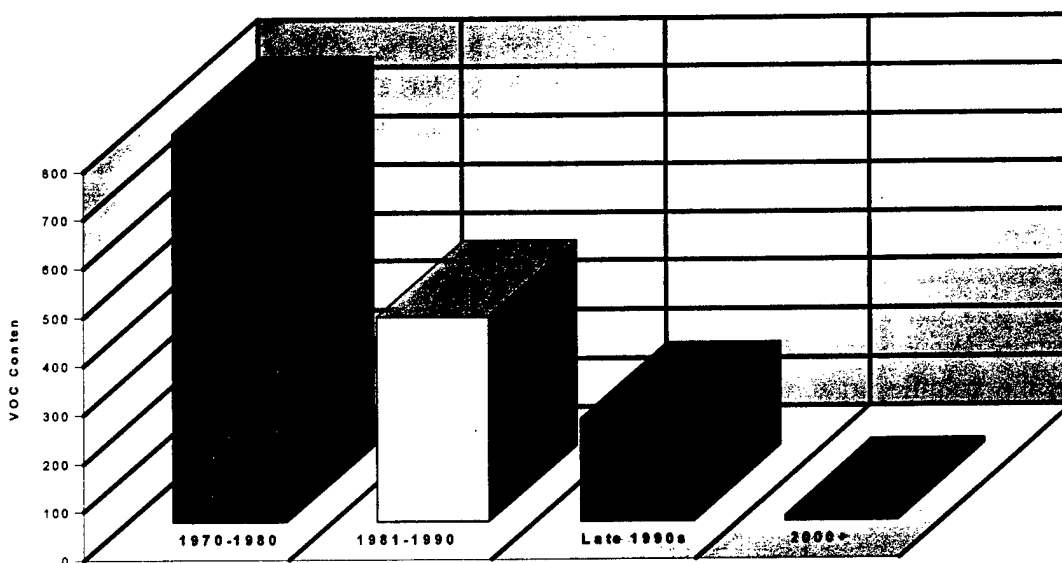


FIGURE 3. Summary of VOC levels in standard military coatings for past, present and future systems.

described in Reference (29). Three categories of non-chromated conversion coating alternatives have been studied in the Navy: inorganic non-chromated solutions, chromium (III)-based treatments, and sol-gel formulations. The first category includes solutions based on permanganate, cobaltamine, and ceric ion (among others) as the active corrosion-fighting agent. At this time, the performance of these materials is marginally comparable or inferior to conventional CCCs in adhesion and corrosion resistance. A Navy-developed chromium (III) treatment (30,31) has shown corrosion resistance and paint adhesion properties comparable to CCCs in laboratory evaluations; broader testing and in-service demonstrations of this technology are underway. Sol-gel formulations, although still in the initial phases of development, show promise for favorable conversion coating properties. These materials are organic/inorganic polymers based on the hydrolysis and condensation of metal alkoxides. Figure 4 illustrates how, for example, silicon alkoxides (of general formula $\text{Si}(\text{OR})_4$) can be reacted to form a barrier film strongly bonded to an oxidized aluminum surface.

The chemistry of sol-gel films also allows a great deal of flexibility in modifying adhesive and other properties. While some of these alternatives have shown promise, an across-the-board replacement for chromate conversion coatings has not yet been achieved.

A self-contained pen (Alodine 1132 Touch-N-Prep) has been approved by NAVAIR and the Air Force for the repair and touch of chromate conversion coatings. The pen significantly reduces waste related to conventional chromate wiping since the formulation requires no rinsing and eliminates the need for brushes or rags. Non-chromate versions of the pen will be available for evaluation soon.

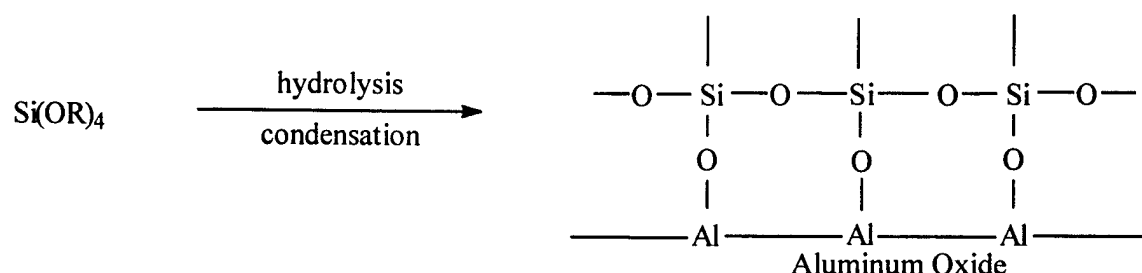


FIGURE 4. Formation of a silicon oxide barrier film to bond to an oxidized Al surface.

Chromic acid anodizing (CAA) has been widely used in aerospace production and maintenance operations. However, due to the increasing restrictions on hexavalent chromium, several potential alternatives have been identified. These alternatives are sulfuric/boric acid anodize (SBAA) and thin film sulfuric acid anodizing (TFSAA), as well as the standard Type II sulfuric acid anodizing. General information on these processes can be obtained from References (32-35). Several Navy laboratory investigations were performed on these alternatives as described in references (36-38). After a full-scale successful demonstration of SBAA at the Naval Aviation Depot at North Island, CA, it has been approved for use and incorporated into the MIL-A-8625 specification as Type IC (sulfuric/boric acid-anodize). Also, the laboratory studies have resulted in the definition of acceptable performance parameters for the TFSAA alternative which was incorporated into MIL-A-8625 as Type IIB. NAWCADPAX is also investigating the performance of trivalent chromium pretreatment as a sealer for Type IC, II and IIB anodized aluminum.

3.3 Waterborne Technology Water has long been used as a carrier for organic coatings. The polymers for these coatings are usually modified with hydrophilic groups and dispersed in water to form either solutions or emulsions. Most latex paints are based on thermoplastic resins that are suspended in water to form spherical particles. These particles, whether pigmented or neat, are usually covered with a thin layer of emulsifier to maintain a stable dispersion. When applied to a surface, these spheres coalesce into a continuous film as the water of the emulsion coating evaporates. This film formation mechanism tends to lead to longer drying times in high humidity environments. Other effects of using water as the diluent include: smoother surface finishes due to greater flow times, less overspray when using air application equipment (due to the higher density of water), and easier clean up (usually accomplished with soap and water). Unfortunately, these coatings have some disadvantages. For example, they are more sensitive to surface contamination, like oils and greases. Also, these films tend to be porous and their high

affinity for water can lead to poor resistance in moisture environments resulting in coating failure when wet, or exposed to high humidity conditions.

Waterborne or water-reducible, high-performance coatings are unique in the way that they contain resins that are usually not soluble in water. The resin exists in its own micellar phase. Figure 5 illustrates the resin micelle in a waterborne coating. As shown in Figure 5, neutralized carboxylic groups and surfactants stabilize the particle. Excess amine and solvent distribute between the phases. Because the polymer exists in its own organic phase surrounded by water, the solvent distributes between the organic phase and the aqueous phase. This solvent, called the coalescing solvent or co-solvent, aids in film formation as the water evaporates by allowing binder and pigment particles to fuse in a continuous film (39). Because water is used as the primary liquid medium or as a diluent, formulations based on waterborne resins have much lower VOC levels than their solventborne counterparts. Recent advances in urethane and additive chemistries have shown that coatings approaching zero VOC are feasible, consisting of low viscosity, water-soluble reactants (40).

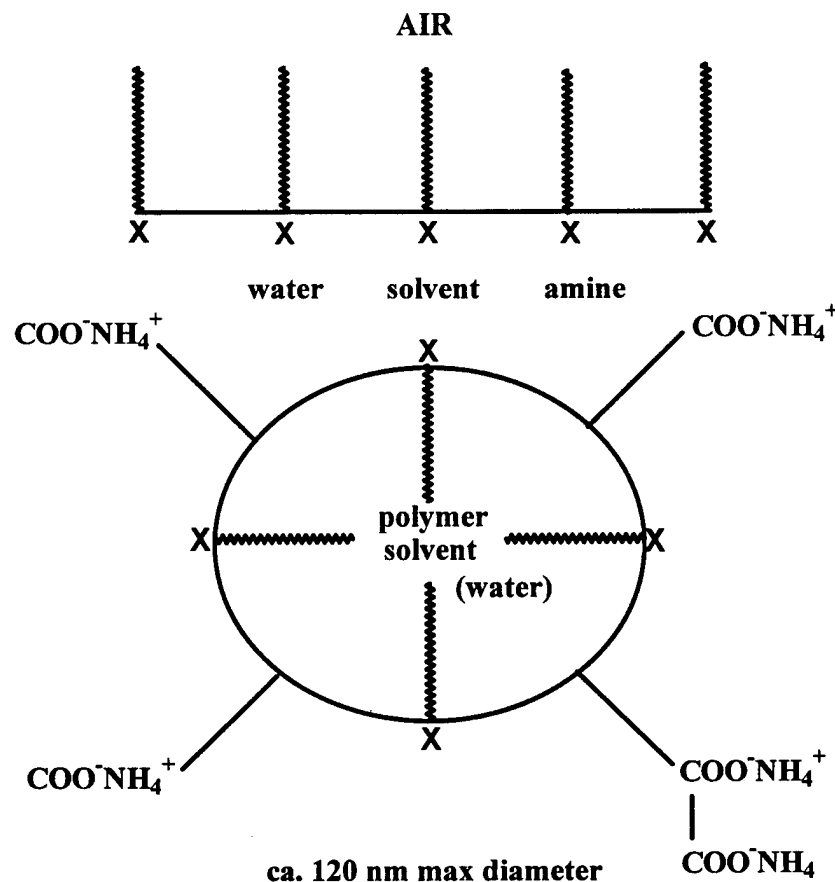


FIGURE 5. Schematic diagram of a resin micelle in a waterborne coating.

Polyurethane coatings comprise an area where high performance waterborne coatings have been investigated. One-component polyurethane dispersions have been in existence for some time and generally consist of fully reacted polyurethane resins which are predominately thermoplastic. Since urethanes are not readily compatible with water, these systems are modified ionically and non-ionically with hydrophilic groups to aid in the stability of the dispersions. After application, these films form by the coalescence of the long chain urethanes. Although some work has been performed to investigate ways of crosslinking these systems, they tend to have lower crosslink densities and are not as chemically resistant as their solventborne counterparts.

Recently, resin manufacturers have shown signs of success in working with two component water based polyurethane resins for high performance coatings. One example is based on an aliphatic polyol prepolymer and a polyisocyanate. The polyols are pre-reacted with a diisocyanate and emulsifying agents to form a linear hydroxy-terminated prepolymer. The hydroxy-functional groups aid in the stabilization of the polyurethane dispersion. In addition, a water dispersible polyisocyanate has been synthesized which has a preferential affinity for the polyol over the water competitor. The two components are mixed with an excess of isocyanate to form the final high-performance polyurethane product. Government laboratories and the commercial resin industry are investigating other variations on water-based urethane chemistry; coating manufacturers have begun to formulate finished products from this technology. The U.S. Army Armament Research, Development and Engineering Center (ARDEC) is currently investigating a water-reducible chemical agent-resistant coating (CARC) under SERDP with multi-service participation (PP-1056).

3.3.1 Low VOC Waterborne Topcoat In conjunction with the Sherwin-Williams Company (formerly Pratt & Lambert), engineering studies to investigate resins, formulate coatings from these resins, test, and demonstrate low VOC waterborne topcoats were conducted. These studies were initiated from a previous effort at the Naval Air Warfare Center Aircraft Division, Warminster, PA (NAWCADWAR). A low VOC waterborne topcoat was applied to a P-3 aircraft in 1994 that had a VOC content of 210 g/L. This VOC content is 50% lower than the limit outlined in the current Aerospace National Emission Standard for Hazardous Air Pollutants (NESHAP). The material exhibited sagging during application and was applied to the wings only. The laboratory at NAWCADWAR was relocated to the Naval Air Warfare Center Aircraft Division in Patuxent River, MD (NAWCADPAX) and evaluations at NAWCADPAX resulted in an optimized topcoat formulation that meets all the specification requirements and demonstrates good film-forming properties. The reformulated topcoat is currently under field assessment on a cargo bay door of a CH-47 helicopter at NADEP Cherry Point, NC. This demonstration was initiated in August 1998 under the Navy's Pollution Prevention Demonstration/Validation Program (W2210). Other aircraft platforms, such as the AV-8B, are being approached for potential demonstrations. A coating inspection of the original material on the P-3 revealed that the coating was performing at an acceptable level as compared to other aircraft with similar coating life.

3.3.2 Zero-VOC Waterborne Topcoat A zero-VOC topcoat has been developed under a joint Navy-industry effort funded by SERDP (PP-65). This topcoat, formulated by Deft Coatings, Inc., is based on a novel urethane chemistry that requires no co-solvent. Through manipulation of the polymer backbone chemistry and the involvement of new surface-active and rheological additives, a water-reducible polyurethane binder system was developed that contains no organic solvents and emits no hazardous air pollutants (HAPs). The zero-VOC topcoat offers the potential for the DOD to go beyond environmental compliance in its painting operations.

After achieving "Proof of Principle" for zero-VOC coating technology under SERDP, the project transitioned to the Environmental Security Technology Certification Program (ESTCP) whose office funded NAWCADPAX to demonstrate and validate the topcoat for use on military aircraft. Successful implementation of this topcoat would result in the elimination of approximately 120 tons of VOCs per year based on GSA estimates of MIL-PRF-85285 usage throughout the DOD. The primary objective of this ESTCP-sponsored project is twofold: to eliminate hazardous materials and VOCs in the topcoating process and to maintain the high-performance characteristics found in the current VOC-containing topcoats.

A joint group led by NAWCADPAX and consisting of technical representatives from the Naval Aviation Depots, Warner-Robins Air Logistics Center, and other government agencies reached technical consensus on engineering, performance, and testing requirements for topcoats. The joint group defined critical tests with procedures, methodologies, and acceptance criteria to qualify alternatives against these technical requirements. This joint test protocol (JTP), developed for the ESTCP (Project No. 199802), is currently being used to evaluate the current candidate topcoat and will be employed in evaluations of future candidates. The JTP contains two sets of requirements and tests. The first summarizes a common set of requirements and tests agreed upon by the joint group. Some of these requirements (and associated tests) include adhesion, weatherability, cleanability, fluid resistance, flexibility, and viscosity. The second includes program-specific, or "extended," requirements and tests identified by at least one of the affected programs. Examples of these extended requirements (and associated tests) are chemical agent resistance, corrosion resistance, more stringent tests for cleanability and flexibility, and signature issues.

The earliest versions of the zero-VOC topcoat experienced poor drying characteristics, including leveling, gloss, flexibility, and use time (pot life). New dispersing agents and rheology additives were able to rectify the majority of the problems; however, at this time, it appears that a property trade-off situation exists between pot life and flexibility. The latest two versions of the topcoat (camouflage gray) each exhibit a shortcoming in one of the two properties. One version passes all flexibility requirements, but has a pot life of three hours (one hour short of requirement); the other passes the pot life requirement, but displays a GE impact flexibility of 20% (40% required) at ambient conditions. Both versions demonstrate excellent low-temperature flexibility: no cracking was observed when coated panels were bent over a 1/2" cylindrical mandrel at -60°F.

Two solutions were proposed. The first involves optimizing the formulation to achieve the best results in both pot life and flexibility. The second solution involves using plural-component spray equipment. With plural-component spraying, both components (see Section 2.3) are placed in separate material-storing compartments. Hoses lead from each compartment to a "mixing

area". The mixing area consists of a network of intertwining tubes that blend the components. The admixed coating exits the mixing area and proceeds directly to the spray gun's nozzle. Therefore, excess waste is eliminated because only the amount used is admixed. Also, pot life is not an issue because the admixed material is applied seconds after mixing.

Although the advantages of the plural-component spray equipment are significant, its use is not recommended here for the following reasons. Plural-component spray equipment exerts a high shear force on the mixture as it passes through the mixing area. Work at NAWCADPAX showed that when combining the components of the current zero-VOC coatings with high-shear (e.g. high-speed mixer), excess carbon dioxide bubbles were generated, resulting in a surface finish with bubbles. This phenomenon is observed when mixing waterborne polyurethane coatings in a similar manner, whereas bubbles are not observed when mixing solventborne coating systems. The zero-VOC coating would have to be reformulated to be compatible with the new spray equipment. Also, the average plural-component spray unit can accommodate up to three spray guns. The largest aircraft painted by the Navy is the P-3 Orion, which requires eight painters, or three units. Because the units are on the order of \$40,000 each, a capital investment of \$120K per paint hangar would be necessary. Air Logistics Centers' investments would be even higher for sites that refinish large cargo aircraft such as the C-5. Because reformulation is necessary to achieve either the required pot life or sprayability with plural component equipment, it is significantly more cost-effective to pursue pot life extension at this time.

Under ESTCP, technology demonstrations will be conducted at NADEPs in Jacksonville, FL; Cherry Point, NC; and North Island, CA. Throughout this two-year evaluation, several Navy aircraft will be painted with the zero-VOC topcoat at the Naval Aviation Depots (NADEPs). Periodic inspections for performance will be scheduled with NAWCADPAX and NADEP representatives present for evaluations and if reformulations may be necessary to maintain current standards. Additionally, Warner-Robins ALC has agreed to demonstrations on USAF weapon systems component parts. Aft engine cowlings were painted at Warner-Robins in October 1998 and will be exposed outdoors at that facility for one year. The cowlings will be washed and rinsed every 60 days according to the T.O. 1-1-8 protocol. Assessments will be made of topcoat degradation before and after all washings.

The zero-VOC topcoat will be substituted for the standard topcoat when the aircraft is scheduled for its final painting at the NADEP. Performance of the new material must, at a minimum, perform comparably to aircraft painted with the standard finishing system at approximately the same time frame. Based on the results of these demonstrations and meetings of the joint group, the JTP may be modified to reflect the optimized performance with regards to pot life and flexibility.

3.4 High Solids Technology Another method to attaining a lower VOC coating is through the use of high solids technology. Several paths to increase coating solids are possible. The first and most obvious reduction comes from simply lowering the solvent concentration. While this approach reduces the VOC content, it shortens the pot life and significantly increases the resin viscosity when traditional raw materials are used. Also, the surface finish tends to be rougher

from decreased flow characteristics. Another option to lower VOC is through the use of reactive diluents. These materials are low-viscosity, low-molecular weight compounds that act like a solvent for viscous resins. On curing, the reactive diluent becomes part of the polymer backbone and is not driven off as a VOC. Using low molecular weight resins can produce a high-solids coating with lower viscosity and better flow properties. However, these materials tend to have shorter workable pot lives and lower flexibility when cured with traditional polyisocyanates. This lower flexibility is related to the increase in crosslink density resulting from the smaller backbone structures between functional groups. Using narrow molecular weight distribution isocyanate terminated prepolymers as the isocyanate source produces low VOC coatings with good performance and processing characteristics. These prepolymers yield coatings with lower viscosity, shorter drying time, and longer pot life.

A further approach utilizes blocked polymers. These yield a longer pot life, but they tend to be less mobile with slower reaction rates. Their decreased reactivity leads to long drying times, which is not desirable. In addition, high-boiling solvents can be used to replace convention solvents. By incorporating these materials, the applied films retain the solvent longer giving smoother surface finishes. However, this solvent retention leads to longer drying times and can allow the coating to continue to flow. This characteristic has produced a new phenomenon where sharp edges can be exposed with time. Finally, solvent retention can result in eventual porosity in the film, decreasing chemical resistance properties.

Two approaches to formulate low VOC coatings were pursued by the laboratory at NAWCADPAX using high-solids technology: reactive diluents and low molecular weight resins. These efforts were part of a SERDP effort (PP-65).

Reactive diluents were explored for use in the development of a low-VOC epoxy topcoat. Epoxy resins are among the binders that allow the formulation of high-solids paints. For more than 30 years, epoxy/polyamide systems have been used as the standard binder for coatings requiring superior chemical and corrosion resistance. The performance standard for these coatings utilizes an epoxy resin, cured with a standard high-viscosity polyamide curing agent. The epoxy resin is based on the glycidyl ether of bisphenol-A (DGEBA); its structure is given below in Figure 6.

Here, the value of "n" is between 2 and 3 and the epoxide equivalent weight (molecular weight divided by functionality) is approximately 500. In formulations containing such systems, 40-50 volume percentage solvent is necessary to attain a sprayable viscosity, significantly contributing to VOCs. Two reactive diluents were explored, one was monofunctional and the other was difunctional. The number of epoxide groups contained in the molecule defines the functionality. The monofunctional cresyl glycidyl ether (CGE) and the difunctional neopentyl glycol, diglycidyl ether (NGDE) are pictured below in Figure 7.

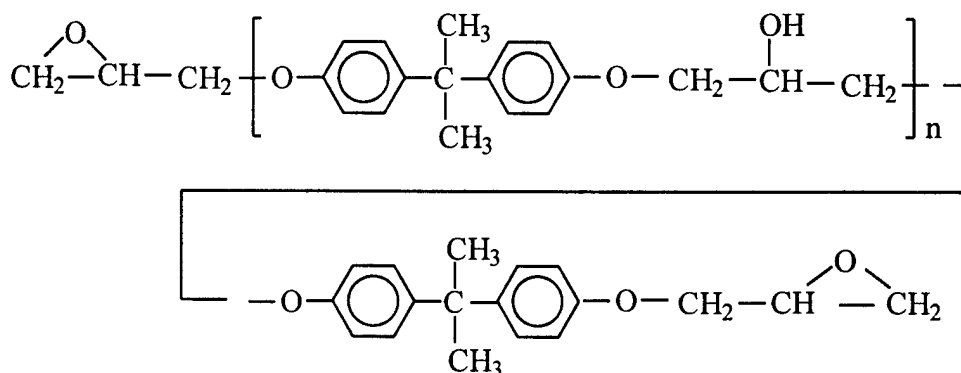


FIGURE 6. Chemical structure of an epoxy resin based on the glycidyl ether of bisphenol-A.

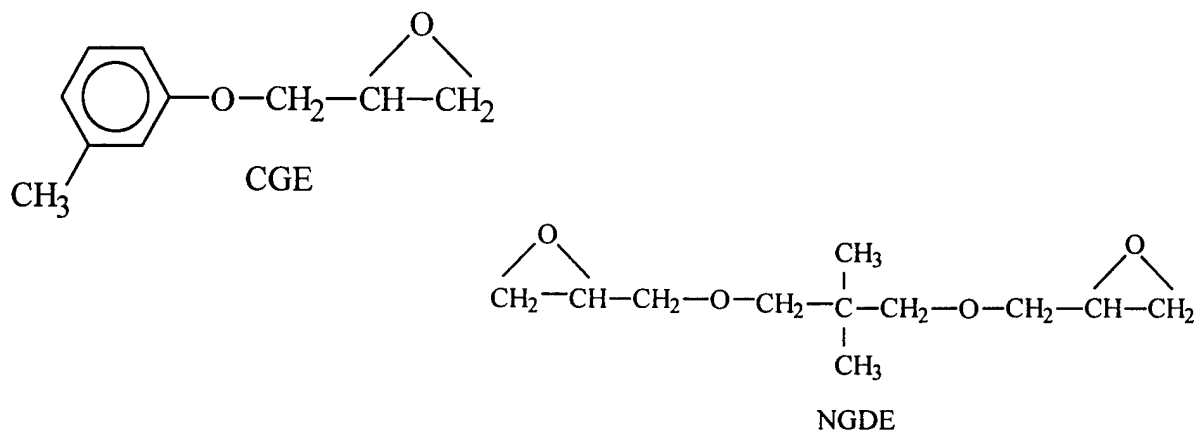


FIGURE 7. Chemical structures of the reactive diluents cresyl glycidyl ether (CGE) and neopentyl glycol, diglycidyl ether (NGDE).

Coatings prepared with CGE were unacceptable due to poor surface properties and possible fluid migration through missing crosslinks. Two successful formulations were prepared using NGDE, exhibiting superior performance and reducing VOC content to 60% of the standard epoxy topcoat. The formulations were submitted to a paint manufacturer for possible scale-up. The reactive diluent effort was summarized in a technical report. (41)

Low molecular weight resins based on aldimine chemistry were employed to develop low VOC coatings. Aldimines are reaction partners for isocyanates, which replace the polyols in the reaction scheme (see Section 2.3). Aldimines have viscosities that are so low that the standard polyester polyol is more than 50 times more viscous; this allows for a significantly less solvent usage to reach a sprayable viscosity.

Aldimine use for coating binder systems resulted from studies by a resin manufacturer on using ketimine-isocyanate reactions to produce clearcoats. These reactions produced a major product, azetidinone, and some minor products according to the scheme in Figure 8.

The minor products reacted further with the isocyanates resulting in coatings that varied in stability and color. Substituting aldimines for the ketimines resulted in the formation of the crosslinked azetidinone polymer film only (no minor products) that demonstrated good color and stability with 100% retention of solids.

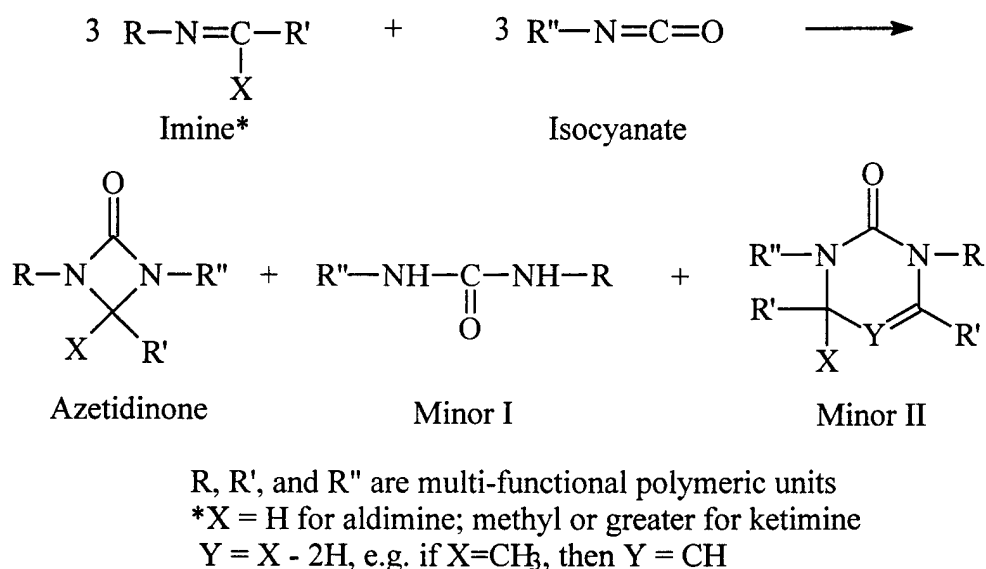


FIGURE 8. Imine-isocyanate chemical reaction scheme.

Pigmented formulations were prepared at NAWCADPAX at VOC levels of approximately 200 g/L. These formulations failed to produce workable coatings even after numerous optimizing attempts.

In summary, each individual approach has identified deficiencies that present a challenging problem to resin companies. However, a combination of these technologies appears to have the greatest potential for success and is being pursued by numerous manufacturers.

3.5 Low VOC Technology Status Numerous military and commercial specifications have been written to cover materials based on these technologies. However, in light of the proposed CTG and the ozone depleting substances problem, these material specifications are currently being modified to eliminate the type allowing exempt solvents and all other non-compliant

versions. This will authorize only low VOC materials for use. High performance VOC compliant primers, topcoats, and self-priming topcoats are required to have a maximum VOC content of 340, 420, and 420 g/L, respectively.

Waterborne and high-solids technologies have allowed for the development of protective coatings that contain a significantly reduced amount of VOC; some of these are currently under evaluation both in the laboratory and in the field. At present, it does not appear that VOC levels of less than 200 g/L can be attained with high-solids technology for aerospace coatings using present application methods. Novel polymeric water-based resins suggest that the development of zero-VOC coatings, which meet or surpass all existing requirements, is plausible and should be available within the next ten years.

3.6 Non-Toxic Inhibitive Primer Until recently, chromates were virtually the sole source for active corrosion inhibition in aircraft coatings. This was due to their outstanding performance in protecting nearly all metals in a large range of environments. However, chromates have been shown to be carcinogenic, and their use and disposal are becoming severely restricted. This has led to much research and development of non-toxic inhibitors for use in coatings, including those for aircraft. Pigments that have been investigated as alternatives include phosphates, borates, molybdates, nitrates, and silicates.

The mechanisms by which these inhibitors perform have not been thoroughly defined. Proposed mechanisms for zinc phosphate include the adsorption of ammonium ions, complex formation on the exposed surface, passivation through a phosphating process, and anodic/cathodic polarization. Phosphates, borates, and silicates are generally regarded as anodic passivators that reduce the rate of corrosion by increasing anodic polarization. Molybdates also have been classified as anodic inhibitors and especially effective at inhibiting propagation of pits. At high concentrations, the oxidizing action of molybdates is the main factor behind its corrosion inhibiting ability. Molybdate ions migrate into anodic areas and accumulate there, especially in pitted areas. Although these pigments individually provide some level of corrosion inhibition, in general, one for one substitution for chromates has not resulted in coatings with equivalent corrosion prevention capabilities. However, synergistic effects from combinations of some inhibitors provide nearly equivalent or superior properties to chromates (35, 42-44).

Non-chromated, non-toxic pigment packages were developed under SERDP by a joint Navy-industry effort. One such package was incorporated into a waterborne epoxy binder at NAWCADWAR. This primer passed all the requirements of MIL-PRF-85582 and was field-tested on a P-3 "beaver tail" component in February 1995 at NAWCADPAX. No discernible differences were observed between the in-house formulation and the chromated control after 236 flight hours. Resin quality and variability resulted in the cancellation of this part of the project, however, the beaver tail remains in service with no reported problems to date.

A non-chromated waterborne primer developed by Spraylat Corporation (now PRC-DeSoto) qualified to MIL-P-85582, Class N, a new classification that allows for non-chromated materials. A field demonstration was initiated on a T-2 aircraft at NADEP, Jacksonville, FL in March 1996 and an F-18 access panel painted at NAWCADPAX in September 1996. There have been no



FIGURE 9. Application of non-chromated, waterborne epoxy primer to a T-2 aircraft at NADEP Jacksonville, FL in March 1996.

reported problems to date and a full evaluation of the T-2 was performed in late July 1997. There were no significant differences between the T-2 painted with the non-chromated primer and those painted at similar times with the standard primer/topcoat system. Application of the non-chromated primer to the T-2 is shown in Figure 9.

In 1994, the Joint Logistics Commanders chartered the Joint Group on Acquisition Pollution Prevention (JG-APP) to coordinate joint service issues identified during the acquisition process. The group's (now called Joint Group on Pollution Prevention or JG-PP) objectives are to reduce or eliminate hazardous materials, share technology, and avoid duplication of effort. Their focus is on contractor design and manufacturing locations. One product is a Joint Test Protocol that establishes the critical requirements necessary to qualify alternative technologies. The Boeing Company organized a joint industry/government team to evaluate proprietary, non-chromated, epoxy primers for aircraft application. The Navy, Air Force, and National Defense Center for Environmental Excellence are participating.

Military specifications MIL-PRF-23377 and MIL-PRF-85582 define the performance requirements for high-solids and waterborne primers, respectively. Paint manufacturers were asked to submit samples of non-chromated primers for evaluation under either of the

specifications. Seven companies responded with thirteen different products. The corrosion inhibitors were typically blends of several compounds described above (phosphates, borates, molybdates, etc.). Primers were evaluated by NAWCADPAX in viscosity, pot life, drying time, surface finish, adhesion, flexibility, cure time, fluid resistance, corrosion resistance, and strippability tests. The non-chromated primers generally exhibited more corrosion in salt-spray and filiform tests in comparison with control primers containing chromates. Only one candidate, the water-borne coating from Spraylat Corporation mentioned above, met all of the qualification requirements.

Boeing St. Louis (formerly McDonnell Douglas Aircraft) conducted similar tests on these materials. They also included additional properties such as sprayability, heat resistance, humidity resistance, thermal-shock resistance, and compatibility with sealants, topcoats, and non-destructive inspection techniques. They confirmed NAWCADPAX's results and recommended a waterborne primer from Dexter Corporation as a second candidate for the service demonstration.

The demonstration included eight F/A-18 aircraft, two F-15 aircraft (wings only), an AV-8 aircraft, and several T-45 aircraft (touch-up painting). The Spraylat or Dexter primer was applied to one side of each aircraft and a standard chromated primer was applied to the other side. A MIL-PRF-85285 polyurethane topcoat was used over all of the primers.

Another team was formed to inspect the demonstration aircraft and document the results over a two-year period. The aircraft are currently based with operating squadrons at Naval Air Stations in Beaufort, SC, Cecil Field, FL, Lemoore, CA and Tyndall Air Force Base, FL. Early inspections indicate no significant differences in corrosion resistance between the chromate and non-chromate primers.

In summary, current available primers are based on two-component high solids or waterborne epoxy systems and corrosion inhibitors similar to those discussed above. These include molybdates, nitrates, borates, silicates, and/or phosphates as well as a variety of metal cation systems. These primers have shown promise in general corrosion resistance and adhesion tests; however, most of these primers have had problems providing adequate filiform corrosion resistance. In addition, many of these experimental coatings have exhibited flexibility, strippability, viscosity and storage stability deficiencies. Further investigation of these materials is being conducted to alleviate these problems. Finally, a better understanding of the corrosion inhibiting mechanisms associated with these non-toxic inhibitors, both individually and as multiple inhibitor systems, needs to be attained to formulate corrosion preventive primers more effectively and efficiently. A multi-service effort sponsored by SERDP (PP-1133) was begun in 1999 to address these concerns.

3.7 Touch-up Paints One approach which has been used to reduce VOC and hazardous waste from painting operations has been the development of self-contained touch-up paint applicators. Maintenance personnel must treat corrosion by removing oxidation products and loose paint, then repairing the original paint finish. Aircraft paints, such as MIL-P-23377 or MIL-PRF-85582 epoxy primer and MIL-PRF-85285 polyurethane topcoat, are supplied in two-component kits. Each component is taken from a quart or gallon can, mixed in a specific volume ratio, and

sprayed with air-atomized equipment. Workers tend to use more material than necessary to assure sufficient coverage. Excess paints must be processed as a hazardous waste. Improper mixing ratios often yield poor film properties. Spray application requires respiratory protection for all personnel in the area. Usage beyond damaged areas adds weight to the aircraft, thereby reducing its speed and range.

A unique kit designed to store, mix, and apply small quantities of two-component paints has been developed. Approximately 10 cc of the base and curing agent are contained in a clear, plastic tube separated by an impermeable barrier. When the barrier is displaced, the two components are easily mixed by shaking. A narrow brush on one end is used to dispense and apply the mixed material. A wider brush is also included. This kit, known as a "SemPen" and developed by Courtaulds Aerospace (now PRC DeSoto), can be used to touch-up areas of 1-2 square feet. The SemPen is shown schematically in Figure 10.

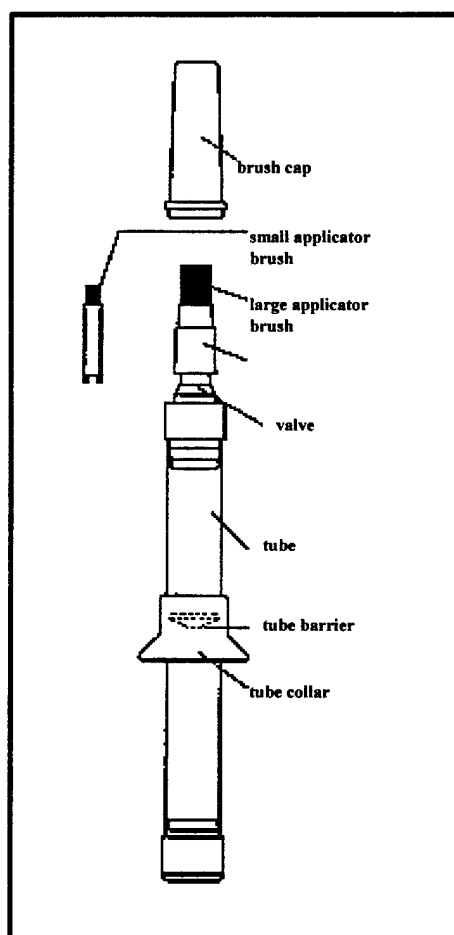


FIGURE 10. Schematic diagram of the "SemPen" self-contained paint applicator pen.

It has a number of advantages over spray application techniques using bulk materials:

1. The small, touch-up kit restricts maintenance personnel from mixing large quantities of paints that may be applied to excessive areas or disposed of as a hazardous waste.
2. Brush application minimizes airborne concentrations of the toxic solvents, isocyanates, etc. in paints. Other personnel can work nearby without protective equipment.
3. The individual components are pre-measured to assure precise mixing and optimum properties.

A number of kits containing MIL-PRF-85582 epoxy primer or MIL-PRF-85285 polyurethane topcoat (FED-STD-595, Color 36375) were supplied to operating squadrons for aircraft touch-up. The materials were used during normal maintenance operations to repair painted surfaces that were cracked, chipped, or corroded. Personnel observed the ease of application, appearance of the applied paint, and its durability over a six-month period. Fleet activities were enthusiastic about the kits, requesting their inclusion in the NAVAIR 01-1A-509 Manual (aircraft corrosion-control). National Stock Numbers have been obtained to allow procurement within the Federal Supply System. Because of the success of the kits, the development of a "corrosion control kit" has been proposed. This kit will contain the abrasive pads, rags, self-contained pretreatment applicator, and the primer and topcoat SemPens.

3.8 Adhesive Films Protective film technology has been used for specific applications in Naval aviation for many years. One of the primary means of protecting aircraft radomes and leading edges from rain-erosion is the use of elastomeric tapes. These tapes are flexible films bonded to painted surfaces with an attached adhesive. Recently, manufacturers of these types of materials (3M, etc.) have developed an appliqué film aimed at replacing aircraft exterior topcoats. These appliqué materials provide a durable, weather-resistant finish and are intended for application over a standard, corrosion-resistant primer. The material consists of a polymeric layer (can be multiple layers) and an adhesive layer with a plastic sheet over the adhesive. After removing this sheet, the film is bonded to the primer in adjoining or overlapping sections. During application, only simple measuring and cutting tools are needed. The work can be done in any enclosed area with minimal training. Nearby personnel can perform installation and maintenance work at the same time, since no safety or environmental hazards are present.

The technology progression is following the "Crawl-Walk-Run" philosophy. The "crawl" stage includes technology feasibility studies on single aircraft to demonstrate evolving laboratory products while resolving safety-of-flight concerns. The appliqué has exhibited good adhesion and excellent durability after exposure to aircraft fluids, weathering, high altitudes, and supersonic speeds. The next stage, or "walk" stage, will include multiple aircraft demonstrations where such questions as maintainability, removability, and cost effectiveness of the material will be addressed. The "run" stage will be entered upon successful completion of the walk phase. Those aircraft that are identified as good candidates based on performance and affordability will enter implementation on a squadron level scale. Full-scale operational issues will be finalized during this stage and the necessary efforts for implementation will be pursued.

Following exposure to weathering, high altitudes, and supersonic speeds, flight-testing to date has shown that appliqué materials can be made with good adhesion and durability. In many cases, the flight clearances for these demonstration aircraft have been extended for these tests to obtain more information. A high sensitivity to surface characteristics has been identified and is being addressed to expand the versatility of appliqué technology.

3.9 Electrodeposition Coatings And Powder Coatings Electrodeposition of paint works on a similar principle as that of the chrome plating of metal. Charged paint particles are electrically plated to an oppositely charged conductive substrate. The object to be coated is dipped into the electrodeposition tank and the current is turned on. This causes the paint solids to deposit onto the substrate as a paint film. During the operation, the paint coats every conductive surface, regardless of shape, with a uniform film whose thickness can be controlled very accurately. The paint film then insulates the substrate, preventing any further deposition of the coating. More detailed descriptions of the electrodeposition (e-coat) process can be found elsewhere. (45-47)

Because waterborne coatings are used in the e-coat process, VOCs are kept to a minimum. Also, no flammability hazards exist and no elaborate ventilation systems are required as with conventional spray techniques. A significant hazard does exist, however, with the enormous power required. The tank area must be enclosed and have fail-safe controls. The technique is also limited to small, conductive parts in aircraft applications. Also, typically temperatures around 149°C (300°F) or more are required for cure of these coatings.

Powder coatings can be applied by a variety of methods, including dip coating-fluid bed; electrostatic dip coating-cloud chamber; and the most ideal, spray-electrostatic spray. With electrostatic spray, as the powder passes the high-voltage electrode at the tip of the spray gun, it picks up the electrostatic charge and is attracted to grounded work. There, the powder adheres and will remain until fused and cured in an oven. More detailed descriptions of powder coatings and application techniques can be found in the literature. (46,48)

As with e-coats, film thickness of powder coatings is controlled by the insulating effect of the powder film as it builds up on the substrate. Overspray is considerable, but it can be collected and reused, so losses are low. Because the material is a solid, there are no VOCs, but an explosion hazard potential exists due to the fine dust overspray. Therefore, careful grounding of the booth and all equipment is required.

An operational, small-scale batch e-coat process line was established at the Naval Aviation Depot Jacksonville, FL (NADEP JAX) under SERDP. The line utilizes a cathodic electrodeposition epoxy coating that is cured in a conventional oven at 300°F for 20 minutes. Aluminum panels and scrap aircraft parts were successfully coated to verify such properties as consistent film thickness and throwing power. Corrosion tests of e-coated non-pretreated aluminum panels revealed undercutting of the coating on exposure to neutral salt spray. Because the e-coat exhibits superior adhesion as compared to typical coating systems, it was presumed that corrosion inhibitors in the bath would not be necessary. However, even pretreated aluminum panels exhibit some degree of undercutting. NADEP JAX, along with the National Defense Center for Environmental Excellence (NDCEE), Boeing St. Louis, and PPG Industries, is pursuing

newer formulations of e-coatings that incorporate non-toxic corrosion inhibitors in the bath. This investigation is still on going. The e-coat process line area at NADEP JAX is pictured in Figure 11.

A Nordson® powder coating spray booth with an electrostatic spray gun was installed at NADEP JAX under SERDP. Both steel and aluminum substrates have been successfully coated, as well as condemned aircraft parts. The coated parts are cured in a convection oven at 375°F for 15 minutes. The powder coating spray booth is pictured in Figure 12.

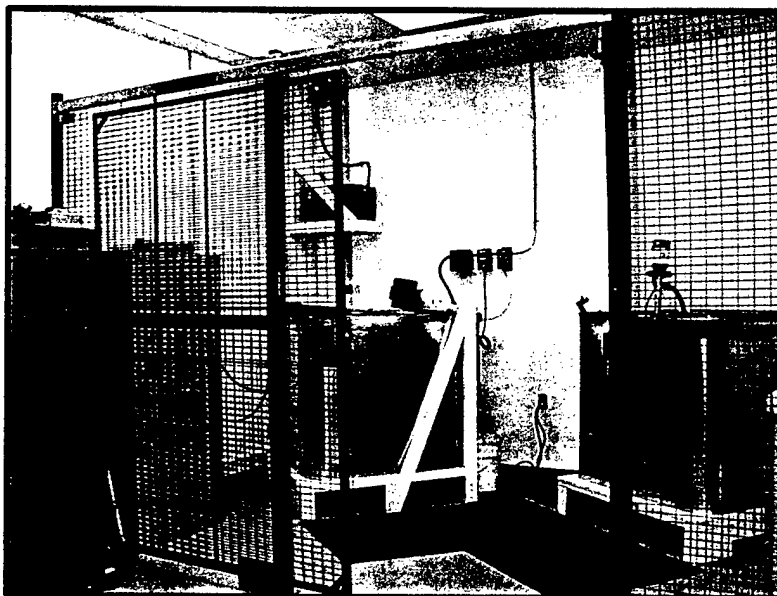


FIGURE 11. Small-scale e-coat process line at NADEP Jacksonville, FL.

Because of concerns affecting substrate properties at elevated temperatures (e.g. temper), investigations continue for powder coatings with lower cure temperatures. Materials that cure between 250-300°F are under test so to determine if any serious property trade-offs will occur on lowering the cure temperature. Cure temperature affects cross-link density; therefore, it will be necessary to address such properties as fluid and chemical resistance, corrosion resistance (limited barrier properties due to fewer cross-links), and adhesion.

Several parts have been e-coated and powder-coated and placed in service for field-testing. These include the following: 1) aerial refueling system – external fuel tank parts, 2) outer moldline access panels, 3) ejection seat parts, and 4) ground support equipment parts. Corrosion tests continue on e-coated and/or powder-coated steel and aluminum panels in salt spray and studies have begun on both strippability and reparability. Evaluations are continuing for electrocoating for applications under JSF funding. JSF, other NADEPs, and the Air Force have shown interest in the processes. NADEP JAX is currently pursuing e-coating and powder coating as approved alternatives to painting for small component parts.

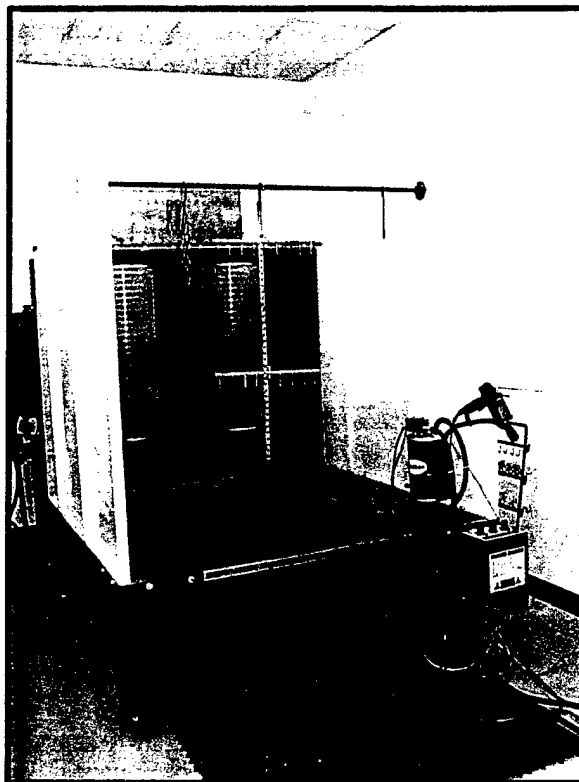


FIGURE 12. Powder coating spray booth at NADEP Jacksonville, FL.

3.10 Paint Application Equipment As part of the CAAA Aerospace CTG, conventional air spray application equipment will no longer be authorized for applying paints. Conventional air spray equipment has a transfer efficiency of approximately 28%. The types of paint application equipment authorized for these materials will be similar to those specified by the State of California's AQMD Regulations which require minimum transfer efficiencies of 60% to 85% and maximum gun tip air pressures of 10 psi. A number of alternative technologies have been proposed to meet this requirement and were assessed under SERDP at NADEP JAX. The only two spray application techniques authorized were electrostatic and high-volume low-pressure (HVLP) spray guns. These are summarized in Figure 13. Both of these techniques have improved transfer efficiencies over conventional air spray. Roller, brush, dip, and other non-spray methods are also acceptable. Each of these techniques has its unique capabilities and limitations. Some methods can be used in combination (i.e. plural component, air-assisted airless with electrostatic) to yield even higher efficiencies. Because the NADEP JAX study demonstrated HVLP to be the most cost effective, the technology has been implemented at all NADEPs.

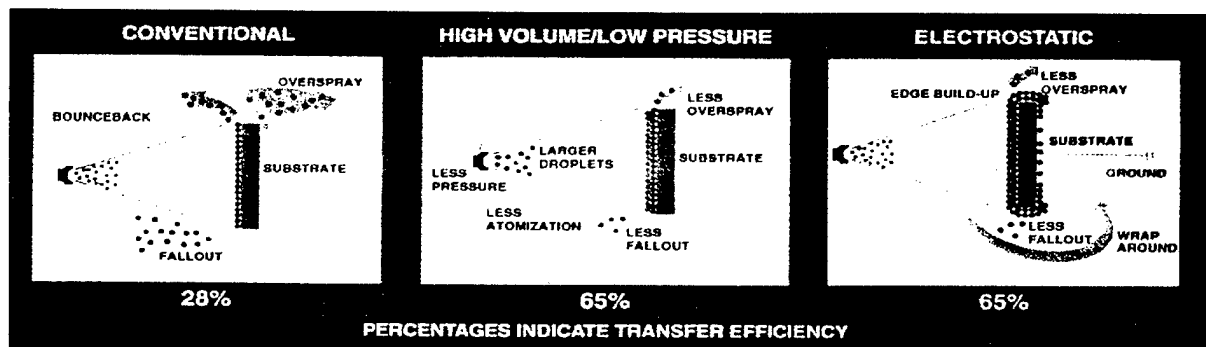


FIGURE 13. Comparison of paint spray-application techniques.

The method of cleaning spray equipment is also being regulated under the CTG. The old solvent wash method, which generated large quantities of hazardous waste and was time consuming, is being prohibited. Some type of enclosed cleaning method, which captures the majority of the cleaning solvent, has to be used. Paint gun washers that meet this requirement have been identified. In addition to drastically reducing the solvent emissions, these enclosed cleaning operations take approximately one fourth of the working time as compared to the old method.

3.11 Non-Chromated Sealants Hexavalent chrome-inhibited sealants were developed under Naval Air Systems Command (NAVAIR) sponsorship to provide additional corrosion protection beyond that provided by standard aircraft fuel tank sealants. The most effective inhibited sealants were formulated from polysulfide polymers, soluble chromates, manganese dioxide curing agents and other additives and fillers. Military specification MIL-PRF-81733 was the result of this effort and most of the products on the qualified product list (QPL) were qualified in the 1978-80 time frame. Inhibited sealants were applied to prevent faying surface corrosion and dissimilar metal corrosion and were also applied as corrosion resistant coatings. Since the best of these chromate inhibited sealants had excellent application, performance and shelf life properties, there was reverse engineering by some suppliers but little incentive to develop new inhibited sealants until the mid-1990s when the elimination of the use of soluble heavy metal compounds (such as chromates) was required.

Polythioether polymers and sealants were also developed under a series of NAVAIR research and development contracts in the 1980s. The polythioether sealants have several advantages over polysulfide types such as faster curing rates and a higher temperature performance range. This effort resulted in a military specification, MIL-S-29574, Sealing Compound, Polythioether, for Aircraft Structures. MIL-S-29574 has a Type II category for a corrosion inhibitive, fuel resistant sealant, but development of corrosion-inhibitive polythioether sealants did not progress until the SERDP program was initiated.

A direct replacement for the soluble chromate was not found so combinations of two or more chemicals were necessary to make up the new inhibitor packages for sealants. Inhibitors found to be effective replacements for chromates in paint primers and other corrosion prevention materials were not directly transferable to sealants. Because of the interactions of the polymers, curing

agents, adhesion promoters, fillers and other ingredients, it was difficult and expensive to effectively formulate new inhibited, non-chromated sealants with all the necessary sealant properties. As a result, most of the reformulated inhibited sealants released by sealant suppliers had limitations that needed to be resolved before even considering the sealants for military fleet use. When deficiencies were too severe, the products obviously were not acceptable. But because of the limited market for corrosion inhibited sealants (primarily naval aircraft), these "non-optimal" inhibited sealants were the only suitable replacements available.

Initial SO₂-Salt Spray Corrosion Study - A comprehensive study was undertaken under SERDP to determine the relative corrosion protection provided by available sealants, both corrosion inhibiting and non-corrosion inhibiting, from Courtaulds, a major supplier of aircraft sealants. Corrosion specimens were prepared at the NAWCADPAX in accordance with the requirements of MIL-PRF-81733. Duplicate set of specimens were exposure tested in SO₂-salt spray at NAWCADPAX and Boeing St. Louis (formerly McDonnell Douglas Aerospace [MDA]). Both 2-week and 4-week exposure results are presented for NAWCADPAX-exposed specimens, while only 4-week week results are given for MDA exposed specimens. These results are shown in Table 1.

Overall, NAWCADPAX's panels had significantly more pitting on the surrounding aluminum even at 2 weeks than the MDA panels, indicating a less severe environment in the MDA test chamber. PR-1875, a non-chromated polythioether, provided good corrosion resistance when tested both at NAWC and MDA. PR-1828, a low adhesion windshield sealant with no corrosion inhibitors and PR-1826, a high temperature polythioether (also with no corrosion inhibitors) also performed well. Discoloration, an early signal for corrosion, was the most common condition of the panels but pitting was minimal for almost all of the sealants. Because of these results, showing equal (or in some cases better) corrosion protection from sealants with no corrosion inhibitors to those with corrosion inhibitors (chromate or non-chromated), a new test method for evaluating corrosion protection is being developed. The pristine system tested per MIL-PRF-81733 is not necessarily representative of conditions in the fleet.

Galvanic Corrosion Prevention (Copper/Aluminum) - In order to evaluate the corrosion inhibiting abilities of a new non-curing, non-chromated sealant, CA-1000 (Courtaulds), mixed metal specimens were exposed to the SO₂-salt spray environment for 4 weeks using MIL-PRF-81733 as a guidance. In MIL-PRF-81733 only magnesium/aluminum coupled specimens are tested. This effort, using copper and aluminum panels, was undertaken to simulate the aluminum wing bulkhead/beryllium copper bushing found on some Navy aircraft. Degradation at the aluminum bulkhead and the force fit beryllium copper bushing occurs despite application of PS-870 because the bushing rotates within the bulkhead breaking the sealant and allowing moisture intrusion. Corrosion has been a major source of concern at this interface. The non-curing CA-1000 would be able to move with the bushing and provide continuous corrosion protection. PR-1875, a rapid-curing, non-chromated, inhibitive polythioether was included in the testing. A duplicate set of galvanic corrosion panels was prepared for mounting on racks on aircraft carriers to determine sealant effectiveness under severe natural conditions.

Table 1. SO₂-Salt Spray Corrosion Test Results

SEALANT	SOAK TIME	RESULTS/DESCRIPTION
PS-870	2 weeks	No discoloration; 1 pit at top edge of sealant
	4 weeks	10% discoloration; 2-3 pits around bottom shim
	4 weeks/MDA	1% discoloration; no pits
PS-890	2 weeks	1% (light) discoloration; no pits
	4 weeks	10% discoloration; no pits
	4 weeks/MDA	10% discoloration (slightly purple); no pits
PR-1750	2 weeks	1% discoloration; no pits
		2-3% discoloration; no pits but several "holes" in Al at center
	4 weeks/MDA	2-3% discoloration; no pits
PR-1775	2 weeks	No discoloration; no pits
	4 weeks	10% discoloration; no pits but several shallow "shiny" spots at edge of discoloration
	4 weeks/MDA	No discoloration; no pits
PR-1776	2 weeks	No discoloration; no pits
	4 weeks	No discoloration; 3 pits at edge of sealant
	4 weeks/MDA	No discoloration; no pits
PR-1820	2 weeks	1% discoloration; no pits
	4 weeks	10% discoloration (light); no pits
	4 weeks/MDA	5-7% discoloration; no pits
PR-1826	2 weeks	No discoloration; no pits
	4 weeks	No discoloration; no pits
	4 weeks/MDA	1% discoloration; no pits
PR-1828	2 weeks	10% discoloration; no pits
	4 weeks	10-12% discoloration; no pits but several shallow "shiny" spots at edge of discoloration
	4 weeks/MDA	10-12% discoloration; no pits but several shallow "shiny" spots at edge of discoloration
PR-1829	2 weeks	No discoloration; no pits but several "holes" in center
	4 weeks	No discoloration; no pits
	4 weeks/MDA	1-2% discoloration; no pits but one "hole" near fastener hole
PR-1875	2 weeks	No discoloration; no pits
	4 weeks	No discoloration; 1 pit at edge of sealant
	4 weeks/MDA	No discoloration; no pits

Specimens in the following table were prepared for exposure to ASTM G85 SO₂-salt spray for 28 days in accordance with MIL-PRF-81733. Each corrosion sample consists of a 7-mil thick layer of sealant placed between one small (2-inch x 3-inch) metal plate on a larger (4-inch x 6-inch) metal plate. For each of the eleven samples listed below, the small metal plate (anode) is

Table 2. Aluminum/Copper Mixed Metal Assemblies

Sealant	Copper Plate Coating
CA-1000	Nickel/Zinc alloy
CA-1000	Electroless Nickel plating
CA-1000	Dull Cadmium plating
CA-1000	Tin/Zinc alloy
CA-1000	Uncoated
PR-1875 B-2	Electroless Nickel plating
PR-1875 B-2	Dull Cadmium plating
PR-1875 B-2	Uncoated
PS-870 B-½	Electroless Nickel plating
PS-870 B-½	Dull Cadmium plating
PS-870 B-½	Uncoated

Table 3. Aluminum/Copper Mixed Metal Assemblies Exposed to ASTM G85 SO₂ Salt Spray for 28 days

Sealant	Coating	Corrosion Test Result
CA-1000	Cadmium	Cadmium coating eaten away in approximate semicircles along sides; small, raised mounds throughout region still coated by cadmium
CA-1000	Nickel	No corrosion, no erosion of coating
CA-1000	Tin/Zinc	Many small raised mounds like in cadmium sample; coating is eroded around edges
CA-1000	Nickel/Zinc	Lots of small, raised bumps throughout region still coated; coating is eroded around edges, black/white splotches on edges of what remains of coating (white substance on top of black substance), no corrosion in exposed copper
CA-1000	None	Discoloration around edges, no corrosion
PS-870	Nickel	No corrosion, no erosion of coating
PS-870	None	Discoloration around edges, no corrosion
PR-1875	Cadmium	Coating has eroded slightly from edges; pitting in some areas near edge of region still coated; no corrosion in copper exposed by erosion
PR-1875	Nickel	No corrosion, some very slight erosion of coating around edges
PR-1875	None	Discoloration around edges, no corrosion

chromated conversion-coated aluminum and the large metal plate is copper (cathode) with one of five different coatings. The various plating materials for the copper were chosen from the options currently under investigation for replacement of cadmium plating. The types of sealant used and the copper plate coating for each sample are listed in Table 2.

Test results and observations are shown in Table 3 for specimens exposed to ASTM G85 SO₂ salt spray for 28 days in accordance with MIL-PRF-81733.

Results from the three sealants evaluated in this study, PS-870, PR-1875, and CA-1000 were very similar. The sandwich specimens of bare copper and aluminum indicated some discoloration of the copper around the edges (under the sealant) but no corrosion was noted with any of the sealants. The cadmium plated copper specimens exhibited no corrosion but the cadmium plate, as the sacrificial coating, appears eroded from the edges of the specimen with the least amount of erosion under the PS-870 and PR-1875. The bare and nickel-plated copper specimens appear to have been the least affected by the corrosion testing especially with PS-870 and CA-1000. This study indicates that CA-1000 should perform as well as PS-870 in preventing corrosion but the CA-1000 has the added advantage of remaining as a gel (non-curing) to accommodate rotation of the bushing. The results of ongoing field-testing will be the final test of this new material.

Shipboard Exposure - The following non-chromated sealant specimens were attached to corrosion racks exposed onboard and aircraft carries. PR-1761 is a non-chromated EMI sealant that showed considerable promise in EMI shielding effectiveness and previous corrosion testing. PR-1775 (polysulfide) and PR-1875 (polythioether) are non-chromated corrosion inhibiting sealants designed to replace MIL-PRF-81733-qualified sealants. CA-1000, again, is a non-curing polythioether. The specimens are summarized in Table 4.

Table 4. Assemblies for Shipboard Exposure

Sealant	Mixed Metals
PR-1761 B-2	Aluminum/Graphite-epoxy Composite
PR-1775 B-2	Aluminum/Magnesium
PR-1775 B-2	Aluminum/Magnesium
PR-1875 B-2	Aluminum/Magnesium
PR-1875 B-2	Aluminum/Magnesium
CA-1000	Aluminum/Bare Copper
CA-1000	Aluminum/Electroless Nickel-Plated Copper
CA-1000	Aluminum/Zinc-Plated Copper

Preliminary test results were satisfactory again showing PR-1875 and CA-1000 to be effective non-chromated inhibited sealants. Final results will be available after test racks are returned to NAWC and the specimens are disassembled and analyzed.

Alternative Supplier for Sealants - Fifteen corrosion samples were made with Morton sealants placed between magnesium plates (anode) and alodine-coated aluminum (cathode). These samples are listed in Table 5; MC-730, a non-chromate corrosion-inhibitive sealant, was evaluated as an alternative to MIL-PRF-81733 chromate inhibited aircraft faying surface sealants. MC-665 contains chromates and was to be evaluated as a second source for Courtaulds' MIL-PRF-81733-qualified products. MC-275 was evaluated as a rapid-curing fuel tank sealant.

Table 5. Magnesium/Aluminum Assemblies

Sealant	Specimen Number
MC-665 B-2	12-16
MC-730 B-2	17-21
MC-275 B-2	22-26

Evaluations of Morton sealants were suspended when the polysulfide business was sold to Advanced Chemistry and Technology (ACTech). It was later determined the formulated sealants developed by Morton could not be marketed by ACTech, so this task was terminated.

Fleet Evaluations - The service evaluations of PR-1875 (non-chromated inhibited polythioether sealant) were conducted at NADEP North Island and NADEP Cherry Point. The materials performed satisfactorily on F-18 aircraft and H-53 and H-3 helicopters (floorboard applications). Field testing of CA-1000, PR-1875, and PS-870 bulkhead/bushing sealants was started in August 97 and is continuing. Field evaluations of new non-chromate-inhibited sealants from ACTech and Courtaulds will be performed at North Island and Cherry Point depots, and various Naval Air Stations under Operations and Maintenance, Navy (O&M,N) funding and other programs.

Transitions - The best alternative materials were identified from the laboratory evaluations and have been service demonstrated. These non-chromate inhibited sealant aircraft sealant compounds are being transitioned to fleet use through specification modification, technical manual revision, and design changes. Industry coordination throughout the development and evaluation of these materials and processes will insure availability for implementation. Most of the sealants are now covered under commercial AMS specifications maintained by the G-9 Committee of the Society of Automotive Engineers (SAE).

4. SUMMARY

Chromate elimination from aluminum pretreatments is continuing through multiple efforts. Alternative aluminum pretreatments are currently in the demonstration and validation phase on Naval aviation platforms and will soon be included on others in the Army, Air Force, NASA and private industry. Non-chromated sealers for Type II anodized aluminum are under evaluation as part of ESTCP project 199701 led by ARDEC.

Many new innovations in protective coatings technologies have emerged during the past few years including corrosion sensors; pressure sensitive, preferentially strippable coatings; and appliqué technology. As with pretreatments, the biggest driver in coatings research and development has been and will continue to be the implementation of more stringent environmental regulations which limit the types and amounts of materials used in coatings formulation and application processes. For organic coatings, these regulations mainly affect volatile organic compounds and heavy metals, although other types of chemicals have come under scrutiny. These policies are causing dramatic changes in how coatings are formulated as well as the raw material from which they are derived. Organic coatings based on non-heavy metal containing low- and no-VOC polymer binder systems are currently under demonstration and validation on operational aircraft. Research and development of novel low-VOC polymer systems (i.e., high solids, waterborne, powder coatings, etc.) and non-heavy metal compounds will continue well into the next century and the advances from these fundamental efforts will be translated to changes in coatings technology. In addition, the approach to improve aircraft finishing system performance will be attained through investigation and utilization of high performance polymers, pigments, and additives.

5. ACKNOWLEDGMENTS

The authors gratefully acknowledge the support of the Strategic Environmental Research and Development Program (SERDP); the Environmental Security Technology Certification Program (ESTCP); the Office of Chief of Naval Operations Environmental Protection, Safety, and Occupational Health Division (N45); and the Office of Naval Research (Code 332) Exploratory Development Program in sponsoring the research, development, testing and evaluation of the Naval Air Systems Team's protective coatings efforts.

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