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NAVAL AIR WARFARE CENTER AIRCRAFT DIVISION AT WARMINSTER ENVIRONMENTAL MATERIALS PROGRAM - PHASE II

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As the World's environmental consciousness continues to increase, more efforts are being devoted to finding safe, compliant solutions to past, current, and future environmental problems. Driving forces such as the Clean Air Act Amendment of 1990 and the Federal Facilities Compliance Act, have led the Department of Defense (DoD) to expand its efforts to reduce the amounts of hazardous materials generated from its cleaning, pretreating, plating, and painting and paint removal processes used in maintenance depots and operations (major DoD sources). The Navy has set a goal of near zero discharge of hazardous waste by the year 2000. In support of this goal, the Naval Air Warfare Center Aircraft Division at Warminster has a number of on-going efforts that deal with the elimination or reduction of hazardous materials used in aerospace processes. The Environmental Materials Program includes a variety of research, development, test and evaluation projects covering a wide range of technologies (volatile organic compounds reduction, chlorofluorocarbon elimination and toxic heavy metal replacement). These programs are aimed at solving environmental problems encountered by the fleet. A summary of previous environmental efforts performed at the Center are provided in the Phase I report. The following is an update to these programs along with a brief description of present efforts.

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Abstract

As the world's environmental consciousness continues to increase, more efforts are being devoted to finding safe, compliant solutions to past, current, and future environmental problems. Driving forces such as the Clean Air Act Amendment of 1990 and the Federal Facilities Compliance Act, have led the Department of Defense (DoD) to expand its efforts to reduce the amounts of hazardous materials generated from its cleaning, pretreating, plating, painting and paint removal processes used in maintenance depots and operations (major DoD sources). The Navy has set a goal of near zero discharge of hazardous waste by the year 2000. In support of this goal, the Naval Air Warfare Center Aircraft Division at Warminster has a number of on-going efforts that deal with the elimination or reduction of hazardous materials used in aerospace processes. The Environmental Materials Program includes a variety of research, development, test and evaluation projects covering a wide range of technologies (volatile organic compounds reduction, chlorofluorocarbon elimination and toxic heavy metal replacement). These programs are aimed at solving environmental problems encountered by the fleet. A summary of previous environmental efforts performed at the Center are provided in the Phase I report. The following is an update to these programs along with a brief description of present efforts.

INTRODUCTION

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 United States in recent years, has been the Clean Air Act Amendment (CAAA) of 1990. This law significantly effects the type of materials and processes which will be approved for use in the future. This regulation in conjunction with the Federal Facilities Compliance Act, which states that government facilities are no longer exempt from environmental laws, has heightened awareness and concern about federal compliance.

In response to this situation, the Department of Defense (DoD) has expanded its efforts to reduce the amounts of hazardous materials generated from the cleaning, pretreating, plating, painting and paint removal processes used in maintenance depots and operations. The materials associated with these processes have been identified as major sources of hazardous waste in the DoD (Ref 1). The Defense Environmental Restoration Account, Pollution Abatement, and the Strategic Environmental Research and Development Programs have provided the funds for these efforts. However, with the overall decrease in DoD's budget, increased funds alone are not sufficient. Joint service efforts which coordinate projects and eliminate duplication of effort are essential. A Tri-Service Environmental Quality Strategic Plan was developed which combines and coordinates the environmental efforts of the Navy, Army and Air Force. This plan defines user requirements as the driving force for environmental research, development, test and evaluation (RDT&E) projects. The document is divided into four areas of environmental concern: Clean-Up, Compliance, Pollution Prevention, and Conservation. In addition, technology road maps were developed in each area to highlight the transition of materials and processes, from initial development to final implementation into the user community.

The Naval Air Warfare Center Aircraft Division at Warminster (NAVAIRWARCENACDIVWAR) has a number of on-going efforts that deal with the elimination or reduction of hazardous materials used in aerospace processes. These programs are in direct support of the Navy's goal of a near zero discharge of hazardous waste by the year 2000. The Environmental Materials Program includes a variety of RDT&E projects as well as numerous joint efforts with other DoD and industry facilities and active participation in technical societies and environmental working groups. The RDT&E programs cover a wide range of technology areas. These include inorganic pretreatments and surface preparation processes, organic protective coatings and materials, and operational chemicals. These programs are aimed at solving near and long term environmental problems at all levels of fleet operation (depot, intermediate and organizational) and are included in the Pollution Prevention section of the tri-service plan. The primary hazardous materials being addressed by these efforts are chromium VI, high volatile organic compounds (VOC) contents, chlorofluorocarbons

(CFC) and toxic heavy metals. Reference 2 provides a history and summary of previous environmental efforts performed at the Center. The following is an update to these prior programs along with a brief description of present efforts.

Surface Pretreatments

The primary goal of the pretreatment efforts is the total elimination of chromium. This toxic material has been traditionally used 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 naval aircraft (A/C) and aerospace systems and the severe corrosive environment in which these systems operate. Chromium VI has been used widely in aerospace inorganic pretreatment processes and materials such as alkaline cleaners, deoxidizers, conversion coatings and anodizing processes. Chromium VI is a known carcinogen, but it was used because there was no adequate replacement available. Recently, regulatory agencies have enacted rules which will prohibit this practice, thereby requiring alternative materials to be employed.

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 future chemical pretreatments. While current chromated materials used in these operations perform satisfactorily, they need to be replaced with non-chromated alternatives. A laboratory investigation into these alternatives resulted in the recommendation of non-silicated, non-chromated alkaline cleaners and non-chromated deoxidizers for fleet use (Ref 3). Two viable materials identified from laboratory testing have been implemented as direct replacements into existing procedures at the Naval Aviation Depots (NADEP) at North Island, Jacksonville and Cherry Point. These non-chromated alternatives were coordinated with investigations conducted through the Aerospace Chromium VI Elimination Team.

Inorganic coatings are used as surface pretreatments for aircraft substrates because of their enhancement of the overall protective finishing system. These protective pretreatments are called out for virtually every weapon system, platform and support equipment used by the Navy, and are specified by MIL-S-5002 "Surface Treatments and Inorganic Coatings for Metal Surfaces of Weapon Systems." Conversion coatings and anodic films are the two primary surface pretreatments for naval aircraft.

Chromate conversion coatings (CCC) produced in accordance with MIL-C-5541 using materials conforming to MIL-C-81706 are excellent surface pretreatments for aluminum alloys. These materials form a surface oxide film, which enhances the overall adhesion and corrosion prevention properties of the protective finishing system applied over them. While CCCs have been an essential part of the Navy protective finishing system for many years, recent restrictions proposed by environmental agencies mandate that alternative pretreatments must be developed.

Previous non-chromated pretreatment development efforts investigated numerous proprietary non-chromated surface preparation and pretreatment materials to replace the current chromated materials. These experimental materials were evaluated on common aluminum alloys with standard Navy coating systems. Physical performance tests (i.e. corrosion resistance, adhesion, etc.) and electrochemical impedance spectroscopy were used to analyze pretreatment performance. This information is described in Reference 3. The most promising alternative is a proprietary multi-stage, heated bath process from Sanchem Inc. Although this material provides the closest performance to the standard CCC, it is currently limited to a bath process and is not directly applicable for aircraft skins. Efforts to modify the process for spray application are in progress. Incorporating steam generator equipment to provide the necessary process parameters has shown some preliminary success, and is being pursued further in a joint effort with Electrosteam Generators Inc. A pilot scale of this modified Sanchem process line is scheduled to be set up at the National Defense Center of Environmental Excellence to demonstrate the capability to produce a non-chromate surface pretreatment for aluminum.

Anodize processes currently used on Navy A/C form a thicker oxide film which provides more protection against degradation than conversion coatings. MIL-A-8625E "Anodic Coatings, for Aluminum and Al Alloys" describes the performance requirements for this type of film. Type I of this military specification covers chromic acid anodizing (CAA) which is presently used in production and depot level maintenance operations. Two potential alternatives were identified: Boeing Aerospace Corp's Sulfuric/Boric Acid Anodize (SBAA) and thin film sulfuric acid anodizing (Refs 4 - 6). Based on existing test data, the Boeing SBAA process was selected for demonstration as a replacement for chromic acid anodizing.

A lab scale sulfuric/boric acid anodize process line at NAVAIRWARCENACDIVWAR and a 3,200 gallon production scale SBAA line at the North Island Naval Aviation Depot were used in the evaluation of this process. The performance properties of SBAA were compared to those of CAA on various substrates, both sealed and unsealed. In addition, these films were examined as a base for standard Navy coatings and the fatigue characteristics of these oxides were characterized. The results of this study showed that the SBAA process provided equivalent corrosion resistance and paint adhesion while maintaining the existing mechanical properties provided by CAA. Specific details on this anodize investigation can be found in Reference 7. Based on this successful demonstration, the MIL-A-8625 specification was revised to include this anodize type and to transition this alternative for use in the fleet.

Elimination of CAA significantly reduces the total amount of chromium emitted from Navy pretreatment operations and is in direct support of Navy and DoD hazardous waste minimization policies and directives. In addition, the need for expensive control equipment required by California's Air Quality Management District (AQMD) laws effective in 1994 is eliminated, resulting in significant cost avoidance. Control equipment for the six Navy Depots is estimated at $4.5-6M for capitol costs and $2.5-4M for annual operating costs.

Plating Processes

Alternatives to cadmium and chromium plating and pretreatment baths are being isolated and evaluated. Efforts have been concentrated on developing potential alternatives for cadmium plating. Cadmium has been a commonly used coating due to its ease of application and its resistance to many varied environments, including salt spray exposure in sea service. Several Zinc-Nickel (Zn-Ni) electroplating baths of both acidic and caustic nature are being established for test comparison purposes at NAVAIRWARCENACDIVWAR, NADEP Cherry Point, and NADEP Jacksonville. The advantages/disadvantages of both general types of Zn-Ni baths will be recorded and verified through comparative test efforts between all three facilities.

A tin-zinc bath is planned for start-up at NAVAIRWARCENACDIVWAR in late 1993 to evaluate this coating for threaded areas where cadmium has been especially critical. Zinc-nickel is not able to replace cadmium for this application due to its increased minimum thickness requirements. Cadmium has been uniformly coated in threaded fastener areas at 0.0002 to 0.0003 inches per side while providing acceptable corrosion protection. Zn-Ni will require at least twice this thickness per side to offer equivalent corrosion protection. This added thickness will cause interference fits in threaded areas.

In addition to electrolytic plating replacements for cadmium, aluminum manganese molten salt bath plating is being pursued through a Broad Agency Announcement (BAA) released in June 1993. During the initial tests at NAVAIRWARCENACDIVWAR in the early 80's, it was discovered that this metallic glass coating offered protection very similar to cadmium, and provided fatigue values nearly identical to cadmium on steel. The BAA solicits commercial facilities capable of operating this plating system, while simultaneously developing the safety constraints and equipment necessary to allow ease of operation and care of this bath under production conditions. Unlike electrolytic baths, it is anticipated that this coating will be applied by metal treatment firms, such as steel companies, much like other molten salt baths used for metal heat treatment processes. Several companies have expressed interest, and proposals are anticipated over the next calendar year. Contact with the National Institute for Science and Technology has verified that duplication of this effort will not occur.

Additional contacts have been made with companies offering proprietary processes which compete with ion vapor deposition (IVD) of aluminum. One identified process allows many coatings such as cadmium, graphite, nickel and chromium to be applied to all exposed surfaces within a low vacuum plasma chamber with no measurable degree of airborne or water emissions. This effort is being carried out in cooperation with the Environmental Protection Agency (EPA). Additionally, the potential exists for the multi-layering of coating materials, which can not be layered with existing electrolytic, electroless or vapor deposition techniques.

Replacement of hexavalent chromium plating with the trivalent chromium process continues at several NADEPs and many contractor facilities. This will dramatically reduce chromium pollution in the near term and is recognized as the best short term interim solution for those applications where existing alternatives such as hardened electroless nickel are not currently able to meet minimum performance requirements.

This replacement reduces the environmental problems of chromium by about 97-99%. Advances in plating technology, derived from the former Soviet Union, offer potential methods of solving many of the current performance shortfalls, but will require significant funding to commercialize in the near term. One such method has the potential of doubling existing plating hardnesses of nickel, for example, which would allow nickel to replace chromium in many more applications than are currently possible. Additionally, this would allow thicker electrolytic plating to be used instead of the current electroless plating. Funding for these efforts may be supplied by the Office of Naval Research in the next fiscal year.

Organic Coatings

The primary defense against environmental degradation is the organic coating system. Protective organic coating systems are thought to be the rate controlling step in the corrosion of aircraft alloys (Ref 8). Therefore, high performance coatings are essential to the overall operational readiness of Navy aircraft. The environmental efforts in organic coatings can be described by two main thrusts: the development of low volatile organic compound (VOC) content coatings, and the development of non-toxic inhibited coatings. The efforts in low VOC are aimed at reducing the volatile organic compound content of Navy coatings to meet environmental regulations, especially California's AQMD rules and the CAAA Aerospace Control Techniques Guideline (CTG). The development of non-toxic inhibited coatings is concerned with eliminating toxic heavy metal pigments, such as lead, chromates and cadmium used in Navy protective primers, low IR field green coatings and topcoats.

The low VOC versions of the standard Navy primers and topcoats which have already been transitioned to the fleet, will allow the naval aviation community to comply with the CAAA Aerospace CTG. These materials are based on water-borne, high solids and exempt solvents technology. In light of the proposed CTG and the ozone depleting substances problem, these 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 in the fleet. The following is a list of the proposed specification types and VOC contents:

	Specification	VOC Compliance Type	VOC Content
PRIMERS:	MIL-P-23377	High Solids	340 g/l
	MIL-P-85582	Water-Borne	340 g/l
	TT-P-2760	High Solids	350 g/l
TOPCOATS:	MIL-C-22750	High Solids	340 g/l
	MIL-C-85285	Type I: High Solids	420 g/l
		Type II: High Solids	340 g/l
	TT-P-2756	High Solids	420 g/l

In addition to these materials, a number of efforts are presently underway to develop low VOC versions of Navy specialty coatings. One-component polyurethane topcoats have been developed for fleet touch-up operations. These low VOC coatings are easily mixed and applied, then cleaned up with soap and water. In addition, they contain no free isocyanates and minimize waste, since they are used as supplied. Service testing of a Courtalds material is currently in progress at the Naval Air Stations in Oceana, Miramar and Whidbey Island. The MIL-L-81352 lacquer specification is being revised to include this material. Water-borne wash primers from Deft Inc. and Sherwin Williams show promise and are being investigated further. The MIL-C-8514 wash primer specificationwill be revised to include a VOC compliant type. Also, the MIL-P-52905 temporary camouflage and MIL-C-85322 rain erosion resistant coating specificationare being changed to include VOC compliant types based on the results of laboratory testing. The MIL-F-7179 Finishing and MIL-F-18264 applications specificationsare being revised to include these new technologies.

Chromates have been the workhorse corrosion inhibitor for military aerospace coatings, particularly MIL-P-23377 and MIL-P-85582. Unfortunately, the chromate pigments contained in these corrosion inhibiting coatings are being regulated, requiring that non-toxic alternatives be developed. There are currently three efforts in the non-toxic inhibited aircraft coatings area: development of non-toxic inhibited primers, investigation into non-toxic corrosion inhibitor mechanisms, and development of self-priming topcoat technology.

The non-toxic corrosion inhibited primer effort has two methods to transition high performance, 340 g/l VOC primers to the fleet. The first approach is through the development of an in-house coating and the second is through the analysis of commercial available primers.

The in-house formulations are based on 2-component high solids polyurethane primers, and 2-component water-borne epoxy primers.

Although the dry film performance, such as corrosion resistance, adhesion, flexibility, etc., of these experimental high solids polyurethane primers is quite good, the viscosity and storage stability properties are currently deficient. Future efforts will be directed to alleviate these problems. Current water-borne epoxy primer formulations have performed well in laboratory testing and after the completion of long term corrosion tests, this material will be field tested in 1994. The analysis of commercial materials has yielded two promising candidates. The first product is a 2-component high solids epoxy primer manufactured by Courtalds Aerospace Coatings. The second material is a 2-component water-borne epoxy primer manufactured by Deft, Inc. Both of these materials, although promising, have problems related to filiform corrosion resistance, flexibility, and strippability. Further investigation by the manufacturers is in progress, and when complete, these materials will be evaluated again.

The non-toxic corrosion inhibitor mechanisms study is aimed at determining the mechanisms associated with individual inhibitors and multiple inhibitor systems. A thorough understanding of these mechanisms will allow for the subsequent development of predictive corrosion models. These models will be used to formulate corrosion inhibitive coatings more effectively and efficiently. To date, borate, molybdate, phosphate, and silicate as well as standard chromate corrosion inhibitive pigments have been analyzed using a direct current polarization analytical technique. A fundamental model of the electrochemical properties (i.e., corrosion current and corrosion potential) of these pigments has been developed. Further research in the characterization of the corrosion inhibition mechanisms will be generated from the analysis of accelerated environmental exposure, interfacial surface energy, electrochemical surface response profile, and continued direct current polarization experiments.

Self-priming topcoats (SPT) are low volatile organic compounds (VOC), non-toxic pigmented single coating systems that provide equivalent performance to the standard epoxy primer and polyurethane topcoat system. TT-P-2756 specifies the performance requirements for a 420 g/l VOC, two component polyurethane SPT which has been described in several publications (Refs 9-13). This environmentally compliant technology was first demonstrated on an operational F-14 at NADEP Norfolk, VA in February 1988. To date, over 130 operational Navy and Air Force aircraft have been painted with the SPT material and this technology is being transitioned to the entire aerospace community. Current developmental efforts include extending this technology to steel substrate applications (i.e., support equipment and structures) at 340 g/l, and also development of a 200 g/l version for aerospace applications. Experimental formulations for steel applications using a two component high solids polyurethane resin with a novel corrosion inhibiting pigment system have exceeded the performance requirements of the standard coating systems for steel substrates. Service testing of this material is planned for FY-94. In addition, an experimental 200 g/l SPT based on a two component water-borne polyurethane has shown promise. This ultra low VOC material is comparable to current TT-P-2756 qualified materials, with the exception of flexibility, optical properties, and long term storage stability. Solutions to these deficiencies are currently being investigated, and field testing of this material in scheduled for FY-95.

The transitioning of the non-toxic corrosion inhibited primers at 340 g/l and the SPT materials (the 340 g/l and subsequently the 200 g/l versions) to the fleet will be facilitated through the modification of appropriate specifications and manuals. Standard Navy primer specifications (MIL-P-23377, MIL-P-85582, TT-P-2760, and TT-P-1757) are in the process of being changed to include non-chromated classifications. The primary corrosion control manual (NAVAIR 01-1A-509) at the organizational and intermediate maintenance levels will be updated to include these specification changes. Also, a requirement to eliminate the use of cadmium pigments (typically used for optical properties) has been implemented in MIL-C-85285. Similar requirements for other Navy topcoats and lacquers, such as MIL-C-22750, MIL-C-85322, MIL-L-19537, and MIL-L-19538 are expected to be completed in FY-94.

An effort was recently initiated to develop non-toxic inhibited zero-discharge organic coatings. This program is a joint effort being conducted with NAVAIRWARCENACDIVWAR, Hughes Missle Systems Co., Hughes Aircraft Co., Lehigh University and the University of Arizona. Powder coatings, radiation curable coatings and electrocoatings are being developed to address future VOC requirements.

Paint Application Equipment

As part of the Clean Air Act Amendment of 1990, the EPA has developed a CTG for the aerospace industry (one of 174 source categories). Under this CTG, conventional air spray application equipment will no longer be allowed for applying paints. Conventional air spray equipment has a transfer efficiency of approximately 28%. The type of paint application equipment authorized for these materials will be similar to California's AQMDs. The transfer efficiency regulations require minimums 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. The only two spray application techniques authorized will be electrostatic and high-volume low-pressure (HVLP) spray guns. 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 own 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. Also, with the development and transition of a number of new coatings to meet these impending laws, the interaction of the compliant coatings with this type of application equipment must be evaluated. These application techniques are currently being investigated in conjunction with NADEP Jacksonville.

The method of cleaning spray equipment is also being regulated. 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. A spray gun washer that meets this requirement has been identified. In addition to drastically reducing the solvent emissions, the cleaning operation with this equipment takes approximately one fifth the working time as compared to the old method. These gun washers have already been incorporated into the NAVAIR 01-1A-509 Aircraft Weapons Systems Cleaning and Corrosion Control manual (Appendix B).

Alternative Paint Removal Technology

The protective finishing system on Navy aircraft is completely removed when the aircraft undergoes reworking at an aviation depot. This process occurs approximately every 3 to 6 years. Traditionally, chemical paint strippers are made up of methylene chloride, phenols, chromates and other hazardous materials, which are used to remove the paint system. With the acceptance of the CAAA of 1990, many of the traditional strippers are now considered to be hazardous air pollutants (HAP). The Aerospace CTG under the CAAA has a zero HAPs restriction. Consequently, traditional paint stripping which results in the generation of large quantities of hazardous waste, will no longer be acceptable. To address this problem, both non-hazardous chemical paint strippers and alternative mechanical paint removal methods are being investigated.

Solvent characteristics, rapid penetration, and non-flammability make methylene chloride the solvent of choice for paint stripping. Since this particular combination of properties does not exist in other solvents or blends, non-chlorinated paint strippers are necessary compromises. Vendors have taken two approaches to date: 1) N-methyl pyrrolidone-based removers (with an alkaline activator, usually an monoethanolamine) and 2) benzyl alcohol-based removers (with either an acid-activator, such as formic acid, or an alkaline activator, such as ammonia). The pyrrolidone removers are typically used in hot tank stripping processes because they are slow to penetrate at room temperature, but readily soften urethane paints at 140 to 200°F. Such products are available under MIL-C-83936 and have been used for small components for several years.

Recently, NAVAIRWARCENACDIVWAR evaluated two benzyl alcohol based products, Turco 6776 (acid-activated) and Turco 6813 (alkaline-activated). Although Turco 6776 stripped laboratory panels in less than one hour, it had the typical problems associated with acid strippers: hydrogen embrittlement on high strength steel and magnesium corrosion. Although the product passed all of the MIL-R-81903 (acid stripper specification) corrosion requirements, tests have shown that even the vapor from this product can embrittle C-ring test specimens in less than one hour. Turco 6813, an alkaline-activated remover, was very slow to strip laboratory test panels, taking about 24 hours to remove an epoxy primer/gloss urethane topcoat. Since the product passed MIL-R-81294 (alkaline stripper specification) corrosion requirements, it was recommended for further testing at the NADEP's. In April 1993, field evaluation of Turco 6813 at NADEP Jacksonville proved successful on a high gloss painted P-3C aircraft. However, evaluation of a sample of the product from the field demonstration revealed hydrogen embrittlement failures, when tested using the ASTM F519 Specimen 1d (C-Ring test). Production batches of this product are currently under evaluation for embrittlement. Additional demonstrations will be planned once it has been shown that the product can be manufactured with consistently acceptable properties.

Alternative mechanical paint removal methods under investigation include plastic media blasting (PMB), carbon dioxide pellet blasting, flash lamp, bicarbonate of soda stripping, wheat starch blasting, high pressure water jet blasting and combinations of these technologies. Substrate effects, particularly on thin aircraft skins, are of primary concern in this program since these blasting techniques can potentially cause surface damage, which can cause catastrophic structural failure. In addition, stripping rates, waste generation, capitol equipment costs and operating costs all play a part of this evaluation.

Accomplishments in alternative mechanical paint removal methods include PMB, waterjet and flashjet. One primary concern with the use of PMB is its effects on composite skins. A test plan was formulated to determine the effects of PMB on the mechanical properties of composite skins. To date, specimens have been blasted and are undergoing mechanical property testing. Specimens were blasted at predetermined blast parameters of:

Angle of Impingement: 45 and 90 degrees
Media Flow Rate: 500 lb/hr
Stand-off Distance: 18 inches
Nozzle Diameter: 1/2 inch
Nozzle Pressure: 30 psi

One variable in the testing was the number of times the specimens were stripped (5X, 10X, 20X, etc.).

Another alternative method is the FLASHJET system developed by McDonnell Douglas. Flashjet is the combination of the flashlamp and carbon dioxide pellet blasting methods. The flashlamp "burns" the paint and the CO_2 washes the residue away. NAVAIRWARCENACDIVWAR is sponsoring a test program for this technology as an add-on to the Air Force contract for development. The test plan covers the effect on mechanical properties of both metallic and non-metallic substrates. A twelve inch lamp has been developed as a result of the NAVAIRWARCENACDIVWAR test plan, which significantly increases the paint removal rate.

Determination of the feasibility of a high pressure waterjet process for Navy aircraft depainting was initiated, specifically for Navy composite substrates. Waterjet offers the potential for hazardous waste minimization, cost reduction and operational safety. Characteristics of the process were examined by stripping painted composite panels. Microstructural investigation and preliminary mechanical property tests are planned for the test panels which were stripped.

Another effort this year has been data gathering to accurately compare the various alternative paint stripping methods. A matrix for comparison of all methods is shown in Table 1. A primary conclusion is that the evaluation of the alternatives has been very harsh, using criteria based on control samples that have never been stripped. The recommendation from this effort is to compare alternative technologies to past stripping methods.

Adhesives and Sealants

Chromates are widely used in adhesive bonding metal pretreatment processes, as well as adhesive primers. These materials act as etchants, surface passivators and corrosion inhibitors. Phosphoric acid anodizing (PAA) is the aluminum surface bonding pretreatment most frequently used to replace the Forest Products Laboratory's (FPL) etch and other chromate containing solutions. However, some unanswered questions remain as to the effectiveness of PAA when used with non-chromated primers. The most effective structural adhesive primers contain large amounts of VOC's and soluble chromates (hexavalent chromium). In order to comply with federal, state and local regulations, new primers have been developed with reduced VOC and non-chromated inhibitors. Laboratory durability tests were conducted to determine the effectiveness of the new primers. The tests performed included wedge crack extension tests and lap shear stress durability. Primers were evaluated in three groups: (1) American Cyanamid's non-chromated, water borne BR250NC and BR350NC, and 3M's solvent borne EC3960, (2) Dexter Hysol's non-chromated, water borne EA9289 and solvent borne EA9205, (3) 3M's water borne EC3983 and solvent borne EC3924. The first group of primers were evaluated with American Cyanamid's FM300-2K film adhesive. The second group of primers were evaluated with Dexter Hysol's EA9689 film adhesive. The third group of primers were evaluated with 3M's AF131-2K and AF143-2 film adhesives. Table 2 contains a list of the systems evaluated.

Specimens primed with the non-chromated water borne BR250NC exhibit properties that are comparable to the solvent based EC3960. The specimens primed with BR250NC showed impressive resistance to 672 hours of humidity conditioning. Specimens primed with the water borne BR350NC system exhibited residual lap shear strengths comparable to the solvent based system.

TABLE 1. PAINT REMOVAL METHOD COMPARISON

	CHEMICAL	SANDING	PMB	WHEAT STARCH	ROBOTIC PMB	FLASHLAMP /CO2	WATER JET
# OF LABORER	6		1 per nozzle	1 per nozzle	1 per robot	4 per head	
TRAINING			1 week	2 weeks	6 weeks	1 week	
METAL DAMAGE			none	none	none		
COMPOSITE DAMAGE			matrix pitting	matrix pitting	matrix pitting		beyond primer fiber breakage fiber pullout
INITIAL COST			$600K		$4 million	$1.3M + $3/ft^2	
MAINTENANCE HOURS			0.5 man year		100 hrs/yr	150 hrs/yr	
MAINTENANCE COST			50K/yr		$40K/yr	$0.10/ft^2	
SAFETY REQ.			dust ventilation	dust ventilation	interlocks to doors/emergency stops	UV protection hearing protection	
FACILITY REQ.			exhaust floor recovery	humidity controls	supports for robots	Effluent capture system	
SAFETY HAZARDS			dust	dust		fumes noise	
WASTE AMOUNT			2000 lbs		2000 lbs	1 yd^3/plane	
WASTE REMOVAL $						$250/ yd^3	
AIR EMISSIONS						1%	
PREPARATION			1 hour		1 day	1 hr	
STRIP RATE(sqft/min)			1.0	1.0	2.5-5.0	2.0	
POST REQ.			1 hour		1 day	1 hr	
THROUGH-PUT TIME			16 - 24 hours 3 nozzles		3-4 days 2 robots		
PROCESS LIMITS						curved surface and tight areas	
REPEATABILITY					95%	±0.025"	
ROBOTICS			no	no	yes	yes	
STRIP PARAMETERS			Available	Available	Available	Available	
SOURCE OF INFO.			Cherry Point Depot	Hunting Aircraft	Southwest Research	McDonnell Douglas	

TABLE 2. PRIMER SYSTEMS USED IN STUDY

ADHESIVE	PRIMER	CARRIER	INHIBITOR
FM300-2K (Am.Cy.)	EC3960 (3M)	SOLVENT	CHROMATED
FM300-2K (Am.Cy.)	BR250NC (Am.Cy.)	WATER	NON-CHROMATED
FM300-2K (Am.Cy.)	BR350NC (Am.Cy.)	WATER	NON-CHROMATED
EA9689 (Hysol)	EA9205 (Hysol)	SOLVENT	CHROMATED
EA9689 (Hysol)	EA9289 (Hysol)	WATER	NON-CHROMATED
AF131-2K (3M)	EC3924 (3M)	SOLVENT	CHROMATED
AF131-2K (3M)	EC3983 (3M)	WATER	CHROMATED
AF143-2 (3M)	EC3924 (3M)	SOLVENT	CHROMATED
AF143-2 (3M)	EC3983 (3M)	WATER	CHROMATED

Wedge crack extension specimens that were primed with water borne EA9289 exhibited less growth than the specimens primed with the solvent based EA9205. However, the solvent based primer showed higher lap shear values in all of the test conditions. The primer to adherend failure that was seen in the water borne systems is an area of concern that require further attention.

Specimens primed with the solvent based EC3924 exhibited better overall properties than those primed with the water borne EC3983. Again, the primer to adherend failure that was seen in the water borne systems is an area of concern that needs to be addressed.

Overall, the water borne systems evaluated have shown great promise except for low temperature performance. Additional studies are planned to determine adhesion and peel strength (a measure of toughness) at -67^{o}F.

The sulfuric/boric acid anodizing (SBAA) process has not been as effective as PAA as an aluminum pretreatment prior to structural adhesive bonding. Lap shear tensile and peel strengths were 10-20% lower with SBAA. There is still interest in SBAA since this aluminum surface pretreatment has the possibility of better corrosion resistance (passivation) than PAA. An evaluation of a modified SBAA specifically for prebond treatment has been initiated and will be continued.

An inhibited non-chromated aircraft fuel resistant polysulfide sealant, PR 1775, was compared to the standard chromate inhibited polysulfide sealant PROSEAL 870 which meets MIL-S-81733 requirements. The corrosion study showed PR 1775 as less effective for corrosion prevention as either PROSEAL 870 or PR 1826, an unihibited, fast-cure polythioether base sealant. Typical corrosion specimens for this study consisted of magnesium panels fastened to aluminum panels with nylon fasteners. The magnesium is separated from the aluminum by a sandwich layer of sealant. The sandwich assemblies are exposed to SO2-salt spray for standard lengths of time, then disassembled and evaluated for corrosion.

PR 1775 has now been reformulated to improve adhesion and water resistance, as well as corrosion protection. Evaluations of the new reformulated PR 1775 will continue. A new water base sealant primer, PR 182, will be evaluated for its ability to enhance adhesion and performance of both inhibited and standard sealants. The PR 182 primer will replace PR 148 and other solvent containing primers.

Low/No-VOC Cleaners/Preservatives

Federal, state, regional and local regulations covering air and water pollution, as well as discharge permits and occupational health studies, continue to force change in this area. Elimination of solvents which are ozone depleting substances (ODS's), hazardous air pollutants (HAP's), or VOC's are obviously desirable. Current efforts include turbine engine gas path cleaners, corrosion preventives, and exterior aircraft cleaners.

MIL-C-85704, the aircraft turbine engine cleaner spec, was revised in Nov 92 to include requirements (under Types II and IIA) for an aqueous detergent cleaner containing at least 90 percent water in the use dilution, and prohibiting the use of hydrocarbon solvents. Due to the requirements for storage stability of the concentrates, up to 10 percent coupling solvent may be required (such as a glycol ether) in these cleaners. It should be noted that, although listed as one of the 189 HAPs under EPA, no regulations have yet been proposed covering this type of cleaning operation under the Aerospace Industry's National Emission Standard for Hazardous Air Pollutants (NESHAP). MIL-C-85704 will be further revised to include a Type III product to clean running turbine engines for shipboard applications.

The VOC content of existing corrosion preventives (MIL-C-81309, MIL-C-85054 and MIL-C-16173) was determined. These compounds were compared to products with low VOCs. Although low-VOC products usually do not displace water effectively, trial formulations with ingredients from Alox Corporation may prove useful. A new specification will be written to cover such products as Fluid Film, a low-VOC product based on wool wax.

A new non-VOC cleaning compound formulation, based on a blend of amphoteric and non-ionic surfactants, is being developed for use as an aircraft exterior cleaner with performance equivalent to the existing MIL-C-85570 Type II. In addition, a wheel well cleaner control formulation is being developed for inclusion in MIL-C-85570 as a Type VA, to meet San Diego AQMD requirements for a 10 percent limitation on solvent content in the use dilution.

Ozone Depletion Program

Ozone depleting substances (ODS's), such as chlorofluorocarbons (CFC's) and certain chlorinated solvents have been used for many years as non-flammable, fast-evaporating, effective solvents and propellants for many applications. The CAAA of 1990 established a schedule for gradual phaseout of CFC's and 1,1,1-trichloroethane (TCA) to be completed by 2000 and 2005 respectively. However, a Presidential executive order requires that CFC's be phased out by 1 Jan 1996 and hydrochlorofluorocarbons (HCFC) by 2000, with special restrictions on HCFC use prior to phaseout. There are currently 13 NAVAIR ODS replacement projects: avionics/electrical components applications, military specifications, oxygen systems cleaning, aircraft and precision bearing cleaning, non-destructive inspection, vapor degreasing, hydraulic fluid contamination testing, pre-bond cleaning, pre-plate cleaning, pre-paint cleaning, hydraulic and fuel filter cleaning, peroxide testing, and specialty items. NAVAIRWARCENACDIVWAR is the team leader for three replacement projects: avionics and electrical components, military specifications and peroxide number testing.

ODS's have been used in avionics and electrical component applications for solder flux removal and precision cleaning. In addition, ODS's have been used in aerosol propellent systems for electronic dusters, spot chillers and as carrier solvents for electronics lubricants. The following paragraphs are summaries of the status of each subtasks in this area:

FLIR cleaner. CFC-113 has been a very successful cleaner for removing accumulated greases from cryogenic helium lines in a FLIR (forward-looking infrared radar) detector system. Five solvent alternatives have been evaluated for cleaning Braycote 601 grease from babet balls (now done using CFC-113). Field trial of the best, 3M PF-5060, proved inadequate in cleanliness testing (vacuum stability test). Soil composition is being reevaluated.

Alternative soldering technology. Flux removal from plated through hole (PTH) boards and surface mount technology boards is achieved using azeotropic blends of CFC-113 or 1,1,1-trichloroethane with methanol. NAWC China Lake has completed an evaluation of HF-1189 water soluble flux. Included in the evaluation were practical soldering tests, acceptability to MIL-STD-2000, ionic cleanliness and surface insulation resistance, durability of solder joints after artificial aging and thermal shock, and identification of thermal degradation products. HF-1189 has been recommended for use in PTH mounting where water rinsing is tolerated. Currently, NAWC China Lake is evaluating 3 additional water soluble fluxes and no clean (or low residue) fluxes.

Electrical connector plug cleaning. Failure in plug and edge connector continuity can occur during the maintenance of avionic equipment at the squadron level. Connectors are typically cleaned with pressurized spray cans of CFC-113, then protected with MIL-C-81309 Type III corrosion preventive compound. Removal of salt deposits or residual corrosion preventive is an important function of this type cleaning procedure. Four solvents for cleaning cannon plugs were evaluated. Cleaning ability using corrosion preventive, hydraulic fluid, silicone oil, and sea salt soils was verified, as was compatibility with elastomers. A low pressure aerosol package (propellent = HFC-134a) with brush attachment was successfully field tested. Currently, Microcare, Inc. is developing an improved aerosol package to prevent plastic head breakage.

General purpose degreaser. Prior to repair, avionic equipment is often given a general cleaning to remove soils which have accumulated in service, such as fingerprints, silicone lubricants, dielectric fluids, corrosion preventives, and hydraulic fluid. Vapor degreasing with CFC-113 is commonly performed, as well as cleaning with aqueous solutions of non-ionic detergent. After aqueous cleaning, CFC-113 vapor degreasing functions as a water-displacer and drying agent. Seven aqueous non-ionic detergents were tested for their ability to clean Coolanol (dielectric fluid), and hydraulic fluid. An optically stimulated electron emission (OSEE) cleanliness tester was obtained for further study.

Freezing compound. Pressurized spray cans of CFC-12 and HCFC-22 are used as freezing compounds for diagnosing thermally intermittent failures. Six freezing compound compositions were tested for cooling rate, minimum temperature achieved, and electrostatic charging. A future report will recommend the use of HFC-134a with 4.9% addition of methanol to prevent electrostatic discharge damage.

Cleaner lubricant. Key pad contacts or other devices requiring intermittent electrical contact occasionally exhibit corrosion failures, therefore, preventive measures are taken by applying a lubricant/corrosion preventive such as MIL-C-81964 or MIL-C-83360. These products are currently available in pressurized spray cans and contain CFC-113 as a carrier solvent. A survey of electronics manufacturers and lubricant vendors did not identify spray applied products for electronics use. A potential candidate for non-flammable solvent spray is a DuPont or Allied Signal hydrofluorocarbon, which will not be available for testing until March of 1994.

Solder flux remover. Frequently, bench technicians resort to spot cleaning with pressurized spray cans of pure CFC-113 to remove soils deposited during the course of reworking a part. Flux remover for bench repair technicians is extremely important for component reliability. Solder flux residue from avionics repair has resulted in debonding of conformal coatings, and subsequent failure, due to accumulation of moisture and corrosion. Currently, pressurized spray cans of flux remover contain an alcohol with CFC-113 or 1,1,1-trichloroethane as the carrier solvent. The IPC Phase II test program at the Electronics Manufacturing Production Facility at Indianapolis has identified 13 products for manufacturer's in-line flux removal cleaning processes. Nine aerosol solder flux removers for printed wiring board (PWB) rework have been tested. OSEE is being used to identify the best available products for bench top use. MIL-C-85447 on solder flux remover will be revised to include an HCFC and a non-HCFC formulation.

Electrical equipment cleaner. Generators, transformers, switches, relays, motors, etc. have been cleaned using CFC-113. New cleaning techniques and materials will be studied in FY-94.

Conformal coating remover. Prior to PWB repairs, conformal coating removal is occassionally necessary and is accomplished by softening the coating with CFC-113 or TCA, then scraping with various tools. NAWC Indianapolis is developing test methods for evaluating 3 solvent-type conformal coating removers for use on various MIL-I-46058 coatings (acrylic, epoxy, silicone and polyurethane).

A number of efforts are underway with respect to military specifications which call out ODSs. HFC-134a and HCFC-22 have been tested as non-ODS propellants for aerosol use in corrosion preventives and spray kits. MIL-S-22805 spray kit and MIL-C-81309 corrosion preventive were revised to include both of these propellants, although it now appears that HCFC's will be prohibited after 1 Jan 94. The corrosion preventive compound formulation in MIL-C-85054 has been modified to eliminate CFC-113 but cannot be rendered non-flammable. Attempts to suppress the flash point using fluorinated solvents raised only closed cup flash points, not open cup flash points. This specification will be issued shortly as a flammable material. Coating specifications defining types containing ODS's (typically 1,1,1-trichloroethane as a non-VOC solvent) are being revised to eliminate that type, and alternative types (notably, high solids types) which already exist. In addition, amendments to 22 first level specifications were drafted for comment. A specification is under development for parts washer cleaning compounds. Requirements have been developed based on 26 candidate products (5 were fully successful).

Peroxide number testing is another area where ODS's have traditionally been used. To identify a non-ODS test method for determining peroxide number in fuels, the Naval Research Laboratory (NRL), Geocenters (an NRL contractor), Wright Patterson

AFB, University of Dayton (a WP-AFB contractor) and NAWC Trenton were contacted. The University of Dayton has developed a portable cyclic voltammetry test device to determine peroxide in fuel. The tester has been ordered from University of Dayton and will be compared with the existing method to validate its performance. A round robin testing program will be developed after proving the method at NAWC Trenton.

Composites

High temperature organic matrix composites used in Navy aircraft rely on methylene dianaline (MDA) as a curing agent. MDA is a multiple threat, in that it is both a carcinogen and a mutagen. As part of the 6.2 materials block, a program to characterize five resin systems that do not contain free MDA is underway. The materials being evaluated are X3009 (American Cyanamid), Primaset (Allied Signal), TRW-800 (HYCOMP), EX-1509 (Bryte Technologies), and Phthalonitrile (NRL). The out time, processability, mechanical properties, and thermal oxidative stability of each composite is being evaluated. The results of the study will be a material property database for the 2 systems with the best combination of properties. This will allow for the substitution of non-MDA systems on current and future Navy aircraft.

NAVAIRWARCENACDIVWAR has been requested to participate in an OP-40 sponsored group to develop a program to address environmental concerns related to the repair of naval aircraft. Small Business Innovative Research and other developmental programs are being formulated that will commence in FY-94.

RDT&E Transition and Implementation Methodology

The materials and processes developed under this program are being transitioned to full implementation for fleet maintenance operations in conjunction with NAVAIR and the Lead Maintenance Technology Center for Environment (LMTCE) through the development or modification of military specifications, the revision of maintenance manuals and by changing aircraft and system design plans. Traditionally, the transition from RDT&E to fleet use is accomplished through a long involved process requiring several years. In today's rapidly changing environment, this is no longer acceptable.

Several efforts to shorten this transition process have been established. One method to increase the rate of implementation of RDT&E efforts is to begin the specification revision in the final optimization stage of the project. This enables a mechanism for transition when the product demonstration is complete. Normally, a specification change takes from 6 to 12 months to complete. By starting the change process early, the revisions are being made concurrently with the product optimization and implementation. Another way to shorten the transition process is by using Rapid Action Changes (RAC) for the technical manual revisions. RACs can be issued quickly to amend manuals in the interim between overall revisions, which can take as long as two years. This ensures that the product information reaches the fleet in a rapid and timely manner. A third important aspect of technology transfer is to have coordinated demonstration plans that are agreed to by the approving authorities, prior to the demonstration initiation. This avoids needless delays for additional testing after the main demo is complete. Finally, market of new funds to accelerate the RDT&E efforts can lead to accomplishing milestones ahead of schedule.

Future Acquisition Programs

While pollution prevention and source elimination for existing materials and processes are important goals of any environmental program, another important aspect is to eliminate or minimize any hazardous material from any future acquisition. Therefore, reviews of environmental impact assessment plans for future aircraft and weapon systems are part of the NAVAIRWARCENACDIVWAR Environmental Program. Active programs being reviewed include: the F-18E/F, AX, JSOW and UAV BQM-145A. Materials and processes proposed for these systems are evaluated relative to their effect on the environment. Several developmental and joint evaluation efforts are currently on-going.

SUMMARY

All of these programs have lead to the development of non-hazardous or less hazardous materials, processes and equipment for current aerospace maintenance and manufacturing. Many of these materials and processes have been successfully demonstrated at naval aviation depots, intermediate maintenance depots and organizational maintenance levels, through cooperation with the Naval Air Systems Command (NAVAIR) and the LMTCE. The use of these new maintenance materials and processes allows the Navy to meet stringent environmental standards while maintaining operational readiness and efficiency of system performance. In addition, significant cost savings are being recognized by the implementation of these environmentally compliant materials.

LIST OF ACRONYMS

A/C	Aircraft
AQMD	Air Quality Management District
BAA	Broad Agency Announcement
CAA	Chromic Acid Anodizing
CAAA	Clean Air Act Ammendment
CCC	Chromate Conversion Coating
CFC	Chlorofluorocarbon
CTG	Control Techniques Guidelines
DoD	Department of Defense
EPA	Environmental Protection Agency
FLIR	Forward Looking Infrared Radar
FPL	Forest Products Laboratory
HAP	Hazardous Air Pollutant
HCFC	Hydrochloroflourocarbon
HVLP	High Volume Low Pressure
JSOW	Joint Standoff Weapon
LMTCE	Lead Maintenance Technology Center for Environment
MDA	Methylene Dianaline
NADEP	Naval Aviation Depot
NAVAIR	Naval Air Systems Command
NAWC	Naval Air Warfare Center
NAVAIRWARCENACDIVWAR	Naval Air Warfare Center Aircraft Division Warminster
NESHAP	National Emission Standards for Hazardous Air Pollutants
NRL	Naval Research Laboratory
ODS	Ozone Depleting Substances
OSEE	Optically Stimulated Electron Emission

LIST OF ACRONYMS (Continued)

PAA	Phosphoric Acid Anodizing
PMB	Plastic Media Blasting
PTH	Plated Through Hole
PWB	Printed Wiring Board
RAC	Rapid Action Change
RDT&E	Research, Development, Test & Evaluation
SBAA	Sulfuric/Boric Acid Anodize
TCA	1,1,1-Trichloroethane
VOC	Volatile Organic Compounds

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