AGARD-R-816

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ADVISORY GROUP FOR AEROSPACE RESEARCH & DEVELOPMENT

7 RUE ANCELLE, 92200 NEUILLY-SUR-SEINE, FRANCE

AGARD REPORT 816

Environmentally Compliant Surface Treatments of Materials for Aerospace Applications

(les Techniques de traitement de surface conformes à la réglementation sur la protection de l'environnement pour les matériaux destinés aux applications aérospatiales)

Papers presented at the 83rd Meeting of the AGARD Structures and Materials Panel, held in Florence, Italy, 4-5 September 1996.

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North Atlantic Treaty Organization
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Environmentally Compliant Surface Treatments of Materials for Aerospace Applications

(AGARD R-816)

Executive Summary

Traditional surface treatments for aerospace materials are becoming unacceptable due to pressures exerted by national and international environmental and health organizations. For example, the applied volatile organic compound (VOC) content of organic coatings is now limited by law in several countries. Cadmium and chromium compounds that provide excellent corrosion inhibition, as well as desired surface interaction properties, are targeted for reduction to levels that may make them impractical for long-term use.

Throughout the Workshop it was shown that in recent years, research and development efforts in environmentally compliant surface treatments for cleaning, surface preparation, coating and electroplating have resulted in new or modified materials and processes for the aerospace community. Widespread substitution of this new technology is limited because many of the new materials/processes have some characteristics that may not fully meet traditional performance standards. Also, some of the newly developed processes are less controllable or robust and may have problems when production scale-up is required.

The conclusions and recommendations of the Workshop stated that continued research and development efforts are required in order to successfully develop and implement new environmentally compliant surface treatments for aerospace applications.

Les techniques de traitement de surface conformes à la réglementation sur la protection de l'environnement pour les matériaux destinés aux applications aérospatiales

(AGARD R-816)

Synthèse

Aujourd'hui, les traitements de surface classiques sont difficilement acceptables pour les matériaux aérospatiaux en raison des pressions exercées par les organisations nationales et internationales de l'environnement et de la santé. A titre d'exemple, dans plusieurs pays, le contenu en composés organiques volatiles (VOC) des revêtements organiques est actuellement fixé par decret. Il est prévu de réduire le contenu en composés de cadmium et de chrome des revêtements organiques à des niveaux qui risquent de les rendre inefficaces à terme. Or, ces composés sont d'excellents inhibiteurs de corrosion et ont toutes les caractéristiques d'interaction surfacique demandées.

Tout au long de l'atelier il a été démontré qu'au cours des dernières années, tous les travaux de recherche et développement entrepris en techniques de traitement de surface conformes à l'environnement pour le nettoyage, la préparation des surfaces, le revêtement et la galvanisation ont débouché sur des matériaux et des procédés nouveaux ou modifiés, au profit de la communauté aéronautique et spatiale. La substitution généralisée de ces nouvelles technologies est pourtant limitée puisque bon nombre des matériaux et procédés ont certaines caractéristiques qui ne correspondent pas tout à fait aux normes de performances traditionnelles. Aussi, certains procédés nouveaux sont moins contrôlables ou moins robustes et risquent de poser des problèmes lors du lancement de la production à grande échelle.

En conclusion, les membres de l'atelier ont recommandé la continuation des efforts de recherche et développement qui sont faits, afin de développer et de mettre en œuvre de nouveaux traitements de surface conformes à la réglementation sur la protection de l'environnement, pour des applications aérospatiales.

Contents

SESSION I: OVERVIEW

SESSION II: CLEANING, SURFACE PREPARATION

SESSION III: COATINGS, PAINT, PLATING

Preface

The current focus to develop and implement environmentally compliant materials and processes is primarily aimed at developing technology that requires the use of less hazardous materials and processes, while increasing process efficiency and decreasing costs.

The SMP held a Workshop on Environmentally Compliant Surface Treatments of Materials for Aerospace Applications. The purpose of this Workshop was to review and assess the latest progress in environmentally compliant surface treatments for aerospace applications. This includes processes involving surface cleaning, preparation and modification and coating (e.g. paints) and plating technology.

The Workshop format consisted of presentations of the environmental legislation and regulations, as well as overviews of the work on environmentally compliant surface treatments in several NATO countries. These were followed by presentations of specific work dealing with cleaning, surface preparation, coatings, paint and plating.

On behalf of the Structures and Materials Panel, I would like to thank the authors, session chairmen and technical evaluation reporter whose participation made possible the success of the Workshop.

Dr. Jeffrey Waldman
Chairman, Sub-Committee on
Environmentally Compliant Surface Treatments
of Materials for Aerospace Applications

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TECHNICAL EVALUATION REPORT

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1. SUMMARY

This report provides a technical evaluation of the workshop on "Environmentally Compliant Surface Treatments of Materials for Aerospace Applications," held during the 83rd meeting of the AGARD Structures and Materials Panel on 4-5 September, 1996, in Florence, Italy.

2. CONTENTS OF PRESENTATIONS

2.1 Environmental Issues and Perspectives

With the implementation of the Montreal Protocol and independent nation initiatives, Ozone Depleting Substances (ODSs) are severely restricted and banned from production in some cases. Other organic, semi-aqueous and aqueous alternative solvents are implemented and are resulting in monetary return on investment. However, the introduction of non-ODS alternatives has created a flammability problem for users. The US Clean Air Act amendments of 1990 and European clean air and clean water initiatives are now the major concern for the aerospace facilities.

Environmental and human health regulations that impact surface treatments of materials are primarily focused on three major areas; 1) organic air emissions, 2) inorganic air emissions and 3) water discharge standards. Papers that focused on these areas were presented from the USA, Canada, France and the United Kingdom. Organic coatings and cleaning solvents are the major target of most environmental standards and the limit on volatile organic compound (VOC) for primers and topcoats varies between nations. Waterborne or water-reduced primers and topcoats are under development and some are successfully implemented. Inorganic air emissions result from metal treating and coatings processes including anodizing, pickling and electroplating. Limits on cadmium and chromium air emissions are of greatest concern due to their extremely small allowable levels and the threat to decrease these levels to the point where the use of cadmium or chromium processes may no longer be practical. Current levels in the USA are 5.0 $\mu g/m^3$ for cadmium and 0.5 mg/m^3 for chromium. Proposed levels fall to 0.5 - 5.0 $\mu g/m^3$ for chromium prior to the next century. Water pollution restrictions are usually defined as release standards that set limits on the concentrations of organic and inorganic pollutants discharged from a surface treatment facility to a waste water treatment facility. Hexavalent chromium is restricted to a concentration of less than 0.1 mg/l in France while standards in the USA vary between States.

Each NATO country identified restrictions on cadmium and chromium as their top concern and the technology specific presentations echoed that concern.

2.2 Cleaning

Papers were presented from Canada and the USA. A general concern about the substitution of flammable solvents for non-flammable ODS solvents was described in both papers. Many effective substitutes for ODS solvents are developed and implemented. Most of these are organic wipe solvents that consist of oxygenated hydrocarbon blends or terpene/parafinnic hydrocarbon mixtures. Although these substitutes are effective, tradeoffs must be made between evaporation rate (relating to vapor pressure and user acceptance) and flammability. Non-liquid substitutes were also discussed but are in the preliminary research and development (R&D) phase. These include ultraviolet light with carbon dioxide pellet blasting, ultraviolet light in an elemental oxygen atmosphere as well as CO_2 and excimer laser processes.

2.3 Surface Preparation

Several technologies are under evaluation as substitutes for chromate based adhesive bond pretreatments, conversion coatings and de-oxidizers. Wet chemistry processes are the standard for surface preparation and papers from Germany, the United Kingdom, and the USA presented the latest status and summary of results of materials substitutes and new processes under research and development. Cerium formate, nickel metavandate and tetra-ethyl ammonium thiotungstate were evaluated as alternatives for strontium chromate corrosion inhibition. Phosphoric Sulfuric Acid (PSA) anodizing, additions of cerium and potassium permanganate to standard sulfuric acid anodize baths were presented as promising substitutes for chromic acid anodize while, ion beam enhanced deposition, sol-gel deposition, excimer laser oxidation, plasma polymerization and plasma spray techniques were discussed as innovative techniques that were explored as alternatives for chromated adhesive bond pretreatments.

Replacements for chromate anodize operations were presented by Germany and the United Kingdom. It was concluded that the PSA anodize process could be used for applications that do not require a hot water seal. The process requires a shorter immersion duration and has some potential economic benefits, however, the need to operate a recycling facility to keep the content of dissolved aluminum within the desired limits offers a challenge to large production scale-up. Chemical additions (at 7.5 g/l) to the standard sulfuric acid anodize process were evaluated against the neutral salt fog results of chromic acid anodize. The addition of cerium (III) or cerium (IV) provided high (but not yet comparable) levels of corrosion protection. More work needs to be pursued in this area to vary concentrations, study alternative additions and define the fatigue and salt fog/SO_2 performance of other aerospace alloys that undergo these novel processes.

Among the new adhesive bond pretreatments discussed, the sol-gel technology showed particular promise since it appears to be the easiest, most economical process to scale-up. Sol-gel materials also provided the best materials performance properties (wedge and lap shear tests of adhesive bond strength) as reported by the USA.

2.4 Organic Coatings

Advances in environmentally compliant topcoats and primers include the identification, evaluation and service use of some non-chromate inhibited and low-VOC coatings. Papers presented by the UK and Germany primarily focused on the re-evaluation of accelerated performance tests required to meet the most common coatings specifications as well as requirements for future coating systems. The UK presented an overview and analysis of the industry accepted standard tests for corrosion inhibition. The selection of revised standards in accelerated corrosion test requirements and the need to continue comparisons to the long-standing neutral salt fog test ASTM B117 were emphasized. Also, some benefits and drawbacks of intermittent neutral salt fog testing were discussed. Near term coatings systems in Germany and the USA must contain less than 350 g/l VOC in primers and 420 g/l VOC in topcoats. The acceptance of waterborne coatings is troubled by their sensitivity to application conditions (mostly operator skill and atmospheric humidity).

2.5 Electroplating

Cadmium electroplating remains the preferred protective coating for aerospace steel components and fasteners because of cadmium's lubricity properties and outstanding sacrificial qualities. Cadmium compounds are also considered one of the most toxic substances used in aerospace metals finishing. Damage to liver, kidneys, and lungs is attributed to very small amounts of cadmium inhalation and ingestion. European Union and USA environmental groups and regulatory bodies are considering an effective ban on the use of cadmium in industrial operations before the year 2000.

Substrate corrosion resistance, hydrogen embrittlement tendencies, fatigue life degradation, chemical resistance, paint adhesion and lubricity properties must be considered for any environmentally compliant substitute for cadmium electroplating. Papers from the United Kingdom and the United States outlined a spectrum of R&D efforts including investigations of electrodeposited zinc-cobalt-iron, aluminum, tin-zinc and acid/alkaline zinc-nickel. Tension-tension fatigue tests of coated substrate materials were performed as well coating adhesion testing. The most promising electroplated substitutes to date include alkaline zinc-nickel (the process is more robust in production than the acid nickel process). A molten aluminum manganese salt bath is also under evaluation but has the drawback of a 400^0 F bath operating temperature.

Electroplated chromium remains the standard aerospace coating on steel that requires excellent corrosion resistance and wear properties. Alternatives now in R&D include electroless nickel, electroless nickel (nanocrystalline diamond impregnated), physical vapor deposition, thermal spray (HVOF) materials, nickel-tungsten-boron electroplating as well as ion beam implantation and deposition assisted processes. Comparisons of the wear, adhesion and fatigue properties of these coatings were presented. HVOF and electroless nickel is now implemented and replacing some uses of electroplated chromium. The thermal spray processes (like HVOF) have good thickness buildup characteristics and are currently the most desirable candidates for chrome replacement. However, thermal spray and ion beam assisted technologies have limitations on their ability to coat inner diameters. Thermal spray coatings (especially ceramic/metal materials) are difficult to machine but usually quite controllable during application therefore desired thicknesses are often obtained by a skilled artisan.

Because of the unique properties of electroplated chromium and cadmium, their low operating cost and application versatility, no one substitute for either coating is on the horizon. A spectrum of materials and methods are under evaluation. Due to the high toxicity of chrome and cadmium, continued research and development efforts are needed to find environmentally compliant substitutes that are practical and economical.

3. CONCLUSIONS AND RECOMMENDATIONS

In recent years, a great deal of important materials and process R&D has resulted in new or modified aerospace materials that are more environmentally benign. These new materials are implemented on a limited basis, however, wide spectrum materials substitutions are rare because many of the new materials have characteristics that may not fully meet traditional performance standards. Also, as is the case with the phosphoric sulfuric acid anodize process as a substitute for the chromic acid anodize, some processes are less controllable or robust and therefore may suffer when production scale-up of laboratory developed technology is attempted.

While low VOC, water-reduced and non-chromate inhibited organic coating technology is developed and being optimized, inorganic finishing and electroplating technology is still immature and many different technologies are under evaluation. Widely implementable materials and process substitutes for electroplated cadmium and chromium are not currently available and therefore require continued investment in research and development.

The AGARD SMP should host a workshop or sponsor a technical exchange that specifically addresses the elimination of cadmium and chromium from aerospace materials and process operations. More work is needed in three major areas of inorganic metal finishing and electroplating. First, the identification and optimization of mechanisms at work in promising non-chrome anodize and pretreatment processes. The areas of cerium and potassium permanganate additions to standard sulfuric acid anodize solutions as well as the sol-gel approach to application of adhesive bond pretreatments are of particular interest. Second, multi-process strategies must be selected, scaled-up and validated in the effort to eliminate the requirement for cadmium and hard chrome electroplated coatings in aerospace manufacturing or maintenance facilities. One for one substitution initiatives have proven unsuccessful and multi-process studies with the goal of the total removal of chromium or cadmium electroplating from one aerospace facility should be a target of future efforts. Third, the elimination of chromate conversion coatings that provide corrosion protection and promote paint adhesion may result from the validation of new wet chemical processes, alternative coatings or revisions to rigorous materials performance standards. More likely, the next generation corrosion protection system for metal airframes will include a combination of these three approaches. Future aerospace corrosion protection systems for aluminum alloys may include electrocoated organic as well as polymeric powder coatings combined with non-chromated pretreatment processes.

From an environmental perspective, within these three major technical areas lies the highest priority needs of the aerospace community and the greatest beneficial impact will be gained through focusing AGARD's near term efforts in these areas.

ENVIRONMENTAL PERSPECTIVES FROM A CANADIAN AEROSPACE COMPANY

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SUMMARY

In Canada, the Federal, Provincial and Municipal governments have assumed responsibilities for different aspects of establishing and enforcing environmental legislation.

As a partner in the largest aerospace company in Canada, Bombardier-Canadair uses various materials and processes which are regulated, such as organic coatings, resins, sealants, solvents, deoxidizers, chromic acid anodizing, cadmium plating, chromium plating, etc.

The work done at Bombardier-Canadair over the last five years concentrated in eliminating ozone depleting compounds, reducing emissions of volatile organic compounds, reducing the amount of hexavalent chromium (Cr 6+) in our effluent, and replacing hazardous air pollutants. New issues are also being addressed, such as the replacement of methylene-based chemical strippers and the replacement of electrolytic cadmium plating.

This purpose of this paper is to provide an overview of the various levels of environmental legislation facing Canadian Aerospace companies in general and Bombardier-Canadair in particular. The paper also summarizes the technical problems presented by such legislation and the work done by Bombardier-Canadair and Bombardier-de Havilland to solve these problems and achieve compliance.

1. INTRODUCTION

In Canada, the Federal, Provincial and Municipal governments have assumed responsibilities for different aspects of establishing and enforcing environmental legislation.

The following is a general breakdown of the responsibilities:

a) The Federal government (Environment Canada) is responsible for legislation driven mostly by international agreements, particularly in the following areas:

    (F1) Ozone Depleating Compounds (ODCs)
    (F2) Dangerous Goods
    (F3) Federal Programmes for Pollutants
    (F4) Federeal Programme for "Greenhouse" Gases

b) The Provincial government (Quebec's Ministry of Environment and Wildlife) is responsible for the following aspects:

    (P1) Certificates of Authorization (CAs)
    (P2) Air Pollution (Transferred to Municipal level)
    (P3) Water Pollution (Transferred to Municipal level)
    (P4) Ground Pollution
    (P5) Solid Waste

c) The Municipal government (Montreal Urban Community) is responsible for approving permits in the following areas:

    (M1) Air Quality (By-Law 90)
    (M2) Water Quality (By-Law 87)

As a partner in the largest aerospace company in Canada, Bombardier-Canadair uses various materials and processes which are regulated, such as organic coatings, resins, sealants, solvents, deoxidizers, chromic acid anodizing, cadmium plating, chromium plating, etc.

The following sections describe the different areas of environmental regulations affecting Bombardier-Canadair under the various governments.

1.1 Ozone Depleating Compounds (F1)

Bombardier-Canadair participated in the federal government's Program for Elimination of 1,1,1-Trichloroethane (TCA). This program was driven by the Montreal Protocol which banned production of TCA by January 1, 1996.

Bombardier-Canadair's emissions of TCA were produced by vapour degreasing (73%) and manual cleaning (27%). As of today, TCA is no longer used at Bombardier-Canadair. Aqueous degreasing solutions have replaced vapor degreasing. Manual cleaning with TCA has been replaced with more environmentally acceptable cleaning products, depending on the application.

1.2 Pollutants (F3)

Bombardier-Canadair participates in the federal government's Program for National Inventory of Pollutant Waste.

Paper presented at the 83rd Meeting of the AGARD SMP on "Environmentally Compliant Surface Treatments of Materials for Aerospace Applications", held in Florence, Italy, 4-5 September 1996, and published in R-816.

This program requires companies to keep inventory on waste containing any of 178 substances.

Some of the substances used at Bombardier-Canadair are Methyl Ethyl Ketone (MEK), nitric acid, sulphuric acid, cadmium, chromium and its derivatives, toluene, etc. Annual reports must be furnished to the federal government.

Bombardier-Canadair just started participating in Programme ARET (Accélération de la Réduction ou de l'Élimination des Toxiques). This programme is based on voluntary participation of companies and was designed to accelerate the reduction of their use of toxic substances.

1.3 Certificates of Authorization (P1)

Certificates of Authorization are approved by the Quebec Ministry of Environment and Wildlife. They are required for any construction, processing or increase of production that will result in emissions to the atmosphere or waste into the environment.

Certificates of Authorization issued to Bombardier-Canadair are based on forcasted production levels for 1998. They apply to storage of dangerous goods, assembly operations (Plant 1), fabrication of tubing, chemical surface treatment, machining operations, sheet-metal forming operations and storage of raw materials.

Certificates of Authorization for the areas of tooling, assembly operations (Plant 3), and fabrication of composites are being renewed.

1.4 Ground Pollution (P4)

Responsibility for the quality of the soil belongs to the Quebec Ministry of Environment and Wildlife, but the responsibility for the storage of petroleum products was transferred to the Quebec Ministry of Energy and Resources.

The law requires that undergound steel reservoirs more than 25 years old and above-ground reservoirs not in use be removed before 1996. Under this legislation, Bombardier-Canadair has removed more than 50 reservoirs.

1.5 Solid Waste (P5)

Under the curring provincial legislation, Bombardier-Canadair has completed the following projects regarding solid waste:

a) Writing of procedures for management of dangerous waste.
b) Distribution of colour-coded containers for temporary storage of dangerous waste.
c) Training of supervisory personnel.
d) Implementation of waste reduction programme.
e) Computerization of waste management.
f) Recycling of waste from composite materials

At the same time, other projects have been started for recycling of solid waste and relocation of warehouses .

1.6 VOC Reduction (M1)

Under By-law 90, Bombardier-Canadair presented a programme for reduction of VOCs to the Montreal Urban Community (MUC) in 1990. This 5-year programme proposed a 90% reduction of VOC emissions from 1989 levels by reducing at the source. In order to achieve this, the following measures were taken:

1) Conventional paint guns were replaced by HVLP guns.
2) A cover was placed on the chem-milling maskant tank.
3) The solvent-based epoxy primer was replaced with a water-reducible version in Canadair and Boeing programs.
4) Recycling of spent solvents.
5) A peelable, water-based temporary protective coating was implemented in Boeing programs.
6) The lacquer used for spraying locating dots was replaced with a water-based coating.
7) Use of high-solids polyurethane topcoats.

Other projects currently in progress at Bombardier-Canadair to further reduce VOCs include use of high-solids fuel tank coating, use of low-VOC solvents, evaluation of water-based bonding primers, capture and destruction of toluene emissions from chem-mill maskant, and re-design of the paint shops.

1.7 Waste Water Treatment (M2)

By-law 87 established the following limits for the waste waters going to the sewer:

i) pH must be between 6 and 10.5
ii) Total Chromium must be less than 5 ppm
iii) Total amount of mineral oils and greases must be less than 30 ppm
iv) Reduction in water usage for cooling

Bombardier-Canadair already complied with the requirements for pH, mineral oils and greases, and Chromium content. In order to meet the limits for Chromium content, Bombardier-Canadair started a programme for Chrome reduction.

Since the largest amounts of Chrome came from rinsing of Chrome-based solutions, the programme concentrated on the following:

a) A system to allow parts to drain properly into the tank before rinsing them.
b) Evaluating non-chromated deoxiders to try and replace the chromated ones in use today.

Eight systems have been installed to help the operators control the drain-time prior rinsing. These very simple systems consist of a red light that comes on when the operator finishes raising the parts out of the solution. The red light stays on for 20 seconds. When it comes off the operator moves the parts over to the rinsing tank. An alarm sounds if the operator does not respect the 20 seconds waiting period.

The implementation of these systems has brought a 50%-60% reduction in Chrome content in the rinse water of the tanks where they were installed.

About 35% of the overall Chrome content in the effluent at Bombardier-Canadair came from rinsing after the deoxidizing and desmutting steps in the chemical milling line. Another 30% came from rinsing after the deoxidizing step in the chromic acid anodizing/conversion coating line.

Therefore, several non-chromated deoxidizers were evaluated at Bombardier-Canadair over a 2-year period for these applications. As a result, the deoxidizer/desmutter in the chem-milling line has been successfully replaced with a non-chromated product. The non-chromated solution has been in operation for over 14 months.

Replacement of the deoxidizer in the anodizing/conversion coating line, however, has been more difficult. The work in this area continues, and the goal at Bombardier-Canadair is to have a non-chromated alternative for this application in the tank before the end of 1996.

As part of the effort to meet the requirements of By-law 87, Bombardier-Canadair reached an agreement with the Montreal Urban Community to reduce the amount of water used for cooling by at least 116 million gallons. To date, water usage for cooling has been reduced by 100 million gallons, and a project is in progress to reduce it by another 50 million gallons in the next couple of years.

PROCÉDÉS DE PROTECTION ET ENVIRONNEMENT
PROBLÈMES ET SOLUTIONS

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1 - SOMMAIRE

Différents produits et procédés de fabrication couramment employés dans l'industrie aéronautique sont ou risquent, à des degrés divers, d'être visés par les réglementations liées à la protection de l'environnement et de la santé humaine :

- le nettoyage des surfaces en phase solvant organique,
- les traitements en phase aqueuse (décapage et anodisation)
- les revêtements métalliques,
- l'application de films organiques (peintures et vernis),
- l'usinage chimique des métaux (bains et masques),
- les produits d'étanchéité,
- les agents de démoulage,
- les traitements de ressuage,
- les produits de freinage.

Ces réglementations ont des origines diverses car l'industrie aéronautique s'exerce dans un contexte international. De façon générale, la législation française de plus en plus lourde s'applique à la plupart des produits utilisés en traitement de surface, que ce soit les solvants organiques ou à base aqueuse, les installations de traitement de surface (rejet d'effluents aqueux), certains traitements électrolytiques (cadmium en particulier) ainsi que les composés organiques volatils et les pigments de peinture. Enfin la législation sur les déchets concerne à la fois leur stockage et leur traitement aux fins de destruction et, si possible, de recyclage.

L'entrée en vigueur de ces nouvelles réglementations oblige les industriels, à développer d'abord de nouvelles technologies (phase de recherche), puis à intégrer ces dernières dans leurs chaînes de fabrication (phase d'industrialisation).

Cet exposé présente, pour les procédés de protection cités ci-dessus, un bref rappel de la réglementation et les premiers résultats des études actuellement développées par Aerospatiale et Dassault Aviation pour mettre au point ces technologies.

2 - NETTOYAGE DES SURFACES EN PHASE SOLVANT ORGANIQUE

Jusqu'à une date récente les 4 principaux solvants de nettoyage utilisés dans l'industrie aéronautique française étaient : le trichloroéthylène, le trichloroéthane T 111, le trichlorotrifluoroéthane CFC 113 et le perchloréthylène. La consommation totale de ces produits était d'environ 2 000 000 litres.

En quelques mois la situation a notablement changé puisque les échéances du règlement européen 3093/94 ont conduit comme prévu à l'arrêt de la production de CFC 113 et de T 111 respectivement fin 1994 et fin 1995.

Les demandes de dérogation pour usage essentiel présentées par l'industrie aéronautique française n'ayant pas abouti, il a fallu se résoudre à développer de nouvelles solutions pour tous les types de nettoyage.

On a donc assisté depuis 1994 à l'accélération du processus de remplacement des solvants CFC 113 et T 111 engagé depuis plusieurs années. Afin d'éviter au maximum les redondances, de limiter le nombre de produits, chaque entreprise a mis en place une action coordonnée rassemblant diverses composantes (technique, industrielle, commerciale, médicale, hygiène et sécurité). Un plan d'action en 3 grandes étapes, comportant chacune un certain nombre de tâches a été défini.

La *première étape* a consisté à recueillir l'information nécessaire. Elle comprenait 3 tâches principales :

Tâche 1 - Prendre la mesure du problème, avec 2 sous-tâches :

- le recensement des applications utilisant du T 111 et du CFC 113,
- l'identification des contraintes réglementaires (santé, sécurité, environnement).

Tâche 2 - Prendre connaissance du marché des substituts potentiels :

- les fournisseurs,
- les produits,
- les procédés.

Tâche 3 - Créer des banques de données rassemblant un maximum de données physico-chimiques, toxicologiques et environnementales afin de pouvoir opérer les premières sélections parmi la masse de produits présentés.

La *deuxième étape* avait pour objet de préciser le besoin. En effet, lorsqu'il s'est agi de remplacer des produits utilisés universellement, il est apparu que c'était l'expérience qui tenait lieu de spécification. L'élaboration de spécifications pour les différents usages était donc nécessaire.

Paper presented at the 83rd Meeting of the AGARD SMP on "Environmentally Compliant Surface Treatments of Materials for Aerospace Applications", held in Florence, Italy, 4-5 September 1996, and published in R-816.

Plusieurs documents ont donc été créés pour des applications spécifiques, par exemple:

- l'usage général à froid,
- l'usage à chaud (en cuve),
- le nettoyage de composants électroniques.

La *troisième étape* a consisté à sélectionner les produits correspondant aux différents besoins. Elle comportait 3 tâches :

- une présélection sur dossier,
- des essais de faisabilité industrielle,
- des essais complets de qualification.

Où en est-on actuellement ?

Ces trois étapes ont été franchies pour la plupart des applications. Citons parmi celles-ci :

- l*e nettoyage des composants électroniques :* procédés aqueux, solvants perfluorés, HCFC 141b,
- le *nettoyage à chaud* : lessiviels, hydrocarbures isoparaffiniques,
- le *nettoyage à froid* en atelier de mécanique : hydrocarbures additivés, mélanges de solvants oxygénés, trichloréthylène avec des équipements appropriés, HCFC 141b (utilisation en circuit fermé).

Des problèmes subsistent-ils ?

Oui, sans nul doute, tous les problèmes ne sont pas résolus. En particulier il faut bien insister sur le fait que, dans de nombreux cas, un double transfert de risque s'est opéré :

- les COV ont remplacé les CFC, c'est à dire que le risque de destruction de la couche d'ozone est devenu un risque de pollution de la troposphère,
- le remplacement des produits ininflammables par des produits inflammables.

Quelle que soit la réglementation, il est clair qu'il en résultera d'une façon ou d'une autre une augmentation du coût de production qui devra prendre ces éléments en compte.

Et puis il faut noter qu'à tort ou à raison la législation ne cesse de se durcir. Par exemple des menaces sérieuses planent sur l'avenir des HCFC et pire encore sur celui des solvants halogénés. Cela signifie que bien des portes vont encore se fermer, sans que des solutions de remplacement soient réellement disponibles.

Et pour le futur ?

Il est difficile de savoir de quoi il sera fait tant les pressions de toutes sortes exprimant des intérêts pas toujours convergents rendent les prévisions hasardeuses. Quoi qu'il en soit, les voies actuellement les plus intéressantes semblent bien être :

- les traitements par voie aqueuse, encore que cette solution porte elle-même ses propres inconvénients (coût de dépollution en particulier),
- les traitements sans solvant tels les traitements par laser, plasma froid, l'utilisation du CO_2 à l'état supercritique, etc., à condition qu'ils soient techniquement et économiquement intéressants (un contrat européen Brite-Euram débute pour évaluer l'intérêt de ces procédés),
- les nouvelles molécules, notamment basées sur la chimie du fluor, à condition que les législations futures ne fassent pas barrage à leur utilisation.

3 - TRAITEMENTS EN PHASE AQUEUSE

Les gammes de traitements de surface des alliages d'aluminium, matériaux les plus couramment utilisés en aéronautique, comportent 3 étapes principales: dégraissage(s), décapage(s) et traitement de conversion chimique ou électrochimique. Pour réaliser ces opérations, des bains à base de chrome hexavalent sont généralement employés : décapage sulfochromique, anodisation chromique, chromatation.

Si d'un point de vue législatif il n'existe pas d'interdiction d'emploi de bains contenant du chrome hexavalent, des mesures visant à limiter la pollution des eaux et de l'atmosphère ont été prises (arrêté ministériel du 26/09/85) : concentration limite dans les effluents de 0,1 mg/l et teneur limite dans les gaz et vapeurs rejetés 0,1 mg/Nm^3.

Les études en cours ont pour objectif le développement de traitements de décapage et d'anodisation non polluants et qui permettent de réduire significativement le coût de fonctionnement des installations de traitement de surface.

Décapage

Différents bains de décapage sulfochromique sont utilisés dans les gammes de préparation de surface des alliages d'aluminium. Les objectifs visés sont essentiellement :

- l'attaque ménagée du substrat avant des opérations de protection (anodisation, chromatation) ou de contrôle des pièces par ressuage,
- la neutralisation de la surface après une attaque du substrat dans des bains alcalins avant des opérations de protection ou de masquage des pièces usinées chimiquement.

Les études, conduites sur un grand nombre de formulations de bain en faisant varier divers paramètres (la concentration des éléments actifs, la température ou la durée d'immersion), ont abouti à une première sélection de procédés. Cette sélection a été réalisée sur la base de 2 critères : une vitesse de décapage comparable à celle d'un bain sulfochromique et une diminution des attaques localisées de la surface des substrats par rapport à un décapage sulfochromique. En effet ces piqûres qui résultent de l'attaque des composés intermétalliques présents à la surface sont à l'origine d'une diminution notable de la tenue en fatigue des matériaux traités.

A l'issue de cette première phase, des procédés susceptibles d'assurer les fonctions décrites ci-dessus ont été retenus :

- l'attaque ménagée du substrat dans bains alcalins (sodiques à faible vitesse d'attaque) ou acides (mélange acide sulfurique/sulfate ferrique à chaud),
- la neutralisation après attaque alcaline dans des bains acides (acide nitrique ou mélange acide sulfurique/sulfate ferrique à froid).

La seconde phase de travail qui doit aboutir à la sélection finale d'un procédé est en cours. Elle aborde des aspects plus industriels en particulier :

- la conduite des bains (durée de vie, méthodes de dosage, méthodes et fréquence des réajustements),
- le bilan économique (modifications à réaliser dans les installations actuelles et estimation des coûts de montage, d'entretien et de rejet des bains).

Anodisation

Le traitement d'anodisation chromique non colmatée est principalement employé pour élaborer une couche d'oxyde d'aluminium poreuse favorisant l'adhérence de la peinture qui est ensuite appliquée sur celle-ci. C'est la peinture qui joue le rôle protecteur vis-à-vis de la corrosion.

Comme pour les traitements de décapage, la première phase de l'étude a consisté à évaluer différentes formulations de bains. Le principal critère de sélection a été d'éviter une attaque localisée de la surface trop importante afin de limiter la chute de la tenue en fatigue observée après une anodisation chromique.

Ces travaux, qui ont débuté dans le cadre d'un programme européen Brite-Euram, ont abouti au développement d'un procédé d'anodisation en milieu alcalin dans un bain à base de tétraborate de sodium.

La figure 1 présente l'état de surface d'un alliage 2024 T351 après une anodisation avec ce nouveau procédé par comparaison à une anodisation chromique. La réduction de la quantité et de la profondeur des piqûres en surface est très importante.

Des essais de fatigue ont été réalisés sur des éprouvettes cylindriques entaillées (Kt=1,7) en 2024 T351, prélevées dans le sens TL et sollicitées en traction ondulée avec R=0,1. Les résultats de la figure 2 confirme l'intérêt de ce nouveau procédé d'anodisation sur le comportement en fatigue des alliages d'aluminium (des résultats similaires ont été obtenus avec l'alliage 7175 T7351).

La structure de la couche de type poreuse, semblable à celle formée lors d'une anodisation chromique, conduit à une adhérence de la peinture sur la couche satisfaisante.

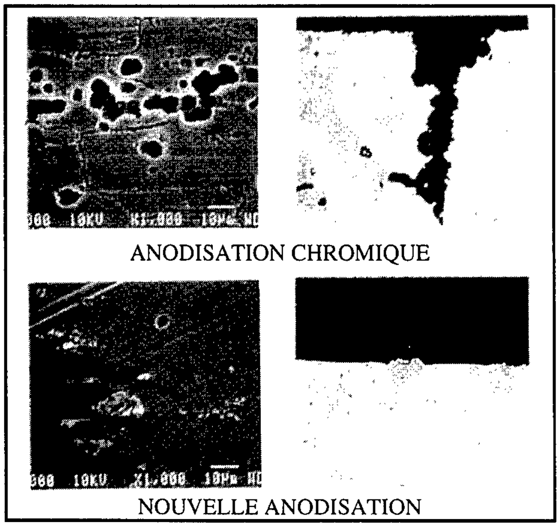

Figure 1 - Etat de surface après anodisation

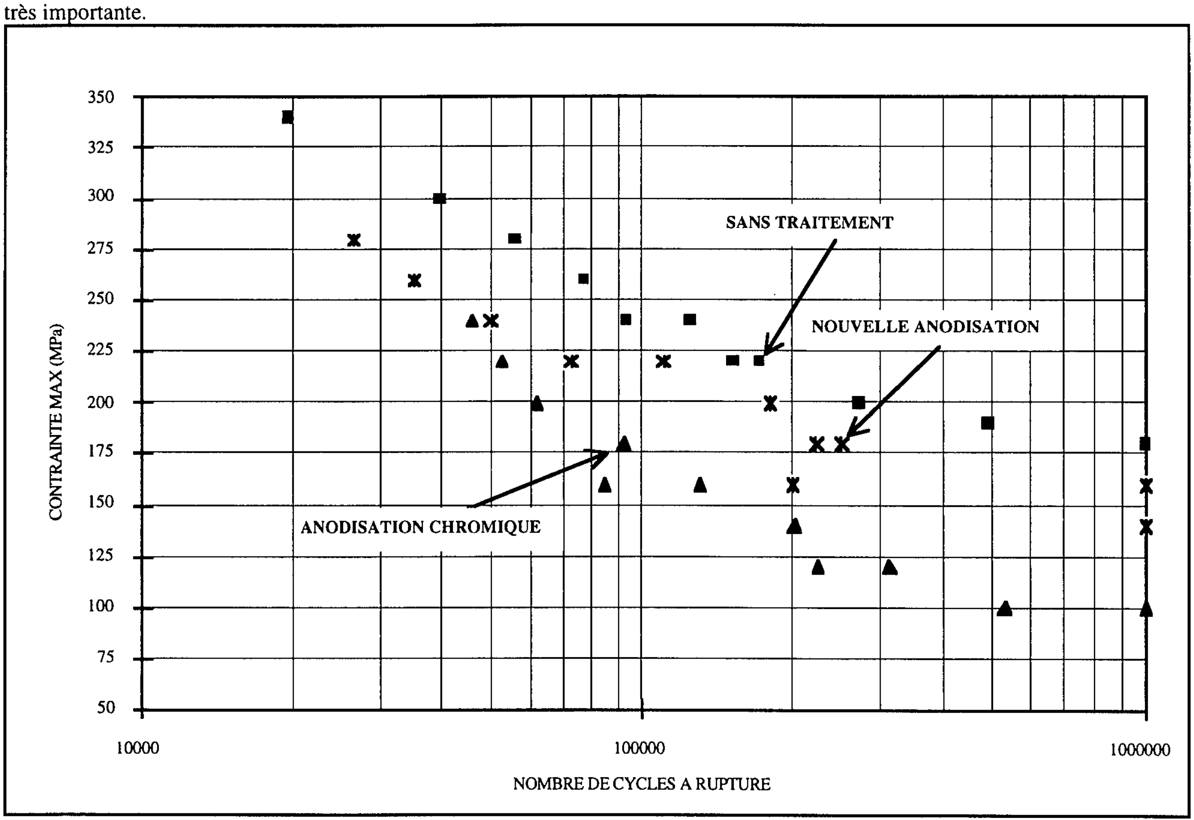

Figure 2 - Courbes de Wöhler

4 - REVÊTEMENTS MÉTALLIQUES

Parmi les revêtements métalliques, le cadmium est le plus couramment employés dans l'industrie aéronautique. Les autres revêtements (nickel, chrome, zinc, ...) ont des applications très spécifiques et limitées. La principale application du cadmium est la protection contre la corrosion des aciers faiblement alliés.

Une directive européenne (n°91/338/CEE) transposée en droit français (décret n°94-647) réglemente sévèrement son utilisation. Elle prévoit que la mise sur le marché des produits finis cadmiés ou des composés de ces produits cadmiés est interdite dans de nombreux cas. Elle n'est pas applicable aux produits et composants des produits utilisés dans l'aéronautique. Cependant, une éventuelle suppression de ces dérogations est à craindre et la recherche de revêtements de substitution du cadmium est une de nos préoccupations.

Au niveau des installations, la réglementation (arrêté du 26/09/85) limite la concentration en cadmium dans les eaux à 0,2 mg/l et le flux de cadmium à 0,3 g/kg utilisé.

Les revêtements de substitution devront posséder des propriétés comparables à celles du cadmium en particulier dans les domaines de :

- la résistance à la corrosion : le revêtement doit présenter, non seulement une bonne résistance intrinsèque à la corrosion, mais aussi un caractère sacrificiel par rapport au substrat,
- la fragilisation des aciers à haute résistance : la possibilité d'éviter ce phénomène grâce à l'utilisation de bains à haut rendement et de traitements de dégazage est impérative.

L'aspect sacrificiel est fondamental, il limite les possibilités aux métaux plus électronégatifs que les aciers utilisés pour les fabrications aéronautiques. Il en résulte que les revêtements envisageables seront, soit à base d'aluminium, soit à base de zinc. Ce sont essentiellement :

- les revêtements d'aluminium applicables par procédé physique ou électrolytique (milieu non aqueux),
- les revêtements de zinc et de zinc allié réalisés par procédé électrolytique classique,
- les revêtements à base de pigments d'aluminium ou de mélanges de pigments d'aluminium et de zinc dans des liants minéraux ou organiques. Ils sont réalisés par trempage ou pistolage puis cuisson à des températures proches de 200°C.

Le tableau 1 présente une synthèse des résultats obtenus sur des éprouvettes en 35NCD16 de formes simples. Ils font apparaître que les revêtements les plus prometteurs sont :

- l'aluminium quel que soit le procédé d'élaboration utilisé (électrolyse, dépôt physique en phase vapeur ou pigment dans un liant minéral),
- le zinc-nickel déposé par procédé électrolytique.

REVÊTEMENTS ÉTUDIÉS	CORROSION			FRAGILISATION PAR H2
	POTENTIEL DE CORROSION PAR RAPPORT AUX ACIERS	COMPORTEMENT INTRINSÈQUE DU REVÊTEMENT	CARATÈRE SACRIFICIEL PAR RAPPORT AUX ACIERS	
Zn alc	■	□	□	□
Sn + Zn alc	■	□	■	□
Ni + Zn alc	■	□	□	■
ZnFe alc (Fe<1%)	■	□	□	□
ZnCo ac (Co<1%)	■	□	□	□
ZnCo alc (Co<1%)	■	□	□	□
ZnNi alc (Ni≈8%)	■	■	■	■
SnZn alc (Ni≈30%)	■	▨	■	□
Al électrolytique	■	■	■	■
Al PVD	■	▨	■	■
Pigment Al + Liant minéral	■	▨	■	■
Cd	■	■	■	■
ZnNi ac (Ni≈15%)	■	■	■	■

ac = bain acide alc = bain alcalin

LÉGENDE	■	▨	□
	SATISFAISANT	INSUFFISANT A OPTIMISER	MAUVAIS

TABLEAU 1 - Synthèse des résultats d'évaluation de revêtements susceptibles de remplacer le cadmium

5 - REVÊTEMENTS ORGANIQUES

Dans un contexte industriel, où les coopérations et les travaux de sous traitance sont organisés à l'échelle de la planète, l'utilisation des peintures comme revêtement de protection des structures métalliques et composites doit satisfaire de plus en plus aux exigences réglementaires. A l'heure actuelle, l'ensemble des constituants (pigments, résines, solvants) est visé par ces dispositions et si l'on se projette dans un futur proche (2 à 10 ans), l'ensemble des peintures que nous utilisons actuellement seront remplacées par des produits plus respectueux de l'environnement et de la santé humaine. C'est dire l'ampleur de la tâche à laquelle formulateurs et utilisateurs sont confrontés. A ce titre de nombreux programmes de recherche en collaboration avec les principaux fournisseurs ont été initiés. Les principaux résultats sont présentés ci après.

Pigments : remplacement des chromates

L'aéronautique reste l'une des rares industries à utiliser encore des primaires anticorrosion chromatés en raison des niveaux d'exigences demandés et de la spécificité des mécanismes de corrosion des alliages Al-Cu. Or deux pressions s'additionnent aujourd'hui rendant indispensable, à terme, la substitution des chromates par d'autres inhibiteurs :

- des problèmes d'approvisionnement en matières premières,
- leur toxicité reconnue.

Après des années de recherche, basée sur la substitution des chromates par des phosphates de Zn ou Al diversement dopés, une voie directrice se dessine aujourd'hui. Elle consiste à incorporer à la peinture des complexants de l'aluminium et du cuivre, susceptibles de s'adsorber fortement à la surface du substrat métallique et de former des sels insolubles stables dans la gamme de pH généralement rencontrée dans les cellules de corrosion naissantes ($3<pH<8$). Sans participer directement aux réactions électrochimiques, leur action se traduit par une modification des cinétiques et par un abaissement extrêmement important des courants de corrosion. Bien entendu dans ce contexte, l'adhérence en milieu humide du système de peinture au substrat métallique doit être optimale soit en raison des propriétés intrinsèques du liant soit par ajout de promoteurs d'adhérence.

Si l'examen de la littérature laisse entrevoir de nombreuses potentialités, le choix des substituts aux chromates dans les peintures, comme l'a montré une étude menée avec MAPAERO et l'École de Chimie de Toulouse, se révèle limité en raison des problèmes liés à :

- la compatibilité de l'inhibiteur avec les résines (effets catalytiques, gélification, etc.),
- leur solubilité en fonction du pH (trop forte (cloquage), trop faible (faible protection)),
- la coloration des inhibiteurs ou des complexes formés,

Des solutions prometteuses sont en cours d'évaluation.

Résines : moindre toxicité

Deux objectifs guident actuellement les recherches :

- le remplacement des systèmes standards par des systèmes à excellente durabilité
- l'utilisation de résines à faible toxicité (ex: remplacement des isocyanates)

Le premier point peut être considéré aujourd'hui comme acquis grâce à la sélection de matière première contenant moins d'impuretés et de composés insaturés. Néanmoins il faut souligner la disparité des méthodes d'évaluation entre les constructeurs aéronautiques. Une harmonisation des cycles de vieillissement associée à une meilleure compréhension des mécanismes de dégradation doit permettre de mieux corréler vieillissements accélérés et naturels.

Les travaux réalisés ces dernières années se sont plus particulièrement focalisés sur la formulation de peintures utilisant des chimies autres que celles des polyuréthannes ou des époxydes dont la toxicité (allergie, affections des voies respiratoires)est reconnue. Le tableau 2 présente deux exemples de recherches menées dans le cadre de programmes européens Brite-Euram.

FORMULATEUR	CHIMIE	AVANTAGES	INCONVÉNIENTS
COURTAULDS	Anhydride	Pas d'isocyanate Faible teneur en VOC Très faible toxicité Bonne tenue aux UV Faible toxicité Bonne stabilité Faible coût	Polymérisation à 90°C Pas de réticulation à 23°C Odeur
AKZO	Ketimine	Séchage air Faible teneur en VOC Temps de gel : 2h Adhérence Résistance chimique Protection corrosion Faible toxicité Faible perméabilité à l'eau	Faible tenue aux UV Rétention de solvant Contraintes internes Odeur Coût

Tableau 2 - Exemples des recherches menées sur la formulation des résines de peinture

Solvants : réduction des émissions

Les répercussions des réglementations en matière de rejet d'effluents gazeux ont motivé depuis maintenant 20 ans des efforts de recherche et développement importants de la part des fabricants de peinture. Ainsi les peintures à faible VOC qui étaient présentées comme "la réponse" aux problèmes solvants ne vivront vraisemblablement qu'un nombre limité d'années pour être par la suite remplacées par des technologies et des produits plus respectueux de l'environnement, ceci d'autant plus rapidement que l'industrialisation de ces peintures s'avère parfois laborieuse.

Les constructeurs aéronautiques se sont depuis de nombreuses années investis dans la recherche de peinture à faible teneur en solvant. Ces travaux, généralement effectués en étroite collaboration avec les fournisseurs, s'orientent vers les produits hydrodiluables (application par pulvérisation ou électrodéposition) et les peintures poudres. Le tableau 3 décrit les transitions probables entre un passé proche et un proche futur.

Hier	Forte VOC
Aujourd'hui	Faible VOC
Demain	Hydrodiluable Poudre

Tableau 3 - Evolution des systèmes de peinture

Bien entendu des peintures poudres ou hydrodiluables sont déjà qualifiées en aéronautique pour des applications très spécifiques, mais leur généralisation se heurte, notamment dans le cas de l'aviation civile :

- aux exigences des cahiers des charges notamment de résistance aux fluides hydrauliques à base d'esters phosphoriques, d'adhérence et de protection contre la corrosion,
- aux conditions de polymérisation des peintures (150-180°C pendant 30 min pour les poudres) incompatibles avec les matériaux (120°C au maximum pour les alliages d'aluminium).

6 - CONCLUSION

Bien que la prise de conscience des problèmes soulevés par l'utilisation industrielle de produits ou procédés présentant des risques pour l'Environnement et pour l'Homme soit encore récente, des progrès significatifs ont été réalisés dans la mise en place de technologies "propres". Dans pratiquement tous les domaines qui ont été évoqués au cours de cet exposé, les études de laboratoire sont bien avancées voire terminées et les procédés sont en phase d'industrialisation.

Néanmoins il apparaît que dans beaucoup de cas, il est illusoire de penser remplacer un produit ou un procédé polluant par un unique autre produit ou procédé. Les solutions qui se dessinent font au contraire apparaître que plusieurs procédés de remplacement sont envisageables et qu'il faudra probablement les utiliser de façon complémentaire en tenant compte de leurs avantages, de leurs inconvénients et des exigences requises pour les pièces à traiter. Dans certains ces,

On s'efforcera de profiter de ces changements pour optimiser autant que possible les coûts de fabrication. On ne pourra éviter cependant, dans certains cas, une augmentation de ces coûts. De toute façon il y aura lieu de prendre en compte les coûts de recherche et de qualification de ces produits ou procédés.

ENVIRONMENTALLY COMPLIANT SURFACE TREATMENT ACTIVITIES IN THE UNITED KINGDOM

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SUMMARY

Environmental legislation is having a major impact on surface treatment activities in the United Kingdom (UK). This paper summarises current UK legislation and aims to show, through a specific example of relevance to the UK Ministry of Defence (MOD) work undertaken to ensure that environmental compliance is achieved. This covers the introduction of paints, with reduced solvent levels, into the various branches of the Armed Forces, and general results and conclusions from the task are summarised. Paint removal issues are also discussed with regard to UK MOD operations. Two broader case studies are also presented to demonstrate that environmental compliance does not have to involve increased costs either at the manufacturing stage or during unnecessary 'pollution clean-up' activity.

1. INTRODUCTION

In the 1980s there was still some in the UK who doubted whether the issue of 'the environment' would last. They have been proved wrong, since it remains one of the big issues of the 1990s throughout the world.

It is a big issue in political terms, since protection of the environment is a high priority for the 1990s and looks to continue as such into the next millennium. It is also big in terms of the size of the problems faced and the solutions required; global warming, low level ozone, the destruction of the ozone layer, acid rain and toxic waste are all problems that impinge on the surface finishing industry and require a global response. To address these many environmental issues, nations have introduced a number of environmental laws and the UK has also created specific, dedicated organisations to assist industry with environmental compliance.

It is also an issue which is open to both misunderstandings and ignorance. To quote an example, a sock was promoted in the UK as "ozone friendly", with a label claiming: "Helps prevent foot odour which is probably a major cause of the destruction of the ozone layer"! This story emphasises the need for education among the general population whilst workshops and seminars of this type can inform and promote information exchange within the scientific community.

Both environmental legislation and general public awareness is forcing all industrial sectors to review the potential impact of their business on the environment and to embrace alternative, greener technologies (processes, practices and materials). In particular there are a numbers of activities within the surface treatment industry of concern including:

- Alternatives to Cadmium
- Chromate free materials for the corrosion protection of aircraft
- Reduction of waste discharge (land, water and air)
- Environmentally friendly pretreatment and cleaning
- Removal of chemicals from air and water
- Alternatives to tin-based anti-fouling paints

This list is by no means exhaustive and some of these issues will be discussed in detail in papers presented at this workshop.

This paper will outline the current UK environmental legislation influencing surface treatment activities and it will also discuss government initiatives introduced to assist UK industry. By way of an example, and of particular relevance to this workshop, the challenge faced by UK MOD (which is not immune from embracing the changes required of industry in general) with regard to painting processes will be covered. In conclusion, more general case studies are highlighted to demonstrate that environmental compliance can result in cost savings.

2. BACKGROUND LEGISLATION

The UK has a history of environmental controls. Medieval statutes have been followed by a number of acts including the Public Health Act 1875 (arising from the Industrial Revolution), the Alkali Act 1863 to control atmospheric emissions primarily from the caustic soda industry and water pollution controls contained within the Rivers Pollution Prevention Act 1876. In these early years, law making tended to be very ad hoc and reactive, without much thought for wider developments or implications and one effect of this long and unplanned history is that Britain has inherited a far less coherent system of pollution control than many other countries. The emphasis has also, in the main, been directed at health and safety issues.

This picture is changing with the introduction of two particular acts in the 1990s. The focus of this legislation - as far as the surface treater is concerned - is on the control of pollution, the control of hazardous substances and processes and the minimisation and management of waste. That is to control the by-products of the modern technological age.

The two main pieces of legislation recently introduced are:

- The Environmental Protection Act 1990 (EPA). This is a wide ranging act covering, amongst other subjects, the discharge of substances to air, water and land. Of particular interest to the surface treatment industry (suppliers and coaters), and to end users of equipments that have themselves been coated, are the sections governing: The recovery of non-ferrous metals such as

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cadmium, the use of acid processes, processes involving halogens, inorganic chemical processes that involve a number of listed metals as well as coating and printing processes. The act also sets out the proscribed substances for release into water and into land.

- The Environment Act 1995. This, perhaps, stands alongside the 1990 Environmental Protection Act as the second plank of modern UK environmental law. This act sets up a new Environmental Agency, bringing together the National Rivers Authority, Her Majesty's Inspectorate of Pollution and other bodies into a single, all embracing agency. It also introduces new legal provisions in relation to liability for contaminated land. This in itself may have major consequences for both the coating industry and the end users of coated equipment. The latter where stripping, repairs or re-coating has been done in buildings and on open land. It is interesting that, as part of this act, public access to environmental information will be enhanced.

It is also important to note that the European Commission is a major and increasing source of British environmental protection law. It has a central and profound influence on the direction of environmental policy, both at Community level and within each Member State. As a result most, if not all, of recent UK environmental legislation has been strongly influenced by a pan European approach.

To assist and support the surface finishing industry with the impact of environmental legislation two initiatives have been introduced. Through the Department of the Environment and the Department of Trade and Industry (DTI), an Environmental Technology Best Practice Programme (ETBPP) has been created to promote the use of better environmental practices throughout UK industry and commerce. The National Surface Engineering Centre (NASURF) is a DTI initiative, managed by the Defence Research Agency, aimed specifically at the surface engineering industry. With a primary role of being a national advice centre to support surface engineering within the UK it encompasses environmental issues.

3. SPECIFIC EXAMPLES OF SURFACE TREATMENT ACTIVITIES REQUIRING ENVIRONMENTAL COMPLIANCE

With the background legislation in mind, this section focuses on a particular surface treatment activity, painting and paint removal processes undertaken by the armed forces, as an example of how UK MOD is reacting to the environmental pressures.

3.1 Example 1 - UK MOD Painting Processes

3.1.1 *The Challenge To UK MOD*

The EPA includes restrictions on the atmospheric discharge of volatile organic compounds (VOCs) which contribute to the formation of low level ozone pollution. VOCs are, in general terms, organic solvents with boiling points below 110°C and a major source of VOCs is from paints. Unsurprisingly the UK MOD is a large user of paints and allied materials - during 1991 the RAF, for example, purchased 330,00 litres of paint and nearly 500,000 litres of thinners and paint removers (Ref 1).

In contrast to more straightforward paint requirements in, for example, the automotive industry where corrosion protection and aesthetic appearance tend to be the critical demands, a military paint system can have a range of unique requirements. In general, corrosion protection is a basic prerequisite, however, front line equipment also needs camouflage which is literally a life-saving property. Other unusual requirements demanded of defence paint systems include:

- Non slip coatings for HM Ship's flight decks
- Erosion Resistant Coatings for jet aircraft
- High flexibility coatings for rubber grenades

In addition to specific, and unusual requirements, many paints developed for UK MOD need to be suitable for use in a variety of environments. Although at new build stage, paint can be applied under 'ideal' conditions (fully equipped spray booths with carefully designed drying conditions and pre-treatment areas) during the lifetime of most equipment re-painting will occur under a range of often hostile environments. Maintenance painting occurs in the middle of the world's oceans as well as in front-line positions by Army personnel - materials, therefore, need to be user friendly for non-skilled applicators. Rapid re-deployment of military hardware also necessitates quick changes in paint schemes for operational reasons.

On top of these specific requirements for a paint system are the pressures of environmental legislation and increased awareness of the environmental risks. To solve the various problems created by stringent environmental guidelines, alternative materials and processes need to be technically assessed for performance prior to use in the critical applications associated with UK MOD equipment. This section highlights the introduction of environmentally compliant paint materials and the supporting technical work undertaken to ensure the products are fit for purpose.

3.1.2 *Legislation Specific To Painting Processes*

As painting processes are used in a wide range of industrial finishing applications a set of Process Guidance (PG) notes have been issued by the Department of the Environment to assist with the implementation of the EPA. The PGs cover activities such as 'Coating and Recoating of Aircraft and Aircraft Components' (PG 6/40), 'Paint Application in Vehicle Manufacturing' (PG 6/20) and non specific painting processes are covered in the general 'Coating of Metal and Plastic' (PG 6/23). The PG documents also contain guidance on the use of VOCs at the surface pre-treatment and paint removal stages.

To reduce the VOC discharge to atmosphere the user has two options. The VOC emissions can either be reduced through the addition of an arrestment plant prior to release to the atmosphere or, alternatively, the user can specify the use of 'compliant coatings' which are, generally, paints with a reduced VOC content.

3.1.3 *Alternative Solutions*

Although end of pipe abatement is a valid alternative for reducing VOC discharge, the plant required is very expensive and is, in many applications an impractical alternative for UK MOD units. Arrestment plants can rely on absorption, condensation or incineration processes but absorption and condensation techniques are preferred as they offer recovery of the solvent. This solution can be implemented in dedicated paint shops in which the investment would be returned and some industrial sites have chosen this solution e.g. automotive finishing plants.

UK MOD users have decided to pursue the compliant coatings route. These do not involve the investment of expensive plant although this new generation of materials may prove to have a more expensive unit cost than the solvent based products in the short term. Compliant coatings can, however, be considered a greener technology which reduce the VOC content at source. VOC limits are expressed as grams per litre (g/l) of VOC content within the paint and typical values for current paint formulations are 450g/l for primers and 560g/l for a finish coat. For comparison, the limits quoted within the current PG 6/23 for these generic materials are 250g/l and 420g/l respectively and these provide initial targets for new materials.

The precise definition of a compliant coating is contained within the relevant PG of interest. In general, it means that the paint product has a reduced solvent content although it is recognised that in certain circumstances the adoption of a solvent reduced alternative is not possible in the immediate short term and some coatings may prove to be 'compliant' with existing product technology. To reduce the solvent content various alternatives are available to the paint manufacturer but two principle materials are being offered:

- High Solids Paints - Solvent levels are reduced by increasing the solid content (typically 60-80% solids are used). To retain a product with acceptable rheological properties further formulation changes may be required which can affect other properties of the material.

- Water Based Paints - These essentially use water instead of an organic solvent as the carrying medium although other formulation changes are required to cope with such a significant change in the chemistry of the paint system. Small quantities of solvent still remain within most formulations but these materials could be classed as a greener alternative than high solids products. Examples of this product include decorative emulsions common to many domestic situations.

As direct replacements for solvent based products, paint manufacturers have developed products which are either high solids are water borne. In fact the appropriate route to follow has caused considerable debate in the paint industry.

Other types of paint technology which can be used to overcome solvent use are powder coatings which are paint formulations in powder form which are cured thermally - these products have no solvent content at all. Radiation cured coatings are also an alternative in which the paints (in wet form) are cured using radiation such as UV or even electron beam - this method of curing also requires less energy than thermally cured materials. Although radiation cured coatings have not been used by the UK MOD, powder coating materials are used for finishing certain components - the powder coated aircraft is not a viable option at this stage!

The remainder of this section covers the technical assessment of compliant coatings as alternatives to the solvent based products used in Defence applications. Different PG documents, and hence differing definitions of compliant coatings, relate to the three Services within UK MOD and the areas are therefore covered separately. The general results obtained in the different areas show similar trends and are summarised in a single sub-section to avoid repetition.

3.1.4 *Paints For Land Based Equipment*

PG 6/23 (Coating of Metal and Plastic) covers the majority of land based applications such as painting front line vehicles (tanks, armoured vehicles etc), support vehicles and ground support equipment. Both the army and the RAF have an interest in such equipment and the DRA has undertaken work in this area on behalf of the Army Technical Support Agency, the branch responsible for maintenance painting at Base Workshops, and the RAF Surface Finishing Support Authority.

The paint scheme with the highest volume use in this area is the Nato Green Infra Red Reflecting finish applied to most vehicles and support equipment and is covered by the UK Defence Standard 80-41. This is a performance based specification detailing the requirements of the scheme covering a range of properties. In addition to corrosion resistance and other more standard paint film properties a critical requirement of this material is the camouflage attributes that need to be retained in any alternative product. It is also critical that the material is easily applied by brush as Army units undertake touch-up operations under non-workshop conditions.

The DRA has undertaken laboratory work to test the compliant products (mainly water borne to achieve the 250g/l primer limit within the PG) offered by paint manufacturers against a draft Defence Standard containing the same tests as 80-41. The performance assessment covers a range of physical, mechanical, corrosion and durability tests of the coating - examples include the scratch test, salt spray test and fuel resistance test.

3.1.5 *Aircraft Paints*

The repainting of aircraft is covered by a separate PG (PG 6/40) This document has a range of VOC limits depending on the exact nature of the paint product and examples are:

• Epoxy Primer	350g/l
• Erosion resistant coatings	800g/l
• 'Other speciality Coatings'	840g/l

The most commonly used materials by the RAF for aircraft refinishing are epoxy based primers based around the British Standard specification (BSX 33) and matt polyurethane top coats (classed as 'other speciality coatings' due to the necessary infra red camouflage requirements) based around the British Standard specification (BSX 34) although smaller quantities of a number of other products are also specified by the RAF.

The RAF Surface Finishing Support Authority are now specifying compliant materials in their procurement contracts and to assist the RAF, the DRA has undertaken material approvals, provided general advice and specific laboratory support to the Service.

'Other speciality coatings' have a relatively high VOC limit and current materials meet this limit easing the pressure on a significant proportion of the RAF paint inventory. There are, however, other paints with lower VOC limits that require work to evaluate new products offered by paint manufacturers. The epoxy based primers have been assessed against BSX 33 and glossy polyurethane top coats, which also have demanding VOC content limits, have been evaluated and subsequently approved for use

In parallel with the adoption of low VOC paints an additional way to reduce solvent use in a painting operation is to minimise waste and this can be achieved using paint application techniques with higher transfer efficiency. Transfer efficiency is the amount of paint solids sprayed from the gun that actually ends up on the object being coated. Aircraft refinishing is traditionally undertaken using standard spray application which has a relatively low transfer efficiency. Although brush application offers the highest transfer efficiency this is impractical and more efficient spray techniques have been implemented by the RAF. In particular 'High Volume Low Pressure' (HVLP) spray application is now preferred by the RAF, this necessitates an investment in new application equipment and also has training implications for personnel however the higher transfer efficiency (increases from 30-45% for conventional spray to 55-80% for HVLP are reported (Ref 2)) yields significant benefits.

Another area in which the RAF are addressing the need to reduce VOC waste is during the cleaning of paint application equipment. Solvent recovery units and specialised spray gun cleaning equipment have been introduced, both of which yield significant savings in terms of solvent use.

3.1.6 *Paints For Naval Equipment*

The painting of Naval equipment is essentially covered by PG 6/23 and the Directorate of Naval Architecture & Future Projects (the technical authority for Naval paints) in conjunction with the DRA has undertaken a number of technical investigations related to compliant coatings. The work has included trials on board HM Ships in addition to laboratory based assessments. In common with the other Services, priority has been placed on the high volume use materials and these include the weatherwork coatings applied to the superstructure of ships, flight deck coatings and paints schemes used on the internal surfaces of vessels.

The laboratory work undertaken to date has concentrated on the evaluation of high solids and water borne materials against the Defence Standards covering the weatherwork paint system This material has a number of critical requirements including the achievement, and retention, of high gloss levels. It is also a material that is applied under adverse conditions using unsophisticated equipment during Naval operations. Further work is also underway to investigate coatings used for internal structures and on flight decks and any new coatings introduced into service have to meet future environmental legislation in addition to meeting other technical requirements.

Trials on board working ships are difficult to arrange and the Navy has taken advantage of various museum ships. Although these vessels do not mirror the exact conditions experienced by operational ships, the increased availability offered is useful from a testing point of view. In these trials the application characteristics are carefully monitored as well as regularly examining specific properties (depending on the paint scheme) such as colour and gloss retention and non-slip properties over time. Due to the successful performance of certain materials on the museum ships, trials of a range of paints (e.g. weatherwork and anti-fouling) on operational vessels are in progress.

3.1.7 *General Results*

As stated previously, a summary of the general performance of the compliant coatings assessed will be presented as many of the trends observed were common to the various paint schemes irrespective of the particular end use of the coating.

It was generally found that the water borne materials offered poorer corrosion protection than the solvent based products. Although the high solids materials performed better than water borne they did not match solvent based paint schemes. The types of corrosion tests used were salt spray and sulphur dioxide resistance tests designed to accelerate external exposure of coatings. The generally inferior corrosion protection performance of water borne materials is not unexpected as the presence of water contributes to corrosion.

Another problem with water borne products was their relatively lower tolerance to imperfect substrate preparation. It was found that these materials require scrupulously clean surfaces otherwise adhesion of the paint films is compromised - leading to corrosion of the substrate. Again this is a critical property as many paint schemes are applied in adverse conditions within the military environment. Surface tolerance was less of a problem with high solids materials.

Another factor that needs to be recognised with water borne products is the drying conditions required which are more important than with solvent based materials which dry relatively easily. It is important that these paints are allowed to dry with a sufficient flow of air - humidity is also a factor that needs to be considered.

An important property of the weatherwork paint system used in Naval application is both high initial gloss levels and retention of these values. The trials on board HM Ships was used to monitor these properties and a wide variation in results was observed.

In addition to general trends, specific problems were noted with certain products. One sample exhibited both poor heat and fuel resistance which would obviously be unacceptable for a vehicle finish. Another example, with regard to an aircraft scheme, was poor resistance to hydraulic fluids.

3.1.8 *Conclusions*

General conclusions can be drawn from the results obtained in the assessment of the compliant coatings. Firstly, the performance of the products tested do not match that of the current solvent based paints with the high solids samples offering more potential than water borne at this stage. It should be remembered, however, that water borne products are more desirable from an environmental point of view as they reduce solvent levels (VOC content) to the bare minimum.

As two of the main drawbacks noted with the compliant materials were poorer corrosion resistance and lower surface tolerance, a potential solution is to use a 'hybrid' paint system consisting of solvent based primer and compliant top coat. This would result in lower VOC use whilst retaining acceptable performance although work would need to be undertaken to check the compatibility of the coats.

Although *current* compliant coatings do not match the performance of solvent based materials, this is readily recognised by the paint industry and all manufacturers are investing heavily in the production of new materials as replacements for solvent based paints. In fact one of the problems with assessing the performance of compliant paint schemes is that laboratory work would commence on the samples supplied by manufacturers and newer improved products would be offered prior to completion - it is a rapidly changing scene.

The impact of the move towards compliant coatings also requires the UK MOD user to carefully consider the particular purpose of a paint scheme. With solvent based coatings a particular material could be used in a wide range of applications. For example, material conforming to Defence Standard 80-41 is used to paint various military vehicles as well as static ground support equipment sited in the middle of airfields. Current compliant coatings do not show such versatility and in future different materials may need to be used for the different situations. This poses problems with regard to an increase in the inventory of paints held and may lead to differing process instructions for the different materials. It is important that expert advice is sought during deliberations on such changes. It is easy to specify single source, proprietary materials but for continuity of supply, assurance of product quality and to assist with competitive tendering the use of performance standards (e.g. Defence Standards) are essential.

With regard to paints for military vehicles, a more recent approach has been to evaluate commercial vehicle re-finishing products. Although these materials need specialist application facilities and initial work has concentrated on non-camouflage coatings, the laboratory results are very encouraging and full scale trials are planned. If the performance of these products is confirmed, work will commence, in conjunction with paint manufacturers, to formulate camouflage materials.

3.2 Example 2 - Paint Removal

At some stage in the life cycle of a paint system it needs to be removed. This could be for an operational requirement, as part of a maintenance cycle (check for corrosion) or for any number of other reasons. However, it is recognised by UK MOD that paint removal is also subject to environmental regulations and pressures.

3.2.1 *Background*

Traditionally, paint removal has been achieved using chemical strippers such as compositions based on methylene chloride. The PG documents include some guidance on reducing VOC use in paint stripping processes and the all embracing EPA covers discharge of substances in general which requires recognition of the various waste streams attached to any process. Use of chemical strippers contributes a waste stream that needs to be tackled.

In addition to environmental considerations, from a Health and Safety perspective, the types of substances contained within chemical paint removers pose risks to operators involved in the process.

3.2.3 *Alternative Solutions*

To avoid the use of chemical methods, physical methods for the removal of paint have attracted considerable interest.

In particular, investigations by the RAF revealed that the majority of VOCs used on their stations emanated from paints strippers and other solvents such as thinners and cleaning materials (Ref 1). Consequently the RAF has invested heavily in the use of Plastic Media Stripping (PMS). This method involves subjecting the paint surface to a high pressure stream of acrylic particles resulting in physical removal of the paint film. This technique is now widely used for the stripping of aircraft around RAF stations and the technique has developed from the stripping of components to the procurement of equipment able to strip whole aircraft.

Although PMS is a success story (it is reported that the 'down time' for aircraft has been reduced to 2/3 of previous times) it has not eliminated chemical removers as they are still required in particular situations such as small area airframe inspections and work is underway to evaluate environmentally friendly chemical paint strippers.

Other possibilities are variations on PMS involving the use of natural products as the stripping medium. Walnut shells and wheat starch have been evaluated and offer a greener medium although quality control of natural substances is more difficult than synthetic acrylic materials currently used in PMS.

The Navy are also investigating physical methods of paint removal using media such as 'pure water', garnet grit and 'sponge jet'.

The search for alternative paint removal techniques continues with vigour and imagination and two other techniques which have been explored to varying extents are:

a. Cryogenic Blasting - This involves using dry ice particles (carbon dioxide) as the abrasive media.

b. Laser Pulse - This technique uses a laser to vaporise the paint film and although feasibility studies have been undertaken it is currently a slow process to strip a large, complicated surface and would require significant investment in processing equipment.

4. CASE STUDIES WITH COST SAVINGS ('THE SILVER LINING')

Although environmental compliance can involve considerable investment, longer term cost savings can result. Advice is available both with the introduction of new technologies (materials, processes and practices) and to assist with solving existing pollution problems. The two case studies presented in this section illustrate how cost savings can be achieved and how technical support activity can prevent unnecessary expense in 'pollution clean-up' operations.

4.1 Effluent costs eliminated by Water Treatment (Ref 3)

A small company producing specialist electrical connectors for military and aerospace applications use electroplating methods for coating articles with gold, cadmium, copper, silver, nickel and tin. Large quantities of rinse water are used during the electroplating process but prior to discharge to drain it must be treated to meet environmental regulations. To conform to the legislation, the company recognised that they would have to invest in a range of measures including chemicals for effluent treatment, waste collection by licensed contractors, maintenance of the treatment plant and compliance testing - as well as the substantial water consumption costs. The main problem identified was the cadmium discharge and the company investigated a number of ways of eliminating this waste stream. They decided on an ion exchange closed-loop water treatment system and this has resulted in significant savings to the company without any adverse affects on product quality. Investment in the plant will be repaid in 16 months and the company will then realise year-on-savings of greater than £100,000 per year. This illustrates that the need for environmental compliance can act as a spur to investigate new technologies resulting in significant cost savings.

4.2 Lead in Paints

As well as a long history of pollution control, the UK has a long history of pollution. This has left a legacy of problems that require urgent action, such as abandoned waste tips, derelict and contaminated land, discharge of toxic waste, and many other matters of relevance to the surface treaters. Many such problems have stemmed from the fact that discharges were not perceived as problems in the past, or that lower standards were accepted

An example is the historical use of lead-based primers which were extensively used for the protection of ferrous substrates. Due to the established health hazards, limits on the lead content of paint have been imposed and alternative anti-corrosive pigments are now used. However, a number of older structures still contain lead which during maintenance activity either has to be sealed or removed. The Royal Navy were concerned that older ships in the fleet, about to undergo refit, contained lead primers but confirmation was needed as the precautions necessary to remove lead-based paint are more involved and, hence, more expensive. The DRA has undertaken surveys of several ships to advise the Navy of the presence, or otherwise, of lead. The Navy are then able to plan the most cost-effective paint removal and re-painting activities process.

5. SUMMARY

It is clear that the surface treatment industry faces a significant challenge to meet environmental legislation and to react to environmental pressures. In particular UK MOD has to meet the challenge without compromising military effectiveness. and this paper has concentrated on the issues relating to the MOD's use of paint but many other materials and processes face a similar challenge. It is important to realise that environmental legislation is likely to become increasingly restrictive in future years and the challenge will not disappear.

However, within the UK, government funded initiatives have been created (e.g. NASURF and the ETBPP) to assist with the transition to greener technologies and a range of other technical facilities and consultancies are also available.

In particular, although technologies are rapidly developing and product, and process, performance are improving, in the short term compromises may need to be accepted in order to meet imminent legislation. In these cases advice from technical experts can assist the non-specialist to minimise any risk involved with the adoption of a new technology.

Finally, it is important to realise that the adoption of new technologies in response to environmental pressures can lead to cost savings and not to cost penalties.

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OVERVIEW OF CLEANING/SURFACE PREPARATION FOR METALS IN THE US

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SUMMARY

Environmentally acceptable cleaning and surface pretreatment are being implemented in the US in order to reduce the costs of production and maintenance of weapon systems. The application of good business practices and decisions are central to meeting customer requirements, improving performance, reducing costs, environmental acceptability of materials and process and maintaining occupational health and safety. The key factors involved in any material or process change include, environmental acceptability, performance and affordability. The use of semi-aqueous and closed system volatile organic solvent cleaning has found widespread application within the US aerospace community. Metallic surface preparations including conversion coating, anodizing, adhesive bonding or electroplating are presently being converted the those not requiring the use of hazardous and toxic materials as well as large amounts of process water. Research and development activities are presently at a high level to develop new environmentally acceptable and safe processes for the long term.

1 INTRODUCTION

There are four major activities or environmental thrusts presently active within the US Aerospace community. (See illustration 1) These are risk analyses, cleanup, compliance and prevention. Prevention is concerned primarily with front of the pipeline activities such as materials and process changes/substitutions in order to reduce or element our dependence upon hazardous and toxic materials in the production and maintenance of our weapon systems. Prevention is the longer range activity designed to change the way we do business in the cleaning and metal surface preparation technology area. All of the activities involved in the implementation of substitute materials and processes are shown in illustration 2. In most instances as can be seen the substitution of a new material and or process must be proceeded by the development of an engineering data package showing the impact of the change on, affordability, functional effectiveness, the environment as well as safety and health. Illustration 3 shows a pictorial of waste stream generating processes involved in the production and maintenance of a weapon system. Prevention research and

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development is geared to reduce to as close to zero as possible these waste streams.

2 DISCUSSION

Metal finishing operations include cleaning and degreasing, plating and finishing, painting and paint stripping, anodizing and conversion coating. Illustration 4 shows three of these operations along with the associated hazardous and toxic materials that are associated with the process. Research and development, illustration 5 shows the prioritized technology thrust areas involved in meeting the objectives set forth by the Montreal Protocol as well as various laws, regulations and presidential directives that have been imposed on the manufacturing community in the US. The objectives and thrust area organization within the R&D strategy for pollution prevention is shown in illustration 6. The effort is broken down into subareas. These cover metal surface finishing, ordnance manufacture demil and refrigerants, fire fighting agents, and non-hazardous solid wastes.

Metal surface preparation R&D programs include efforts on cleaning and degreasing, illustration 7. Plating and finishing illustration 8, non-chromate conversion coating, illustration 9 and Paint Stripping, illustration 10 the projects are separated in to 6.2 Tech. base or applied/exploratory R&D and 6.3 technology demonstrations. The projects are also described by title and the performing organization (AF), Air Force (N) Navy and (A), Army are also identified.

Cleaning and degreasing work covers advanced technology cleaning processes that do not require the use of VOC's, water or hazardous and toxic chemicals. The cleaning processes under development or study include; laser cleaning, atomic oxygen, ultra-violet, oxygen plasma, particulate C02, as well as SCC02. Plating and finishing R&D includes advanced processes not requiring water, VOC's or hazardous and toxic chemicals. Under study are a number of thin-film technology processes including sol-gel oxide deposition, ion-beam deposition as well as physical and chemical vapor deposition of oxides, carbides and heavy metals such as chromium and nickel. Conversion coatings for steel and aluminum involve the use of rare earth's and other inorganic film formers to replace the presently used chromates.

Paint stripping R&D includes the development of advanced enzyme base strippers as well as the use of flash lamp-C02 particles as a process for paint removal.

3 CONCLUSIONS

Pollution prevention R&D is coordinated among the DoD armed Services in two ways. First, is the preparation of the tri-service strategic Environmental Quality Plan in which all environmentally related R&D is roadmapped. Second, is the strategic Environmental R&D Program which funds and coordinates high priority DoD environmental research. The DoD R&D program is driven by high priority needs received from the user community. The user community is involved in the operation, maintenance and repair as well as the design and production of weapon systems. The focus of the pollution prevention R&D program is on front of the pipe line work to reduce our dependence on the use of ODS's, VOC's hazardous and toxic chemicals as well as large water using processes.

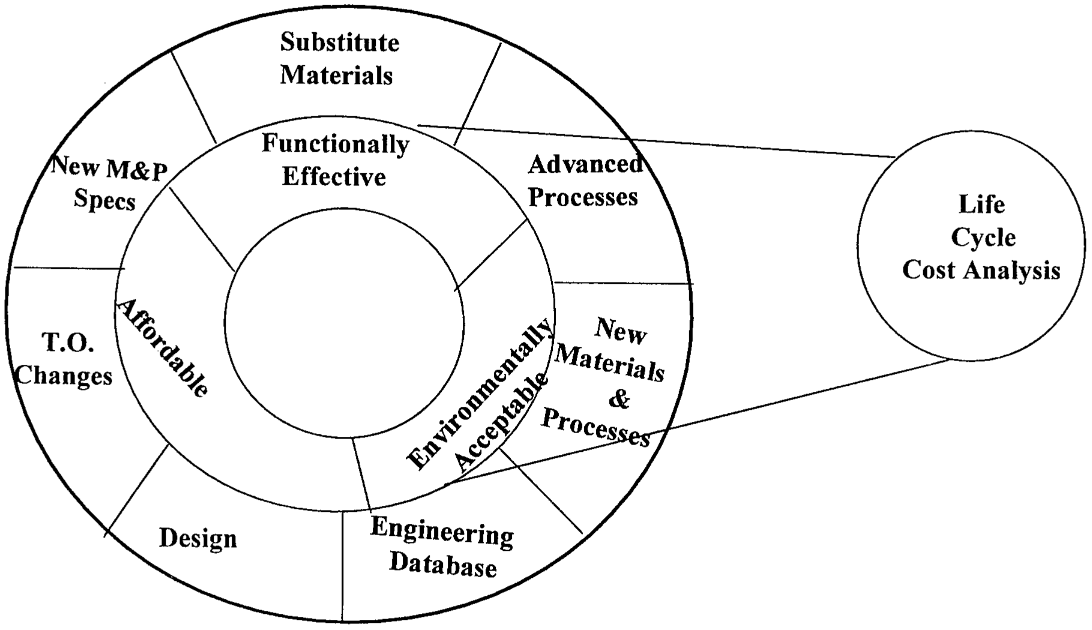
ILLUSTRATION 1

ENVIRONMENTAL THRUSTS

- Four Major Activities
  - Risk Analysis
  - Cleanup, Site Restoration
  - Compliance
  - **Prevention, Future Technology**

ILLUSTRATION 2

POLLUTION PREVENTION R&D
Alternative Materials & Processes Development
Illustration 2



DEFINING POLLUTION

ILLUSTRATION 3

POLLUTANT UNIVERSE AS SEEN IN WEAPON SYSTEMS

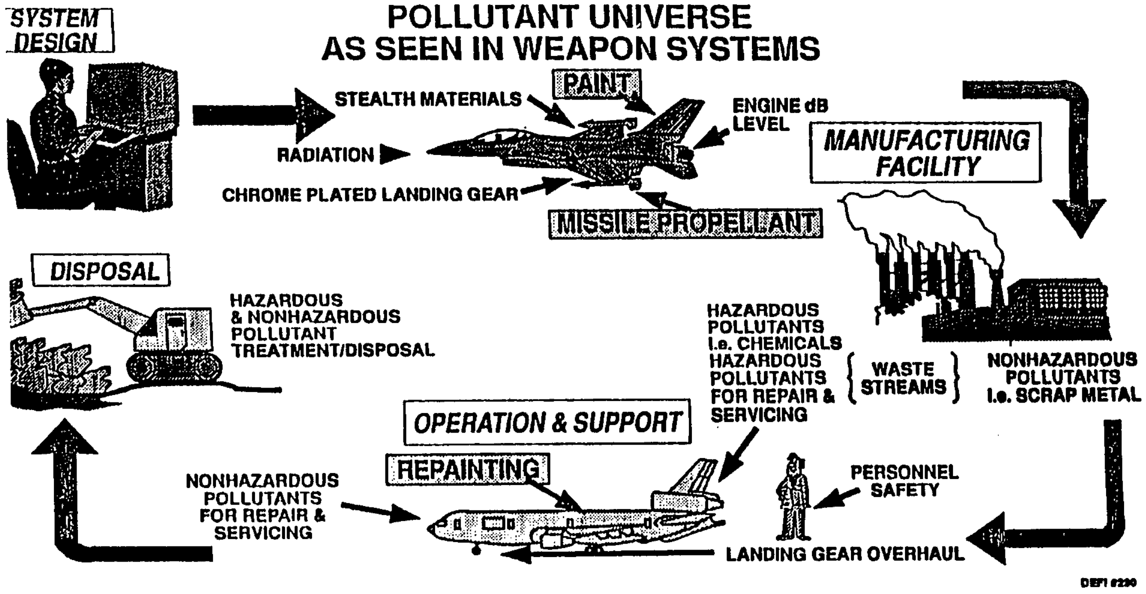


ILLUSTRATION 4

DoD METAL FINISHING TECHNOLOGY R&D

<u>CLEANING/DEGREASING</u>

- SMALL COMPONENTS
    - BEARINGS
    - GYROS
    - ELECTRONICS
- LARGE COMPONENTS
    - ENGINES
    - MOTORS
    - AIRCRAFT
    - SHIPS
    - TACTICAL SYSTEMS
    - HEAVY EQUIPMENT

<u>PLATING/FINISHING</u>

- CHROMATES
- CYANIDES
- NICKEL
- CHROMIUM
- CADMIUM
- ACIDS/BASES
- ANODIZING
- CONVERSION COATING

<u>PAINTING/STRIPPING</u>

- ISOCYANATES
- VOC,s/ODC,s
- CHEM. STRIPPERS
- CHROMATES
- LEAD/COPPER
- HAP,s

ILLUSTRATION 5

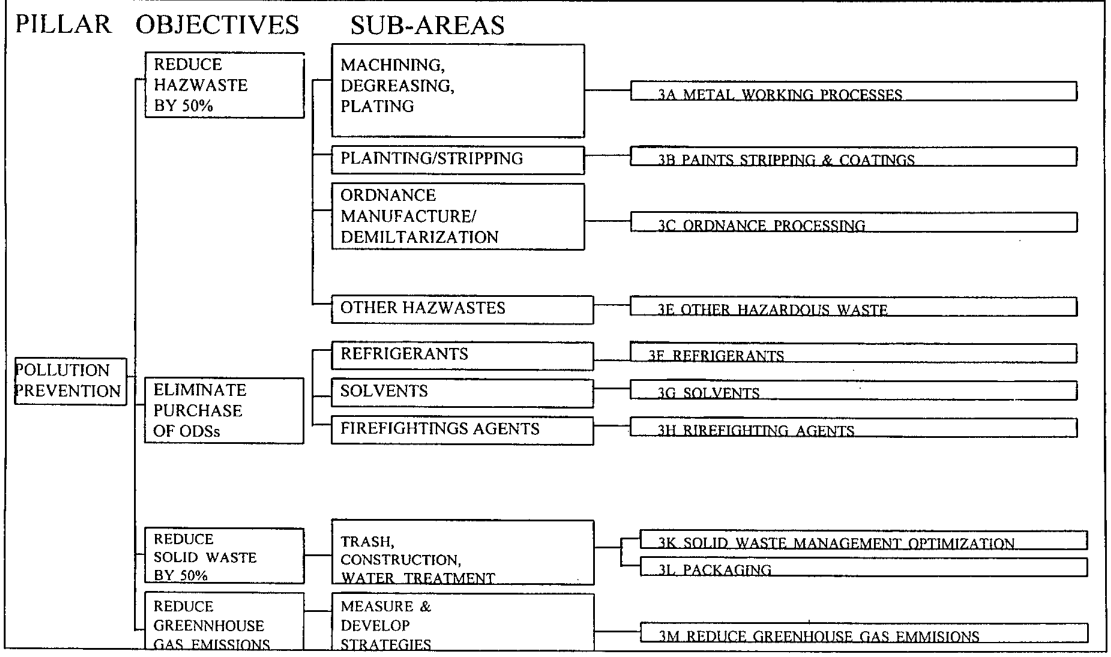
DoD METAL FINISHING TECHNOLOGY
R&D

PRIORITIZED TECHNOLOGY THRUST AEAS

- ELIMINATION OF OZONE DEPLETING CHEMICALS
- HAXTOX MATERIALS/PROCESSES/COMPONENTS REPLACEMENT
- HAZTOX WASTE STREAM REDUCTION
- VOLATILE ORGANIC COMPOUND ELIMINATION

ILLUSTRATION 6

R&D Strategy for Pollution Prevention



PILLAR
OBJECTIVES
SUB-AREAS

POLLUTION PREVENTION

REDUCE HAZWASTE BY 50%
- MACHINING, DEGREASING, PLATING
  - 3A METAL WORKING PROCESSES
- PLAINTING/STRIPPING
  - 3B PAINTS STRIPPING & COATINGS
- ORDNANCE MANUFACTURE/ DEMILTARIZATION
  - 3C ORDNANCE PROCESSING
- OTHER HAZWASTES
  - 3E OTHER HAZARDOUS WASTE

ELIMINATE PURCHASE OF ODSs
- REFRIGERANTS
  - 3F REFRIGERANTS
- SOLVENTS
  - 3G SOLVENTS
- FIREFIGHTINGS AGENTS
  - 3H RIREFIGHTING AGENTS

REDUCE SOLID WASTE BY 50%
- TRASH, CONSTRUCTION, WATER TREATMENT
  - 3K SOLID WASTE MANAGEMENT OPTIMIZATION
  - 3L PACKAGING

REDUCE GREENNHOUSE GAS EMISSIONS
- MEASURE & DEVELOP STRATEGIES
  - 3M REDUCE GREENHOUSE GAS EMMISIONS

ILLUSTRATION 7

DoD METAL FINISHING TECHNOLOGY R&D CLEANING DEGREASING

TECH. BASE (6.2)

- SOLID STATE CLEANING TECHNOLOGY (AF)
  (LASER,ATOMIC 02,UV+02,PARTICULATES,SCC02)
- SURFACE CLEANLINESS MEASUREMENT &STANDARDS(AF)

- NONTOXIC SHIPYARDS DEGREASING(N)

TECH DEMO(6.3)

- SOLVENT SUBSTITUTION & LOW VOC CLEANERS(N)

- NON PERSISTENT EMULSIFYING DEGREASER(N)

6.2 APPLIED R&D; 6.3 TECHNOLOGY DEMO.
(AF) AIR FORCE; (N) NAVY; (A) ARMY

ILLUSTRATION 8

DoD METAL FINISHING TECHNOLOGY R&D PLATING & FINISHING

TECH BASE(6.2)

- NON-CHEMICL SURFACE PREPARATIONS(AF)
  (SOL-GEL OXIDE, PLASMA SPRAY, ION BEAM OXIDE DEP.
  LASER OXIDE GROWTH)

- ADVANCED METAL DEPOSITION PROCESSES FOR CHROMIUM & NICKEL
  - PVD/ION BEAM ENHANCED COATINGS(A)
  - SPRAY CASTING (AF)
  - ELECTROMAGNETIC POWDER SPRAY(AF)
  - LASER DECOMPOSITION OF METAL ORGANICS (AF)

TECH DEMO(6.3)

- CADMIUM REPLACEMENT FOR SMALL PARTS(N)
- PLATING BATH REGENERATION/RECYCLE (N,A,AF)

ILLUSTRATION 9

DoD METAL FINISHING TECHNOLOGY R&D

NON CHROMATE CONVERSION COATINGS

TECH BASE(6.2)

- NON CHROMATE CONVERSION COATINGS/SEALERS(A)
- NON CHROMATE METAL ETCHING (A)

TECH DEMO(6.3)

- AIRCRAFT MAINTENANCE CHROMATE REPLACEMENT (N)
- NON CHROME CONVERSION COATING FOR SHIP REPAIR (N)
- NON CHROME CONVERSION FOR IVD ALUMINUM (AF)
- NON CHROME CONVERSION COATING FOR AIRCRAFT Al (N,A,AF)

ILLUSTRATION 10

DoD METAL FINISHING TECHNOLOGY R&D

PAINT STRIPPING

TECH BASE(6.2)

- ADVANCED HULL MAINTENANCE(N)
- ENZYMATIC PAINT STRIPPING (N,AF)

TECH DEMO(6.3)

- AIRCRAFT DEPAINT TECHNOLOGY (N,AF) (FLASH LAMP-C02)
- PLASTIC MEDIA RECYCLE/REUSE (AF,A,N)
- AIRCRAFT PAINT STRIPPING (AF)
- HULL & HEAVY VEHICLE PAINT STRIPPING (N,A)

ILLUSTRATION 11

DoD METAL FINISHING TECHNOLOGY
R&D
SUMMARY

- POLLUTION PREVENTION R&D IS WELL COORDINATED AMONG THE SERVICES
- R&D FUNDING IS FOCUSED ON HIGH PRIORITY USER NEEDS
- FOCUS IS ON AVOIDANCE AS A MEANS OF REDUCING CONSUMPTION & WASTE STREAM ELMINIATION

TRAITEMENTS DE SURFACE ET ENVIRONNEMENT : IMPACT DES RÉGLEMENTATIONS SUR LA POLITIQUE INDUSTRIELLE D'AEROSPATIALE

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1. INTRODUCTION

L'augmentation croissante et continue depuis 1970 des réglementations environnementales d'une part, la sensibilité accrue des opinions publiques et des pouvoirs politiques aux questions d'environnement et de santé d'autre part, ont induit des contraintes économiques, techniques et industrielles qui menacent aujourd'hui la pérennité de nombreux produits, matériaux et technologies utilisés dans les fabrications industrielles, aéronautiques en particulier.

Ainsi a-t-on vu successivement interdire des productions et des utilisations industrielles, au titre du principe européen de précaution, les substances appauvrissant la couche d'ozone comme les CFC (CFC 113), le T111, puis récemment, l'amiante.

Différentes autres substances, également limitées d'emploi, comme le cadmium, les COVs, les chromates, induisent les principaux fournisseurs à abandonner progressivement ces substances toxiques au profit de substituts moins dangereux pour l'environnement ou la santé.

Pour faire face à cette situation et s'adapter à ces évolutions dans une dynamique de compétitivité et de réduction des coûts, Aerospatiale, dans le cadre d'une organisation interne et en partenariat avec les constructeurs aéronautiques français, a mis en place une démarche stratégique originale visant à maîtriser les risques industriels ainsi générés.

2. PRINCIPALES CONTRAINTES RÉGLEMENTAIRES AFFECTANT LA PRODUCTION OU L'EMPLOI DES PRODUITS

Les différents pays occidentaux (Europe, USA) ont récemment engagé des programmes de réduction massive des émissions polluantes, en raison des menaces que ces émissions incontrôlées font peser sur l'environnement et sur la santé des populations exposées.

Parmi les polluants les plus visés, nous citerons successivement.

2.1 Les Composés appauvrissant la couche d'Ozone (Ozone Depletion Substances ou ODS)

Dès 1920, la découverte par CHAPMAN de possibles interactions entre le chlore et le cycle de formation/destruction de l'ozone avait préparé le terrain réglementaire.

En 1974, MOLINA et ROWLAND associaient à la déplétion possible de l'ozone une origine industrielle : les Chloro-Fluoro-Carbones (CFC).

Le protocole de Montréal, dès 1987, condamnait ces produits et prévoyait des calendriers d'élimination progressive.

Le réglement européen n°3093/94 avançait encore les échéances en interdisant la production du CFC 113 au 31/12/1994 et du T111 au 31/12/1995. Les Chloro-Fluoro-Carbones Halogénés (HCFC) étaient en même temps contrôlés et interdits d'utilisation en système ouvert.

Des processus s'exercent actuellement pour modifier l'article 5 de ce réglement, en particulier pour supprimer l'ensemble des usages solvants des HCFCs dès 1998 (aujourd'hui autorisés en système confiné jusqu'en 2015).

La suppression de production, voire d'utilisation de ces substances, a rendu nécessaire depuis 1992 la recherche et la qualification de substituts à de nombreux produits/matériaux.

On peut citer à titre d'exemples :

- les agents de nettoyage
- les promoteurs d'adhésion
- les agents de démoulage
- les agents d'expansion des mousses
- les mastics

2.2 Les Composés Organiques Volatils

Les Composés Organiques Volatils (COV), solvants émis par les différentes activités industrielles selon la définition européenne (projet de directive version de mai 1996), sont suspectés de conduire par recombinaison aux oxydes d'azote, à un enrichissement d'ozone au niveau troposphérique, et à la formation de Peroxyacylnitrates

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(PANs) toxiques pour les plantes et les populations exposées.
C'est la raison pour laquelle un objectif de 30% de réduction globale d'ici à l'an 2000 a été défini dans le cadre de la convention de Genève sur la réduction des pollutions transfrontalières.
Pour y parvenir, les états signataires ont engagé simultanément des plans d'actions et mettent en place des dispositions réglementaires visant sélectivement les installations industrielles générant des émissions de solvants organiques.

En France, plusieurs dispositions ont été édictées pour limiter les émissions de COV dans l'atmosphère. Parmi ces dispositions, il convient particulièrement de souligner :

- l'arrêté du 26/09/1985 (en voie de révision) impose pour les installations de traitement de surface des limitations d'émissions des polluants
- l'arrêté du 1/03/1993 relatif aux rejets des installations classées soumises à autorisation, impose déjà pour les installations nouvelles assujetties (atelier de peinture), des limitations drastiques de nombreux solvants utilisés usuellement comme le trichloroéthylène, le perchloroéthylène, des bilans d'effets sur l'environnement, voire des surveillances atmosphériques en continu ou discontinu selon la nature des substances et des flux de polluants émis. Des arrêtés complémentaires devront être pris par les autorités préfectorales d'ici le 28/03/1998 pour étendre ces dispositions à l'ensemble des installations industrielles existantes concernées
- le décret et l'arrêté du 3/05/1995 instituant une taxe parafiscale sur les émissions de polluants atmosphériques (en particulier sur les COVs) de 180 Francs par tonne émise pour les installations classées soumises à autorisation rejetant plus de 150 tonnes/an
- la récente loi sur la protection de l'air ambiant

En Europe, plusieurs textes en préparation, dont un projet de directive sur les émissions de COV, conduiront en cas d'adoption en l'état à un durcissement des contraintes industrielles, à la mise en place à terme de Plans de Gestion de Solvants (PGS) pour chaque installation émettrice concernée, et à la suppression progressive des principales substances toxiques.
Par ailleurs, différentes conventions notamment sur la protection de la mer du Nord (PARCOM) et du Rhin (CIPR) incitent à l'abandon pur et simple des voies solvants.

Aux États-Unis, des mesures de lutte particulièrement sévères contre les pollutions atmosphériques (Clean Air Act, National Emission standards for Hazardous Air Pollutants, rule 1124 et 1171) ont été récemment adoptées (1/09/1995) par l'agence fédérale de protection de l'environnement (EPA) et par certains états comme la Californie.
Certaines mesures s'appliquant spécifiquement aux industries aéronautiques devraient induire d'ici 1998 de profonds changements dans les technologies industrielles utilisatrices de solvants.

Les effets des polluants (CFC et COV) sont résumés sur la figure ci-après.

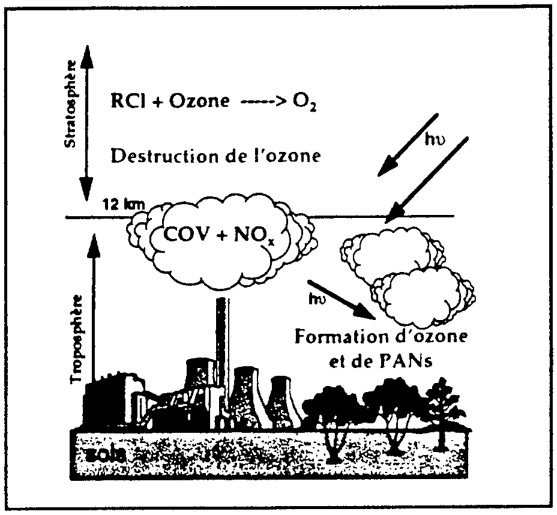

Figure 1 : Principaux effets des polluants sur l'atmosphère
Protection de la troposphère
- convention de Genève
- projet de directive COV
- convention PARCOM et CIPR
- arrêté du 1/03/93
- NESHAP - USEPA (1/09/1995)

Protection de la stratosphère
- protocole de Montréal
- réglement européen n°3093/94
- arrêt de production des CFCs (1994) et T111 (1995)

2.3 Les substances toxiques pour l'environnement ou la santé des populations

Les classifications des différentes substances utilisées par les industriels ont été multipliées et renforcées par :

- les différentes adaptations aux progrès techniques de la directive de base CEE n°67/548 (79/831) à la classification et l'étiquetage des substances et préparations dangereuses
- l'arrêté français du 20/04/1994 et le code du travail

De nombreuses substances et préparations sont désormais classées cancérogènes, mutagènes, tératogènes ou toxiques pour l'environnement, obligeant ainsi la mise en place de mesures de prévention et de protection des travailleurs ou populations exposés et de l'environnement. Face à la lourdeur et aux coûts générés, de nombreux fournisseurs et utilisateurs choisissent de traiter le risque à la source en décidant de supprimer l'emploi ou la commercialisation de ces produits.

C'est le cas en particulier :

- de l'amiante, récemment interdit d'emploi par le ministère du travail français
- des chromates
- du cadmium

3. CONSÉQUENCES POUR LES PRODUITS, PROCÉDÉS ET INSTALLATIONS DE TRAITEMENT DE SURFACE À AEROSPATIALE

Les réglementations environnementales conduisent, comme cela a été précisé précédemment, à :

- l'interdiction ou la menace d'interdiction de produits utilisés (contenant du CFC113, T111, amiante, chromates, cadmium, ...),
- la mise en conformité des installations industrielles (quantité des émissions COV).

La figure 2 montre la prédominance des produits et procédés de traitements de surface touchés par les contraintes réglementaires (CFC ou produits toxiques) à Aerospatiale, par rapport à la totalité des produits et procédés.

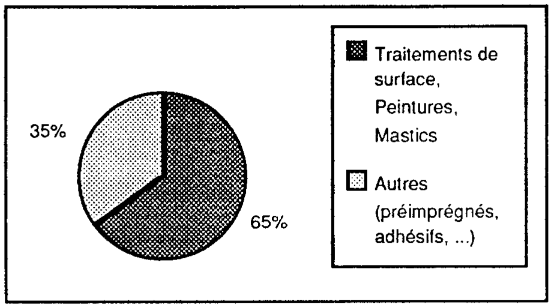

Figure 2 : Produits et procédés touchés par les contraintes réglementaires

L'interdiction, ou la menace d'interdiction, d'utilisation de produits et procédés nécessite leur adaptation, voire leur remplacement.
Cela passe par la recherche de substituts aux produits et procédés critiques, à leur qualification par rapport aux exigences techniques, et éventuellement, à l'adaptation ou le remplacement des installations.

Aerospatiale Aéronautique disposent de 4 sites de production, situés à Toulouse, Nantes, Saint-Nazaire, et Méaulte L'impact des réglementations sur les émissions polluantes des installations est illustré sur la figure 3.

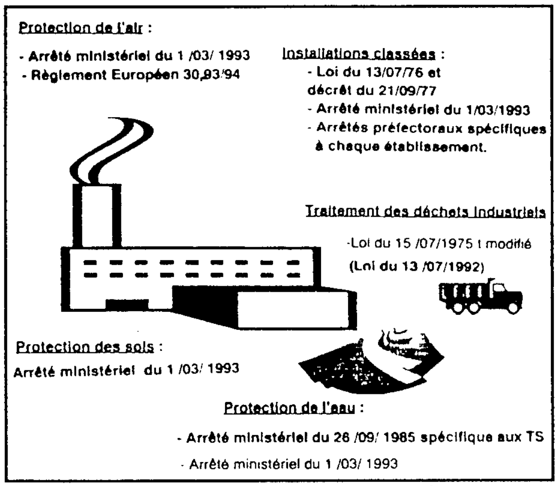

Figure 3 : Application des réglementations aux installations

Le respect des réglementations nécessitera dès 1998 en France, des mesures des émissions polluantes.

4. ORGANISATION MISE EN PLACE À AEROSPATIALE ET À AIRBUS INDUSTRIE

Les problèmes environnementaux ne sont pas traités en tant que tels, mais de façon plus globale, dans le cadre des actions visant à assurer la *Pérennité des matériaux, procédés et installations.*

Assurer la pérennité de matériaux, procédés et installations, c'est mettre en place les actions nécessaires afin de garantir la production des avions pendant la durée de vie des programmes.
Les causes de non pérennité ont des origines diverses :

- environnementales
- hygiène et sécurité
- économiques

Les *réglementations environnementales* ont été explicitées au §2.

Les problèmes d'*hygiène et sécurité* concernent l'arrêt d'utilisation de produits à risque (inflammables par exemple).

Les *causes économiques* englobent les arrêts de commercialisation de produits par les fournisseurs, suite à des réorganisations ou par souci de rentabilité.

A ce jour, 200 produits et procédés sont touchés au sein d'Aerospatiale Aéronautique par des problèmes de pérennité.
La répartition des problèmes de non-pérennité avérés, selon leur origine, est montrée sur la figure 3.

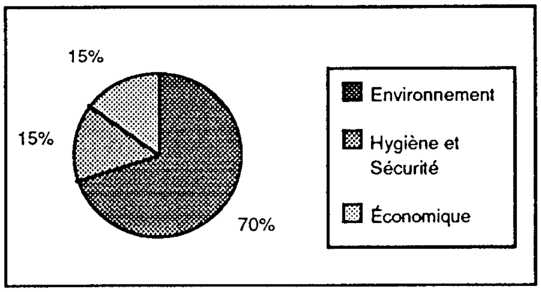

Figure 4 : Causes de non pérennité

4.1 Aerospatiale Aéronautique

L'organisation "Pérennité-Environnement" d'Aerospatiale Aéronautique est une organisation multi-compétences, enrichie de la collaboration avec le Centre Commun de Recherches, et regroupant les fonctions :

- recherche
- étude
- production
- hygiène et sécurité
- moyens généraux
- achats
- qualité
- normalisation

Cette organisation est chargée de :
- l'analyse des réglementations
- l'évaluation de la pérennité des matériaux et procédés
- la recherche de substituts aux matériaux et procédés critiques
- la qualification des substituts
- l'adaptation des installations
- la normalisation des procédures

Quelques exemples d'actions...

Outil d'évaluation des risques industriels

Un outil développé dans le cadre de travaux pour le Service Technique des Programmes Aéronautiques (détail des travaux au §5), permet de hiérarchiser les risques industriels selon un indice de pérennité des produits, et donne ainsi un ordre de priorité dans les actions à lancer.
Après avoir été expérimenté sur les matériaux composites, cet outil d'aide à la décision est actuellement utilisé pour évaluer la pérennité des peintures employées par Aerospatiale.

Commission d'Evaluation des Nuisances Chimiques (CENC)

Avant tout lancement d'essais de qualification, un produit est évalué sur la base de données Sécurité, des réglementations en vigueur ou à venir, afin de l'éliminer immédiatement s'il présente des risques.

Atelier pilote de maîtrise des COVs

Afin de répondre à la demande des autorités régionales et nationales, une étude a été lancée en 1995 visant à implanter des ateliers pilotes dans les usines de Toulouse et Nantes.
Le premier atelier pilote, l'atelier de peinture finale, comprend :
- l'analyse des flux de produits
- la sélection de méthodes d'analyse
- l'étude de méthodes de réduction des COVs
- l'écriture de la documentation d'inspection
- l'extension à tous les ateliers

L'autre atelier pilote, l'atelier d'usinage chimique, concerne la mise au point d'un masque d'usinage chimique sans solvant.
L'étude, d'une durée de 2 ans et d'un coût de 8.5MF, est menée en partenariat avec les fournisseurs.

Diminution des déchets de traitement de surface

Un projet en cours, impliquant toutes les usines d'Aerospatiale Aéronautique, a pour objectif de diminuer de 50% les déchets, et donc les coûts des traitements.
Ce projet, d'une durée de 5 ans et d'un coût de 24MF, verra la mise en place de technologies de recyclage ou de diminution des rejets.

4.2 Airbus Industrie

Depuis plusieurs années, des groupes de travail associant les partenaires Airbus Industrie ont pour vocation de définir des spécifications communes, décrites dans une documentation Airbus Industrie.
Cette documentation est spécifique aux matériaux, aux procédés, aux méthodes d'essais, utilisés au cours de la production des avions.

Il s'agit des :
- Airbus Industrie Material Specifications (AIMS)
- Airbus Industrie Process Specifications (AIPS)
- Airbus Industrie Test Methods (AITM)

Les qualifications des nouveaux produits se font désormais en commun, dans le cadre du partenariat Airbus Industrie.
Cela concerne les produits de nettoyage, les décapants, les procédés de traitement de surface, les peintures, mais aussi les matériaux composites et métalliques.

Des tests spécifiques ont été récemment introduits, afin de répondre aux réglementations environnementales et aux questions d'hygiène et sécurité.
Des substituts à des produits arrêtés ont été qualifiés selon ces nouvelles spécifications.

D'autre part, les produits consommables recommandés par les partenaires sont inclus dans la Consumable Material List (CML), document Airbus Industrie spécifique à la maintenance des avions en compagnie.

5. DÉMARCHE ADOPTÉE POUR MAÎTRISER LES RISQUES INDUSTRIELS

Différentes actions ont été menées ou sont en cours pour maîtriser les risques industriels. Il s'agit d'actions d'anticipation des problèmes.

La démarche présentée ci-après, est le résultat d'une étude sous la responsabilité du Service Technique des Programmes Aéronautiques (STPA), regroupant les principaux partenaires du domaine aéronautique français (Aerospatiale, Eurocopter, Dassault Aviation, Hispano-Suiza, Hurel-Dubois, et SNECMA).
Le but de cette étude était de déterminer les différentes actions à conduire afin de maîtriser les risques.

L'étude a été organisée en 5 phases :

Phase 0	Bilan des problèmes critiques urgents	Eurocopter
Phase 1	Recensement des produits et collecte des informations	Aerospatiale
Phase 2	Évaluation du risque industriel et de la non pérennité	Aerospatiale
Phase 3	Analyse des conséquences industrielles	Dassault Aviation
Phase 4	Recommendations et actions correctives à engager	STPA

Une méthodologie commune d'analyse du risque industriel a été développée, avec notamment un outil d'aide à la décision permettant d'évaluer le niveau de risque que représente pour l'entreprise la non-pérennité d'un matériau.
Cela repose sur l'évaluation séparée de :
- la probabilité d'apparition (P) d'évènements extérieurs pouvant affecter la pérennité des matériaux et procédés
- les conséquences industrielles (C) d'une telle apparition

Le risque pour un matériau M s'exprimera par :

$$R_M = P_M \times C_M$$

La connaissance de ces composantes permet de mieux appréhender la stratégie à conduire pour un matériau donné.

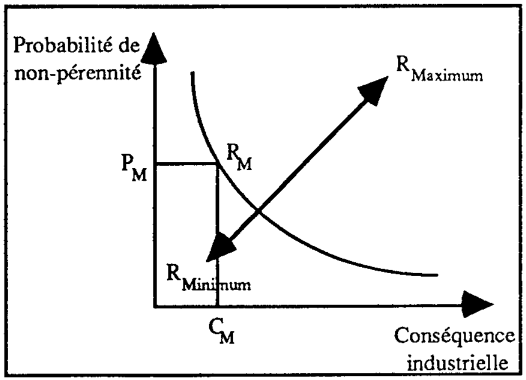

Figure 5 : Risque Industriel R_M

Si P_M est grand et C_M est petit, aucune disposition particulière de recherche de substituts ne sera engagée. Seule une vigilance accrue sous la forme d'une veille technologique et stratégique, accompagnée d'un éventuel lobbying, pourrait être décidée.

Si P_M est faible et C_M grand, il sera obligatoirement décidé des actions à mener afin de prévenir la détection d'un effet industriel de gravité élevée.

On détermine ainsi des zones correspondant à des niveaux de risques plus ou moins importants.

Parmi les méthodes d'aide à la décision, la méthode des déclassements comparés est apparue comme un moyen simple pour traiter les informations recueillies et effectuer un classement comparatif des matériaux, selon une échelle qualitative du risque industriel.
Le principe général repose sur :

- la sélection d'un panel d'experts du domaine étudié
- la sélection de critères pertinents
- une appréciation qualitative des valeurs de chaque critère
- une hiérarchisation des critères
- la construction d'une échelle graduée et facilement exploitable

A partir d'informations collectées auprès des fournisseurs, un groupe d'experts a dégagé un ensemble de critères pour évaluer la probabilité d'apparition (P) d'évènements extérieurs pouvant affecter la pérennité des matériaux et procédés :

- disparition inéluctable du produit
- difficultés potentielles d'utilisation ou de production
- dépendance économique des substances majeures constitutives du produit
- évaluation sommaire des risques liés aux variations et spécificités du marché
- évaluation du procédé

Les conséquences industrielles (C) sont évaluées de la même façon, à partir de critères, même si il est apparu que le choix de critères pertinents dépend de l'industriel et de la nature de ses activités.

Les critères retenus sont :

- existence d'un matériau de remplacement
- type de programme concerné
- compatibilité avec les délais
- coût global de substitution
- importance fonctionnelle des pièces concernées

La construction de l'échelle, nécessaire à la mise en oeuvre de la méthode des déclassements comparés, découle de l'inventaire des critères pertinents, et de l'affectation à chaque critère de valeurs qualitatives traduisant la gravité.

Le produit analysé peut alors être caractérisé par une valeur, qui permettra de le situer comparativement aux autres produits connus ou analysés.
Cela ne constitue pas une quantification absolue du risque industriel, mais permet néammoins de dégager une tendance.

Dans le cadre de l'étude, cette démarche a été appliquée aux matériaux composites.

6. CONCLUSIONS

Pour faire face à des réglementations environnementales interdisant de plus en plus de produits, régulant progressivement les installations industrielles, Aerospatiale Aéronautique a mis en place en interne une organisation multi-compétences, tout en développant des collaborations avec les partenaires d'Airbus Industrie, avec les partenaires aéronautiques français, ainsi qu'avec les fournisseurs.
L'objectif est minimiser les risques industriels générés par la disparition possible de matériaux montés sur avion ou l'interdiction de procédés de fabrication, et de diminuer ainsi les coûts de qualification de substituts et de mise en conformité d'installations.

C'est la raison pour laquelle les industriels doivent unir leurs efforts pour :

- anticiper les risques industriels,
- mener des actions communes pour la recherche et la qualification de substituts,
- travailler en étroite collaboration avec les fournisseurs et leur remonter le plus possible les problèmes,
- faire du lobbying auprès des autorités politiques pour assouplir les réglementations.

Il faut souligner l'importance de l'anticipation des problèmes.
La méthodologie d'analyse du risque industriel présentée précédemment permet de donner des priorités dans les actions correctives.
L'anticipation des réglementations devraient permettre, de plus, d'orienter les activités de recherche vers des produits ou procédés pérennes, et contribuer à la minimisation des risques industriels.
Le suivi et l'anticipation des réglementations sera une des vocations de l'observatoire des contraintes, outil qui sera développé en 1997 avec le soutien de la Délégation Générale pour l'Armement, en partenariat avec des industriels aéronautiques français, et qui pourrait être étendu au niveau européen.

US ENVIRONMENTAL TRENDS AND ISSUES AFFECTING AEROSPACE MANUFACTURING AND MAINTENANCE TECHNOLOGIES

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SUMMARY

The exploration, development and implementation of new aerospace maintenance and manufacturing technologies is partially driven by the increasingly strict environmental regulations and issues. In the United States, innovative technologies are competing for acceptance as the new generation aerospace materials or process standards. The selection of new manufacturing or maintenance processes is largely based on environmental acceptability, but increasingly centered on efficiency, rapid implementation, monetary payback, and most importantly on the ability of the technology to improve an aircraft's mission. In the near future, human health issues may dominate new technology projects funded through environmental programs as new studies show the possibility of the health risk of extremely small quantities of airborne toxics and particulate matter.

LIST OF SYMBOLS AND TERMS

CAA	Clean Air Act
CAM	Compliance Assurance Monitoring
CFR	Code of Federal Regulations
CTG	Control Techniques Guidelines
DoD	Department of Defense
DOE	Department of Energy
EO	Executive Order
EPA	Environmental Protection Agency
EPCRA	Emergency Planning and Community Right to Know Act
HAP	Hazardous Air Pollutant as defined in
ISO	International Standards Organization
MACT	Maximum Achievable Control Technology
NAAQS	National Ambient Air Quality Standards
NESHAP	National Emission Standards for Hazardous Air Pollutants
OSHA	Occupational Safety and Health Administration
PM	Particulate Matter
PMB	Plastic Media Blast
PEL	Permissible Exposure Limit
SERDP	Strategic Environmental Research and Development Program
TSCA	Toxic Substances Control Act
VOC	Volatile Organic Compound

1.0 INTRODUCTION

In the 1980s and early 1990s, a shift in focus occurred within the environmental technology community to include a materials and process approach in the move toward cleaner aerospace manufacture and maintenance facilities. Prior to that time, environmental and civil engineers pursued primarily new construction or modified treatment facilities to decrease the uncontrolled release of pollutants. Since then, materials, industrial, chemical, civil, environmental engineers and scientists have shifted the emphasis of aerospace related RDT&E to address the procedures, materials and techniques that are the source of the pollutants handled in abatement or treatment equipment. A large part of this change in direction is the result of regulations that are designed to prevent pollution which often is less expensive than cleaning-up afterwards. Recent rules and policy are geared toward pollution prevention, community partnership and human health. Successful pollution prevention means substituting or eliminating in-efficient processes. Since many of these processes are proven safe to flight critical aerospace components, often the implementation of a new pollution preventing technology requires innovative development, test and validation. Since in-efficient processes are defined as wasteful, many times the implementation of pollution preventing technology is a good business decision and in some cases may improve the operational availability of the aerospace vehicle.

2.0 RECENT TRENDS AND ISSUES

2.1 Clean Air

US clean air principles were established in 1967 by the Clean Air Act and they are extensively modified in the amendments of 1970, 1977 and 1990. The three major categories of this act are sources that fall under ambient air regulation, new sources and sources that are specific pollution problems, including hazardous air pollutants (HAPs).[1]

2.1.1 Aerospace NESHAP

The latest aerospace NESHAP was released 1 September 1995 and requires three years for full implementation. The NESHAP regulates by placing requirements on materials and processes, including cleaning, painting, depainting or paint stripping, and chemical milling maskants. Facilities covered under this regulation include all major facilities

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with any aerospace activity resulting in the potential to emit ten tons per year of any single HAP or twenty-five tons per year of any combination of HAPs.

For the purpose of this paper, the promulgated aerospace NESHAP standards are summarized in Annex A.[2]

2.1.2 National Ambient Air Quality Standards

Particulate Matter

The EPA currently regulates coarse particulates, or those 10 micrometers or smaller in diameter, and is known as the PM-10 standard.[3] The agency is expected to propose a revised version in November that will add a new standard controlling particulates that are 2.5 micrometers or smaller [PM-2.5].[4] Adoption of a fine particulate matter standard by the EPA will significantly increase the number of states and localities subject to particulate matter regulation as well as imposing new financial burdens.[5] As of 9 August the date for submitting a proposal to establish the new fine particulate matters standard is 30 September. There is no EPA proposal at this time. The numbers being considered are only recommendations contained in an EPA staff paper[6] from the Clean Air Science Advisory Committee [CASAC].[7]

These recommendations remain highly controversial, even within CASAC where half the committee members felt EPA may have "overstated" its case for a PM-2.5 standard.[8] It was finally agreed that the PM-2.5 standard should include both a 24-hour and an annual component to address short-term and long-term health effects. The upper range for the 24-hour standard is proposed at 65 micrograms per cubic meter and the lower end of the range is set at 20 micrograms.[9] A major concern is accommodating regional variations in the natural background against which the standard numbers will be measured. Three types of natural events are recognized as affecting whether an area meets the PM-10 standard: volcanic or seismic activity, wild land fires, and high winds.[10]

The method used by the EPA to determine whether areas are in attainment with federal standards for ozone or PM would be replaced under a draft report being considered. The subcommittee for Ozone, Particulate Matter, and Regional Haze Implementation Programs designates two types of areas for regulation, "areas of violation" [AOV] and "areas of influence" [AOI]. The principle benefit of this approach is that it factors in the regional nature of ozone and PM pollution problems. The boundaries of AOV should be defined by the geographical location of ambient air quality monitors recording violations of the standards, rather than by political boundaries under the existing framework. The committee also recommends a requirement that areas make an additional 3% in reductions each year after 1996.[11]

Assuming EPA proposes the rules in November and makes a final decision on standards by June 1997, nonattainment designations should be made by June 1999, and nonattainment areas would be required to submit plans to EPA for meeting the standard by June 2002.[12] This issue may be of particular importance to EPA, given the passage of the Small Business Regulatory Enforcement Fairness Act, which requires a congressional review of final rules expected to have an impact on the economy of $100 million or more. Through the act, Congress can block rules it determines will have an overly burdensome impact on small business.[13]

2.1.3 Air Toxics Program

EPA intends to amend its regulation and move the deadline for sources filing initial notification requirements for EPA air toxics rule to 1 Sept 1997 or one year before sources are required to come into compliance with the rule. Subpart A of 40 C.F.R. 63 sets initial notification requirements for air toxics standards. The aerospace standard gives sources 3 years to comply, which differs from most air toxics rules. This rule is estimated to affect 2,869 major source manufacturing and rework facilities and is expected to reduce emissions of HAPs by 59% [123,700 tons] from levels that would occur in 1998 without the standard. HAPs targeted include chromium, cadmium, methylene chloride, tolulene, xylene, methyl ethyl ketone, ethylene glycol, and glycol ethers.[14]

The US Federal budget battle of 1996 had an affect on the EPA's air toxics program. The 40% cut in funding projected was expected to have a major impact on the agency's ability to promulgate MACT standard schedules for completion in 1997 [7-year standards]. The agency planned to propose 22 7-year standards in '96, but would only get to 8 under current funding levels. Work could not even begin on developing any of the 87 MACT standards [10-year] due for completion in 2000.[15] In a regulatory schedule established by the agency in Dec '93, EPA set a deadline of Nov 15, 1994 for completion of the 4-year standards, and a deadline of May 15, '96 for submission of 112(j) operating permits in the event a 4-year standard was not complete. Deadlines for 7-year standards are Nov 15, 1997 & May 15, 1999 respectively. For 10-year standards, deadlines are Nov 15, 2000 & May 15, 2002.[16]

This is important as facilities required to report under the Emergency Planning and Community Right-to-Know Act [EPCRA] released 2.26 billion pounds of toxic chemicals into the environment in 1994 according to the latest EPA report released 26 June. This is an 8.6% decline from 1993 levels. Since 1988, overall toxic releases have declined by 44.1%. Under Executive Order 12856, federal facilities were required to report for the first time, and 191 facilities filed. The top 5 states for releases in 1994 were Texas, Tennessee, Louisiana, Mississippi, and Ohio.[17]

EPA staff identified 37 hazardous air pollutants that are considered high priorities for regulation under the air toxics program. Under section 122 of the CAA, the agency is required to set air toxics standards controlling emissions of 189 HAPs. The 37 hazardous air pollutants on the list are:

acetaldehyde; acrolein; acrylamide; acrylonitrile; arsenic and compounds; antimony and compounds; benzene; beryllium and compounds; bis(2-chloroethyl) ether; 1,3-butadiene; cadmium and compounds; coke oven emissions; 2,3,7,8-TCDF; dioxin (2,3,7,8-TCDD); ethylene dibromide; ethylene dichloride; ethylene oxide; formaldehyde; glycol ethers; hydrazine; lead and compounds; manganese and compounds; mercury and compounds; methylene chloride; MDI; nickel and compounds; phosgene; POM (PAHs); styrene; tetrachloroethylene; trichloroethylene; toluene; 2,4-toluene diisocyanate; vinyl chloride; and xylenes.[18]

An EPA memo released Jan 23 gave notice of the agency's intention to issue a direct final notice moving the permit deadline established. by Section 112(j) for sources subject to the agency's "four-year" maximum achievable control technology standards from May 15, 1996, to Nov 15, 1996. Sec 112(j) is designed to act as a "hammer" by requiring sources to set emissions limits for hazardous air pollutants in the event EPA fails to promulgate a MACT standard covering a source in a timely manner.[19]

A series of proposed revisions to new source review regulations under the Clean Air Act are expected to reduce the number of permitting actions sources must undergo by more than 50%. EPA's proposal retains a requirement that facilities use a "top-down" approach to selecting best available control technologies under the prevention of significant deterioration program. This method of selecting BACT has generated considerable controversy, with many in industry maintaining it is overly stringent and counter to congressional intent behind the act. The top-down approach requires sources to either select the most stringent emission controls available or justify the use of less stringent controls.

Under EPA's rule, a determination of best available control technology must meet two core criteria:

> 1) the source must consider all available control systems, including the most stringent
>
> 2) the selection of a system that is not the most stringent available must be justified in terms of a number of factors, including economic and environmental impacts.[20]

EPA is considering a plan for potential to emit determinations that would place the burden of proof on sources to prove their potential emissions effectively keep them below the thresholds for determining major sources. Sources that rely on limits that are not federally enforceable would be presumed to be major unless they demonstrated otherwise per industry officials. By limiting their potential to emit, many sources can avoid designation as a major source under the act and avoid more stringent permitting and control requirements. Until recently, only controls deemed federally enforceable could be used to determine the limits on a source's potential to emit, precluding the source from counting state or locally mandated controls, or physical limitations, in their determinations.[21]

2.2 Credible Evidence

The EPA does not intend to repropose a rule that will allow the agency to use any credible evidence to establish violations of the Clean Air Act [CAA], instead issuing a final version later this year. The EPA believes it has the legal authority to move forward with a final rule because the rule stems from provisions of a previously proposed rule on enhanced monitoring.

This rule would allow the agency to use credible evidence (as defined by individual state or federal rules of evidence) to prove violations of the CAA regulations. Currently, enforcement personnel must rely on reference test methods contained in regulations to prove a violation has occurred. The agency outlined the proposal in a position paper released March 22 (26 ER 2245). The proposal resurrects a portion of a controversial enhanced monitoring rule proposed by EPA in 1993, but later abandoned under pressure from industry. The CAM rule is designed to replace EPA's controversial enhanced monitoring proposal with a more relaxed monitoring approach based on operation and maintenance procedures.[22] Industry representatives maintain that certain standards, such as some new source performance standards, require compliance only under certain conditions when performance tests are run. They hold that EPA never proved sources could achieve continuous compliance with these standards. Companies believing they are in compliance through their compliance assurance monitoring [CAM] plans could be blindsided by the credible evidence rule if some unanticipated information, beyond the scope of data collected pursuant to CAM, is introduced in an enforcement action.[23]

DoD joined several companies and industry groups in calling on EPA to back away from the use of any credible evidence to establish violations of CAA standards. The changes EPA is suggesting would make it difficult for sources to defend themselves from citizen law suits, allow "dubious or marginal" enforcement actions to go forward, and allow states to unnecessarily increase fines for alleged violations of state implementation plans.

Perhaps the foremost concern raised by opponents of the proposal is its potential impact on the stringency of clean air standards. They maintain the proposal fails to account for factors that lead to variability in air emissions by substituting current test methods based on periodic monitoring with an enforcement mechanism that looks for violations 100% of the time a source is in operation.[24]

2.3 ISO 14001

The International Standards Organization [ISO] is a Geneva-based federation of national standards bodies and is affiliated with the American National Standards Institute. ISO is developing the standard 14001 as a new international standard for environmental management systems. The standard is expected to become final later this year. As of 23 Feb 96, EPA had no intention of adopting ISO 14001 into regulation, in part because it is not a performance standard. EPA also believes parts of the standard need to be clarified, including the term "prevention of pollution."[25] This standard has twofold importance, both on its own terms, and as an example, by analogy, of similar problems with voluntary self-auditing.

Companies considering implementing ISO 14001 should be aware of the possible conflict between the standard and confidentiality of environmental compliance audit results, and consider measures they will use to preserve the confidentiality of as much audit information as possible. ISO 14001 differs from current environmental management systems in the U.S. It requires public involvement. Those items not required to be documented may still need to be demonstrated to an auditor. This would result in an extreme "chilling" effect on self-audits if the results could be routinely used in enforcement actions.

Facilities should work closely with their legal counsel to determine what methodologies will be feasible and necessary to maintain confidentiality prior to implementing ISO 14001. They should also hold discussions with environmental enforcement to determine regulatory changes that would permit implementation without waiving confidentiality.[26] An excellent analysis of the impact is found in the article "Implementing ISO 14001 May Destroy the Confidentiality of Environmental Compliance Audits" by Jack H. Goldman, BNA Analysis & Perspective 6/7/96 pp. 426-430.[27]

A working group has been formed at the EPA to make recommendations regarding any connections between agency policy on environmental audits and the ISO's environmental management benchmarks. Participants on two agency projects have expressed interest in connections between EPA enforcement and ISO 14001 - Environmental leadership Program and Project XL.[28] Lucent Technologies, a participant in project XL, is already experiencing difficulties with confidential data.[29]

2.4 Occupational Safety and Health

The Occupational Safety and Health Administration (OSHA) has set standards for PEL for employees working with and around hazardous materials. These limits (see Table 2) are based on a TWA for an eight hour period. Proposed new standards are listed in Table 3 with possible aerospace materials or processes affected.

Table 2. Current OSHA Limits[30]

Substance	CAS Number	PEL
Cadmium	7440-43-9	5.0 $\mu g/m^3$
Chromium	7440-47-3	0.5 mg/m^3
Methylene Chloride	75-09-2	500 ppm

Table 3. Proposed OSHA Limits and Some Related Processes[31]

Substance	PEL (mg/m3)	Processes Affected
Cadmium	0.5 $\mu g/m^3$	electroplating, blasting
Chromium	-	electroplating, blasting, anodizing, acid cleaning, conversion coating, primer coating
Methylene Chloride	25 ppm	chemical paint stripping, organic cleaning

3.0 AFFECTS ON TECHNOLOGY

3.1 High Payback Technologies

Cleaning, painting and paint stripping are among the most wasteful and time consuming processes in aerospace maintenance and manufacturing. Figures (1) and (2) identify the percentage of HAPs and VOCs released from the aerospace industry.

Figure 1: Aerospace HAP Emissions[32]

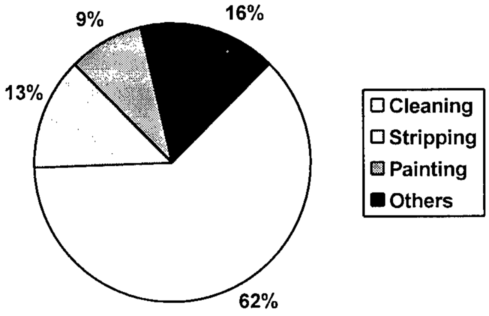
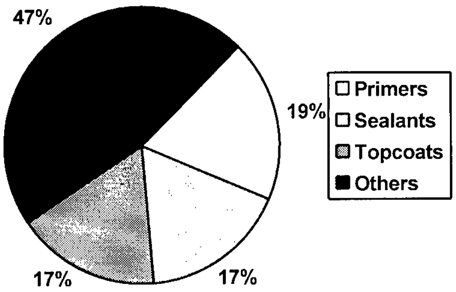


Figure 2: Aerospace VOC Emissions[32]



In the US DoD, an extraordinary effort is ongoing to find substitutes for these most hazardous, wasteful and expensive processes. Low VOC/HAP coatings, electro-coatings, powder coatings and long life coatings are under evaluation through funded RDT&E projects. Concurrently, the quest for a substitute for chromated corrosion inhibiting compositions addresses the OSHA and Air Toxics standards. A revolution in the cleaning of aerospace parts is partially the result of the elimination of ODSs and the push EPA and local push toward low vapor pressure solvents that contain little or no HAPs.

At the beginning of this decade, the identification of methylene chloride as a potential human carcinogen initiated an industry wide push to implement non-toxic paint stripping methods. The chemically resilient, abrasion resistant polyurethane, polysulphide, and epoxy coating systems offered a great challenge to non-methylene chloride based paint removal. However, PMB proved viable and under controlled parameters, resulted in little or no significant degradation in materials properties of sensitive structures necessary for flight. A great majority of aerospace maintenance facilities now utilize PMB to some extent, yet the search for technology that results in a faster output, less waste, and less potential for substrate damage continues.

High intensity light resulting from Lasers or Xenon arc flashlamps are still pursued under funded DoD efforts. The attraction in these technologies results from their inherent low waste and high controllability. Manipulation of these position sensitive methods remains the single largest problem in successful production demonstration. The US Navy, Air Force and Army are, in some cases, teaming up to pursue successful demonstration and validation of these technologies.

3.2 RDT&E Approach Within the DoD

Technical projects involving integrated teams of personnel from Navy, Air Force, Army, academia and private industry are the new standard for successful efforts. CRADAs are an avenue for easily defined team rules and responsibilities and provide for a lawful working relationship among government and the private sector.

In recent years, many leaders in the DoD have pushed for a compressed timeline of technical maturity. The Federal Facilities Compliance Act and the movement of local or state regulating bodies to exceed the EPA or OSHA regulations have impacted operational aircraft units and potentially reduced the quality and frequency of aircraft maintenance.

In 1996, the Director of Defense Research and Engineering, the Honorable Anita K. Jones has said that the DoD's investment in new technology should now accomplish these three objectives; reduction in cost or affordability, rapid transition to the field and dual use application. Dual use projects center on using commercially available technology where we can as well as developing new military technology that is easily converted to private sector benefit.[33]

The Strategic Environmental Research and Development Program is mandated by US law.[34] SERDP addresses matters of concern to the DoD and the DOE. The purposes of the program are:

(1) To address environmental matters of concern to DoD and the DoE through support for basic and applied research and development of technologies that can enhance the capabilities of the departments to meet their environmental obligations.

(2) To identify research, technologies, and other information developed by the DoD and the DoE for national defense purposes that would be useful to governmental and private organizations involved in the development of energy technologies and of technologies to address environmental restoration, waste minimization, hazardous waste substitution, and other environmental concerns, and to share such research, technologies, and other information with such governmental and private organizations.

(3) To furnish other governmental organizations and private organizations with data, enhanced data collection capabilities, and enhanced analytical capabilities for use by such organizations in the conduct of environmental research, including research concerning global environment change.

(4) To identify technologies developed by the private sector that are useful for DoD and DoE defense activities concerning environmental restoration, hazardous and solid waste minimization, and prevention, hazardous material substitution, and provide for the use of such technologies in the conduct of such activities.[35]

Ultimately SERDP is a forum to identify and develop environmentally acceptable technologies and to share that information among other government agencies, and the private sector. While SERDP intends to reduce the environmental risks of its customers, it also strives to improve the mission capabilities of the warfighter.

4.0 CONCLUSIONS

Disagreement remains on the impact of environmental regulations on the US economy and the health of its aerospace industry. The substantial costs of training, reporting and preparing for liability have resulted in the hiring or contracting of additional engineers, scientists, technicians, artisans and lawyers to meet the minimum requirements of recent environmental regulations. In addition, at some facilities the cost of disposal of hazardous waste has increased by an average of 20% per year since 1991.[36] This has contributed to a great deal of research and development of technologies that lower the production and maintenance costs of aircraft and their associated components. It is clear that less polluting materials and processes are by definition more efficient and therefore make our aerospace manufacturing and maintenance facilities more competitive in the long term. On the horizon lies a new emphasis on the human health risks of extremely small airborne particulate matter and quantities of inorganic toxics that near limits of detection devices. Because of these minute quantities proposed, the aerospace RDT&E community must address both immediate and long term technologies that modify or eliminate the source of these hazards.

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Mr. Henry Birdsong, Naval Aviation Systems Team, Lead Maintenance Technology Center for the Environment, NADEP Jacksonville FL, USA

The following is a list of Federal Laws with environmental impacts for facilities and contractors. It is by no means an exhaustive listing and is targeted towards aviation.

Clean Air Act (CAA), 42 U.S.C. §§ 7401 *et seq.*
EPA CAA Regulations, 40 C.F.R. Parts 50-80
Federal Water Pollution Control Act [a/k/a Clean Water Act (CWA)], as amended, 33 U.S.C. §§ 1251 *et seq.*
EPA CWA Regulations, 40 CFR Parts 100-140, 400-700
Federal Facilities' Compliance under CWA, 33 U.S.C. § 1362
Rivers and Harbors Act (RHA), 33 U.S.C. §§ 403, 406
Coastal Zone Management Act (CZMA), 16 U.S.C. § 1456
Safe Drinking Water Act (SDWA), 42 U.S.C. §§ 300f *et seq*
Resource Conservation and Recovery Act (RCRA), 42 U.S.C. §§ 6901 *et seq.*
Hazardous and Solid Waste Amendments of 1984 (HSWA), Pub. L. No. 96-482 (Nov. 8, 1984)
Federal Facility Compliance Act (FFCA), Pub. L. No. 102-386 (Oct. 6, 1992)
Emergency Planning and Community Right-to-Know Act of 1986 (EPCRA), 42 U.S.C. §§ 11001 *et seq.*
Pollution Prevention Act of 1990, 42 U.S.C. §§ 13101 *et seq.*
Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA), 42 U.S.C. §§ 9601 *et seq.*
Executive Order 12580, Superfund IMplementation (23 Jan. 1987), *reprinted in* 42 U.S.C.A. § 9615 at 179 (West Supp. 1990)
Toxic Substance Control Act (TSCA), 15 U.S.C. §§ 2601 *et seq.*
Occupational Safety and Health Act (OSHA), 29 U.S.C. *et seq.*
National Environmental Policy Act (NEPA) of 1969, 42 U.S.C. §§ 4321 *et seq.*
Executive Order 12114, Environmental Effects Abroad of Major Federal Actions, *reprinted at* 42 U.S.C. 4321 note, 44 Fed. Reg. 1957(Jan. 4, 1979)
Endangered Species Act (ESA), 16 U.S.C. §§ 1531 *et seq.*
Noise Control Act (NCA), 42 U.S.C. §§ 4901 *et seq.*
Base Closure and Realignments, 10 U.S.C. § 2687
Defense Authorization Amendments and Base Closure and Realignment Act, Pub. L. No. 100-526 (Oct 24, 1988), as amended, 10 U.S.C. § 2687 note
Defense Base Closure and Realignment Act of 1990, Pub. L. No. 101-510 (Nov 5, 1990), as amended, 10 U.S.C. § 2687 note
Executive Order No. 12088, Federal Compliance with Pollution Control Standards (Oct. 13, 1978)
The Federal Acquisition Regulations (FAR), 48 C.F.R. Ch.1
DoD Federal Acquisition Regulation Supplement (DFARS), 48 C.F.R. Ch.2
Navy Acquisition Procedures Supplement (NAPS), 48 C.F.R. Ch. 52

Annex A

TABLE 1. Process Releated Summary of US National Emissions Standards for Aerospace Manufacturing and Rework Facilities

Cleaning Operations	Standards	Housekeeping measures for all cleaning operations at a facility subject to this subpart. Measures address placing solvent laden cloth or paper in closed containers, storing fresh and used cleaning solvent in closed containers, and minimizing spills during handling and transfer. (63.744(a))
	Test Methods and Procedures	See individual affected sources.
Hand-Wipe Cleaning Operations	Standards	1. Except for spray gun and flush cleaning, all HAP or VOC hand-wipe cleaning solvents must meet a composition requirement, have a vapor pressure less than 45 mm Hg at 20°C, or meet the requirements specified in an alternative compliance plan administered by the permitting authority and approved under Section 112(l) of the Clean Air Act. (63.744(b)) 2. List of cleaning operations exempt from composition and vapor pressure requirements. (63.744(e))
Hand-Wipe Cleaning Operations (cont.)	Test Methods and Procedures	1. Composition determination through manufacturer's data. (63.750(a)) 2. Vapor pressure determination through readily available sources if single component; ASTM E 260-85 and composite vapor pressure determination procedure for multiple component solvents. (63.750(b))
Spray Gun Cleaning	Standards	1. Use one of four specified techniques or an equivalent. (63.744(c)) 2. For enclosed spray gun cleaners, repair as soon as practicable, but within 15 days. (63.744(c)(1)(ii))
	Test Methods and Procedures	None.
Flush Cleaning	Standards	Operating procedures specify emptying into enclosed container, collection system, or equivalent. (63.744(d))
Flush Cleaning (cont.)	Test Methods and Procedures	None. Statement certifying everything is in compliance. (63.753(b)(2))
Primer and Topcoat Application Operations	Standards	Minimize spills during handling and transfer. (63.745(b)) <u>Uncontrolled Primers</u> 1. Organic HAP content limit: 350 g/l (2.9 lb/gal) (less water) as applied. (63.745(c)(1)) 2. VOC content limit: 350 g/l (2.9 lb/gal) (less water and exempt solvents) as applied. (63.745(c)(2)) 3. Achieve compliance through: (1) use coatings below content limits, or (2) use monthly volume-weighted averaging to meet content limits. (63.745(e))

TABLE 1. Process Releated Summary of US National Emissions Standards for Aerospace Manufacturing and Rework Facilities

		Uncontrolled Topcoats 4. Organic HAP content limit: 420 g/l (3.5 lb/gal)(less water) as applied. (63.745(c)(3))
Primer and Topcoat Application Operations (cont.)	Standards (cont.)	5. VOC content limit: 420 g/l (3.5 lb/gal) (less water and exempt solvents). (63.745(c)(4))6. 6. Achieve compliance as in 3. above. (63.745(e)) Controlled Primers and Topcoats 7. If control system is used, must be designed to capture and control all emissions from the application operation and must achieve an overall control efficiency of at least 81%. (63.745(d)) All Primers and Topcoats 8. Specific application techniques must be used. If alternative is sought, can only be used if emissions are less than or equal to HVLP or electrostatic spray application techniques. (63.745(f)(1)) 9. All application equipment must be operated according to manufacturer's specifications, company procedures, or locally specified operating procedures. (63.745(f)(2))
Primer and Topcoat Application Operations (cont.)	Standards (cont.)	10. Exemptions from No. 8 above provided for in certain situations. (63.745(f)(3)) 11. Operating requirements for the application of primers or topcoats that contain inorganic HAP, including control with either particulate filters or waterwash, and shutdown if operated outside manufacturer's specified limits. (63.745(g)(1) through (3)) 12. Exemptions from No. 11 provided for certain application operations. (63.745(g)(4))
	Performance Test Periods and Tests	1. For "compliant" coatings: each 30-day period. For "averaged" coatings: each 30-day period. For "controlled" coatings, non-carbon adsorber: three 1-hour runs. For "controlled" coatings, carbon adsorber: each rolling period. (63.749(e)(1)) 2. Initial performance test for all control devices to demonstrate compliance with overall control efficiency requirement. (63.749(e)(2))

TABLE 1. Process Releated Summary of US National Emissions Standards for Aerospace Manufacturing and Rework Facilities

	Test Methods and Procedures	1. Organic HAP level determination procedures. (63.750(c) and (d))
Primer and Topcoat Application Operations (cont.)	Test Methods and Procedures (cont.)	2. VOC level determination procedures. (63.750(e) and (f)) 3. Overall control efficiency of carbon adsorber system determined using provided prodedures; for other control devices, determine capture efficiency and destruction efficiency. For capture efficiency, use Procedure T in Appendix B to 40 CFR 52.741 for total enclosures and 40 CFR 52.741(a)(4)(iii) procedures for all other enclosures. (63.750(g) and (h)) 4. For alternative application methods, first determine emission levels for initial 30-day period or five aircraft using only HVLP or electrostatic, or a time period specified by the permitting agency. Then use alternative application method for period of time necessary to coat equivalent amount of parts with same coatings. Alternative application method may be used when emissions generated during the test period are less than or equal to the emissions generated during the initial 30-day period or five aircraft. Dried film thickness must be within specification for initial 30-day period or five aircraft as demonstrated under actual production conditions. (63.750(i))
Depainting Operations	Applicability	Applies to the outer surface of aerospace vehicles. Does not apply to parts or units normally removed. Fuselage, wings, and stabilizers always covered. Radomes, parts normally removed are exempt. (63.746(a))
	Standards	1. Unless exempted, no organic HAP are to be emitted from chemical strippers or softeners. (63.746(b)(1)) 2. Minimize inorganic HAP emissions during periods of non-chemical based equipment malfunction. (63.746(b)(2)) 3. Use of organic HAP-containing strippers for spot stripping and decal removal limited to 26 gallons per aircraft per year for commercial aircraft and 50 gallons per aircraft per year for military aircraft. (63.746(b)(3))
Depainting Operations (cont.)	Standards (cont.)	4. Operating requirements for depainting operations generating airborne inorganic HAP, including control with particulate filters or waterwash systems. Mechanical and hand sanding are exempt. (63.746(b)(4) and (b)(5)) 5. Non-exempt organic HAP emissions controlled at 81% efficiency for systems installed before effective date. For newer systems, control at 95%. (63.746(c))
	Performance Test Periods and Tests	1. For demonstrating no organic HAP emissions: each 24-hour period. (63.749(g)(1)) 2. For spot stripping and decal removal usage limits: each calendar year. (63.749(g)(1)) 3. Initial performance test for all control devices to demonstrate compliance with overall control efficiency requirement. (63.749(g)(1), (g)(2), and (g)(3))

TABLE 1. Process Releated Summary of US National Emissions Standards for Aerospace Manufacturing and Rework Facilities

	Test Methods and Procedures	1. Procedures provided for determining gallons of HAP-containing stripper used for aircraft. (63.750(j))
Depainting Operations (cont.)	Test Methods and Procedures (cont.)	2. Overall control efficiency of carbon adsorber system determined using specified procedures; for other control devices, determine capture efficiency and destruction efficiency. For capture efficiency, use Procedure T in Appendix B to 40 CFR 52.741 for total enclosures and 40 CFR 52.741(a)(4)(iii) procedures for all other enclosures. (63.750(g) and (h))
Chemical Milling Maskant Applica-tion Operations	Applicability	Applies only to chemical milling maskants used in Type II chemical etchants. (63.747(a))
	Standards	Minimize spills during handling and transfer. (63.747(b))
Chemical Milling Maskant Applica-tion Operations (cont.)	Standards (cont.)	Uncontrolled Maskants 1. Organic HAP emissions: £ 160 g/l (1.3 lb/gal) (less water) as applied. (63.747(c)(1)) 2. VOC emissions: £ 160 g/l (1.3 lb/gal) (less water and exempt solvents) as applied. (63.747(c)(2)) 3. Achieve compliance through: (1) use maskants below content limits, or (2) use monthly volume-weighted averaging to meet content limits. (63.747(e)) Controlled Maskants 4. If control device is used, system must be designed to capture and control all emissions from maskant operation and must achieve an overall control efficiency of at least 81% for systems installed before effective date. For newer systems, control at 95%. (63.747(d))
	Performance Test Periods and Tests	1. For compliant maskants: each 30-day period. For averaged maskants: each 30-day period. For controlled coatings, carbon adsorber: each rolling period. For controlled coatings, non-carbon adsorber: three 1-hour runs. (63.749(i)(1))
Chemical Milling Maskant Applica-tion Operations (cont.)	Performance Test Periods and Tests (cont.)	2. Initial performance test required for all control devices to demonstrate compliance with overall control efficiency requirement. (63.749(i)(2) and (i)(3))
	Test Methods and Procedures	Procedures provided essentially identical to those for primers and topcoats for organic HAP and VOC content levels. (63.750(g), (h), and (l)-(o))

Research into Chromate-free Treatments for the Protection of Aluminium Alloys

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SUMMARY

Chromate based pretreatments and chromate pigmented primers are extensively used in the corrosion protection of aerospace aluminium alloys. Current design requirements for UK military aircraft specify the use of either a chromate conversion coating or a chromic acid anodising treatment on components manufactured from aluminium alloys. This is followed with the application of an epoxy primer containing a strontium chromate inhibitive pigment. Because of concern about the carcinogenic nature of chromates, a research programme to develop non-chromate pretreatments and protective finishes has been undertaken. The results of research into novel inhibitors for aluminium alloys and their application to pretreatments and aircraft primers are presented. Several promising inhibitors including cerium salts, sulphur containing compounds and oxoanions have been identified. Whilst none of the systems so far investigated give the same level of protection as chromate based treatments, progress towards a chromate-free protection scheme is being made.

1 INTRODUCTION

Aluminium alloys continue to be extensively used in the construction of both military and civil aircraft. Depending on the composition, temper and product form, aluminium alloys may develop various types of corrosion attack in service. Examples of pitting corrosion, intergranular attack, exfoliation corrosion and stress corrosion cracking occurring on aerospace components have been given at previous AGARD meetings[1,2] and are described in detail in the AGARD handbook on aircraft corrosion[3]. To reduce the risk of corrosion, protective treatments and coatings are applied to all aircraft parts. Considerable care is taken during the assembly of the airframe structure to avoid potential corrosion problems such as crevices and dissimilar metal contacts through the use of sealants and jointing compounds. Further protection is given to the assembled structure before the final paint finish is applied.

The protection scheme currently employed on aluminium alloy components consists of a surface pretreatment to which is applied a chromate pigmented epoxy primer. The preferred pretreatment is chromic acid anodising but for some applications a chromate conversion coating is used. The anodising process thickens the air formed film present on the surface of aluminium to produce an oxide film consisting of a thin dense barrier layer at the metal surface and an outer thicker porous layer. The usual UK practice is to apply an epoxy based primer directly to the unsealed anodic film. The primers are normally two pack epoxy materials pigmented with a corrosion inhibitor. UK standards[4] require that the dry paint film should contain at least 15% by weight strontium chromate. The porous structure of the anodic film provides a degree of mechanical keying for the paint primer enhancing the adhesion of the paint to the substrate. A different approach is adopted in North America. After anodising, the anodic film is sealed either by immersion in boiling water or by placing the part in a dichromate bath. Sealed anodic films are more effective barrier coatings giving a greater degree of corrosion protection but do not generally provide the same level of mechanical keying for paint adhesion.

The corrosion protection of aerospace aluminium alloy components depends partly on isolating the metal substrate from the environment and partly on modifying the local environment to make it less aggressive. The surface pretreatments and primers which are used provide some measure of barrier protection. However all paint schemes contain defects and none are totally impervious to moisture. The important feature of the primer is the release of strontium chromate when in contact with moisture. The chromate ions in solution prevent corrosion from initiating on the aluminium alloy substrate at areas where the paint film has become damaged or cracked or where there is poor paint adhesion. Previous work has shown that the level of chromate released from a primer is very low but is sufficient to inhibit corrosion on 2000 series aluminium - copper alloys even when immersed in aqueous solutions containing 600 mmol l^{-1} sodium chloride[5].

There is concern on environmental grounds about the continued use of chromates because of their carcinogenic nature. A number of countries within the European Union are considering introducing restrictions on the use of chromates which will have a major impact on the surface protection of aircraft. The aim of the present research programme is to develop and evaluate alternative protective treatments. The work described in this paper is concerned with the identification of novel inhibitor systems for aluminium alloys and their application to anodising processes and aircraft paints.

Paper presented at the 83rd Meeting of the AGARD SMP on "Environmentally Compliant Surface Treatments of Materials for Aerospace Applications", held in Florence, Italy, 4-5 September 1996, and published in R-816.

2 CORROSION INHIBITORS

2.1 Introduction

Research has been concerned with identifying novel inhibitor systems for aluminium alloys. Much of the early work was based on a simple immersion test carried out in a 1mmol/litre sodium chloride solution to which was added 2mmol/litre of inhibitor[6]. Small coupons of sheet 2014-T6 aluminium alloy were suspended in the test solution for three weeks and the weight loss due to corrosion was determined. Under these conditions coupons tested in chromate containing solutions showed no signs of corrosion attack. Of the many chemicals which were evaluated the most promising group of materials appeared to be salts of some mercaptocarboxylic acids. Zinc salts appeared to give a higher level of corrosion inhibition than either the corresponding barium, strontium or calcium salts[7]. Of all the compounds examined using the immersion test, zinc thioglycollate appeared to be the most promising inhibitor.

In subsequent work attempts were made to incorporate a zinc thioglycollate pigment into a standard epoxy primer formulation[8]. Problems were experienced with the curing of the primer and this was believed to be associated with the presence of the sulphur containing group in the pigment. Corrosion tests were therefore carried out on 2014-T6 sheet panels painted with a polyurethane based primer containing zinc thioglycollate. Results obtained were disappointing and the overall performance of the primer fell well short of a standard epoxy primer containing strontium chromate. In an attempt to analyse the results of the paint tests, experiments were conducted to measure the concentration of inhibitor leached from the paint on exposure to moisture. Results obtained showed that after 40 days exposure to distilled water the total concentration of zinc thioglycollate inhibitor leached into solution was approximately 0.005 mmol/l. In the case of a primer containing strontium chromate the concentration was 0.013 mmol/l. As a result of these tests it was concluded that for paint applications inhibitors which were effective at levels at least two orders of magnitude less than 2mmol/l would be required.

Further research has indentified three groups of inhibitors, cerium (3+) compounds[9], metavanadates[10] and thiotungstates[11] which show high levels of corrosion inhibition when present in low concentrations. Work is described in this part of the paper to determine the minimum concentrations of three inhibitors, cerium(3+) formate, nickel metavanadate and tetra-ethyl ammonium thiotungstate necessary to prevent corrosion.

2.2 Experimental

Details of the inhibitors evaluated are given in table 1. The cerium formate and strontium chromate inhibitors were laboratory grade chemicals whilst the nickel metavanadate and tetra-ethyl ammonium thiotungstate compounds were prepared using standard methods.

Cathodic polarisation sweeps were carried out to enable the effect of inhibitor concentration on corrosion current to be determined. Test electrodes 15mm x 15mm were prepared from small coupons cut from 1mm thick 2014-T6 aluminium - copper alloy sheet. The electrodes were immersed in 600mmol/l of sodium chloride solution to which had been added a known concentration of inhibitor.

Table 1 Corrosion inhibitors evaluated

Compound	Formula
Strontium chromate	$SrCrO_4$
Cerium formate	$Ce(COOH)_3$
Nickel metavanadate	$Ni(VO_3)_2$
Tetra-ethyl ammonium thiotungstate	$(N(C_2H_5)_4)_2WS_4$

The test solutions were aerated and after 30 minutes stabilization the electrode was cathodically polarised at a rate of 2.5mV/20s until the overpotential exceeded 300mV. The corrosion current was estimated from the cathodic polarisation sweep by extrapolating the linear part of the curve to the open circuit potential.

2.3 Results and discussion

Plots showing the effect of inhibitor concentration on corrosion current are given in fig. 1. In the case of the strontium chromate inhibitor the corrosion current remained at a value less than 0.01μA/mm^2 provided the concentration of inhibitor was greater than 0.003mmol/l. At concentrations below this, there is a steady rise in corrosion current towards the level of the non-inhibited salt solution. Estimates of the minimum concentrations for cerium(3+) formate, nickel metavanadate and thiotungstate inhibitors can be made from the plots in fig.1 and are listed in table 2.

Table 2 Minimum concentrations for corrosion inhibition in 600mM/litre sodium chloride solution

Inhibitor	Concentration mmol / litre
Strontium chromate	0.0032
Cerium formate	0.06
Nickel metavanadate	0.018
Tetra-ethyl ammonium thiotungstate	0.016

The data presented indicate that strontium chromate is a more effective inhibitor than the three systems considered but the performances of the thiotungstate and metavanadates in particular are encouraging.

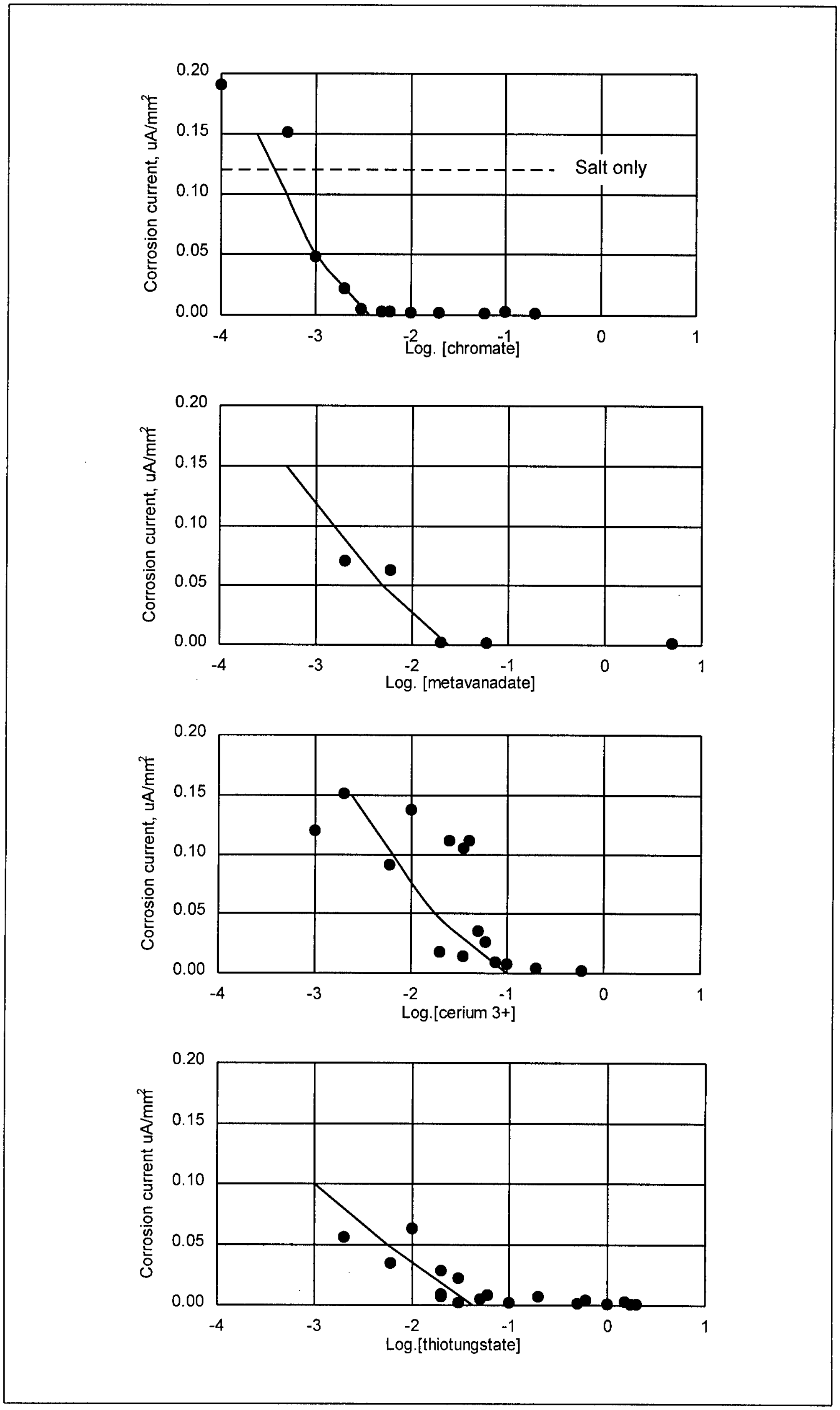

Fig. 1 Effect of inhibitor concentration (mmol / l) on the corrosion current of 2014-T6 aluminium alloy tested in 600 m mol / litre sodium chloride solution. (Currents estimated from polarisation sweeps)

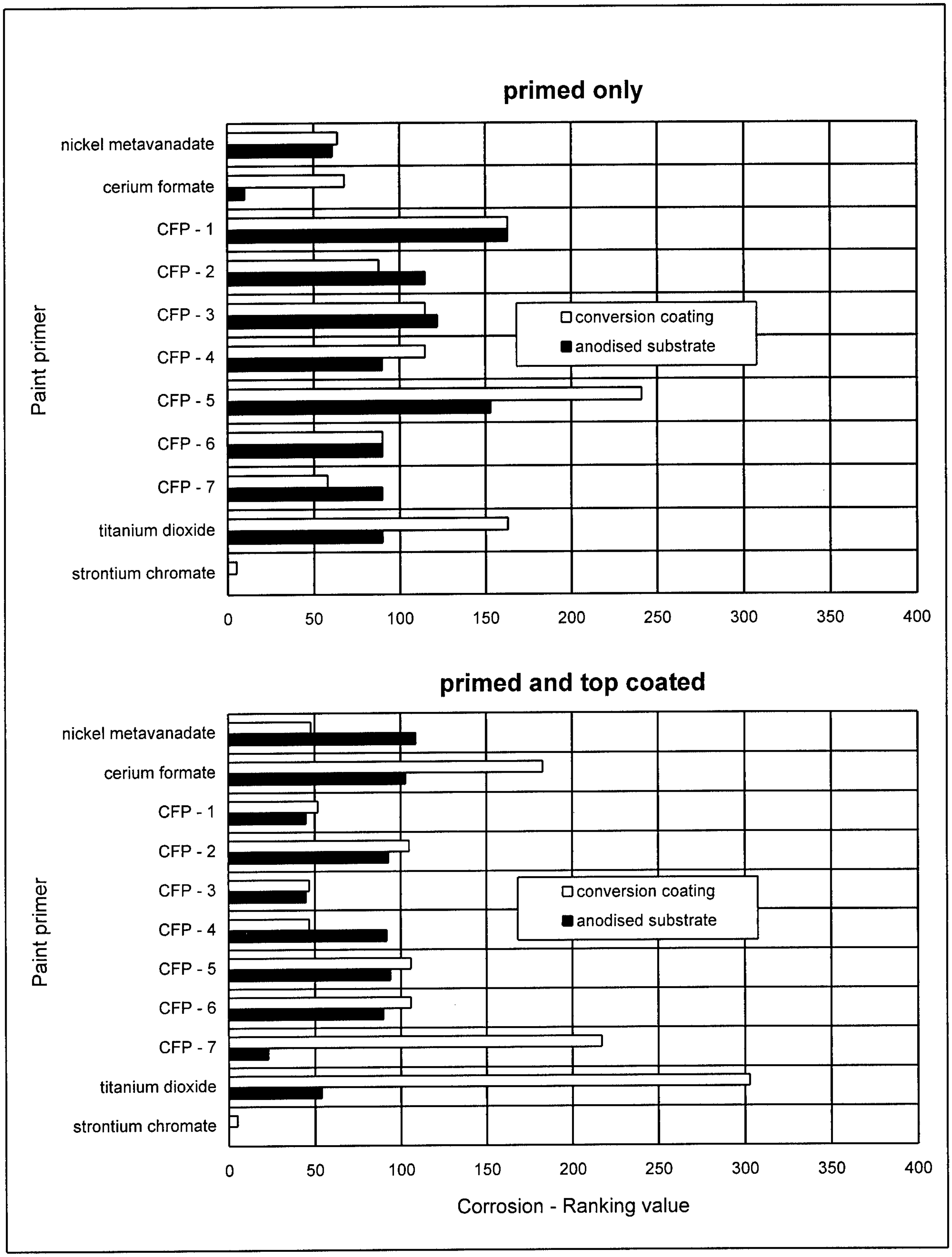

Fig. 2 Corrosion ranking value of painted panels following 2000 hours exposure to neutral salt fog.

3 NOVEL ANODIZING PROCESSES

3.1 Introduction

Research on anodising has concentrated on the development of anodic films with improved corrosion resistance by the incorporation of corrosion inhibitors into the oxide film. The results obtained from preliminary anodising experiments made using a standard sulphuric acid bath containing various inhibitors are presented below.

3.2 Experimental

A series of trials was undertaken in an attempt to incorporate inhibitors into anodic films through through the direct addition of inhibitors to the anodizing bath. The inhibitors examined evaluated are given in table 3.

Table 3 Inhibitors examined in anodising experiments

Inhibitor	Chemical formula
Cerium (III) sulphate	$Ce_2(SO_4)_3$
Sodium metavanadate	$NaVO_3$
Cerium (IV) sulphate	$Ce(SO_4)_2$
Sodium metavanadate+ zinc sulphate	$NaVO_3 + ZnSO_4$
Sodium molybdate	Na_2MoO_4
Molybdic acid	H_2MoO_4
Potassium permanganate	$KMnO_4$
Ammonium thiotungstate	$(NH_4)_2MoS_4$
Zinc thioglycollate	unknown

All were added to a standard sulphuric acid anodizing bath (150g/l H_2SO_4) at a concentration of 7.5g/l. Ammonium thiotungstate proved to be insoluble in sulphuric acid. After anodising the thickness of the film formed was determined using an eddy current technique. Films were analysed using XRF methods to detect elements incorporated into the film. Panels were exposed to continuous neutral salt fog[12].

3.3 Results and discussion

3.3.1 Cerium(III) and cerium(IV) sulphate

Table 4 summarises the results of neutral salt spray tests conducted on aluminium alloy panels anodised in various inhibited sulphuric acid baths. Preliminary experiments carried out in both Ce^{3+} and Ce^{4+} containing sulphuric acid electrolytes have failed to show evidence of cerium pick up in the anodised layer. However the techniques used were not particularly sensitive to cerium and further investigations are proceeding. As indicated in table 4 neutral salt fog tests conducted on anodised films produced in cerium inhibited electrolytes have unusually high levels of protection for unsealed films. The films produced using Ce^{4+} electrolytes are consistently thinner (3-5µm) and appear to afford better protection than those formed in Ce^{3+} even though the films are actually thicker (7-12µm).

3.3.2 Sodium metavanadate and sodium metavanadate + zinc sulphate

The chemistry of the vanadates is complicated and the form of the species that exists in solution is highly dependant on pH. Preliminary experiments carried out in sulphuric acid electrolytes containing vanadates have shown some evidence of vanadium uptake, although the data are inconclusive. In strongly acid solutions, vanadates exist as the VO_2^+ ion rather than the better known VO_3^- species which is an effective inhibitor for aluminium alloys. As indicated in table 4, on exposure to neutral salt spray the anodic films showed poor resistance to pitting.

3.3.3 Sodium molybdate and molybdic acid

Molybdates have been identified as inhibitors for aluminium although they are only effective when present at comparatively high concentrations. Attempts to prepare anodic films in solutions containing either sodium molybdate or molybdic acid yielded very thin films (< 1µm) which gave a poor corrosion resistance. XRF analysis failed to detect the presence of molybdenum in the anodic films.

3.3.4 Potassium permanganate

Data presented in table 4 show that the anodic films produced exhibit a high level of corrosion resistance. The film thicknesses were in the range 2 - 3µm and both potassium and manganese were detected.

3.3.5 Zinc thioglycollate

As discussed in section 2 previous research has identified the zinc salts of several mercapto-carboxyllic acids as effective inhibitors for the 2000 series aluminium alloys. Although the films produced by anodising were comparable in thickness to those prepared in sulphuric acid baths containing potassium permanganate, they showed poor resistance to neutral salt spray (table 4). Niether zinc nor sulphur were detected in the films suggesting that the zinc thioglycollate inhibitor had not been incorporated into the film.

4 CHROMATE-FREE PRIMERS

4.1 Introduction

The development of chromate-free primers remains a prime requirement for both the aircraft constructor and operator. Early trials conducted on primers formulated by specialised aircraft paint makers demonstrated that these materials did not provide a level of corrosion of protection comparable with the chromate pigmented primers used universally by the aerospace industry. The main laboratory accelerated method to assess the performance of a primer is the BS3900 Part F12 (ISO7253) neutral salt fog test. This method has been shown to give a very good correlation with natural weathering for chromate containing primers. The problem is that when non-chromated anticorrosive primers are subjected to this test method, they fail the test drastically. In practice, when these materials exposed to the atmosphere naturally, some of them do perform adequately.

In the current programme an alternate - emersion test has been employed in addition to the neutral salt spray test. These tests have been used to assess the corrosion performance of several commercially prepared chromate - free primers (CFP) and two

Table 4 Neutral salt fog exposure of panels anodised in inhibited sulphuric acid baths

Inhibitor	Film thickness µm	Time to pitting hours	Assessment of attack at various times (hours)			
			24	168	336	504
None	8.2	24	P1	P2,S2	P2,S3	P2,S3
Cerium(III) sulphate	10.6	72	N	P1,S1	P1,S1	P1,S2
Sodium metavanadate	0.6	12	P2	P2,S3	P2,S3	P2,S3
Cerium (IV) sulphate	4.2	>116	N	N	N	P2,S2
Zinc ions + metavanadate	2.5	24	P1	P2,S3	P2,S3	P2,S3
Sodium molybdate	0.8	8	P2,S3			
Molybdic acid	0.6	6	P2,S3			
Potassium permanganate	2.5	72	N	N	P1	P1,S2
Zinc thioglycollate	2.6	3	P2,S3			
Chromic acid anodising	1.2	48	N,E1	P2,S3	P2,S3	P2,S3

N	No attack	P1	Small pits (limited)
		P2	Small pits (extensive)
E1	Slight attack at edges		
S1	Some staining (<20% of surface)		
S2	Staining 20 - 80% of surface		
S3	Staining 81 -100% of surface		

experimental primers, one containing nickel metavanadate and one containing cerium formate. The alternate-emersion test is cyclic in nature involving the repeated wetting and drying of the painted test panels[13]. This is believed to reflect more closely the situation which occurs on aircraft in service.

The corrosion protection provided by a chromate pigmented primer depends mainly on the release of chromate ions into solution. In the case of primers containing strontium chromate there is a high initial leach rate ensuring that their is sufficient chromate available to inhibit corrosion at areas where the paint film has become damaged or cracked exposing the aluminium substrate. In order to gain a better understanding of the performance of the chromate-free primers measurements were made to determine the leaching behaviour of inhibitors from the experimental paints.

4.2 Accelerated paint tests

4.2.1 Materials

Samples of the latest products available at the time were received from four commercial aircraft paint manufacturers. Included in the programme was a standard BS X33A chromate pigmented epoxy primer and a primer containing a non-inhibitive pigment, titanium dioxide, to act as control primers. Two experimental primers formulated by the Paints Reseach Association based on the cerium(III) formate and nickel metavanadate inhibitors studied in section 2 were also evaluated.

4.2.2 Experimental

a) Accelerated paint tests

The primers were applied to test panels cut from 2014-T6 aluminium alloy sheet to BS L157. Prior to painting the panels were either chromic acid anodised or given a chromate filming treatment in accordance with prEN 2437[14]. Half of these panels were then coated with polyurethane finish to BS X 34

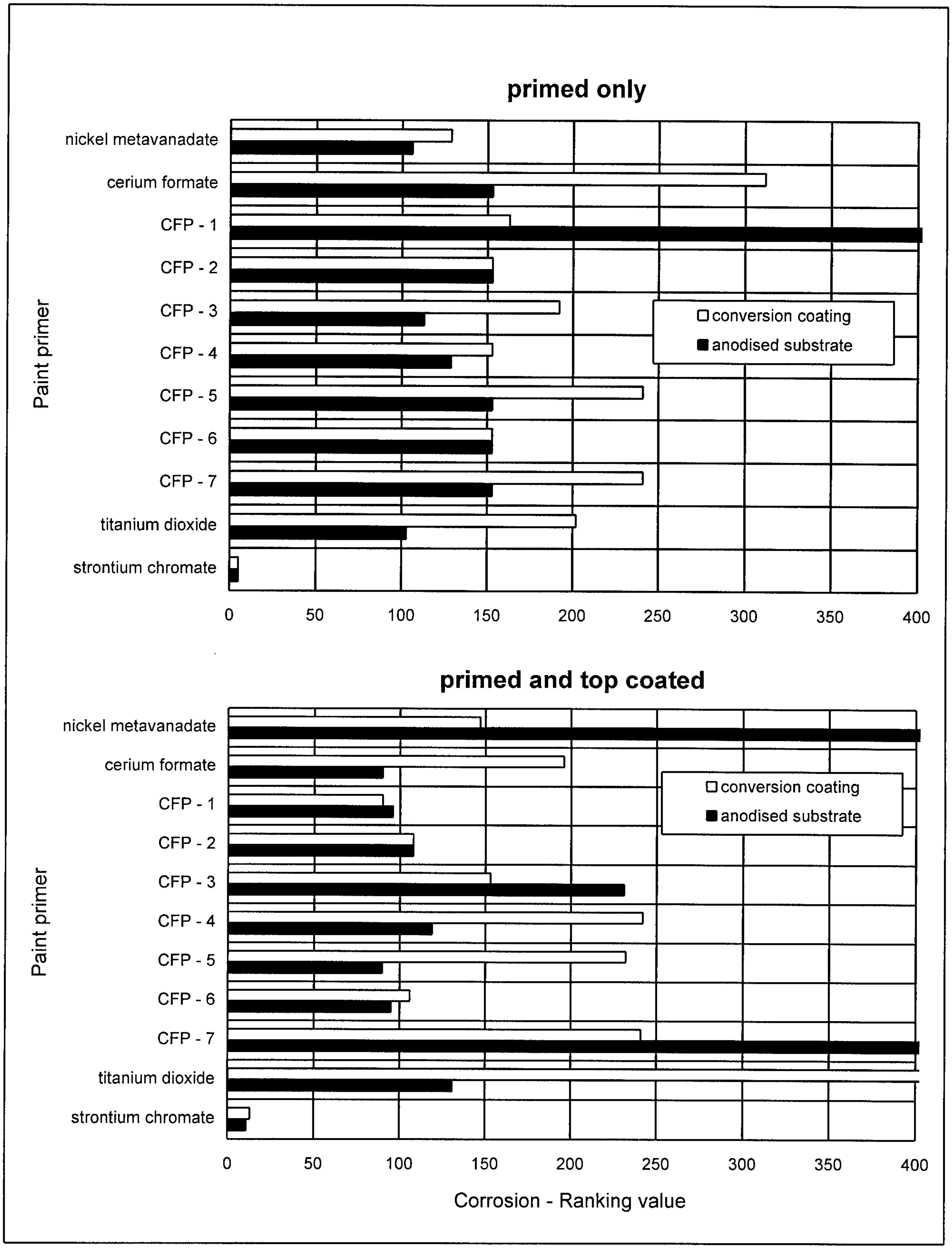

Fig. 3 Corrosion ranking value of painted panels following 2000 hours immersion/emersion testing.

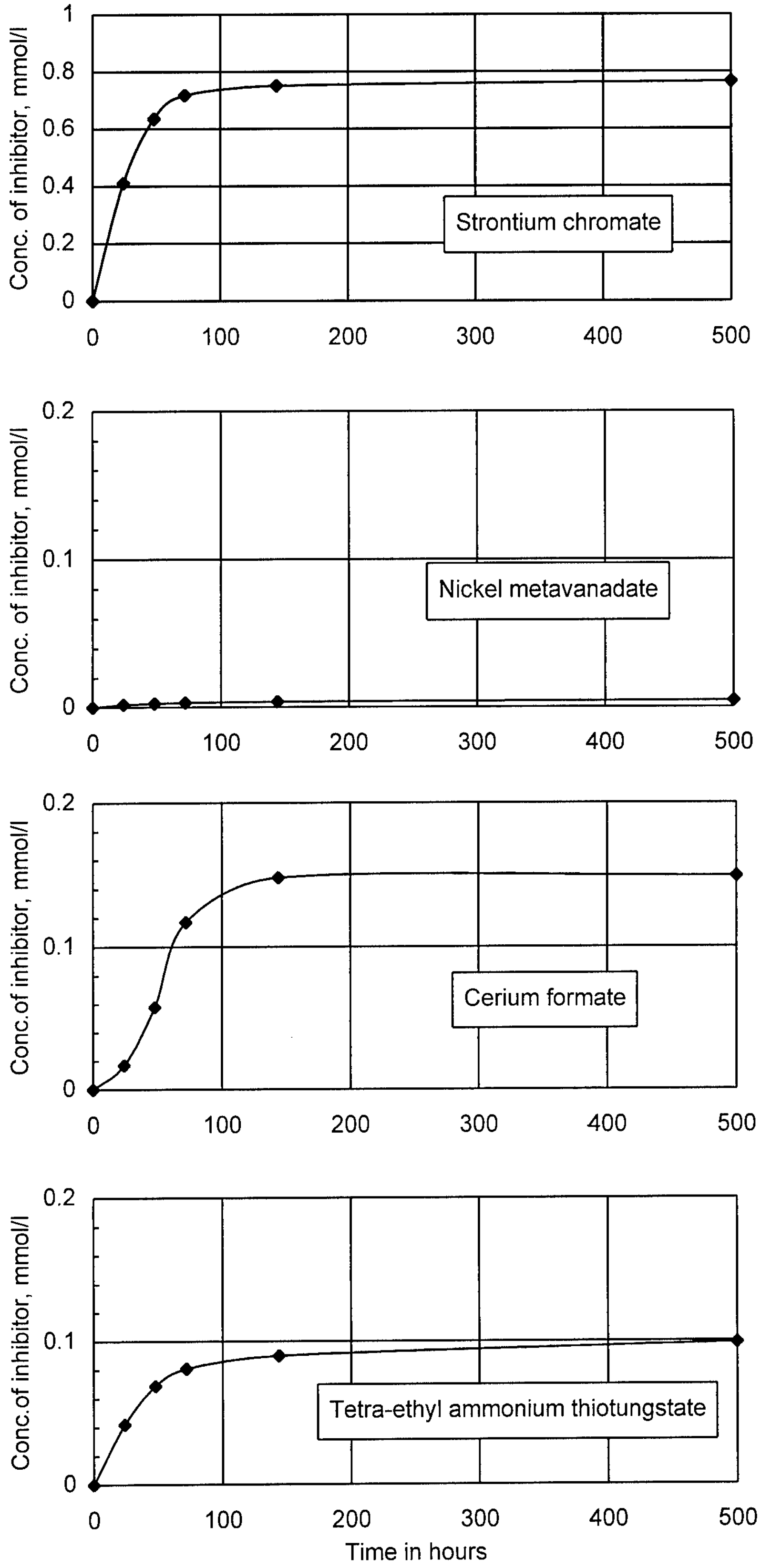

Fig. 4 Leaching behaviour of epoxy based primers containing strontium chromate, nickel metavanadate, cerium formate and tetra-ethyl ammonium thiotungstate. Total concentration of inhibitor as a function of time.

type A[15]. All panels were then prepared before exposure by cutting a 'cross' scratch approximately 1mm wide to within 5 to 10mm of the edges of the panels to a depth sufficient to expose the substrate.

The painted panels were then tested for 2000 hours by exposure to neutral salt spray or alternate immersion / emersion in salt solution buffered to pH 8[13]. At the end of the test period each panel was carefully examined for signs of corrosion in the scratch, for evidence of paint film blistering adjacent to the scratch and for signs of corrosion away from the scratch.

b) Leaching experiments

Leach rate experiments were conducted on panels primed with the standard chromate primer, the two experimental primers containing cerium (III) formate and nickel metavanadate and an additional primer pigmented with tetra-ethyl ammonium thiotungstate. The panels were suspended in glass beakers containing 100ml of 600mmol/l sodium chloride solution. The solution was agitated using a magnetic stirrer. After 24 hours the solution was transferred from the beaker to a storage bottle and replaced with fresh 600mmol/l sodium chloride. This procedure was repeated four more times to give a total of five solutions for each of the primers. The time of agitation varied however being 24 hours for the second solution, 24 hours for the third, 72 hours for the fourth and 360 hours for the fifth. Each solution was then analysed using inductively coupled plasma atomic emission spectrometry to determine the concentration of inhibitor present.

4.3 Results and discussion

Figures 2 and 3 summarise the data obtained from the accelerated corrosion tests. In each case the standard chromate pigmented primer easily gave the highest level of corrosion protection. None of the commercial schemes tested matched the performance of the chromate control. In the primed only condition the performances of the two experimental schemes were generally comparable with the best of the commercial schemes. However when top coated the level of protection deteriorated significantly.

The accelerated corrosion results obtained for the two experimental primers can be broadly interpretted in terms of the minimum inhibitor concentrations necessary to prevent corrosion (table 3) and the leaching characteristics of the paints.

The results of the leaching experiments are summarised in fig.4. The data indicate that total concentration of strontium chromate released, ~0.75mmol/l is much higher than that recorded for the three experimental primers. In addition from table 3 the minimum concentration of chromate required to inhibit the corrosion of 2014-T6 aluminium alloy is 0.0032mmol/l. The shape of the leaching curve suggests that this concentration will be quickly achieved. By contrast the minimum concentration levels of the non-chromate inhibitors are higher. In the case of nickel metavanadate a minimum concentration of 0.018mmol/l is needed but the leaching curve in fig.4 indicates that this level will not be achieved. Data for cerium (III) formate suggest that the minimum concentration level (0.06mmol/l) could be reached after 50 hours.

The poor performance of the experimental primers when top coated with a polyurethane paint scheme is a direct consequence of the reduction in surface area from which inhibitor may be leached. In the case of the strontium chromate primer the small area of paint exposed along the scratch edge will still yield sufficient chromate ions to stop corrosion in the scratch. The concentration of metavanadate or cerium ions however will be very small and well below the levels given in table 3.

5 DISCUSSION

Chromates are extensively used in the corrosion protection of aerospace aluminium alloys both in the pretreatment of surfaces and as inhibitive pigments in paint primers. The research described in section 2 of this report has shown that the minimum level of chromate required to prevent corrosion on a 2014-T6 sheet aluminium - copper alloy is ~0.0032mmol/l. This represents only a fraction of the chromate which may be released from a standard chromate primer when exposed to moisture. Although the compounds identified in this report (cerium(III) formate, nickel metavanadate and tetra-ethyl ammonium thiotungstate) represent significant advances in terms of effective inhibitors for aluminium alloys they are still less efficient than chromates.

The problems associated with the development of chromate-free primers have been recognised for some time. One approach being considered is the introduction of a range of paint specifications providing different levels of corrosion protection. AECMA for example are discussing the possibility of five separate standards. The minimum requirements would be for the protection of the exterior surface of an undemanding aircraft. It is likely that some of the commercial paint schemes examined in the present programme could meet these requirements. At the other extreme would be a chromate-free primer which has high corrosion and fluid resistance with surface tolerance. This might be for use on a military transport aircraft in interior areas where there is possibility of fluid leakage from galleys, toilet areas etc. Clearly the commercial paints evaluated in section 4 would fall well short of fulfilling such a standard.

Another approach might be to make greater use of anodising as a means of providing corrosion protection. The main role of the anodic film is often considered to be simply to promote paint adhesion. Now there is a need to replace chromic acid anodising with an alternative process, the opportunity exists to develop a scheme which provides a greater level of corrosion protection. Work described in section 3 has attempted to incorporate inhibitors directly into the anodic film. Some success has been recorded by making additions of inhibitors to the sulphuric acid anodising bath.

6 CONCLUSIONS

1) Cerium (III) formate, nickel metavanadate and tetra-ethyl ammonium thiotungstate have been shown to be effective inhibitors for a 2014-T6 aluminium alloy immersed in 600mmol/l sodium chloride solution.
2) The minimum inhibitor concentrations required to prevent corrosion are several times higher than for strontium chromate.

3) The addition of cerium(III) and cerium(IV) sulphate to the standard sulphuric acid anodising bath gave a high level of corrosion protection.

4) Anodic films prepared in baths containing potassium permanganate gave much improved corrosion protection. Potassium and manganese were detected in the films.

5) Commercial chromate-free primers and experimental primers containing nickel metavanadate and cerium formate failed to match the overall performance of the standard chromate pigmented primer in accelerated corrosion tests.

7) Measurements made on experimental primers indicate that the levels of inhibitor leached into solution are much lower than from a standard chromate pigmented epoxy primer.

8) Results obtained from accelerated corrosion tests on experimental primers may be interpreted in terms of minimum inhibitor concentrations and leach rates.

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Environmentally Friendly Cleaning Processes for Metal Surfaces

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SUMMARY

Environmental laws, regulations and policies require that traditional cleaners (1,1,1 trichloroethane, Methyl Ethyl Ketone and CFC113) be eliminated from current and future cleaning operations. In order to achieve this goal the Air Force has determined that pollution prevention is the preferred approach. Aqueous cleaning has been the predominant replacement cleaning technology to reduce or eliminate hazardous cleaning waste. However, This tends to shift the waste stream from air to water. The United States Air Force, Wright Laboratory decided to investigate minimal waste cleaning technologies for pre-bonding and precision cleaning processes. Four technologies are being developed to meet the needs of DOD depots, namely, Supercritical CO_2 Convection Flow cleaning, Low-Temperature Oxygen Plasma cleaning, Laser Cleaning and CO_2 / UV light cleaning. Each of these technologies produces no more waste than the contaminant they are removing. Supercritical CO_2 Convection Flow cleaning is much simpler and more flexible than traditional supercritical CO_2 cleaning processes, avoiding high pressure pumps which tend to increase cost, complexity and cycle-time. Low-temperature oxygen plasma cleaning breaks down hydrocarbon contamination in oxygen tubing resulting in benign cleaning residue which is entrained in the vacuum flow and removed from the tube. Laser cleaning utilizes laser energy to remove tightly bound contaminants and coatings. The CO_2/UV light cleaning system has demonstrated its cleaning effectiveness for a large number of shop soils. Surfaces cleaned with this method exhibit excellent bondability.

1.0 INTRODUCTION

Long-term environmentally acceptable cleaning methods are needed to ensure mission readiness of DOD systems now and in the foreseeable future. No maintenance activity can be performed on a system prior to cleaning. The cleaning of weapon system components is recognized as an essential portion of the overall system maintenance activity. Parts must be cleaned prior to inspection, repair, reassembly and bonding to other components or coatings. Many processes exist which can clean components prior to inspection and repair. However, more complex cleaning methods are required to clean and prepare metallic surfaces prior to bonding and coating application operations. This latter category of cleaning requires a much higher level of cleanliness in order to achieve good adhesion between the substrate and the adhesives or coatings. The long term durability of the coating to the substrate is directly traceable to the preparation of the surface. Inadequate cleaning results in disbonding of structural members, as well as the loss of corrosion or wear inhibitors which could cause increased maintenance or system performance failure. Adequate cleaning utilizing environmentally acceptable methods is required to meet mission readiness requirements and achieve long-term environmental compliance.

Unfortunately the most efficient cleaners are those with the least desirable environmental characteristics, such as 1,1,1 trichloroethane, Methyl Ethyl Ketone and CFC113. Alternative processes traditionally require very complex aqueous systems utilizing extensive amount of water. This is an adequate short-term solution, however, the increased use of aqueous cleaners has increased the quantity of waste waters generated at the depots. Simultaneously the United States Environmental Protection Agency has begun to tighten the restrictions on the levels of contamination which can be released in waste water streams. Therefore, increased waste water treatment operations may be required, increasing costs and possibly even limiting operations. Furthermore, depots which are located in water deprived areas may be hindered in their operations due to water conservation efforts.

There is a hierarchy in approaching cleaning with increasing waste and health problems namely:

- Identify the cleaning operation as non-essential and eliminate it
- Minimize the cleaning waste to the contaminant being removed
- Aqueous cleaning to eliminate solvents
- Solvent cleaning using a closed loop system
- Traditional solvent cleaning

The potential deficiencies of aqueous cleaning have led to the development of technologies on the next level of hierarchy, namely those which minimize the waste to the contaminant being removed (see Figure 1). The Army, Navy and Air Force have identified cleaning

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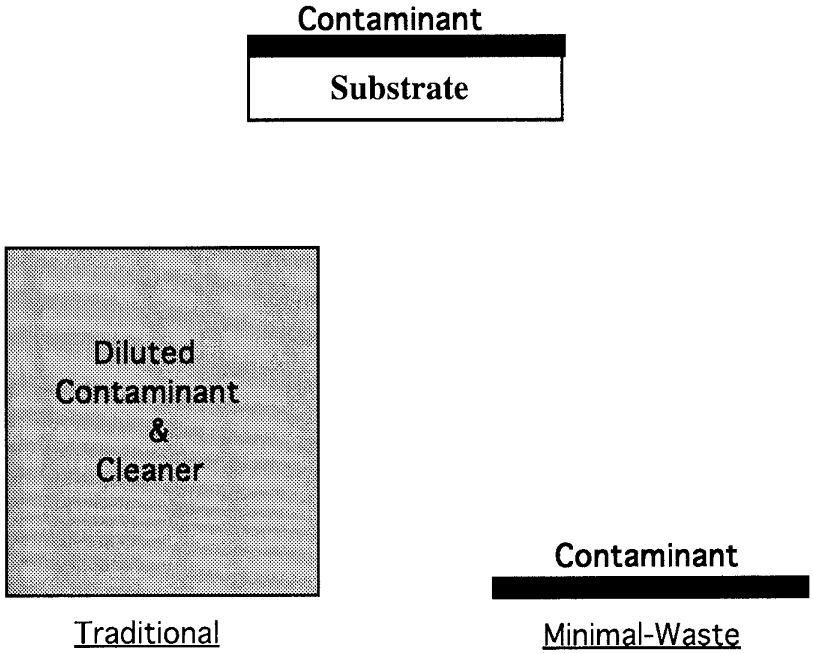

Figure 1 Traditional verses Minimal-Waste Cleaning

alternatives as high priority requirement for pollution prevention. Cleaning methods which meet performance criteria and produce minimal waste are required to provide the depots with a long term environmentally acceptable cleaning solution. Maintenance operations such as adhesive bonding of metal to metal and, metal to composite as well as painting, ion vapor deposition of aluminum (IVD) coating and other related processes require metallic surfaces to be free of contamination. Many of these processes are being redesigned to produce minimal waste (i.e. painting). The implementation of advanced cleaning technologies in conjunction with alternative metal surface treatments and coatings will result in integrated environmentally acceptable metals processes for the depot community.

2.0 CLEANING PROCESSES

2.1 Supercritical Carbon Dioxide Convection Flow Cleaning

2.1.1 Cleaning Theory

Supercritical CO_2 (SCCO2) is carbon dioxide which has been heated above 304.2 Kelvin and at a pressure above 7.39 MPa. Within this temperature/pressure regime the CO_2 has the blended properties of a gas and a liquid. This combination of properties makes it an excellent solvent for many organic contaminants. Some of the benefits of SCCO2 are; 1) no surface tension problems, therefore, it can clean small and hidden orifices, 2) no solvent waste, 3) non-ODS, 4) non-CFC, 5) non-VOC and, 6) non-flammable.

Traditional supercritical CO_2 cleaning technologies exploit the pressure dependent solvating properties of SCCO2. This requires high pressure pumps complicated pressurization cycles and long cycle times. A natural convection flow supercritical fluid cleaning system exploits the temperature dependent solvating properties of SCCO2. Such a cleaning system has been developed which is much simpler and more cost effective than traditional methods. This system utilizes the changes in the solvating properties of CO_2 which changes with temperature as opposed to pressure. (Patent 5,401,322, 20 March 1995)

2.1.2 Cleaning System Operation

The technology has been scaled up from a 5 cm diameter prototype unit to a 30.5 cm diameter pre-production prototype unit (see Figure 2). The pre-production prototype can accommodate items which fit within an envelope of 23 cm diameter, 30 cm long and weigh less than 31.8 kg. The items to be cleaned are placed within the parts basket in the transfer chamber which is pressurized to equal that of the cleaning chamber (9.66 MPa). Once the pressure is equalized, the parts basket is moved into the cleaning chamber.

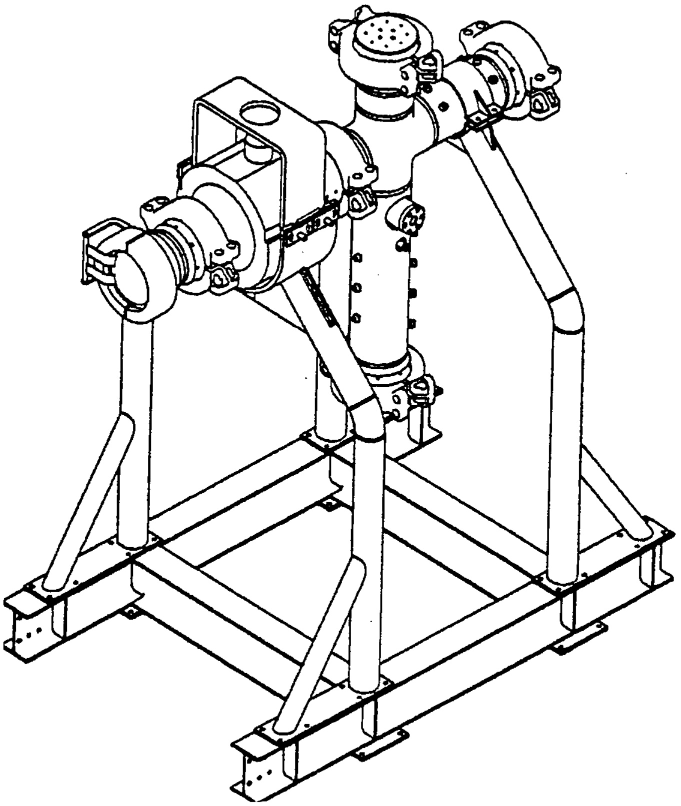

Figure 2 Supercritical CO_2 Convection Flowing System

The cleaning chamber pressure is maintained at 9.66 MPa. The bottom of the cleaning chamber is heated (333^{O}K) and the top is cooler (315^{O}K) creating an 18^{O}K temperature gradient. This temperature gradient creates a convection flow within the chamber. The colder supercritical fluid has greater solvating properties than hot, therefore, the contaminants are removed in the cold zone and circulate down to the hot zone where the contaminants drop out of solution. A flame ionization detector (FID) is used to analyze the supercritical CO_2 to determine the relative concentration of contaminants. At the beginning of the cleaning cycle there is a rise in the baseline level of contamination. As the components are cleaned this level gradually drops and eventually returns to the baseline level. The computer control system alerts the operator that the cleaning cycle has been completed. The parts are brought back into the transfer chamber, the transfer chamber is depressurized and the parts are removed.

Supercritical carbon dioxide is very efficient at removing organic contaminants, but is less efficient at removing inorganics and particulates. Rotating the parts basket creates agitation which aids in particulate removal. The contaminants removed from the supercritical CO_2 can be removed from the bottom of the chamber through a pre-installed valve. This system is greatly simplified, requiring fewer components, less energy with similar cleaning effectiveness when compared to traditional supercritical CO_2 cleaning.

The advanced cleaning system only requires the depressurization of the transfer chamber, while the cleaning chamber remains pressurized. This reduces cycle time and increases the useful life of the unit. Furthermore, the system is highly flexible since it can create higher temperature gradients for more cleaning power, include cosolvents which improve the variety of soils which can be removed and even cleaning with liquid CO_2 is possible in the same unit, when desired.

2.1.3 Technology Developments

Scale-up and validation efforts are currently demonstrating the ability of this system to clean components donated by the depots and industry (Lockheed Martin and Pratt & Whitney). The donated components include contaminated panels, heat pipes, gyroscopes, filters, and precision ball bearings. Through these and other cleaning trials an operational envelope of cleaning effectiveness is being developed. Data are being gathered on the soils, part configurations, and materials which can be cleaned utilizing this technology. Furthermore, data is being collected to document the best operating parameters, as well as system limitations.

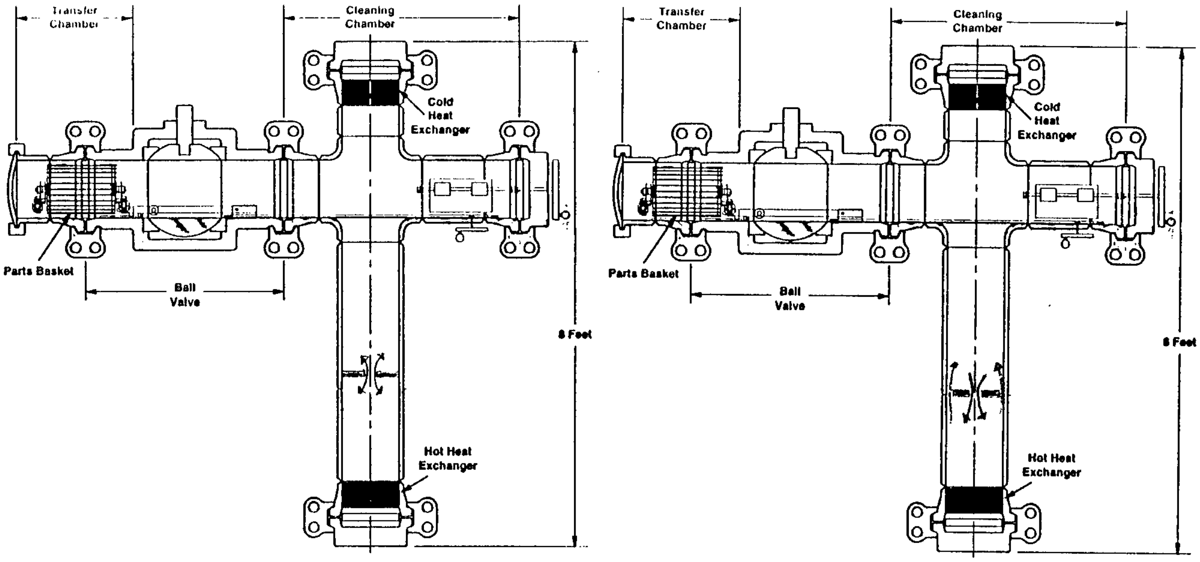

Figure 3A Center Hole

Figure 3B Center Hole & Annular Gap

Figure 3 Baffle Configurations

Preliminary results indicate that the cleaning system removes organic contaminants from the components tested. This cleaning ability has been verified by gravimetric and surface analysis techniques. SCCO2 has some capability to entrain particulates up to 100 microns in diameter. The ability of SCCO2 to entrain particulates of this size has never been demonstrated before. Further investigations are underway.

Extensive convection flow modeling has been able to accurately represent the fluid flow and heat transfer within the chamber facilitating greater understanding on how to improve and tailor the process. Through this effort it was discovered that without some baffle configuration the fluid flowed at a velocity of over 10 cm/sec. This did not allow the fluid enough residency time at either end of the chamber to create a significant temperature gradient. Two baffle configurations were explored, one being a round disk with a center hole and the other adding a circumferential space around the wall of the cylinder in addition to the center hole (see Figure 3).

The center hole baffle configuration achieved the desired result of increasing the temperature gradient between the hot and cold zone of the chamber. Mass transfer was predicted (by a model) and verified to occur by the periodic exchange of fluid from one zone to the other in an oscillating fashion. This method of mass transfer resulted in an unacceptably long cleaning time (hours). Therefore, an alternative baffle design was modeled. This baffle included a center hole and an annular gap around the edge of the cylinder which allowed the natural convection flow of the SCCO2 to continue, hot SCCO2 rising around the edge of the cylinder and cold SCCO2 descending through the center. This configuration produce a good temperature gradient and improved mass flow.

2.1.4 Operational Costs

The cost of operating new cleaning systems is always a concern for potential users. The operational costs consist of operator time, utilities (electricity) and CO_2. The system is computer controlled with an automatic cleanliness detector which can signal the operator when the components are clean. Therefore, minimal operator involvement is required. The electrical costs at the prevailing rate are 13.4 kW during warm-up and 5.0 kW during normal operation. The cost of CO2 is $.13/kg to $.33/kg in the United States. The current system requires 160 kg of CO_2 for the cleaning chamber, this is recycled for multiple cleaning runs. The transfer chamber requires 22 kg of CO_2. The next generation system is anticipated to require less CO_2. Actual costs will vary based on labor rates, electrical rates and the cleaning time for the components involved.

2.1.5 Future Efforts

- Finish the cleaning trials currently underway
- Document the operation envelope of the system.
- Investigate cosolvents
- Design a ruggedized unit that can be used in a production environment

2.2 Low-Temperature Oxygen Plasma Cleaning

The oxygen plasma cleaning technology was originally intended to clean oxygen tubing. Oxygen tubing has inherent unique cleaning requirements which can't be met with traditional cleaning alternatives. Inappropriate cleaning of oxygen tubing can result in fires, explosions, or illness/death of the flight crew. Oxygen tubing is typically cleaned after its fabrication. Fabrication consists of introducing a special hydrocarbon oil into the tube to prevent kinking of the tube during the bending process. These tubes are typically less than 2.54 cm in diameter and shorter than 4.27 m. However, they may be manufactured with a large number of bends. After bending the oil is drained, end fittings are attached and then the tube is cleaned.

Cleaners for oxygen tubing must meet several functional requirements. These cleaners must remove any hydrocarbons down to less than 10.8 mg/.m^2, remove the vast majority of particulates, and any residue cleaning agent must not be flammable or harmful to the flight crew if inhaled. CFC113 has performed this cleaning operation very efficiently in the past The problem is finding a non-hazardous replacement which can meet all of these functional criteria and be implementable in a depot environment. Furthermore, the depot community requires that the oxygen tube cleaning system be able to clean other components in order to increase its utilization.

2.2.1 Cleaning Theory

Low-temperature oxygen plasmas have been used for many years for oxidizing, ashing, etching, pre-conditioning prior to adhesive bonding, polymerization, chemical reactivity investigations and other applications. During space studies it also was learned that atomic oxygen removes hydrocarbon materials. This cleaning technology builds off this extensive base of experience to apply low temperature oxygen plasmas to the cleaning of oxygen tubing of hydrocarbons and particulates.

The exact mechanism and kinetics have not been studied. However, it is assumed that the plasma and its inherent reactive species provide sufficient energy to dislodge and breakdown the organic contaminants which are removed from the tube by the vacuum flow. This cleaning method produces CO2 and water as the major by-products.

2.2.3 Cleaning System Operation

Mechanical methods and low-temperature oxygen plasmas have the potential to clean oxygen tubing for military aircraft. Two alternative processes utilizing low temperature oxygen plasma cleaning are being investigated; tube coupled cleaning and plasma chamber cleaning. Each of these processes are discussed in the following paragraphs.

A - Tube Coupled Cleaning:

1) The oxygen tubing is heated to 104°C. This significantly reduces the viscosity of the hydrocarbon oil. The majority of the oil pours out of the end of the tube.
2) A squeegee device is either pushed or pulled through the tube. This process step accomplishes two things, first it reduces the hydrocarbons to a thin film and second it removes the particulates.
3) A fiberglass coated wire is threaded down the center of the tube.
4) The 13.56 MHz oxygen plasma cleaning system is coupled to the ends of the tube and an oxygen plasma is generated down the length of the tube. The vacuum flow removes all of the contaminants as they are liberated.
5) A sensor system analyzes the effluent and signals when all of the contaminant has been removed.
6) The tube is removed from the system and is ready for installation.

B - Plasma Chamber Cleaning:

1) The oxygen tubing is heated to 104°C. This significantly reduces the viscosity of the hydrocarbon oil. The majority of the oil pours out of the end of the tube.
2) A squeegee device is either pushed or pulled through the tube. This process step accomplishes two things, first it reduces the hydrocarbons to a thin film and second it removes the particulates.
3) The tubing is placed within a plasma chamber which produces an oxygen plasma which can clean the tubing.
4) A sensor system analyzes the effluent and signals when all of the contaminant has been removed.
5) The tubing is removed and can be assembled to the aircraft oxygen system.

Both processes have broader applicability than that of oxygen tubing. Process "A" can clean all types of tubing and process "B" can clean the majority of components which can fit inside the chamber. The user community has expressed the need for a system which can clean oxygen tubing as well as other components in order to increase the utilization of the equipment.

2.2.3 Technology Developments

Initial investigations proved that atomic oxygen alone was insufficient to clean the tubing to the required level of cleanliness. However, an oxygen plasma was able to clean the tubes of all hydrocarbon residue. The operational parameters required were determined during a reactivity study. The operational envelope which efficiently removes oxygen tube-bending oil is depicted in Figure 4.

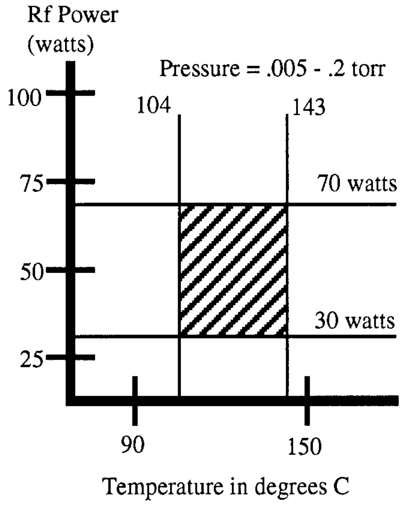

Figure 4 Processing Parameters for Tube Cleaning

Although a low temperature oxygen plasma is very effective in cleaning hydrocarbons, it can not remove particulates. Therefore, low-temperature oxygen plasma cleaning was coupled with a mechanical cleaning method. The current development effort has demonstrated the cleaning on a 91 cm long aluminum oxygen tube with a 1.9 cm diameter to an acceptable cleanliness level (100A cleanliness) within 30 minutes.

According to the user community oxygen tubing on DOD weapon systems range in size from one meter to 4.27 m long. Therefore, major development efforts have been expended to maintain a stable plasma along the entire length of a 4.27 m tube. No method to maintain such a plasma without introducing a conductor into the tube has been found. A preliminary investigation has demonstrated that a simple wire introduced into the tube has been able to maintain such a plasma.

2.2.4 Operational Costs

Operational costs are oxygen for the plasma and electricity to maintain the plasma and operate the vacuum pump and heaters. A life cycle analysis to quantify the operational cost has not been performed. However, the capitol investment for the laboratory system was $20,000.

2.2.5 Future Efforts

Future research efforts will investigate the optimum wire configuration and verify the cleaning effectiveness for a full size oxygen tube (4.27 m long). Furthermore, plasma chamber oxygen tube cleaning will be investigated and validated. Finally, a ruggedized oxygen plasma cleaning system will be designed and delivered to a depot.

2.3 Laser Cleaning

The laser cleaning technology is being pursued to address the problem of very tightly bound contaminants which can not be cleaned by technologies currently in production or development. The DOD depots identified a number of applications for this technology. In addition, the laser system being developed also will be able to remove tightly bound coatings such as HVOF deposited metallic coatings.

2.3.1 Cleaning Theory

Lasers have been used over the last 15 years to remove a variety of materials off of substrates from paints to oils. This effort build upon the research conducted in laser/contaminant/substrate interaction as well as the improvements in control and stability of laser systems. Organic contaminants absorb the energy from IR wavelength light very readily. The CO2 laser produces IR light primarily at 10.6 micron wavelengths. This type of laser is very cost effective. The laser light strikes the contaminant on the surface of the part and the contaminant vaporizes or ablates. Metals reflect over 90 percent of CO2 laser light, therefore a metal substrate is not damaged once the contaminant has been removed. Inorganic contaminants could be removed by IR lasers or other unique laser methods.

2.3.2 Cleaning System Operation

The system (Figure 5) being developed for production use is semi automated to facilitate the wide variety of components which are anticipated to be cleaned. The system will be able to accommodate parts within a 1.2 m x 3.0 m x 1.8 m operational envelope. Parts are placed in a fixture and the laser is moved across the surface of the component (manually or automated program). The laser removes either all or part of the contaminant depending on its nature and thickness. A spectral analyzer examines the contaminant evolution plume to evaluate when the coating has been completely removed. As the laser moves across the surface of the part the feedback control from the spectral analyzer will initiate a clean or no-clean command for each square centimeter of surface area. The effluents are drawn away from the part by a vacuum system near the laser output as well as one located in the flooring. All effluents are treated and where necessary captured in HEPA filters. The system is being designed to be a low-maintenance laser system which can operate in a production environment.

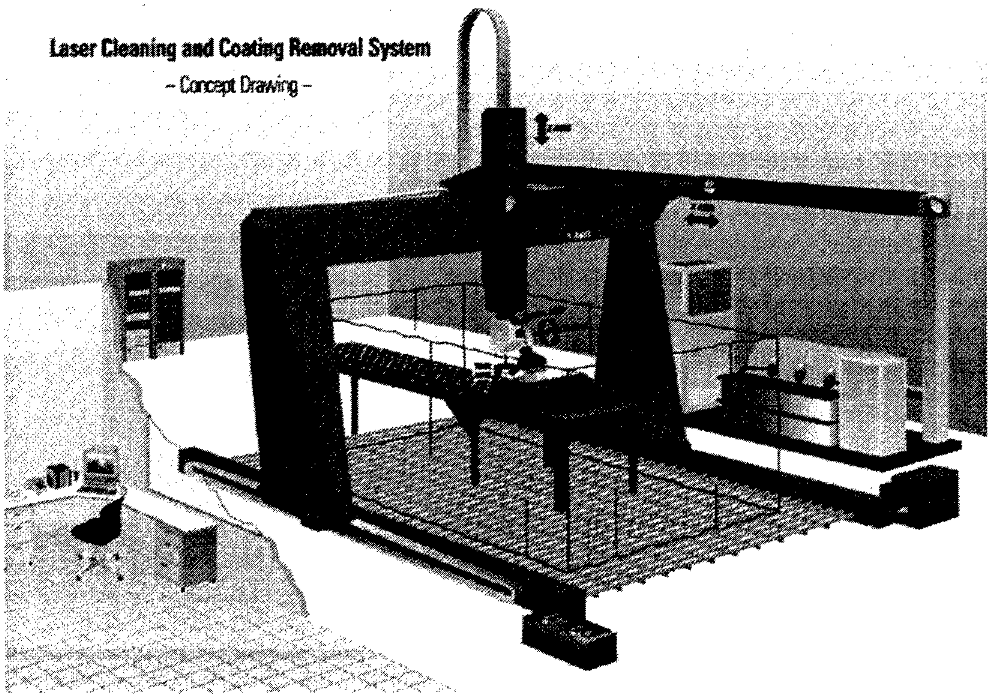

Figure 5 Laser Cleaning System

2.3.3 Technology Developments

The effort is currently in Phase I of a three Phase development program. This initial Phase is using samples submitted by DOD organizations and evaluating 1) which lasers remove the contaminants most efficiently and 2) what operating parameters are required for cost effective removal. Tightly bound coatings, both metallic and ceramic, are being removed in this Phase as well.

2.3.4 Operation Costs

A life cycle analysis will be performed in 1997 to document actual operating and maintenance costs for the system.

2.3.5 Future Efforts

The majority of this effort has yet to be performed. Phase I will establish what types of lasers should be used in the system as well as what range of operating parameters the lasers will need to have in order to clean all of the desired components.

The system will then be built with as much off the shelf equipment as possible. The system will be undergo a rigorous durability test to ensure that it is sufficiently reliable for a production environment.

The cleaning processes will be optimized on the production system for the components submitted by the DOD.

Finally the system will be transferred to a depot environment where the operators and maintenance personnel will be trained.

2.4 Carbon Dioxide / Ultraviolet Light

The CO_2 / Ultraviolet (UV) Light Activated Oxygen cleaning technology is applicable to small and medium sized components which require a surface cleanliness suitable for bonding. The equipment is easy to operate and produces no collectable by-products other than the soil being removed. This cleaning approach combines two established cleaning methods into a single system namely, CO_2 pellet cleaning and ultraviolet light cleaning.

2.4.1 Cleaning Theory

CO_2 pellet cleaning is an established technology which is currently being used at a number of DOD depots. This cleaning method is used to remove carbon and other soils from airframe and engine components prior to inspection and repair. CO_2 food grade gas is converted into pellets measuring approximately 1.6 mm in diameter. These pellets impinge upon the surface of the parts and dislodge the majority of the soils. However, the cleanliness level achieved is not sufficient for bonding operations (the surface is not water-break free).

Ultraviolet light cleaning of organic contamination has been used primarily in the electronics industry for precision cleaning. However, UV light is only effective at cleaning thin film contamination. The UV light creates 10 ppm of ozone. The combined effect of ozone and UV light react with organic molecules on the part surface and in the air. The organic contaminants are broken down and removed from the area via a positive airflow ,The current cleaning process combines these two technologies and applies them to metallic components which require cleaning prior to bonding or coating (metallic/organic).

2.4.2 Cleaning System Operation

The process flow begins by cleaning the components with CO_2 pellets (.103 MPa -.138 MPa at .785 rad). The nozzle is about 20 cm long and 38 mm wide. After 4 to 6 passes the pellets remove the majority of the contamination and then sublime leaving only the contaminant. The parts can be held by hand or placed in a fixture for cleaning. The source of CO2 is a by-product from a food processing operation, therefore, additional CO_2 is not generated to support this process. The pellet blasting reduces the contaminant to a thin film. Other media blasting technologies such as sodium bicarbonate also may be applicable to this process. Once the bulk of the contaminant has been removed the parts are exposed to UV light within a closed chamber. The current chamber measures 60 cm x 91 cm x 91 cm. A serpentine low pressure mercury vapor light is being used to generate the UV light. The primary wavelengths of UV light are at 185 nm and 254 nm. Both wavelengths react with organic molecules on the surface and in the air. During the cleaning process the 185 nm light disassociates a portion of the O_2 creating 10 ppm of ozone (O_3). This ozone also reacts with the organic molecules, and by the end of the process is no longer a reactive product. A positive airflow carries the contaminants away from the parts being cleaned. The primary by-products produced are CO_2 and water vapor. After no more than 30 minutes of cleaning the parts are ready for subsequent operations.

The process does have some minor limitations namely; part sizes are constrained by the size of the UV chamber and that this cleaning method is a line of sight process. However, many components could be rotated during the cleaning to allow all sides to be cleaned. The simplicity of the process as well as building-off of related established technologies lends great strength to its viability as a depot maintenance process.

2.4.3 Technology Developments

The research has investigated various CO2 pellet blasting parameters such as blast angle, pressure, and pellet density to arrive at those used in the process. Both low and high density pellets clean effectively, however denser pellets require fewer cleaning passes. The nozzle configuration has not been optimized.

The UV light cleaning process was investigated with atomic oxygen and ozone as reactive agents. It was determined that ozone although not as reactive as atomic oxygen is more economical. Furthermore, the optimal amount of ozone was investigated. Excess ozone absorbs too much of the UV light preventing it from reaching the surface and cleaning is hampered. It was determined that the 10 ppm which is produced naturally by the 185 nm light is the optimal quantity.

Testing has indicated that the cleaning system is sufficient to provide good adhesion for aluminum and steel substrates and pass the required durability tests. Testing was performed on 2024 Al, 7075 Al and SAE 4130 steel. Panels measuring 7.6 cm by 15.3 cm and 1.5 mm thick were contaminated, cleaned and tested. A set of panels were ion vapor deposition coated with aluminum. The panels were peened with glass beads to increase the density of the coating and test for coating failure. No disbonding at 270,000 Pa is considered passing. All samples passed at 550,000 Pa. Other panels were sulfuric acid anodized and tested in a salt spray chamber for 2 weeks. Another sample set was chromate conversion coated and were salt spray tested for one week or painted and then wet tape adhesion tested. The results of all of these tests are depicted in Table 1.

This process has demonstrated the ability to clean deburring wax, tube-forming oil, machining coolant, preservation oil, zyglo penetrant, simulated dirt, grease, baked on cosmoline. corrosion preventative compound, and forming oil. All of these materials were removed and the metallic surfaces were able to create durable bonds with IVD coatings, conversion coatings, and anodized coatings. Dykem Blue was the only contaminant which could not be thoroughly cleaned. The CO2 removed only minor portions of the contaminant. The UV light changed the nature of the contaminant from hydrophobic to hydrophilic. This

Table 1 Cleaning Results for CO2 / UV Ozone

Material	2024 Al	7075 Al	SAE 4130	2024 Al	7075 Al	2024 Al	7075 Al	2024 Al	7075 Al
Processing	Ion Vapor Deposition	Ion Vapor Deposition	Ion Vapor Deposition	Anodize	Anodize	Conversion Coated.	Conversion Coated.	Conversion. Coated & Painted	Conversion. Coated & Painted
Testing	Peening .55 MPa	Peening .55 MPa	Peening .55 MPa	2 Week Salt Fog	2 Week Salt Fog	1 Week Salt Fog	1 Week Salt Fog	Wet tape Adhesion	Wet Tape Adhesion
Soil									
Deburring wax	pass	pass	pass	pass	pass	pass	pass	pass	pass
Tub Forming wax	pass	pass	pass	pass	pass	pass	pass	pass	pass
MMS 611 coolant	pass	pass	pass	pass	pass	pass	pass	pass	pass
Dykem Blue	pass	pass	pass	pass	pass	pass	pass	fail	fail
Preservation oil	pass	pass	pass	pass	pass	pass	pass	pass	pass
Zyglo Penetrant	pass	pass	pass	pass	pass	pass	pass	pass	pass
Simulated dirt	pass	pass	pass	pass	pass	pass	pass	pass	pass
Mobile grease #28	pass	pass	pass	pass	pass	pass	pass	pass	pass
Backed-on cosmoline	pass	pass	pass	pass	pass	pass	pass	pass	pass
MIL-C-16173	pass	pass	pass	pass	pass	pass	pass	pass	pass
Forming oil	pass	pass	pass	pass	pass	pass	pass	pass	pass

change allowed the visually contaminated panels to pass a waterbreak test following UV cleaning. Furthermore, the panels passed all of the tests presented in Table 1 except for the wet tape adhesion test.

The most complicated component cleaned to date is pictured in Figure 6. This component is about 56 cm long and came fully painted. The paint, primer and conversion coating were removed. Mobile grease was applied to the part and the part was put through the cleaning process. A hand held CO_2 cleaning nozzle was used to facilitate cleaning around the complicated geometry. UV cleaning was performed in the existing chamber without any modifications. The part subsequently passed an IVD aluminum adhesion test.

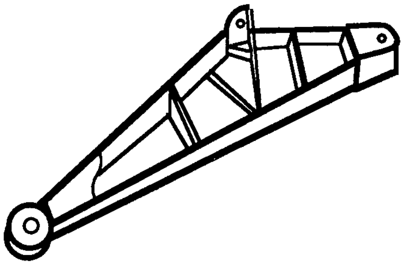

Figure 6 Trainer Aircraft Component

2.4.4 Operation Costs

A preliminary life-cycle economic analysis of operating costs (not capital investment costs) was conducted to determine the cost drivers of the process as well as the cost competitiveness as compared to aqueous cleaners. The UV light cleaning operation is the primary cost driver (74%). The process currently costs many times more than a typical aqueous cleaning process. Longer lasting and more efficient sources of UV lights would reduce this cost significantly.

2.4.5 Future Efforts

The current efforts are exploring optimized CO_2 blasting parameters, nozzles and as well as alternative UV light sources in order to improve the cost effectiveness.

Future efforts will explore the cleaning of more complex components. Part fixturing and effective part transfer methods between the CO_2 blasting and UV cleaning steps.

Furthermore, other developments will be made to enhance the implementation of this cleaning system at a DOD depot.

3.0 CONCLUSIONS

Cleaning processes which produce minimal waste are being developed and optimized. Several approaches have demonstrated the ability to clean coupons and actual components to the required level of cleanliness. Supercritical CO_2 Convection Flow cleaning, Low-Temperature Oxygen Plasma cleaning, Laser Cleaning and CO_2 / UV light cleaning are viable alternative cleaning technologies. Further work is required to optimize the processes, expand the operational envelope and prepare the technology for transition into the depot community.

4.0 ACKNOWLEDGMENTS

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Advanced Surface Preparation for Metal Alloys

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SUMMARY

Current metal surface preparation processes typically rely on materials that are undesirable from environmental or safety perspectives, such as strong acids/bases and hexavalent chromium. In addition, these processes usually produce large wastewater streams. The United States Air Force (USAF) Wright Laboratory is investigating alternate surface preparation approaches in order to develop and transition processes that are environmentally friendly with equal or improved performance. Several technologies are being evaluated, primarily for adhesive bonding of aluminum and titanium. These include: excimer laser, plasma polymerization, ion beam enhanced deposition, plasma spray and sol-gel. These approaches eliminate or greatly reduce the undesirable environmental impact of the currently-approved processes. Most of the candidates deliver bond strength performance equivalent to these existing procedures. As measured by accelerated laboratory testing, none consistently provide the long-term moisture durability of the state-of-the-art. However, some candidates outperform existing, accepted processes and appear to be capable of delivering state-of-the-art moisture durability once optimized. At this time, sol-gel provides the best combination of performance and ease of scale-up for depot and field applications. With this approach, a water-based solution is applied to the metal and dried at elevated temperature without rinsing. Environmentally friendly pretreatment (cleaning and deoxidizing) and post-treatment (priming) steps are used. Future work will continue optimization and scale-up efforts for sol-gel and other viable candidates. Transition to USAF and other users will be pursued. High-temperature titanium bonding and on-aircraft aluminum bonding are potential early transition opportunities.

1.0 INTRODUCTION

Surface preparation is essential for the successful implementation of adhesive bonding technology. Both the initial bond strength and the subsequent bond durability are critically dependent on the interaction between the adhesive (and/or primer) and a pretreated adherend surface. For metals, surface preparation involves both the removal of weak boundary layers or layers that are chemically incompatible with the adhesive and the formation of stable, adherent layers that are mechanically and chemically compatible with the adhesive.[1] Surface preparation is equally critical for the corrosion protection of metal components and the adhesion of coatings to these components.

Current surface preparation technology for aerospace applications primarily relies on wet chemistry techniques. State-of-the-art prebond surface preparations include acid anodization (primarily phosphoric and chromic) and acid or base etch processes. These are generally followed by application of a chromated adhesive primer. For aluminum corrosion protection and preparation prior to priming and/or painting, anodization or conversion coating processes involving both acids and hexavalent chromium are the state-of-the-art. The above wet chemistry processes also produce large wastewater streams.

Recent and pending environmental laws, regulations and policies are beginning to restrict the use of the current surface preparation processes. In particular, there is increasing pressure to eliminate hexavalent chromium from the workplace. As a minimum, the costs associated with the handling, tracking and disposing of chemicals, including chromates and strong acids, are greatly increasing. Finally, due to the use of water-based technologies as replacements for many environmentally unfriendly processes, water waste streams requiring treatment are continually increasing. The United States Environmental Protection Agency

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has begun to tighten restrictions on the levels of contaminants allowable in the waste stream[2].

The United States Air Force (USAF) Wright Laboratory has been active in metal surface preparation pollution prevention research and development since 1993. The intent of the Wright Laboratory effort is to develop, and transition to using customers, new processes that eliminate hazardous and toxic materials and minimize waste streams. It is imperative that the new surface preparations meet or exceed the performance capabilities of the state-of-the-art systems. This is especially true in recent years as it has become desirable to extend the operational lives of many aircraft in the USAF inventory. At the same time, corrosion and fatigue are working to limit aircraft life[3]. Therefore, it would be unacceptable to reduce the level of corrosion protection now available. Also, effective prebond surface preparations, particularly for on-aircraft application, are more critical than ever as adhesive bonding is used for the repair/prevention of fatigue cracking.

The Wright Laboratory efforts in the area of surface preparation for structural bonding are the focus of this paper. The majority of the research has been dedicated to treatment of 2024 and 7075 aluminum alloys and 6Al-4V titanium alloy. Surface preparation of titanium and on-aircraft aluminum preparation are two areas where potential exists for improvements to existing processes. State-of-the-art titanium treatments are not suitable for long-term exposure at high temperatures and cannot withstand the elevated temperature cures of certain adhesives. Most on-aircraft aluminum surface preparations that provide adequate performance contain acids and chromates. These are inconvenient to use, and the effect of acids on aircraft structure is a concern for both embrittlement of high strength steel fasteners and corrosion of aluminum if all acid is not sufficiently rinsed after anodizing or etching.

The Wright Laboratory approach has been to develop several technologies and then downselect and mature the most promising approaches. The intent was to exploit existing technologies, currently used for other applications, by optimizing them for prebond surface preparation. Multiple efforts were funded in several of the technical areas. The areas investigated include excimer laser, plasma polymerization, ion beam enhanced deposition (IBED), plasma spray and sol-gel.

In most cases, bond strength was evaluated using lap shear (ASTM D 1002)[4] and peel (ASTM D 3167)[5] testing. Moisture durability, the most difficult performance characteristic to achieve, was evaluated by the wedge test (ASTM D 3762)[6]. In this test, a crack is initiated in a bonded joint via insertion of a wedge into the bondline. The crack will ideally develop in the adhesive away from the metal surface and surface treatment. The test specimen is exposed to hot/wet conditioning and crack growth is monitored. Although growth data are important, the critical piece of information is the specimen failure mode. Cracks which remain cohesive in the adhesive are desirable since they indicate the surface preparation is not the weak link in the bonded joint. Unless otherwise indicated, wedge adherend thickness was 3.175 mm per the ASTM standard and hot/wet conditioning was at 60°C and 95-100% relative humidity (RH). Performance of candidate surface preparations was compared to that of the applicable state-of-the-art processes.

This paper provides an overview of research efforts ongoing and recently completed. Background information is provided for all of the efforts, however, detailed discussion is limited to select programs.

2.0 EXCIMER LASER TREATMENT

Laser treatment for bonding aluminum and copper was investigated by the Israeli Institute of Metals, Technion, in conjunction with Rafael. The bulk of the work was funded by Wright Laboratory under European Office of Aerospace Research and Development (EOARD) contracts F61708-93-C-0005 and F61708-95-C-0004.

2.1 Laser Treatment Technology and Approach

A UV excimer ArF (193 nm) laser was used to irradiated aluminum specimens (primarily 2024-T3) to both clean the metal surface and modify morphology and microstructure to improve bonded joint strength and durability. The laser radiation, with a fairly discrete wavelength, can rapidly heat material surfaces. At high irradiance levels the laser energy can ablate or vaporize organic contaminants. When properly controlled, the laser can be used to create surface roughness and permit the growth of oxide coatings on metal surfaces. The UV laser wavelength is in the range that can break many chemical bonds and cause free radical chemical reactions. Therefore, the laser was also used to investigate polymerization of polymers (primers) on aluminum substrates. Adherends treated by excimer laser were evaluated using lap shear, peel and wedge tests. The effect of laser parameters on mechanical performance was investigated to optimize the process. Several adhesives were used, including Cytec products FM 73, FM 300-2K and FM 350NA. Controls consisted of unsealed chromic acid anodize and untreated aluminum. Extensive evaluation of laser-treated surfaces was conducted to determine the effects on morphology and microstructure.

The laser process does not create solid or liquid waste streams. Gaseous waste streams can be filtered to remove undesirable components. Current uses of UV lasers include cleaning of surfaces, cutting of materials, ablation and polymerization.

2.2 Laser Treatment Results and Conclusions

Shear strengths obtained using laser treatment approached those of the chromic acid anodized controls. Wedge test results did not equal the controls, and 100% cohesive failures were not achieved. However, great improvement was seen over untreated aluminum. Under optimal conditions, the laser treatment removed organic contaminants and produced an oxide on the surface but did not produce significant morphological changes.

The use of laser irradiation for polymerization of primers on metal surfaces received less attention since the closed system required for this study was constructed late in the effort. The use of the excimer laser for prebond treatment of copper was investigated. Further Wright Laboratory funding to optimize the laser process is not currently planned since technologies easier to scale-up were yielding better performance results at the time of downselection.

3.0 PLASMA POLYMERIZED FILMS

The use of plasma polymerized films as a pretreatments for adhesive bonding and corrosion protection of aluminum is being investigated by the University of Cincinnati under Wright Laboratory contracts F33615-92-D-5812, Delivery Order 066 with Anteon Corporation as prime contractor and F33615-95-D-5615, Delivery Order 0009 with Science Applications International Corporation (SAIC). A small effort on steel is also a part of the latter contract.

3.1 Plasma Polymerization Technology

Plasma polymerization is a vacuum coating process carried out by exposing a solid to a low pressure gas of a "monomer" in which excited species such as radicals and ions are created by application of an electric field. The reactive species impinge on the solid and react with other monomers or excited species to form polymer films[7]. The process is capable of producing extremely thin, defect-free films on metal, polymer and ceramic surfaces. Plasma processes are efficient since polymer synthesis and deposition can be combined. Substrate materials can also be cleaned prior to deposition and post-treated afterward, if desired, in the same vacuum chamber. A large number of monomers can be polymerized, and the properties of the deposited films can be tailored for specific applications.

Plasma polymerization is a dry process without the waste streams associated with typical surface treatment techniques. Plasma etching is used commercially for treating fibers and polymer films, such as polyethylene, to improve adhesion.

3.2 Plasma Polymerization Approach

For aluminum bonding, silica-like films were deposited on aluminum alloy surfaces in both capacatively-coupled radiofrequency and microwave (Figure 1) reactors at a pressure of about 60 Pa. For most of the work, Hexamethyldisiloxane monomer was introduced into the reactors along with oxygen carrier gas. Various processing variables were investigated to determine their effect on thickness, uniformity and composition of the deposited films. These included monomer and carrier gas flow rates, location of ports for introduction of the monomer and carrier gases and reactor power. The films were characterized using x-ray photoelectron spectroscopy (XPS), reflection-absorption infrared spectroscopy (RAIR) and ellipsometry.

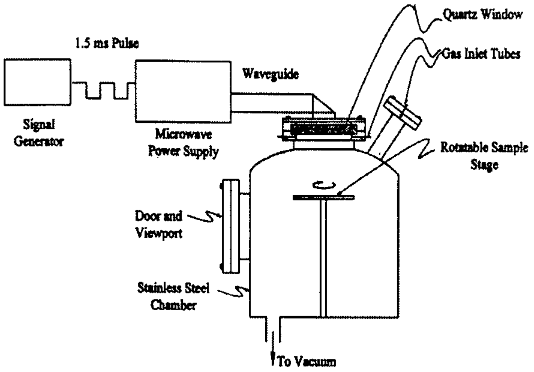


Figure 1: Schematic of Microwave Reactor

Shear and peel tests were used to evaluate the strength of bonded joints fabricated with 121°C-curing epoxy adhesives and moisture durability of the joints was tested using the wedge test. Aluminum substrates were grit-blasted with silicon carbide and then etched in the reactor in argon or argon/hydrogen plasmas prior to coating with the plasma-polymerized film.

3.3 Plasma Polymerization Results and Conclusions

The University of Cincinnati processes are capable of coating aluminum substrates with a fairly uniform silica-like film with a thickness in the 75-80 nm range in 10 minutes. Lap shear tests result in failures cohesively through the adhesive. Wedge test results to date exhibit undesirable adhesive failures. Analysis has shown these failures to occur near the interface of the coating and the adhesive and not at the aluminum surface. Future work will concentrate on improving this interface by introducing functional groups on the deposited coating's surface that can react with the epoxy adhesives. This may be done by post-treating the coatings with a plasma such as ammonia or by changing the monomer and carrier gases.

Application of the silica-like coatings to aluminum as a replacement for chemical conversion coatings is also being investigated. Initial results on 2024-T3 are promising in both adhesion and corrosion protection tests. At this point in their development, the plasma polymerized coatings appear to be better suited to this application. However, that could change if efforts to eliminate failures at the adhesive/coating interface during wedge testing are successful.

4.0 ION BEAM ENHANCED DEPOSITION

The use of ion beam enhanced deposition (IBED) technology for the prebond treatment of aluminum alloys was investigated by CC Technologies, Inc. in association with BeamAlloy Corporation under Wright Laboratory contract F33615-93-C-5323.

4.1 IBED Technology

Ion beam enhanced deposition (IBED) is a process that combines a conventional film deposition technique such as vacuum evaporation or ion sputtering with the bombardment of the growing film by a secondary, high energy flux[8]. The secondary ion flux is usually an inert species such as argon gas. It is used to improve adhesion of the conventional film to the substrate by mixing the first few atomic layers of the conventionally grown film into the substrate surface forming a mechanically alloyed bond layer. In addition, the secondary ion flux controls the morphology of the film as it grows from the substrate surface. The IBED process is carried out in a high vacuum (1.33×10^{-4} Pa or below) and at relatively low temperatures, 50°C or below, with the proper choice of deposition parameters. Figure 2 shows a general diagram of the IBED process.

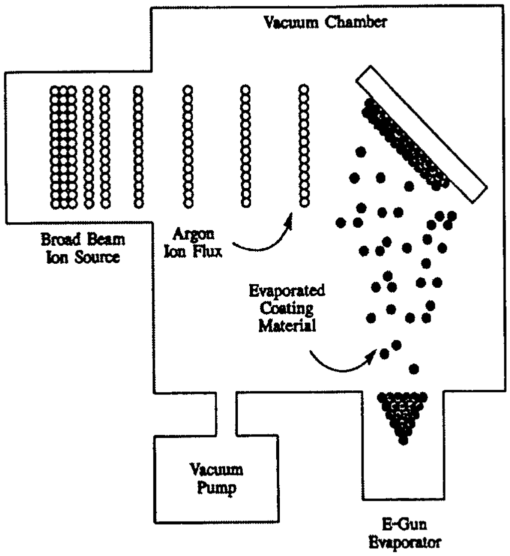


Figure 2: Schematic of IBED Process

IBED can remove and rebuild oxide films on aluminum surfaces without using the wet chemical techniques common with the state-of-the-art surface preparations. With this approach wastewater streams are eliminated. This technology is already in wide use for the deposition of thin insulating coatings on optical components, electronic components, and other thin film devices such as strain and temperature gauges, sensors and transducers[9].

4.2 IBED Approach

Aluminum substrates were degreased and some were grit blasted with 50 µm aluminum oxide. The surfaces were then cleaned by sputtering in the vacuum chamber using high energy argon ions. The IBED process was used to deposit an Al_2O_3 barrier layer on the aluminum surface. This was followed by discontinuation of the secondary argon ion flux and natural growth of a top layer of Al_2O_3 over the barrier layer. Immediately after oxide growth, the vacuum chamber was flooded with dry nitrogen gas. Prepared surfaces were immediately primed or oven dried at 120°C and then primed.

Bonded joints which were prepared using the treated aluminum adherends were tested for peel strength and for durability using the wedge test. Surface analysis was also conducted to determine the nature of the deposited coating.

4.3 IBED Results

Surface analysis showed the IBED layer to be smooth, amorphous or microcrystalline α-Al_2O_3 with a thickness of about 100 nm. The naturally-grown layer was determined to be approximately 300 nm thick crystalline α-Al_2O_3 with a microrough morphology. Peel test results yielded strengths equivalent to those obtained using the phosphoric acid anodize (PAA) controls. Wedge test results, with hot/wet conditioning at 49°C and 98% RH, were initially very poor. This performance was improved when grit blasting was used prior to IBED, however, equivalency with PAA was not demonstrated. When the 120°C oven dry step was added to remove adsorbed water from the oxide surface prior to priming, wedge test crack growth results began to approach those obtainable with PAA and nearly 100% cohesive failures were achieved (Figure 3).

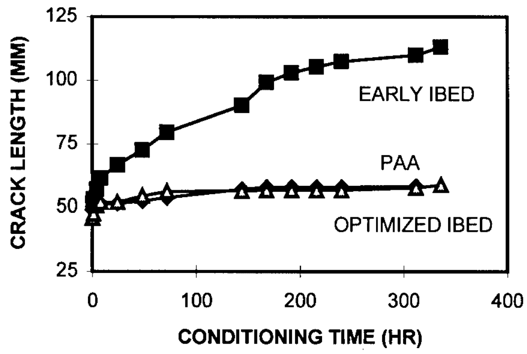


Figure 3: Wedge Crack Growth Versus Time for Early IBED, Optimized IBED and PAA

4.4 IBED Conclusions

This effort demonstrated the feasibility of using the IBED process for surface preparation of aluminum prior to bonding. Good initial bond strengths were obtained, and improvements in bond moisture durability yielded wedge test results nearly as good as those obtained using the PAA surface preparation. However, continued work to scale-up the process is not currently planned. The relative difficulty of fielding a scaled-up high vacuum process and IBED's inability to be used for on-aircraft repair were considerations in the decision not to further fund the effort at this time.

5.0 PLASMA SPRAYED COATINGS

The use of plasma sprayed coatings for the prebond treatment of aluminum and titanium was investigated by the Virginia Polytechnic Institute (VPI) under Wright Laboratory contract F33615-93-C-5321 and DACCO SCI, INC. on contract F33615-93-C-5324. The VPI effort was a feasibility study only and will not be detailed. The information obtained by VPI was shared with DACCO SCI whose ongoing effort, primarily for treating aluminum alloys, is described below.

5.1 Plasma Spray Technology

The plasma spray process involves the rapid heating of powder material to the molten or semi-molten state and then propelling it against the substrate at high velocities. The high impact velocity and molten state provide good bond strength to the substrate. Very little heat is transferred to the substrate with typical substrate temperatures ranging from 100°C to 300°C. Thus metallurgical change, distortion and oxidation are avoided[10]. Metals, ceramics and polymers can be sprayed onto nearly any substrate material. The coating properties can be tailored for a given application, independent of the substrate material, and the coating composition and properties can be graded from the substrate to the surface. Figure 4 is a plasma spray schematic.

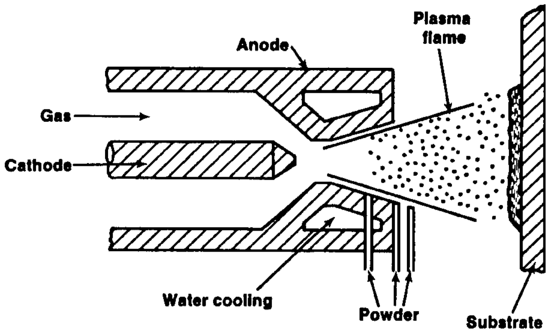


Figure 4: Plasma Spray Process

Plasma spray coatings have been used for thermal barriers for applications such as aircraft engine components. They have also been applied for wear resistance, EMI/RF shielding, slip/slide resistance and biocompatibility. Plasma spray technology has been investigated for prebond surface preparation of aluminum, titanium and steel.

The plasma spray process is a "solid-state" approach that eliminates liquid and gaseous waste streams. In addition, hazardous materials are not required for the pretreatment steps. Priming after plasma spray treatment does not appear to be necessary. If priming is desired, low-VOC nonchromated adhesive primers should be sufficient. Safety and other issues associated with the process have been addressed in production settings since plasma spray is currently used for a number of applications.

5.2 Plasma Spray Approach

Aluminum adherends (2024-T3 and 7075-T6) were sprayed with metal, ceramic and polymeric powders as well as mixtures of the above. Ti-6Al-4V adherends were sprayed with Ti-6Al-4V powder. Within 4 hours prior to plasma spraying, the substrates were grit blasted with a mixture of alumina, silica and silicon carbide. Spray materials and parameters were selected to provide a morphology intended maximize subsequent adhesion of the polymer (adhesive or adhesive primer) to the sprayed coating via mechanical interlocking while also achieving good adhesion to the metal substrate surface. In addition, the coatings themselves had to be tough so they would not be the weak link in a bonded joint. Plasma spraying was conducted using a Metco spray gun mounted on a robot articulated arm. Substrate surfaces were heated to about 100°C by the plasma torch to remove moisture prior to injecting powder into the gun. During plasma spraying, the substrates were air cooled from the back side. The angle of the spray gun to the substrate surface was either 45° or near 90°, and several passes were made to build up the desired thickness. No attempt was made to vary the coating composition as a function of thickness.

Bonded joints were tested primarily with the wedge test, although some lap shear and peel tests were also conducted. Wedge tests were conducted using the following epoxy adhesives: Cytec FM 123, FM 73 and FM 300 as well as 3M Company AF 163-2. The FM 300 is 177°C-curing whereas the remaining three adhesives cure at 121°C. Controls included both FPL etch and PAA for aluminum and Pasa Jell 107 and Turco 5578 for titanium. For most tests, no adhesive primers were applied, although some testing was conducted using Cytec BR 127 and the nonchromated, 0% volatile organic compound (VOC) XBR 6757. The plasma sprayed coatings were characterized using x-ray photoelectron spectroscopy (XPS) as were selected matching failure surfaces.

5.3 Plasma Spray Results

Initially, the best results on aluminum were obtained when spraying 60Al-Si/40polyester and 80Al-Si/20polyester powder, where the Al-Si constituent is an 88%Al-12%Si alloy. Optimal coating thicknesses were in the 50-75 μm range. Pure polyester, pure Al-Si aluminum and other mixes, including 70Al-Si/30polyester, were sprayed with less favorable results. In the wedge test, the lowest initial crack lengths were obtained using the 80Al-Si/20polyester treatments. These initial cracks were predominantly cohesive in the adhesive as desired. However, the crack growth after humidity exposure was significant. This crack propagation was predominantly in the polyester phase of an interphase region where the adhesive and sprayed coating are intermingled. Crack growth data indicated performance better than that obtained with FPL etch but not as good as PAA.

The 60Al-Si/40polyester coatings had much larger initial cracks but less crack growth when bonded with the 121°C-curing adhesives. The reduced crack growth in humidity does not appear to be solely due to lower stress at the crack tip caused by the longer initial cracks (Figure 5).

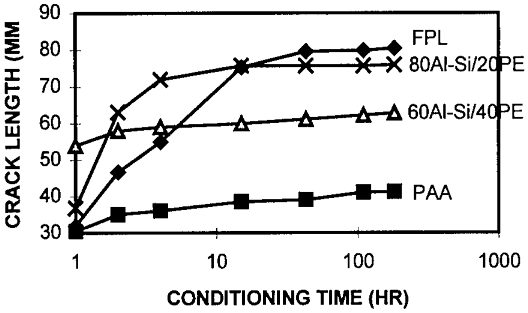


Figure 5: Wedge Test Results for Al-Si/Polyester on Al

For the 60Al-Si/40polyester coatings, both the initial cracks and those after exposure were in the interphase region, primarily in the polyester. These results seem to indicate that an improvement in coating toughness will improve performance results. Furthermore, analysis of the failed surfaces of initial cracks showed greater segregation of the polyester and aluminum components of the sprayed coating than would be expected by random mixing. Steps were taken to achieve better mixing of the aluminum/polyester in the feed powder and to reduce electrostatic charging. These changes produced more homogeneous as-sprayed coatings. The resulting initial, dry cracks were then about 50% cohesive in the adhesive. When bonded with the more brittle FM 300 adhesive, coatings of 60Al-Si/40polyester did give initial crack and crack extension results similar to those obtained with PAA.

Further improvements in performance were sought by eliminating the polymer from the feed powder and depositing a single phase even though very early work spraying aluminum and alumina on aluminum substrates did not produce desirable results and led to spraying mixed aluminum/polymeric coatings. Other early work showed the deposition of titanium coatings (Ti-6Al-4V) on the same alloy titanium substrates yielded wedge test results equivalent to current treatments (Figure 6). Unlike chemically-grown oxides, the chemistry of the sprayed coating is independent of the substrate material, so Ti-6Al-4V was also sprayed on 2024-T3 aluminum substrates. Wedge test performance using this approach was greatly improved. However, the ability to consistently repeat these results must still be shown. For the best specimens, initial cracks were 100% cohesive in the FM 73 adhesive and were shorter than the corresponding cracks obtained with PAA and FPL etch controls. Final crack length after 8 days exposure was similar to that of the PAA controls, however, propagation was visually interfacial between the adhesive and coating (Figure 7). Since spraying Ti-6Al-4V on aluminum appears to be a promising approach, the issue of galvanic corrosion was considered. Electrochemical polarization measurements conducted on titanium-coated aluminum and untreated aluminum yielded identical corrosion rates, indicating that the dissimilar metals of Ti and Al did not promote corrosion of the aluminum.

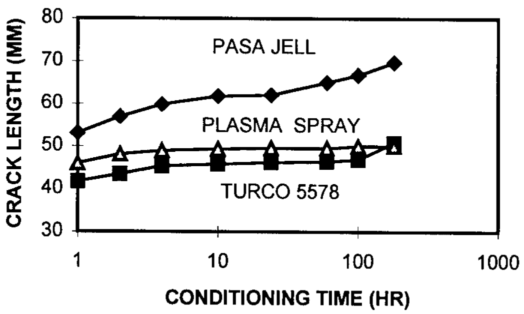


Figure 6: Ti-6Al-4V Sprayed on the Same Alloy

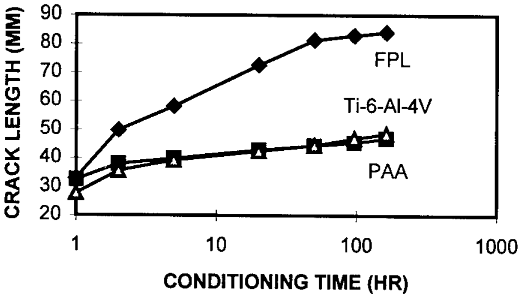


Figure 7: Ti-6Al-4V Sprayed on 2024-T3 Aluminum

5.4 Plasma Spray Conclusions

The feasibility of using existing plasma spray technology for prebond surface treatment of aluminum and titanium has been established. Adherends coated by a plasma spray process yield strength results equivalent to those obtained using state-of-the-art treatments. Moisture durability, as measured by the wedge test, approaches that of the current systems. Although this area still requires improvement, progress is being made, and further improvement should be possible by modifying the titanium coating morphology.

Initial testing indicates treated adherends can be stored indefinitely prior to bonding, with only a simple cleaning by aqueous methods or low impact solvents such as alcohol required after storage. Another advantage of plasma spray technology is the relative insensitivity of the process to the substrate adherend. Also, although on-aircraft repair is possible, many issues would have to be addressed, such as cooling repair areas when only one-side access is available. A downside to the plasma spray technology is the fact that it is a line-of-sight process limited by the ability of the spray head to access the surfaces to be treated.

Further work will concentrate on spraying titanium powder and possibly an optimized aluminum/polymeric powder mix on aluminum. Although plasma spray has been scaled up for other applications in the aerospace industry, work will be conducted to optimize a scaled-up version for adhesive bonding surface preparation. Finally, the high-temperature performance of plasma-sprayed coatings will be evaluated since the state-of-the-art wet chemistry treatments tend to perform poorly in this area. Long-term exposure tests at high temperature (greater than 10,000 hours at 177°C) will be conducted on titanium alloys coated with titanium. Also, the titanium-coated adherends will be tested using a high temperature polyimide adhesive which cures at 370°C.

6.0 SOL-GEL DEPOSITED COATINGS

The largest number of prebond surface preparation efforts funded by Wright Laboratory in a single technology are in sol-gel. Coatings deposited using sol-gel technology are being investigated for adhesive bonding applications on aluminum, titanium and steel, and for corrosion protection of aluminum.

Chemat Technology, Inc. conducted surface preparation for aluminum bonding studies under

Wright Laboratory Small Business Innovative Research (SBIR) contract F33615-94-C-5605. Their work on corrosion protection of aluminum and bonding of titanium has been performed on F33615-92-D-5812, Delivery Order 066 and F33615-95-D-5615, Delivery Order 0008 with SAIC. Chemat also has a small study for bonding steel under this SAIC delivery order. Northrop Grumman is working to scale-up the Chemat aluminum bonding process through Delivery Order 0010 of the above contract with SAIC.

Boeing Defense and Space Group investigated sol-gel for aluminum bonding under Wright Laboratory contract F33615-93-C-5322. Titanium bonding research at Boeing was performed on contract F33615-92-D-5812, Delivery Order 066. Their work continues under F33615-95-D-5615, Delivery Order 0007.

Aluminum adhesive bonding and corrosion protection research has also been performed by Foster-Miller under Wright Laboratory contract F33615-95-C-5621.

The Chemat aluminum adhesive bonding effort and the Boeing titanium bonding work are described below. Early research at both companies involved solvent-based solutions. The work reported here is with water-based sols.

6.1 Sol-gel Technology

The term "sol-gel" refers to a series of reactions where soluble precursors (typically metal alkoxides or metal salts) undergo hydrolysis and condensation to form a sol and then crosslink to become a gel. The precursors can also contain or crosslink with certain organic ligands that are not hydrolyzable during the network-forming process. After hydrolysis and condensation, the resulting metal oxide gel becomes a hybrid organic/inorganic polymer, which can be tailored for specific applications. A drying or pyrolysis step is conducted to remove solvent and densify the final product.

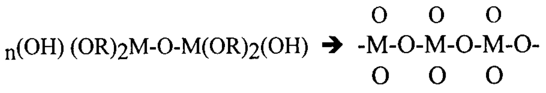
Most metal alkoxides are known to undergo sol-gel reactions. Hydrolysis replaces an alkoxide ligand in metal alkoxides with a hydroxyl ligand during reaction with water:

$$M(OR)_4 + H_2O \rightarrow HO\text{-}M(OR)_3 + ROH$$

where M is a metal atom, such as Si.

Condensation reactions involving the hydroxyl ligands produce polymers that are composed of M-O-M bonds and, in most cases, water or alcohol byproducts:

$$(OR)_3M\text{-}OH + HO\text{-}M(OR)_3 \rightarrow (OR)_3M\text{-}O\text{-}M(OR)_3 + H_2O$$



$$n(OH)\,(OR)_2M\text{-}O\text{-}M(OR)_2(OH) \rightarrow \text{-}\overset{O}{\underset{O}{M}}\text{-}O\text{-}\overset{O}{\underset{O}{M}}\text{-}O\text{-}\overset{O}{\underset{O}{M}}\text{-}O\text{-}$$

One of the big advantages to sol-gel chemistry is its versatility and ability to be tailored for specific applications. Solution chemistry can be controlled to vary deposited film density, porosity and microstructure. In fact, reaction conditions can be varied to produce discrete oxide particulates rather than the network gels which can be used for film formation. Some of the important solution variables include concentration, pH, type of catalyst and solution age. Other key variables are metal pretreatment and the drying time/temperature after coating.

Although the deposited coatings are quite thin, on the order of a few hundred nanometers or less, chemical gradation of the coatings is possible. For instance, a corrosion-resistant inorganic barrier layer can be oriented at the metal substrate interface while an organic functionality tailored for the subsequent bonding application can be present at the top of the deposited coating. Ideally, covalent chemical bonding exists at the coating/substrate interface as well as the coating/polymer (adhesive or adhesive primer) interface.

Sol-gel technology is nearly 60 years old. Automobile rear view mirrors produced by sol-gel thin film techniques have been in production since the early 1950s. Other early applications include antireflective coatings and architectural coatings. Today, sol-gel thin films and coating are being extensively studied for many optical, electronic, protective and other applications. Sol-gel technology is also used for applications other than thin film depostion: synthesis of nanosized oxide particles, ceramic fibers and porous gels and membranes[11].

Though it is a wet chemistry approach, sol-gel technology eliminates most of the negative aspects of the existing aluminum surface preparations. The dependency on strong acids and bases is eliminated with sol-gel. There is no need for hexavalent chromium in the process or in associated processing steps. There are no power requirements as for anodization. Wastewater is greatly reduced over conventional wet chemistry approaches since rinsing is not required. Water usage can be further reduced by employing spray application techniques.

6.2 Chemat Sol-gel for Aluminum Bonding

6.2.1 Chemat Aluminum Bonding Approach

Active alumina coatings were deposited on aluminum alloys (predominantly 2024-T3) from water-based, thermally-active colloidal solutions. Prior to deposition, specimens were degreased with an aqueous cleaner, alkaline cleaned and deoxidized in an acid solution. Deoxidation of adherends during the early work was in a chromated acid solution whereas later work was accomplished using a nonchromated deoxidizer. Deposition of coatings was by dipping or spraying. Coated specimens were dried for one hour at various temperatures. This was followed by application of adhesive primer, Cytec BR 127 or XBR 6757, and bonding with Cytec FM 73M epoxy film adhesive.

Wedge tests and lap shear tests were primarily used to evaluate bonded joints prepared using the coated aluminum. Some peel testing was also conducted. PAA controls were tested with the sol-gel coated specimens. Various techniques, including Auger spectroscopy, were used to characterize the deposited coatings.

6.2.2 Chemat Aluminum Bonding Results

The optimal coating solution, commercially available from Chemat as AL9201, is a colloidal solution made up of aluminum silicate and active organic functional groups. It has a solution oxide content of about 5 weight percent and a pH of about 10.5. This solution is stable, with a shelf life of over one year. AL9201 coatings resulting from both dipping and spraying had thicknesses in the 20-200 nm range. Auger spectroscopic analysis indicated that the coatings were homogenous throughout.

Wedge and lap shear data were optimal when the coating was dried at 121°C for one hour prior to priming. FM 73 lap shear results were in the 38.5 to 41.5 MPa range, and all failures were cohesive in the adhesive. The dependence of shear strength on coating thickness was evaluated. Different thicknesses were deposited on lap shear adherends by varying the speed of withdrawal from solution during the immersion application process; quicker withdrawal rates lead to thicker deposited coatings (Figure 8). Drying temperature and time also effected shear strength, but good results were obtained over a wide range. One hour drying at temperatures from ambient to 125°C produced cohesive failures and strengths in excess of 38.5 MPa. Drying at 150°C caused a reduction in shear strength.

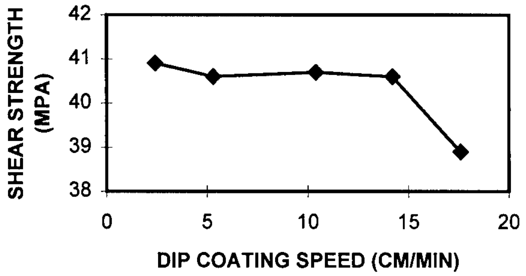


Figure 8: Shear Strength vs. Withdrawal Speed

Wedge test results were also dependent on coating thickness. In these tests, initial, dry cracks were cohesive in the adhesive and shorter than those of PAA controls. After exposure, the best performance (smallest crack growth), was obtained with coating thicknesses of 80 nm or less. Coating drying temperature was a big factor in wedge test performance. Higher drying temperatures yielded less wedge test crack growth in the moisture environment. Optimal results, with crack growth similar to that of PAA-treated specimens, were obtained with drying for one hour at 125°C. Initially, even these results produced adhesive-type failures with the propagating crack shifting to the interface between the sol-gel coating and adhesive primer after 24 to 168 hours of exposure.

It was suspected that the adhesive primer and/or the adhesive were not being fully cured. This situation was remedied, and wedge results improved. However, failures were not cohesive in the FM 73M as desired. Much better results were obtained when the temperature of reaction for creating the sol was increased. This altered the size and composition of the colloidal alumina in solution. It is believed to have resulted in alumina that was of crystalline nature (boehmite) with better hydrolytic stability as opposed to amorphous aluminum hydroxide. Wedge test specimens conditioned for over 30 days produced failure modes that were nearly 100% cohesive with crack growth similar to that of PAA controls (Figure 9).

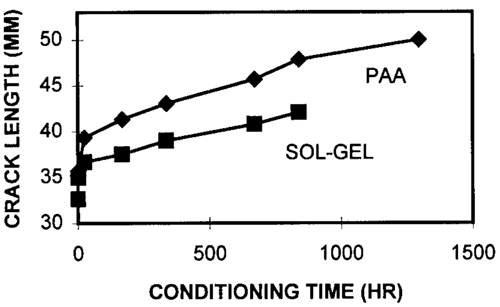


Figure 9: Wedge Test Results for Optimized AL9201

In all tests, specimens deoxidized with the nonchromated product performed as well as those using the chromated deoxidizer. Likewise, specimens primed with 0% VOC, nonchromated XBR 6757 in all cases yielded results as good as those obtained using the chromated, solvent-based BR 127.

6.2.3 Chemat Aluminum Bonding Conclusions

Sol-gel technology has been demonstrated to be a viable prebond aluminum surface preparation option. Shear and peel strength data are equivalent to those obtained using state-of-the-art treatments. Moisture durability, as measured by the wedge test, is nearly equal to that obtained using PAA. Chemat's chemistry is already being commercialized for some nonaerospace applications.

As the Chemat effort continues, further improvement of environmental durability performance will be pursued as will better quality control during solution preparation. Since a need exists for simple on-aircraft prebond surface preparation, much of the future work will be directed at this application. The focus will be to tailor pretreatment steps to on-aircraft usage and reduce the sol-gel drying temperature requirements. In addition, a large part of the effort will focus on optimization of spray application techniques. The aim will be to achieve repeatable, high-performance results with a simple process. Means to verify acceptable on-aircraft coating application must also be developed. The Northrop Grumman work through the SAIC contract focuses on scale-up of the Chemat sol-gel chemistry with heavy emphasis on spray application. The Northrop Grumman work will expand on the Chemat testing and begin to generate the type of data needed to implement sol-gel technology in the aerospace industry.

Ideally, a sol-gel on-aircraft surface preparation process would begin with pretreatment by degreasing/cleaning with an aqueous detergent or low-impact solvent and manual deoxidizing with abrasive pads. The water-based sol-gel solution would be sprayed on the area with a conventional spray gun and allowed to dry, at minimal temperature, with no rinsing required. Priming, if necessary, would be accomplished using a low-VOC, nonchromated product. The sol could potentially be supplied as a concentrate which could be diluted with water and hydrolyzed prior to spraying.

6.3 Boeing Sol-gel for Titanium Bonding

6.3.1 Boeing Titanium Bonding Approach

Sol-gel chemistry was used to deposit coatings on Ti-6Al-4V adherends from a water-based solution of a mixed metal alkoxide containing zirconium isopropoxide and a silane coupling agent. Some of the more critical material and process parameters investigated were chemical composition of the solution, solution age, catalyst, surface pretreatment and activation, application method and post-application drying time. For screening purposes, coatings were applied by immersing titanium panels in solution for 10 minutes, holding at ambient conditions for 15 to 30 minutes, then oven drying for 15 to 30 minutes at 110°C. Dried panels were primed with either Cytec BR 127 adhesive primer or XBR 6757. Bonding of Ti-6Al-4V adherends was accomplished using a 121°C-curing toughened epoxy film adhesive, Cytec FM 73.

Particular attention was given to obtaining the requisite clean, chemically-active metal surface for adhering the deposited coating. In the case of titanium, this is not trivial since titanium produces an extremely passive oxide surface which does not readily hydrolyze to form active metal hydroxides. For this effort, titanium adherends were degreased with an aqueous detergent and then either acid etched or grit blasted with #180 grit alumina followed by detergent cleaning to remove residual grit.

Wedge tests (1.27 mm thick adherends, 60°C and 95% RH conditioning) and lap shear tests (-54°C, 25°C and 82°C) were used for evaluation purposes. Controls were chromic acid anodized and primed with BR 127 adhesive primer. Electron spectroscopy for chemical analysis (ESCA) was used to assess the thickness and composition of deposited coatings.

6.3.2 Boeing Titanium Bonding Results

The optimal solution was a dilute aqueous mixture of tetra-n-propoxyzirconium (TPOZ) and glycidoxytrimethoxysilane (GTMS) coupling agent, with acetic acid as a catalyst. This solution is relatively easy to prepare and apply with reproducible results. Analyses of the applied coatings indicate they are quite thin, 20 to 200 nm, and graded from the titanium substrate (Ti-6Al-4V) surface through a hybrid inorganic/organic mix to the interface with the adhesive primer/adhesive. Dry grit blasting with alumina prior to coating provided the best results for both bond strength and environmental durability.

Lap shear testing at all three temperatures yielded results comparable to those of the chromic acid anodized controls (Figure 10). Failure modes of all specimens were primarily cohesive within the FM 73 adhesive. The performance of sol-gel coatings primed with XBR 6757 was equal to or better than that obtained using BR 127.

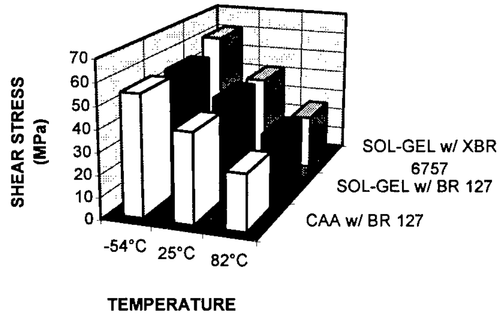


Figure 10: Boeing Sol-gel Lap Shear Test Results

Wedge tests conducted using the sol-gel process compared well with controls from a crack growth perspective. After more than 2000 hours of hot/wet exposure, the crack extension for both processes leveled off at about 2.5 mm (Figure 11). Failure modes, however, were not cohesive in the adhesive as desired.

Initial studies investigating sol-gel application by spraying and drenching show favorable results. There are fundamental differences between the manner of film formation between the immersion and spray techniques; these are being studied. The drenching technique, a hybrid of spraying and immersion, is especially promising. This procedure allows solution to contact substrate surfaces for longer time than the spray process and shorter time than immersion. It takes less skill than spraying and uses much less solution than immersion.

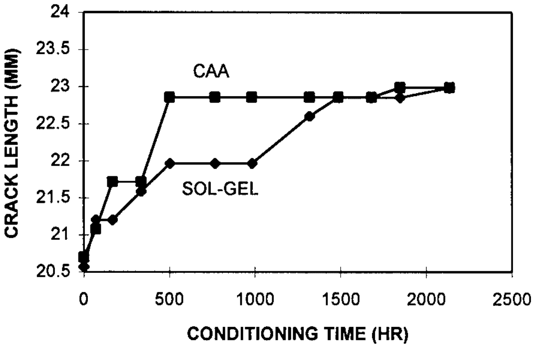


Figure 11: Boeing Wedge Test Results

6.3.3 Boeing Titanium Bonding Conclusions

Strength and moisture durability performance of the best sol-gel coated specimens were essentially equivalent to the state-of-the-art controls for the tests conducted using Ti-6Al-4V adherends and a 121°C-curing toughened epoxy adhesive system. Future work is directed at continued optimization of performance with emphasis on simplifying the process as much as possible. Detailed examination of wedge test failures will be conducted, and further studies on solution age will be undertaken. Also, performance will be evaluated using a lower coating drying temperature than the current 110°C. Pretreatment steps suitable for on-aircraft and in-factory use will be investigated since the grit blast step may not be suitable for all applications. Additional spray and drench coating studies will be conducted. These are a primary area of activity as Boeing scales up their sol-gel process. Scale-up issues include coating of large components and quality control of applied coatings.

Boeing has also been investigating other areas outside of the Wright Laboratory-sponsored work. Testing is being conducted at high temperatures using polyimide adhesives. Cursory evaluation of sol-gel coatings on other titanium alloys is ongoing. Adjustments to solution chemistry will be required to produce optimal results with different alloys and adhesives. Boeing sol-gel chemistry is being evaluated for a number of internal Boeing applications requiring titanium surface preparation for both bonding and painting.

7.0 CONCLUSIONS

Driven by the need to develop environmentally friendly and improved-performance metal surface preparations for the USAF, Wright Laboratory-sponsored research has demonstrated the feasibility of several advanced surface preparation technologies, primarily for adhesive bonding of aluminum and titanium. Multiple approaches have provided bond strengths similar to those attainable with state-of-the-art preparations with moisture durability approaching that of the current processes. The technologies that emerge as the leading candidates will be those that best optimize durability while remaining reasonable to scale-up for depot and/or field use. Sol-gel technology is particularly promising since it appears to be the easiest, most economical process to scale-up and also is providing the best performance to date. Although sol-gel is the only technology evaluated that relies on a wet chemistry approach, with spray application it eliminates or greatly minimizes the concerns with the traditional wet chemistry processes. The best transition opportunities appear to be for titanium bonding and on-aircraft aluminum bonding. One or more of the other candidate technologies could also find application niches within the USAF.

Future work will continue optimization and scale-up efforts. The matured systems will be married with the applicable environmentally friendly cleaning processes for metal surfaces also being investigated by Wright Laboratory. The intent is to transition complete high-performing, environmentally friendly processes to the using community.

8.0 ACKNOWLEDGMENTS

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Phosphoric Sulfuric Acid Anodizing (PSA)

- a Heavy Metal Free Alternative for High Quality Surface Pretreatment of Aluminium

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1. SUMMARY

Chromic Acid Anodizing (CAA) is often applied in the European aircraft industry for pretreatment of Aluminium substrates before coating for corrosion protection and before structural adhesive bonding. By this usage the quality requirements for any alternative process is set with respect to adhesion performance, corrosion protection and fatigue properties, including the compatibility to proven processes and materials.

At DASA the Phosphoric Sulfuric Acid Anodizing process (PSA) was elaborated and verified from laboratory scale up to industrial shop trials. Results reaching from characterizing the oxide morphology by electron microscopy to quality assurance tests on full scale parts are presented.

2. INTRODUCTION

If Aluminium substrates need a high performance corrosion protection Sulfuric Acid Anodizing (SAA) is generally taken as a first choice. Unfortunately this treatment decreases the fatique strength of the substrate, which explains the very limited application in aircraft structures. Instead European aircraft industry mostly utilizes a CAA process developed by Bengough and Stuart in the twenties of this century. Besides for surface protection this CAA process provides, in contrary to the SAA treatment, also a good basis for structural bonding, which is proven by the extremely good in service records; e. g. the Fokker F 27 aircrafts used this technology since 1955. The need to replace CAA derives from the fact that Chromium-VI-compounds are hazardous materials; especially they can cause lungs cancer when they are inhaled. The challenge of today is to develop a less hazardous process, which should find a similar universal application as the CAA treatment.

3. PROCESS DEVELOPMENT

Surface protection and adhesive bonding rely on similar material and process properties like adhesion and corrosion stability. The requirements to be fulfilled are generally more stringent and ambitious in the case of adhesive bonding. This means that if one suceeds to develop a suitable pretreatment process for adhesive bonding the suitability for protective coating with paints is often already given. Therefore we developed an alternative process versus the key properties for adhesive bonding and checked this afterwards against additional requirements from surface protection and fatique.
The today used standard surface treatment for adhesive bonding of Al alloys consists out of several steps (Table 1). Generally the treatment starts with a degreasing in a weak alkaline bath (pH 9) followed by a strong alkaline etch (pH > 11) in order to remove persistently adhering oxides and rolled-in debris. The following treatment in Chromic Sulfuric Acid (CSA) removes

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about another 3 μm of metal as well as the alkaline etch. Finally the substrates are anodized in Chromic acid, which creates on pure Aluminium an oxide layer of 2.5 to 4 μm thickness. Between all this bathes and at the end a thoroughly rinsing with deionized water is performed. In order to avoid any sealing reaction of the oxid the final drying takes place at temperatures not higher than 50°C.

Most important is the porous morphology and mechanical stability of the oxide. The porosity is regarded to be responsible for the good adhesion properties, because primers can penetrate this texture and form a polymer in the pores, thus establishing the intimate contact in the organic/inorganic interface.

The mechanical stability is required for easy handling characteristics during production in the shop. This is e. g. not given with the competitive Phosphoric Acid Anodizing (PAA) process, which creates thinner and even more porous oxide with good bondability properties. On the other hand the oxide built up by the standard SAA process is less porous and therefore not useable for bonding purposes.

The main idea of our developement was to find a process, which creates an oxide layer most similar to that of the CAA process. Recognizing that the morpholoy characteristics of such an oxide is in-between the thicker non porous SAA and the thinner very open texture of the PAA-oxide, we looked at the oxides developed by anodizing in mixtures of Phosphoric and Sulfuric acid. Already the first tests were rather promising. Process parameter studies were performed in order to find an optimum performance. The control tests consisted, besides Scanning Electron Microscope (SEM) investigations, out of wedge tests and floating roller peel tests in dry and wet condition.

The final process parameters were selected also under the aspect to be most forgiving and easy to handle in the production.

These parameters are:

Electrolyte: 100 ± 10 g/l H_3PO_4
100 ± 10 g/l H_2SO_4
Temperature: 27 ± 2°C
Current density: 0,5 - 1,0 A/dm^2
Voltage: 18 ± 2 V
Time: 3 min to 18 V
+ 15 min at 18 V

This process creates an oxide of about 2 μm thickness on Al 2024 clad with a porosity and mechanical stability similar to the CAA oxide (Table 2, Fig. 1).

4. ADHESIVE BONDING

In order to test the suitability of the PSA process for structural bonding the pretreated substrates were evaluated with typical 120°C curing Epoxide (EP) adhesive systems.

These systems were the BR 127 primer (Cytec) in combination with the film adhesives FM 73 M.06 (Cytec) and AF 163-2 K.06 (3M). Some tests were also additionally perform with the system BR 127 plus EA 9628 NW.06 (Hysol Dexter) and the 160°C curing phenol system BSL 101/Redux 775 L&P (Ciba).

The results are given in table 3, indicating a completely satisfactory behaviour. This is especially true for the bondline corrosion test in which floating roller peel specimens are exposed to standard salt spray conditions for up to 300 days. After peeling the corroded area is evaluated. The result are completely in line with the scatter band known from CAA and PAA treated specimens.

5. FATIGUE TESTING

Microscopically technical surfaces are not geometrically plain. Due to the changes of the surficial geometry surface treatment processes influence the fatique properties. This effect can be quite servere, if e. g. selective etching at grain bondarys happens. Also the stiffness of surface layers (e. g. oxide) may influence the properties.

Most important is the question, wether the PSA treatment leads to any decrease of fatique strength in comparison to the CAA process. The selected specimens for testing were on one hand a treated and primed unnotched simple dogbone sample (stress concentration factor $K_t = 1$/Fig. 2) and on the other hand a schematic part representing the actual design of bonded longitudinal lap joints of Airbus wide body aircrafts (Fig. 3). The experimental behaviour of this design with bonded doublers equals to an K_t of about 3,6 and failures take place in the first or third rivet row.

The results are given in Fig. 4 and 5, indicating that there is no substantial difference in the effect of both surface treatment. In the case of the unnotched specimens there is a slight tendency in favour of the PSA treatment. It would be interesting, wether this tendency is realistic. Therefore we currently run tests with specimens notched by an open bore hole ($K_t = 2,5$).

6. SURFACE AND CORROSION PROTECTION

The CAA process is widely applied in corrosion critical areas of aircrafts providing together with a paint system a remarkable protection. For this purpose a replacement process should be applicable to a wide range of Al alloys used in the structure. Such a treatment therefore has to be compatible with the standard coating systems, i.e. it should adhere properly and the protection quality has to be verified.

Table 4 shows the results gained by the PSA treatment of representative Al alloys. Similar to CAA the oxide morphology gets coarser with the amount of alloying elements (Rating see Fig. 6). Also the thickness is reduced. This effect is minimized with Si-containing 6000 series alloys. On all surfaces the standard Airbus paint system consisting out of a Chromate-pigmented EP primer and a Polyureathane (PU) top coat (both RT curing), adhere well with satisfying stability against exposure to water.

Also the corrosion protection reached (Table 5) is of the same quality compared to CAA treated specimens.

The alternate immersion test was perform according to EN 3212 with another specimen design (Fig. 7) in order to test also crevice corrosion effects. Due to the complex appearance also in this case a rating system was applied (Fig. 8).

7. SHOP TRIALS

Before applying the PSA treatment in series production extensive shop trial have to be performed. First target is to verify wether the parameters of the lab tests can be transfered to a full size equipment.

Secondly numerous combinations of the parameters within their allowed scatter band have been tested and thirdly for additional practical aspects final solutions have to be found.

Main addition, from an economic point of view, may be the need to run a recycling facility in order to keep the content of dissolved Al within the desired scatter band of 5 ± 2 g/l. By running a device based on acid retarding technology, we up till now could not determine the tank life limit of the electrolyte. The process turned out to be rather insensitive at a cathode/anode relation from 1:2 to 1:8. As cathode material only few Mo alloyed CRES qualities are suited, otherwise an etching will take place. Nevertheless treated parts can remain in the electrolyte for up to 3 minutes without being significantly damaged. The throwing power of the PSA process is at least as good as with the CAA treatment, but the PSA oxide could not be sealed by a hot water treatment. In this case only white powdery layers were generated.

Also investigated was the ability to bond other alloys than 2024 clad. Sucessfully tested were 2024 bare, 6061 and 7075 material.

8. CONCLUSIONS

The PSA process can be used as a less hazardous replacement for the well proven CAA treatment. This includes the universal applicability for structural adhesive bonding and surface protection. Due to shorter duration and more simple process parameters, economic advantages are determined but specific requirements have to be fufilled (recycling of electrolyte). The generated oxide cannot be sealed with hot water, but such a process is currently not applied in the structure of Airbus aircrafts. Successful shop trials put DASA Airbus in the position to be able to apply this process in series production. A decision to introduce this process will be taken together with the other Airbus partners.

Table 1: Surface treatments for adhesive bonding

Process/ Step	CAA	PAA	PSA
1	Alkaline degreasing	Alkaline degreasing	Alkaline degreasing
2	Alkaline etch	---	Alkaline etch
3	CSA	CSA/FPL[1)]	NAP[2)]
4	CAA	PAA	PSA

[1)] FPL = Forest Product Laboratories
[2)] NAP = Nitric Acid Pickling

Table 2: Main process parameters of anodizing treatments

Process	Oxide thickness on Al 2024 clad [μm]	Temperature [°C]	Voltage program
SAA	10 - 15	18 ± 2	5 min to 15 V + 30 min at 15 V
CAA	1,7 - 3,4	40 ± 2	10 min to 40 V + 20 min at 40 V + 5 min to 50 V + 5 min at 50 V
PAA	0,5 - 0,9	24 ± 2	3 min to 15 V + 15 min at 15 V
PSA	1,7 - 2,3	27 ± 2	3 min to 18 V + 15 min at 18 V

Table 3: **Adhesive bonding test results of PSA treated Al 2024 clad substrates**

Test	Specification	Adhesive System	Results			
			Initial crack[mm]	Failure mode	Propagation [mm]	Failure mode
Wedge test	DIN 65448	BR 127/AF 163-2 BR 127/FM 73	28,4 30,8	C* C	2,7 2,5	C C
Floating roller peel test	EN 2243-2		Peel strength, dry [N/25 mm]		Peel strength, wet [N/25 mm]	
		BR 127/AF 163-2 BR 127/FM 73	257 263	C C	202 264	C C
Lap shear test	EN 2243-1		Exposure	Test temperature [°C]	Bond strength [N/mm²]	
		BR 127/AF 163-2	- - - 2000 h, 70°C, 85 %r.F. 2000 h, 70°C H_2O	- 55 RT + 70 RT RT	49,8 43,2 33,2 41,9 30,5	C C C C C
Bondline corrosion test	EN 2243-5, AITM 5-0009		Corroded area after salt spray exposure [%]			
			45 90	180	300 [days]	
		BR 127/AF 163-2	0 1	6	9	C
		BR 127/FM 73	0 4	5	10	C
		BR 127/EA 9628	0 1	2	6	C
		BSL 101/R 775	0 2	7	11	C

* C = Cohesive failure

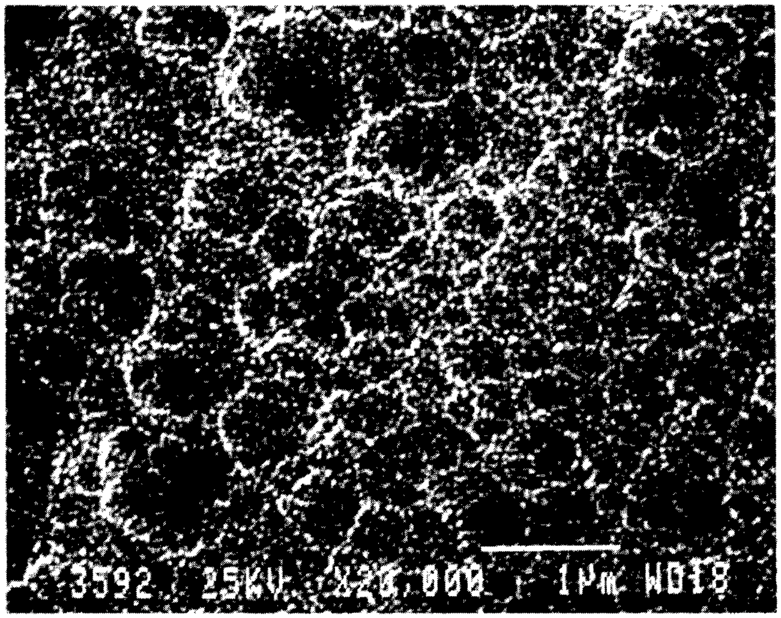
Table 4: **Oxide properties and adhesion of paint, PSA treated substrates**

Al alloy	Oxide		Impact Test (ISO 6772)	Adhesion test (ISO 2409) [Gt]	
	Morphology [grade]	Thickness [μm]	[grade]	dry	168 h H_2O/40°C
2024 clad	1 - 2	1,7 - 3,4	1	0	1
2024	3 - 4	0,5 - 1,0	1	0	1
5052	2	1,5	-	-	-
6013	2 - 3	1,9	-	-	-
6061	3	1,7 - 2,6	1	0	1
8090	3 - 4	1,2 - 1,8	-	-	-

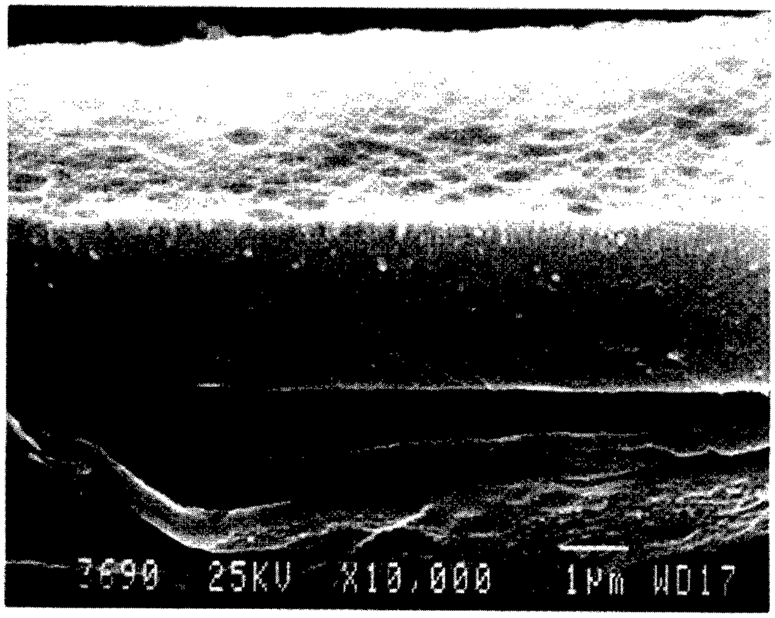
Table 5: **Corrosion test results of PSA treated substrates**

Al alloy	Filiform corrosion (EN 3665) paint undercutting [mm]	Alternate immersion (EN 3212) [grade]	Salt spray (ISO 7253) paint undercutting [mm]
2024 clad	< 1	3	< 2
2024	< 1	3	< 1
6061	≤ 2	1	0
7075	≈ 1	2	0

Fig. 1: SEM images of PSA treated 2024 clad substrates

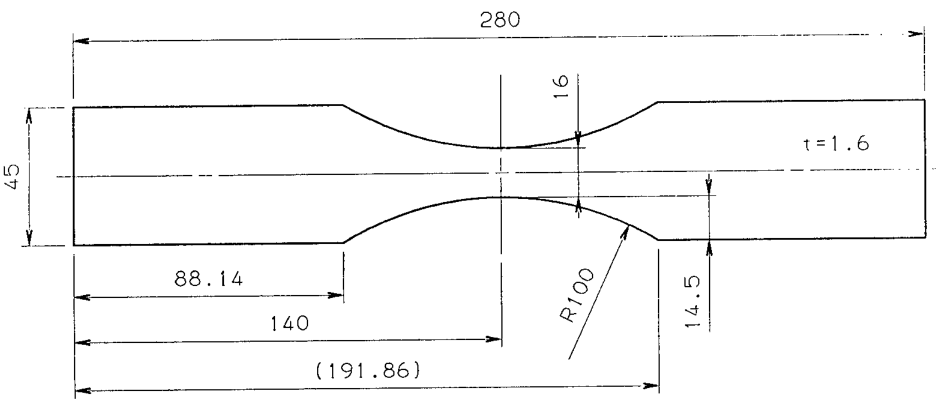


a) Surface image



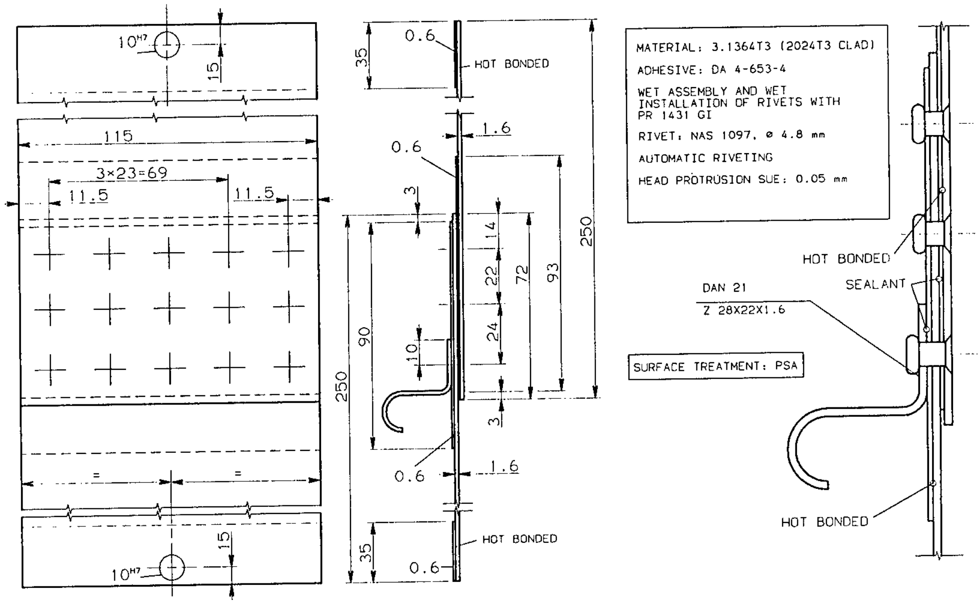
b) Broken sample

Fig. 2: Unnotched specimen for fatigue testing



MATERIAL: 3.1364T3 (2024T3 CLAD)
SURFACE TREATMENT: PSA

Fig. 3: Lap joint specimen for fatigue testing



MATERIAL: 3.1364T3 (2024T3 CLAD)
ADHESIVE: DA 4-653-4
WET ASSEMBLY AND WET INSTALLATION OF RIVETS WITH PR 1431 GI
RIVET: NAS 1097, ⌀ 4.8 mm
AUTOMATIC RIVETING
HEAD PROTRUSION SUE: 0.05 mm

SURFACE TREATMENT: PSA

Fig. 4: Fatigue strength, unnotched specimen, comparison between CAA and PSA

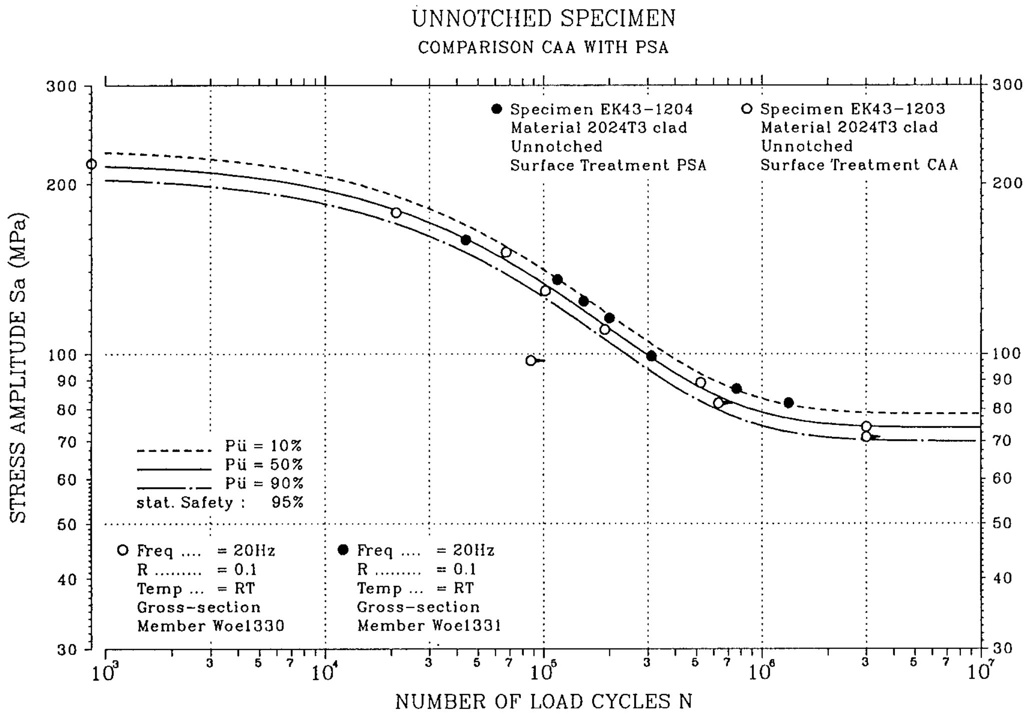


Fig. 5: Fatigue strength, lap joint specimen, comparison between CAA and PSA

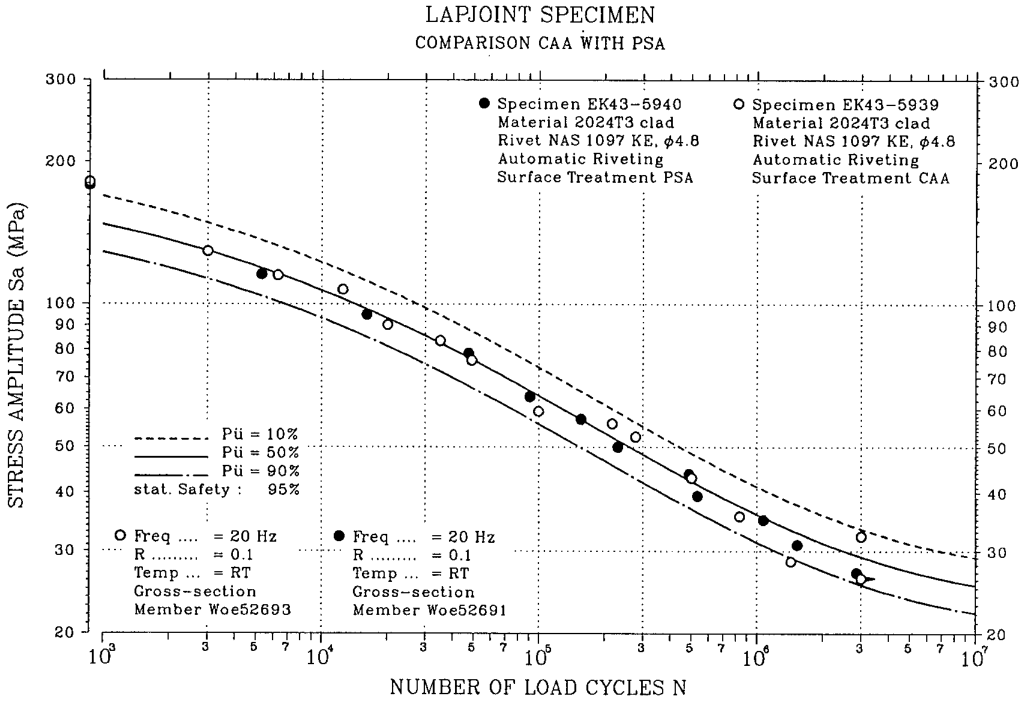


Fig. 6: Rating standards for oxide morphology (SEM/Magnification 20.000 X)

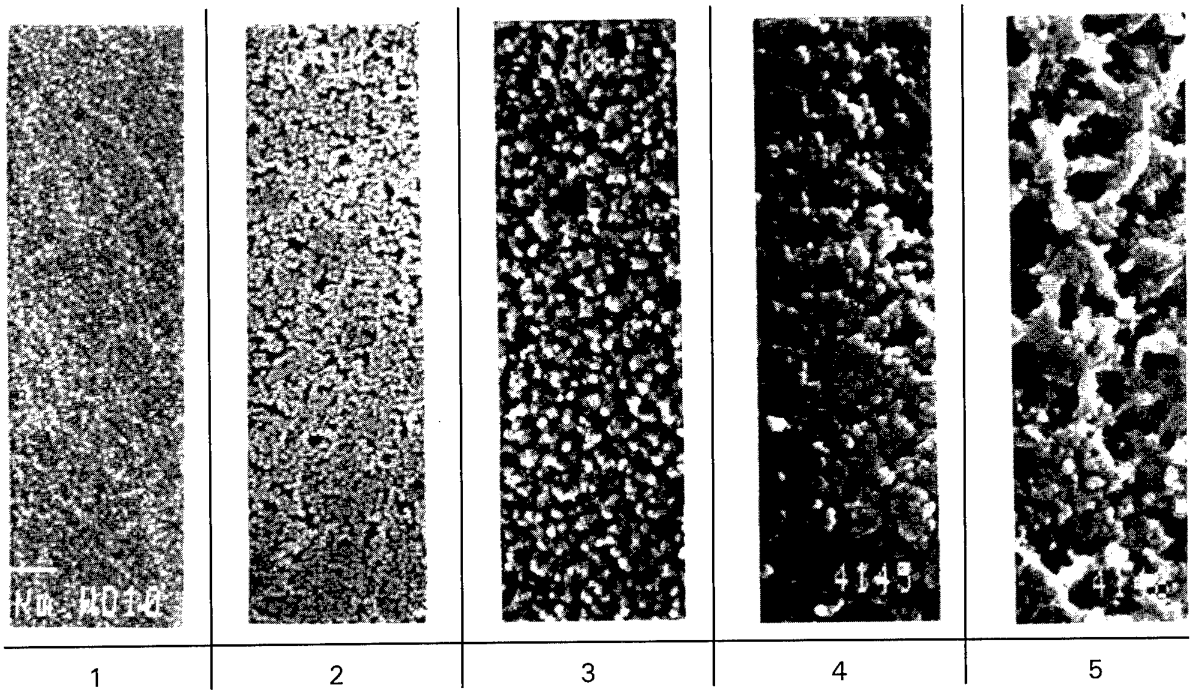


Fig. 7: Test specimen for crevice corrosion test

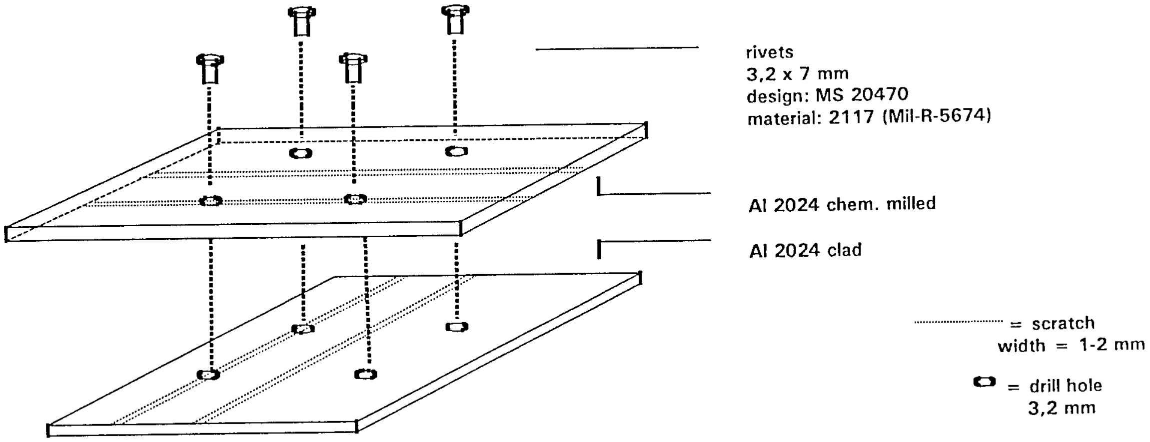
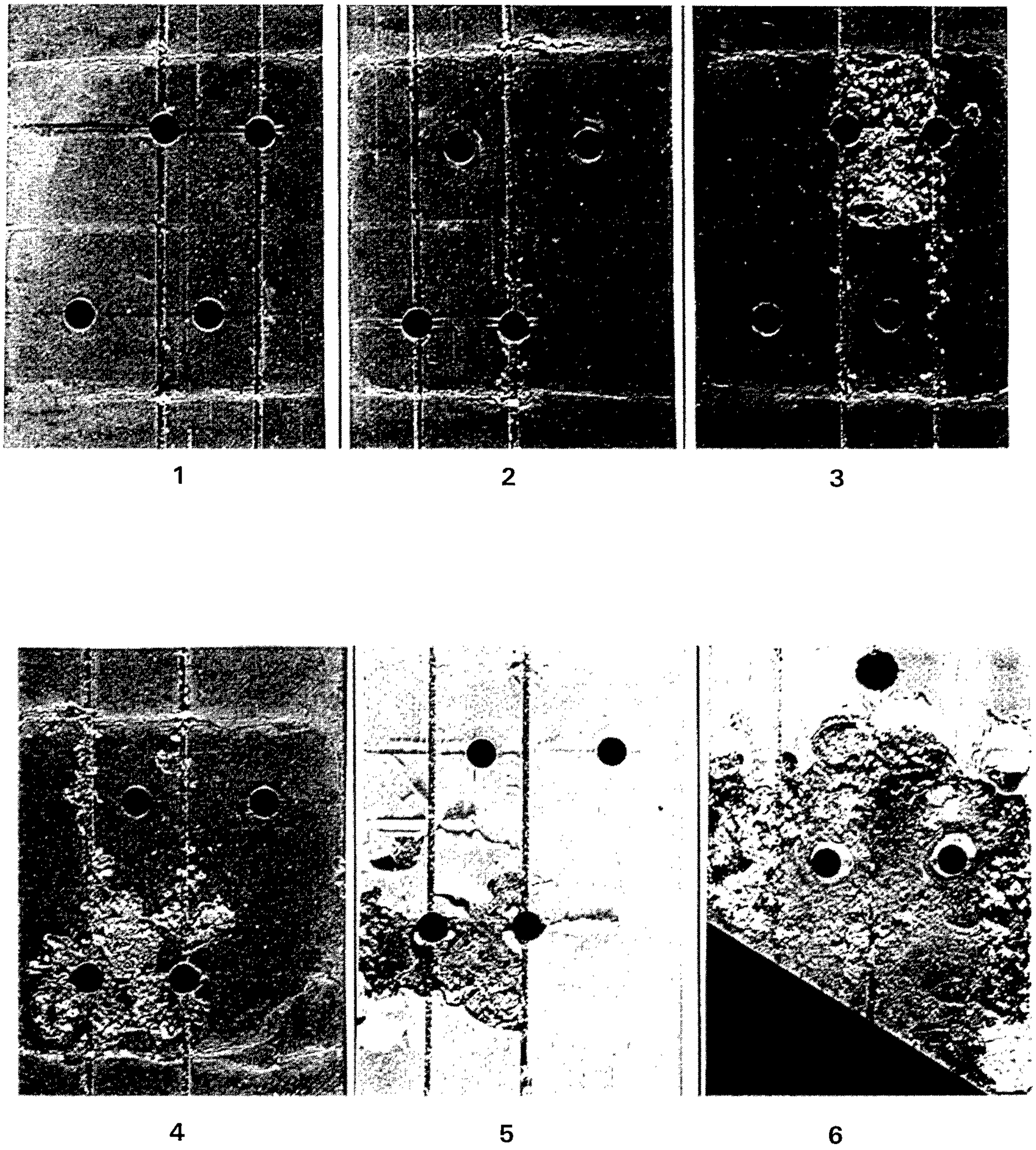


Fig. 8: Rating standards for crevice corrosion test



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ENVIRONMENTALLY BENIGN ION BEAM SURFACE TREATMENTS

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1. SUMMARY

Selected usage of environmentally benign ion beam processes, namely ion implantation and ion beam assisted deposition (IBAD), are discussed in terms of their technical merits, their current status, and the various factors governing their acceptance within the U.S. Department of Defense (DoD) user community.

2. INTRODUCTION

The use of energetic ion beams for beneficially modifying the surface sensitive properties of critical military materiel has been pursued within DoD now for almost two decades. In that time, numerous examples of improved material properties including increased wear-, fatigue- ,corrosion- and oxidation-resistance have been demonstrated in the laboratory. High dose ion implantation was the primary process explored in these early studies of ion beam surface modification. Implantation has been demonstrated to be technically suitable for the treatment of high precision, high cost components. This includes improvements to extend the service lifetime of aerospace bearings (U.S. Navy) and specific metal cutting tools (U.S. Army). More recently, the need to comply with rigid environmental laws concerning electroplating operations common to DoD manufacturing and rework facilities have prompted a re-evaluation of some ion beam based processes as niche substitute processes to supplement or replace Cd/Cr electroplating for specific applications.

The hybrid combination of ion beam bombardment in conjunction with physical vapor deposition, commonly termed Ion Beam Assisted Deposition (IBAD) has emerged as a powerful surface coating technique. It combines many of the positive attributes of ion beam and conventional coating technologies, such as high density, superior adherence and the ability to produce arbitrarily thick coatings. An important feature of IBAD technology is its frequently demonstrated ability to control many generic properties of coatings such as morphology, adherence, grain size, residual stress and stoichiometry. Current applications of ion beam processing for the production of wear-, corrosion-, and fatigue-resistant surfaces are presented here with an emphasis on those pertaining to U.S. DoD needs.

The development of the IBAD process has resulted in a number of DoD applications, ranging from robust optical coatings to surface protective coatings for wear, corrosion and fatigue improvements. Recent DoD thrusts include environmental programs exploring these benign, dry, ion beam techniques for supplanting the wet electroplating processes for Cr and Cd that are under increasing scrutiny at DoD installations for creating hazardous working conditions.

3. ION IMPLANTATION FOR WEAR AND CORROSION RESISTANCE

Ion implantation (Figure 1) appears to be an attractive technique for treating critical components by i) the stabilization of microstructure, preventing a change in wear mode, ii) the stimulation of transformations to a wear resistant mode, or iii) the inducing of chemical passivity to reduce or prevent a corrosive wear mode. Components benefiting from nitrogen ion implantation for improving wear resistance of tool steel alloys include: plastic injection molding tools, metal rolls, piercing tools, forming tools, and other components used in mild-wear applications. Successful utilization of nitrogen implantation requires relatively low tool surface operating temperatures (< 100 ^{0}C) since the nitrogen/defect structures attributed to improvement of wear resistance are not stable at high temperatures. The implantation doses typically used range from 2 to 6 x 10^{17} ions/cm^2 at energies of 50-100 keV.

Ion implantation of metals is becoming more routine on a commercial scale, mainly with nitrogen implantation as an anti-wear treatment of high-value critical components. The primary commercial use to date is for the anti-wear treatment of surgical prostheses such as hips and knees. In use they are in articulating contact against a mating ultra-high molecular weight polyethylene cup and wear is a prime concern for the longevity of the (surgical) prosthesis [1]. Presently more than 70,000 knee, hip and other joint prostheses are being treated each year in the U.S. Implantation for such medical devices is attractive since there is no concern regarding delamination, as there is for sharp interfaces, and nitrogen is considered benign in the human body.

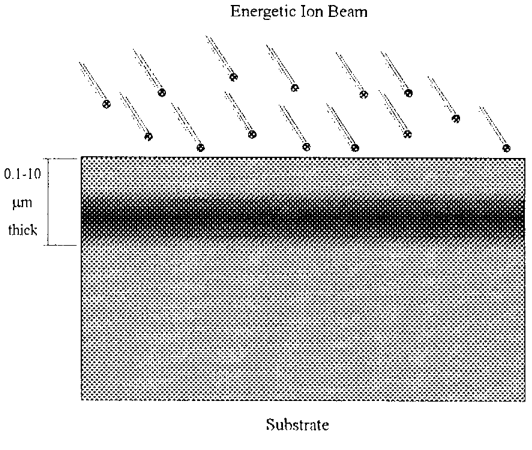

FIG. 1 Schematic of the ion implantation process, showing the injection of atomic species into the near-surface region of a material.

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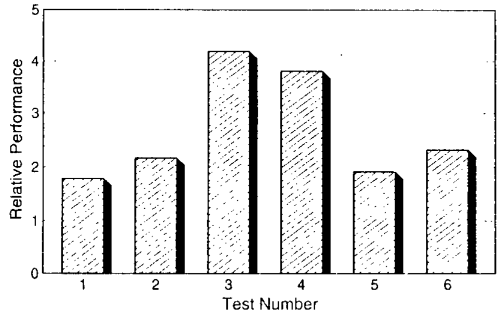

FIG. 2 Relative performance of implanted cutting tools; nitrogen implanted at U.S. Army Research Lab and tested at Corpus Christi Army Depot. From Culbertson et al. [2]

The gap between laboratory wear testing and industrial application trials is extremely difficult to bridge, since there is often little or no control over testing in the industrial environment. Despite these limitations, blind tests of nitrogen-implanted machine tools have been performed involving a collaborative effort between researchers at the Army Research Lab and personnel at Corpus Christi Army Depot (CCAD) [2]. The tests included tool steel taps, dies, punches, and TiN coated WC cutting inserts and were carried out in production machine shops at CCAD where U.S. Army helicopters are refurbished. The tests were performed with computer controlled machines, using specific parameters for feed rates and speeds. Both untreated and nitrogen-implanted tools were tested under given test conditions, without the operators' knowledge of tool treatment, to prevent subjective bias. Figure 2 shows the relative performance of type M4 steel taps and TiN-coated WC cutting inserts.

Tests 1 to 3 involved M4 alloy tools used to tap holes in: AISI 4340 heat treated steel plate, weld seams of aircraft components, and AISI 4130 round stock, respectively. Tests 4 to 6 involved TiN coated WC inserts tools for light (lubricated) machining of 4130 and 321 SS stock. The implanted tools showed lifetime improvements ranging from 1.5X to 4X and no unimplanted tool demonstrated better performance than an implanted tool. Improvements were also observed for implanted tool dies and punches. As a result of these tests, an additional 10,000 TiN coated tool inserts were N-implanted and placed back into the tool supply room for routine use and further evaluation at CCAD.

On the basis of continued reports of lifetime improvements of these tools by CCAD machine shop personnel, the Army contracted for a dedicated nitrogen ion implanter at CCAD for in-house tool treatment. This implanter, installed in 1994 [3], is shown schematically in Fig. 3. This high-current (25-50 mA) implanter is a non-mass-analyzed machine for nitrogen implantation and can produce beam energies from 20 to 100 keV. A multi-aperture bucket type ion source is employed to cover a 75 cm diameter target platen capable of holding a 70 kg load of parts extending up to 60 cm above the platen surface. The platen can be continuously rotated, and tilted with respect to the beam over a 90 degree range, adjustable from outside the vacuum chamber.

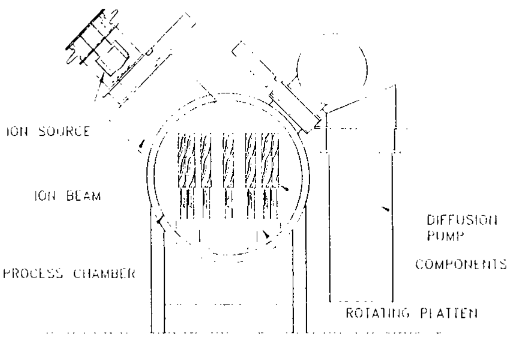

FIG. 3 Schematic of high current nitrogen ion implanter installed at Corpus Christi Army Depot for tool treatment. [3]

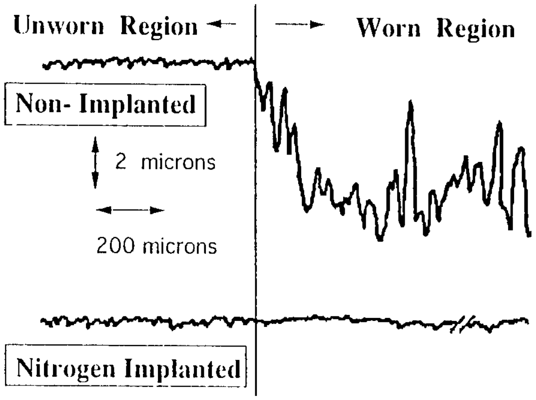

FIG. 4 Nitrogen implantation considerably extends the lifetimes of electroplated Cr, thereby reducing the frequency of rework electroplating normally done for reuseable parts subject to wear. Test shown is from pin-on-disk wear test.

This Model 20N implanter is fully computer controlled, allowing either automatic or manual operation and has run at CCAD since installation with a minimum of maintenance or downtime.

At the present time, the operators of the CCAD implanter are investigating other uses of nitrogen implantation at their facility, including the ion beam treatment of helicopter parts coated with electroplated chromium. Laboratory studies (Figure 4) have shown that this treatment can dramatically reduce the wear rate of the Cr coating, and so reduce the frequency of rework maintenance and the overall use of the electroplating process.

In addition to this directed beam ion implantation, the plasma source ion implantation (PSII) technique [4] offers an alternative means of effectively implanting targets having complex shapes with ions of gaseous species. This method involves the pulsed (high negative voltage) biasing of the substrate in a plasma to attract and implant positive ions within the plasma. This method overcomes the intrinsic line-of-sight limitation of ordinary direct-beam ion implantation by simultaneous bombardment of all surfaces at normal incidence angles. This geometrical feature improves the inherent sputter-limited retained dosage that decreases sharply at non-normal incidence angles in direct-beam ion implantation.

In addition to nitrogen implantation, a number of other ion species, including Ti plus C and Ta have proven effective in reducing wear. Ion implantation of these reactive ions has been actively studied within DoD [5,6] for application to martensitic bearing alloys which are not improved by nitrogen implantation [7]. Ion implantation with such metallic species is frequently desired and is expected to attain wider use commercially with the availability of high current metal vapor vacuum arc (MEVVA) ion sources [8].

One particularly promising demonstration of metal ion implantation has been for the corrosion protection of aerospace bearings, typically martensitic alloys such as AISI 52100 or M50. Rolling element bearings of these common bearing alloys suffer from localized corrosion (from Cl^- ion contaminants in the lubricant) which is prevalent in areas of contact between elements (e.g., rollers and races). The improvement of corrosion resistance of bearings was the focus of a DoD Manufacturing Technology program operated through the Naval Research Laboratory (1983-1986) [9]. This program was performed on contract [10], and demonstrated the technical feasibility and cost benefits of implantation treatment of several types of rolling element bearings. The implant parameters used were based on research performed at NRL on flat coupons of 52100 and M50 bearing alloys. Chromium and Cr plus P ions were the candidate species chosen to improve the pitting corrosion resistance of these low Cr content martensitic alloys. This program resulted in a considerable amount of commercial interest. Related work showed the efficacy of treating the 440C bearing alloy used in the NASA space shuttle oxygen fuel pump to reduce the high level of oxidative wear found in this aggressive environment [11]. This area is presently under review as a possible technology insertion project for the North American Technology and Industrial Base Organization (NATIBO) [12].

4. ION BEAM ASSISTED DEPOSITION

Process Description and Ion Beam Effects

Several aspects of film growth beneficially influenced by ion bombardment during thin film deposition include control and/or improvement of: i) adhesion, ii) nucleation or nucleation density, iii) internal stress, iv) morphology, v) density, vi) composition, and vii) the potential for low temperature deposition on temperature sensitive substrates. IBAD processing allows the attainment of thicker alloyed regions than can be formed by direct ion implantation, and also incorporates desirable features attributable to ion beams, such as superior adhesion due to precleaning and ion mixing during the initial stages of deposition.

Figure 5 shows a simplified schematic of the IBAD process incorporating physical vapor deposition with energetic ion bombardment. In most IBAD systems, the neutral species is normally delivered via physical vapor deposition using either sputter deposition or evaporation. The ion species is typically provided by a low energy (0.2-2 keV) broad-beam gridded ion source producing beam currents up to 1-2 mA/cm^2 (ca. 10^{16} ions/sec/cm^2).

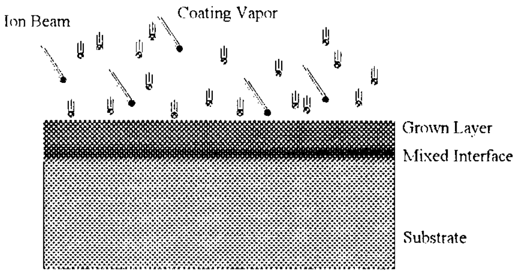

FIG. 5 Schematic Diagram of Ion Beam Assisted Deposition (IBAD) Process.

IBAD processing can be grouped into three different categories:

1) Nonreactive IBAD-where the main purpose of the ions, typically inert gas ions (Ar^+), is to influence the nucleation and growth of deposited elemental or compound coatings.

2) Reactive IBAD-where the purpose of the ion beam is to both influence film growth as well as to provide atoms for the growth of a chemical compound (e.g., Si or Ti deposition with nitrogen ion bombardment to produce Si_3N_4, or TiN).

3) A variation of this reactive technique is to provide atoms in the form of backfilled molecular gas (e.g., N_2 or O_2) while incorporating (i.e., activating) these atoms into the growing film by bombardment with energetic ions (inert or reactive).

This last variation can sometimes be used to create stoichiometric compounds if (and only if) the evaporant is sufficiently reactive [13,14]. It can also be used to make up for the loss of a constituent element (e.g., oxygen) when evaporating compounds (e.g., Al_2O_3 or SiO_2) which tend to decompose at high temperature giving a metal-rich coating in the absence of such an O_2 backfill.

Adhesion

The adhesion of thin films on substrates depends on a variety of factors including: i) interface chemistry, ii) film stress, iii) differential thermal expansion, iv) contaminant levels at the interface, and v) surface morphology. This area has been studied extensively by Baglin [15]. *In situ* vacuum ion beam cleaning offers an excellent means of preparing substrates for coating by removing contaminant layers (e.g., adsorbed water, hydrocarbons, oxides, etc.) and sometimes by selective removal of surface material (texturing) to leave a favorable high bonding surface for either chemical or morphology (texture) influenced adhesion.

The use of high energy ions to mix or "stitch" a metallization onto a substrate has been realized for many years. This technique requires an accelerator capable of producing ions of high enough energy to completely penetrate the film to be stitched, however; this limits practical film thickness to tens to hundreds of nanometers for medium mass ions of energies up to 200 keV.

Low energy ions used in conventional IBAD processing (ion energies typically less than 2 keV) also appear to be effective for enhancing adhesion. Baglin and colleagues have conducted many adhesion studies of Cu on Al_2O_3 by using high energy ions of He and Ne to stitch their films [15]. They found that the improved adhesion could not simply be attributed to a physical intermixing of Cu and Al_2O_3. They were also able to achieve similar results at low ion energies by pre-exposing the Al_2O_3 to a low energy argon beam (500 eV, 50 $\mu A/cm^2$) and then depositing the copper [16].

Densification

The common occurrence of (columnar) microstructural features in low temperature coatings is well documented [17,18]. The use of energetic ion bombardment during low temperature deposition offers a means of essentially eliminating this mode of microstructural evolution. K-H Müller [19] has theoretically modeled the evolution of a two-dimensional lattice under ion bombardment. Using two dimensional molecular dynamics calculations, he shows the microstructure evolving from a highly porous to a highly compact structure as a function of temperature and ion energies. Müller's calculations demonstrated that bombardment of growing films with energetic ions removes overhanging atoms, induces surface movement of atoms, produces local heating, and collapses voids.

Stress

Stress in thin films can be related to microstructure, as well as to incorporated impurities. Typically, thin films with high void fractions are in a state of residual tensile stress. When deposited with the aid of an ion beam, the microstructure initially densifies allowing even higher attractive interactions between adjacent atoms which can further increase the tensile stress to a maximum. As the ratio of incident ions to arriving neutral species increases, the lattice density increases further and the stress may be driven towards a state of compressive stress by the forcible injection of beam atoms or by lattice disorder caused by the energetic beam [20].

IBAD Wear- and Corrosion-Resistant Coatings

IBAD allows processing at significantly lower temperatures than conventional coating processes (e.g., CVD, PCVD). The ion energy can activate chemical and diffusional processes instead of reliance on high temperature activated kinetics normally required for producing tribological coatings such as Al_2O_3, TiN, or TiC. Several researchers have studied the parameters required to obtain hard wear-resistant IBAD coatings (e.g., TiN) by utilizing either i) nitrogen bombardment, or ii) an argon beam to stimulate incorporation of ambient nitrogen gas with a reactive species (e.g., Ti) [21,22].

Conventional corrosion resistant coatings can suffer from poor adhesion and localized defects (i.e., pores) which allow delamination or localized corrosion. Ion implantation can often overcome the problems associated with adhesion and porosity and is also capable of producing unique surface alloys, including amorphous surface alloys, unattainable by any other ambient temperature alloying technique. Implantation by itself, however, is restricted from many commercial applications because of the limited thickness of the alloyed layer that it can produce. IBAD processing surmounts some of these limitations by achieving both excellent adhesion and arbitrary thickness.

Silicon-Containing 'Diamond-Like Carbon' Coatings

Hard amorphous carbon films, such as diamond-like carbon (DLC), appear promising for tribological and corrosion applications because of their high hardness, low friction, and chemical inertness. Conventional DLC and MoS_2 films have unlubricated friction coefficients as low as 0.01 in dry gases, but the friction coefficient of both of these solid lubricant materials increases considerably with increasing humidity (as high as 0.10 to 0.20 with 10% relative humidity) [23,24]. Recently, researchers have examined Si-containing amorphous DLC films, and found that they exhibit extremely low friction coefficients (< 0.05) in both dry and humid atmospheres [25].

Goode et al [26], used a polyphenyl ether liquid precursor and a large area ion beam from a bucket type ion source to produce Si-DLC. Carosella [27] used 150 keV Ti^+ ions and pentaphenyl-trimethyl-trisiloxane (Type 705 Dow-Corning silicone oil) as a precursor. Jones et al. [28] used pentamethyl trisiloxane and polyphenyl ether as a precursor and a 50 keV nitrogen ion beam. Hioki et al [29] combined vapor deposition of pentaphenyl-trimethyl-trisiloxane and simultaneous energetic ions of 1.5 MeV N^+ and 200 keV Ti^+. In each case the films showed coefficients of friction lower than those of conventional DLC films in both dry and humid atmospheres.

Si-DLC coatings have been prepared by an IBAD process at the U.S. Army Research Laboratory [30,31,32]. They were deposited on room temperature Si and steel substrates using energetic ions of Ar^+ to bombard the deposited vapors of tetraphenyl-tetramethyl-trisiloxane (Type 704 Dow-Corning silicone oil) supplied from a heated reservoir. The oil temperature was varied to change the oil arrival rate at the substrate and the growing film surface was continuously bombarded by a slowly oscillating (1 Hz) ribbon (2x20 cm) Ar^+ beam at 40 keV. The peak ion current density in the ribbon beam was varied from 20 to 300 $\mu A/cm^2$.

The average composition of the coatings was $C_{67}Si_9O_6H_{15}Ar_3$, as measured by 2 MeV RBS. The relative amounts of C, Si, and O are almost identical to those found in the precursor. The main effect of the ion beam appeared to be to drive off hydrogen and to add trace amounts of Ar. The fact that no oxygen was lost implies that the siloxane "backbone" of the oil molecule was not destroyed by ion irradiation. The film composition was insensitive to deposition parameters with the amount of each element varying by only a few atomic percent. These films appeared to be featureless when examined under an ordinary optical microscope (1000X), but surface roughness features less than 10 nm in size became clear when the films were examined with a photon tunneling microscope. Transmission electron diffraction revealed that the films were amorphous.

Figure 6 summarizes the microhardness, friction and wear results of the Si-DLC coatings, normalized to the baseline properties of M50 bearing steel (a candidate to be coated with Si-DLC). The combination of high hardness (Knoop microhardness from 1000 to 2100 at 15 g load), along with very low friction (unlubricated coefficients of friction as low as 0.03 against a steel pin, comparable to liquid lubricated systems) led to an extremely low wear rate in pin-on-disc

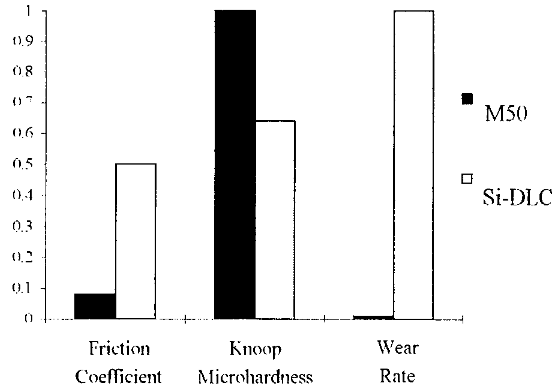

FIG. 6 Relative friction coefficient, Knoop microhardness, and wear rate of Si-DLC films compared to bare M50 steel.

tribological tests. The adherence of the coatings to the silicon and steel substrates was outstanding, as judged by automated scratch tests. Photomicrographs of the wear tracks of the films showed little or no delamination or other film degradation such as cracking. Wear tracks of all of the coatings were barely visible after pin-on-disc testing, including the coatings with the highest friction coefficients.

These films are being examined in greater detail, using a variety of spectroscopic and mechanical tools, to identify the mechanisms of coating formation, oxidation resistance, adhesion, and wear performance. In addition, a process scale-up study has been initiated to allow the uniform coating of large area (50 cm diameter or greater) substrates. These studies may lead to the use of Si-DLC as a protective layer on rolling element bearing materials.

Improved Bearing Materials : Rolling Contact Fatigue Corrosion Resistance

Middleton et al [33] conducted a comprehensive program to improve lifetime performance of gear and bearing materials used within the U.S. Army. This endeavor, combining improved substrate steels with endurance enhancing coatings, was aimed toward development of advanced ceramic/steel hybrid bearings. The program consisted of a two-pronged effort aimed at i) utilization of emerging materials for advanced systems development to meet increased operational requirements, and ii) upgrade improvements of materials used in currently fielded vehicles. In the present economy, emphasis on thrust ii) takes precedence. The replacement and refurbishment of bearings in U.S. Army helicopters represent an expenditure in excess of $10 million per annum [33]. To elevate bearing performance for the operating inventory, surface modification and coating processes are actively being investigated. To date, initial concentration has been on M50 steel, a common bearing alloy for gas turbine engines. Fortuitously, positive results obtained in either program category are not mutually exclusive. Upgrade improvements achieved by surface treatments for the operating inventory may be utilized with substrates developed for advanced systems. The program involved laboratory simulation bearing testing via comparative rolling contact fatigue (RCF) performance of coating/substrate combinations. Adhesion properties and corrosion resistance capability were determined as well. From all the combinations being tested, only the most promising were selected for engine/component testing and eventual insertion in the operating vehicles. Several coatings of IBAD TiN [34], ion plated (IP) ZrN [35] and electroplated thin dense chromium (TDC) were tested using M50 as a substrate. Results obtained were very encouraging.

Rolling contact fatigue testing closely simulates the action of an actual bearing with the exception of one parameter (Hertzian stress). In RCF testing the applied stress is 3 to 4 times higher than that existing under service conditions with an operating bearing. This compromise is made in order to induce enough failures in a reasonable time to elicit statistically significant data. For this reason, the laboratory RCF test is considered a comparison test. That is, the data is not meant to determine a service bearing's endurance but rather, to comparatively rate materials, heat treatments, and surface modifications whose application may improve life performance. The equipment employed is termed a ball/rod rolling contact fatigue rig. The test rig uses a 3/8 in. diameter rod revolving within the constraints of three 1/2 in. steel balls which apply a radial load to the test rod. The ball-loading creates a wear track on the rod circumference and after some time (typically millions of stress cycles), a fatigue spall develops within the wear track. At this time, an accelerometer automatically stops the test and the time to failure is recorded. Normally, 16 to 20 test tracks are created for each sample condition in order to produce enough data for a statistically significant Weibull distribution. Each rolling contact fatigue test was conducted with a 186 kpsi load at 3600 rpm under lubrication.

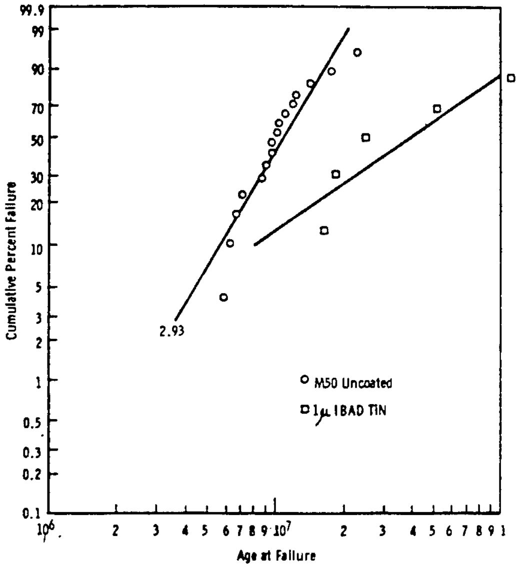

FIG. 7 Weibull distribution of RCF tests comparing M50 alloy uncoated rod vs. IBAD treated rod. Results demonstrate significantly extended lifetime for IBAD TiN at 50% lifetime (B50 lifetime). From [33].

Weibull plots show the accumulated percentage of failed samples versus the time (or stress cycles) to failure and the statistical results are used to rank materials and candidate surface coatings for improving RCF lifetimes. IBAD TiN has demonstrated a four-fold increase in RCF lifetime at B50 (50 % accumulated failure) and electroplated TDC has produced a slightly higher value (Figure 7). ZrN has achieved a better than two-fold increase for the same accumulated percentage failure (B50). It is interesting that IBAD TiN exhibited a thickness dependence for endurance improvement. A coating thickness of 0.25 µm did not display any RCF improvement, whereas a nominal 1.0 µm coating thickness achieved the four-fold increase shown in Figure 7.

Improved corrosion resistance provided by the various coatings has also been considered. Corrosion tests were performed as part of the present effort and entailed crevice corrosion evaluation of materials soaked in lubricating oil contaminated with a very dilute solution of seawater. This is a standard test for aircraft bearing steels subjected to a marine environment where lubricating oil may suffer contamination. The IBAD TiN coating fared very well in this test compared to uncoated M50 steel. The enhanced corrosion resistance found in these tests was substantiated by Ensinger et. al. (36) who evaluated the corrosion potential of TiN films produced by four different techniques: activated reactive ion plating, magnetron sputtering, and arc evaporation in addition to IBAD processing. IBAD TiN recorded the lowest corrosion current of the four processes, out to 400 potential cycles, indicating the lowest corrosion rate.

Chromium Nitride Hard Coatings

Recent environmental concerns regarding the disposal of toxic byproducts from the production of electroplated hard chromium (EHC), widely used as a wear- and corrosion-resistant tribological coating, have led many to consider IBAD and similar coating processes as potential replacements for electroplate technology. Specifically, IBAD chromium nitride (Cr_xN_y) is considered a candidate for EHC replacement because of its good corrosion resistance, high hardness, and overall similarity to EHC. Several studies have investigated the deposition of Cr_xN_y coatings using reactive ion plating [37-40], reactive sputtering [41-42], and IBAD [43,44] and have concluded that Cr_xN_y coatings can be formed with a hardness greater than that of ordinary Cr [37-40,43] and a wear rate an order of magnitude lower [43]. Studies now center on overcoming some of the difficulties often associated with IBAD and other physical vapor deposition (PVD) processes, namely, the optimization of coating adhesion to a given substrate, the optimization of coating hardness and wear-resistance, and the management of residual internal coating stresses [43] to allow the deposition of coatings as thick as those used in electroplating.

Figure 8 shows some results from a recent study at ARL in which Cr_xN_y coatings were deposited onto a variety of substrates using thermally evaporated Cr and a 1200 eV nitrogen ion beam from an RF-type ion source. As with most IBAD processes, the ion/atom arrival ratio was found to have a strong effect on the coating composition (N incorporation), film growth rate, and residual stress. As shown in the figure, the presence of a sufficiently intense nitrogen ion beam aided incorporation of nitrogen into the coatings during deposition (i.e., the formation of nitride phases), and produced coatings that approximated stoichiometric Cr_2N at high ion/atom ratios. This high nitrogen incorporation results in a hardening of the coating through a number of mechanisms, most likely the introduction of ion-induced dislocations and the effects of nitride precipitate growth, and induced a stress state that was highly compressive and less susceptible to cracking than ordinary evaporated chromium. Chromium nitride coatings produced by IBAD are extremely fine-grained, and do not exhibit the columnar structure often seen with PVD films without ion assistance (Figure 9), or the through-thickness cracks often found in electroplated coatings. Coatings produced by IBAD, therefore, can be more corrosion-resistant, since a columnar microstructure can act as a corrosion pathway to the underlying material.

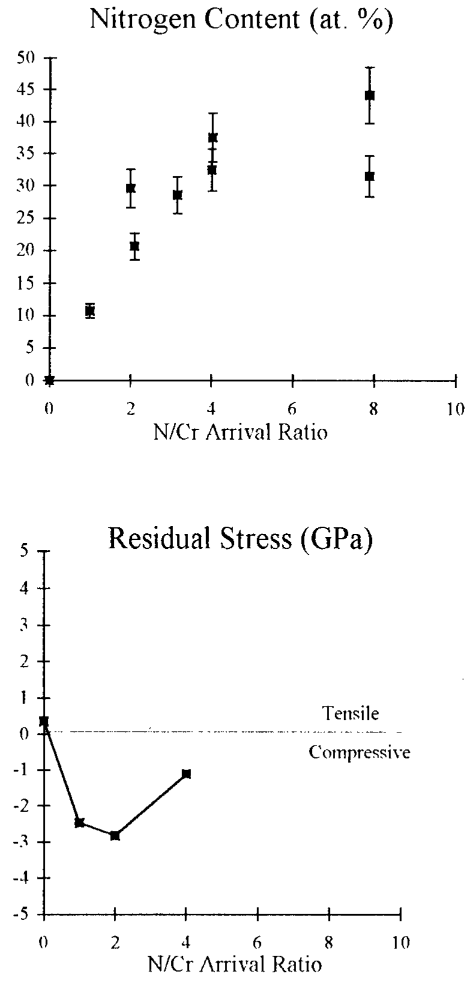

FIG. 8 The effect of ion-to-atom arrival ratio on the composition and stress state of IBAD chromium nitride coatings.

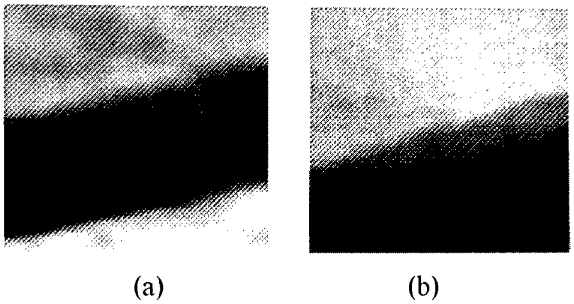

FIG. 9 Coatings of (a) 0.83 μm Cr, evaporated without ion assistance, showing a columnar microstructure; and (b) 0.42 μm $Cr_{70}N_{30}$, showing a dense, featureless microstructure.

This process is the focus of ongoing research at ARL with a goal of identifying the deposition parameters necessary for optimum performance as a wear-resistant hard coating (hardness, adhesion, scratch and scuff resistance, etc.). Once these parameters are identified, this technology will be transferred to a large prototype ion beam facility, discussed in the next section [45], to assess the suitability of these coatings for the replacement of electroplated hard chromium in specific DoD applications. The replacement of either Cd or Cr electroplating has to be assessed on a case to case basis since there is no singular, drop-in substitute for either of these widely used coatings in DoD.

5. ENVIRONMENTALLY RELATED PROGRAMS

Concern over environmental pollution has been a strong driving force in DoD to reduce, supplant or replace operations involving electroplated Cr or Cd. The Army has been tasked with coordinating a DoD wide program consisting of validating and demonstrating environmentally friendly technologies carried out under contract [45] at the National Defense Center for Environmental Excellence (NDCEE) located in Johnstown, PA.

One of the tasks being performed is to demonstrate and validate ion beam processes as environmentally benign alternatives to Cr/Cd electroplating in wide use at DoD facilities. This project is being co-monitored by the Army (ARL- Materials Division) and Navy (NRL). A goal of the program is to demonstrate and validate selected ion beam processes as supplements or replacements for electroplated Cd/Cr for specific niche applications. Initially the program identified the overall usage of various electroplates, including Cd/Cr, at various Army Depots and Navy Shipyards. A second task was to identify candidate components appropriate for treatment by ion beam treatment on the basis of technical feasibility, usage of part(s), ease of treatment, and ability to perform appropriate field service testing. Figure 10 shows a Cr plated aluminum alloy fork assembly from a helicopter landing gear which is under consideration for IBAD treatments to reduce wear and adhesion problems associated with the Cr-aluminum interface.

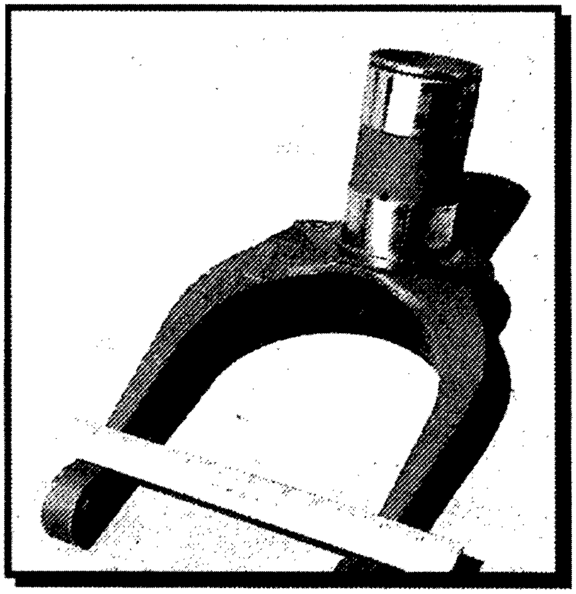

FIG. 10 A Cr plated fork assembly from a helicopter landing gear being considered for IBAD treatment under NDCEE ion beam program [45].

Two general paths were chosen for ion beam treatments: i) N-ion implantation as a means of extending the lifetime of Cr-electroplates thereby reducing the need to replate as often, and ii) selected wear resistant IBAD coatings (e.g., TiN, CrN, and DLC) deposited directly on wear surfaces or on electroplated build-up layers (e.g., Ni) required to restore dimensionality during rework. Several aerospace manufacturers have collectively agreed to various tests of their components to qualify ion beam treatments for use. These include tests for: adhesion, wear, corrosion, fatigue, as well as specialty tests (e.g., drop tests), and field service tests.

The program also includes the design, building, and installation of a prototype manufacturing ion beam processing unit, shown schematically in Figure 11, to enable demonstration of ion beam technologies to DoD users and vendors. The ion beam facility contract was competitively bid and the resultant design [3] includes both high energy [100 keV], high current [20 mA] gas (nitrogen) implantation and low energy [1 keV] ion beam assisted deposition (IBAD) utilizing electron beam evaporators. These components are housed in a large [1.85 M diameter x 1.85 M length] vacuum chamber with a 1 M extension at one end and a 1.2 M length load lock at the other end. This system is currently nearing completion and is scheduled for installation and acceptance in the fourth quarter of 1996.

6. CONCLUSIONS

The issuance of rigid environmental regulations regarding the materials and processes used widely in electroplating at DoD facilities has prompted the examination of several alternative coating techniques, including ion beam processes, for supplanting and/or replacing Cd/Cr electroplating in niche areas. The results to date show that ion beam treated surfaces compare favorably technically as substitutes on a case to case basis and that DoD users and vendors will soon have additional means of evaluating these processes for their particular components and applications.

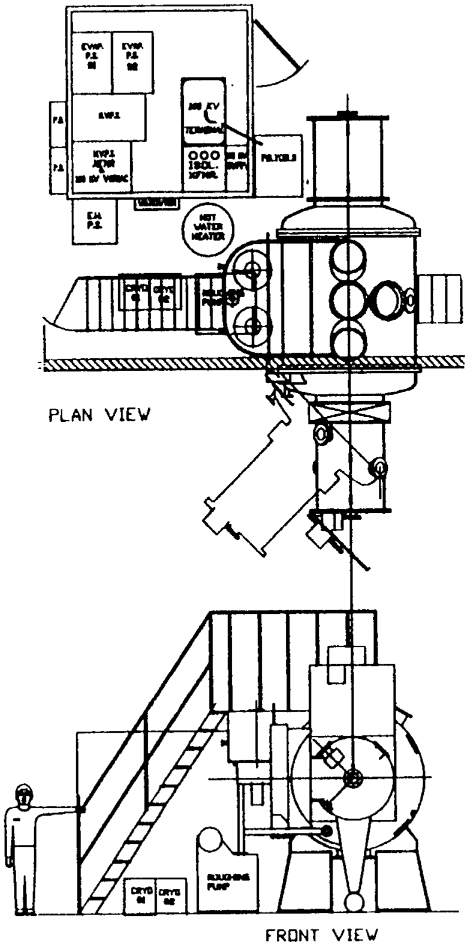

Fig.11 Schematic of ion beam facility being constructed for ion beam demonstration and validation program at National Defense Center for Environmental Excellence in Johnstown, PA.

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EVALUATION OF AQUEOUS DEGREASING AS REPLACEMENT FOR VAPOUR DEGREASING WITH 1,1,1-TRICHLOROETHANE AT BOMBARDIER-CANADAIR

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1. INTRODUCTION

Back in 1990, in view of the environmental regulations in the U.S., and supporting Canada's commitement to the Montreal Protocol, Bombardier-Canadair started investigating the feasibility of using aqueous degreasing to replace vapour degreasing with 1,1,1-trichloroethane (TCA). This paper presents the results of Canadair's laboratory-scale and pilot line evaluations.

Because of the large variety of parts sizes and shapes produced at Canadair, it was decided to evaluate aqueous degreasing by immersion with mechanical agitation or solution recirculation. Seven candidate aqueous degreasers were selected for evaluation based on data obtained from several airframe and aircraft manufacturers who had already evaluated many products. The twelve contaminants most commonly found on parts going through the vapour degreasers at the time of the study were identified and used for the evaluation. Both TCA and an alkaline cleaner already in use at Canadair were used as controls.

From the seven aqueous degreasers evaluated, only three met all the criteria. Laboratory results indicated that, when used as specified, these three degreasers did an acceptable job of removing the contaminants. Therefore, these cleaners were considered acceptable to be used in an immersion process at Canadair as substitutes for vapour degreasing with TCA, and were recommended for pilot line evaluation. One of the three candidates was tested in a pilot line and then successfully implemented into production.

2. LABORATORY EVALUATION

The laboratory scale evaluation was done in three phases. Phase I consisted of evaluating the cleaning efficiency of the candidate degreasers in removing the twelve common soils at five concentrations, three temperatures and three immersion times (ie 5 x 3 x 3 = 45 combinations). In Phase II, candidate cleaners selected in Phase I were evaluated to determine their effects on different aicraft materials. Tests included immersion corrosion, intergranular attack, end grain pitting, sandwich corrosion and weight change. Phase III was used to identify any effects the candidates could have on anodizing and conversion coatings of aluminum alloys. Corrosion resistance was evaluated by salt spray exposure. The weight of anodic coatings obtained by both chromic and sulphuric acid anodizing was also determined.

2.1 MATERIALS

The substrate material selected for Phase I of this evaluation was 2024-T3 bare aluminum. The specimens were cut at 3"x4"x0.020" from in-house stock. In phases II and III, various materials with different finishes were used because of test requirements. Table 1 presents a list of substrate materials, their finishes and the tests for which they were used.

The twelve contaminants most commonly found on parts going through the main vapour degreaser were identified. A list of these soils and their use is given in Table 2.

The candidate cleaners evaluated are listed in Table 3. This list is by no means representative of all the potential replacements for vapour degreasing that were available when this project started. However, because of time and budget constraints, an evaluation of the dozens of products available was not possible.

The selection of candidate degreasers to be evaluated was made based on recommendations from other aircraft and airframe manufacturers who had already evaluated many of those products. The list in Table 3 is not an endorsement of any commercial product.

2.2 PROCEDURE

This evaluation was done in three phases. Phase I consisted of evaluating the cleaning efficiency of the candidate degreasers in removing the twelve common soils. Those found to be effective were selected for further evaluation. Phase II included tests to determine if these degreasers would cause any chemical attack on different aircraft materials. Phase III consisted of identifying the effects, if any, that the candidate cleaners could have on subsequent treatments for aluminum alloys, like anodizing and conversion coatings.

2.2.1 Phase I - Cleaning Efficiency

Laboratory tests used to evaluate cleaning efficiency were conducted in one-gallon, cylindrical, glass beakers. Air agitation was considered but it was discarded because

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most of the candidates foamed excessively. Mild mechanical agitation was provided instead by a magnetic stirrer.

A Cleaning Efficiency Matrix was developed to evaluate the cleaning solutions at five different concentrations. The highest and lowest concentration values were recommended by each supplier as those values at which the products would still clean efficiently. The mid-point of the concentration range was considered the optimum value.

The solutions were tested at three different temperatures. Again, the mid-point was the recommended temperature, while the minimum and maximum values were considered the operating limits for each solution.

Panels were immersed in the solutions for 5, 10, and 15 minutes. Temperatures and immersion times were varied from minimum to maximum at each cleaner concentration. TCA and Turco 4215 NC-LT were used as controls. The cleaning efficiency of Turco 4215 NC-LT at 5, 10 and 15 minutes was only evaluated at the concentration and temperature presently used in production.

Since each soil was tested individually, a total of twelve matrices were completed for each candidate degreaser. For any given combination of concentration and temperature, the same solution was used to determine cleaning efficiency for all three immersion times. The spent solution was then replaced with fresh solution to evaluate the next combination of concentration and temperature.

Each soil was individually applied to specimens. Light oils and lubricants were allowed to drip until a thin film was left on the panel and the dripping stopped. Thicker lubricants and greases were manually extended over the panels and the excess was wiped off.

Once the immersion in the degreasing solution was completed, the panels were rinsed in tap water at room temperature using slight mechanical agitation. Two separate beakers were used for the two-step rinsing operation. The rinse water was replaced every time the cleaning solution was replaced. Panels were rinsed for one minute in each step. The cleaning effectiveness was then determined by visual inspection. The water-break-free surface test was considered the most practical and realistic, since it is the test presently used by operators when processing parts.

A ranking system used at Boeing Wichita during their own investigation was adopted for rating the degree of cleanliness. This system ranks the surface of the panels from 1 (best) to 5 (worst) using the criteria shown in the following table

Rating	Criteria
1	Water-break-free for 30 seconds
2	Clean but not water-break-free
3	Most of the soil was removed
4	Little soil was removed
5	No soil was removed

After vapour degreasing, parts are sent for further processing. At Bombardier-Canadair, this can be heat treatment, more mechanical work or additional chemical processing. In each of these cases, the requirements for the degree of cleanliness of the parts are different. Because of the risk of high temperature oxidation, parts to be heat treated require a surface as clean as that obtained with vapour degreasing. Parts that will undergo additional mechanical work, like deburring for example, require a surface clean enough to be handled and worked on. On the other hand, parts that will be alkaline cleaned as the first step in the required surface treatment have different requirements. If there is any soil residue left on these parts after aqueous degreasing, it should be such that a water-break-free surface can be achieved after 5-10 minutes of alkaline cleaning and rinsing.

Therefore, the cleaning efficiency matrices were completed under the following assumptions:

a) A rating of 1 was the minimum acceptable for parts to be heat treated.
b) A rating of 2 was the minimum acceptable for parts that would receive further mechanical work.
c) A rating of 3 was the minimumn acceptable for parts that would continue for alkaline cleaning prior further chemical processing.

2.2.2 Phase II - Characterization Tests

Candidate cleaners selected in Phase I were then evaluated to determine their corrosiveness on different materials, as well as their etching effects. The corrosiveness of the candidates was evaluated in total immersion per ASTM F483. The degree of intergranular attack and end grain pitting caused by these solutions on aluminum alloys was determined according to BAC 5763, BAC 5749 and BSS 7219. A sandwich corrosion test was done per BAC 5763, Type II, Class 1 to determine if these solutions would cause corrosion between flat surfaces of the same metal alloy.

Finally, the metal etch rate of these aqueous degreasers was determined in accordance with both BAC 5763 and BAC 5749 on different materials.

2.2.3 Phase III - Effects on Corrosion Resistance

The effects of these cleaners on the corrosion resistance of inorganic coatings used on aluminum alloys were investigated , specifically chromate conversion coatings and anodizing.

Aluminum panels were degreased in the candidate solutions, alkaline cleaned and deoxidized. Separate sets of 2024-T3 clad and 6061-T6 bare aluminum specimens were conversion coated per MIL-C-5541, Class 1A, while separate sets of 2024-T3 bare aluminum specimens were chromic acid anodized per MIL-A-8625, Type I, and sulphuric acid anodized per MIL-A-8625, Type II.

The specimens were then tested in salt spray per ASTM B117 at 6 degrees from vertical for 168 hours for the conversion coated and for 336 hours for the anodized. In addition, the coating weights of the anodic coatings obtained by both chromic and sulphuric acid anodizing were determined per ASTM B137.

2.3 DISCUSSION OF RESULTS

Tables 5 to 10 summarize test conditions and results. The cleaning efficiency test used in Phase I reduced the number of candidates from 7 to 3. Three soils were found to be consistently harder to remove than the others. These were Grease Cup No. 3, Sundraw 2020 and Waylube 220.

The three cleaners selected for testing in Phase II achieved ratings of 3 or better when removing these soils, but this was achieved after 10-15 minutes immersion at the higher values of temperature and concentration. Although it is considered an alkaline cleaner, Turco 4215 NC-LT performed surprisingly well when removing these stubborn contaminants.

For each of the three candidates selected, the combination of concentration and temperature found to be the most effective in removing the twelve contaminants was used as the operating parameters for the tests in Phases II and III.

The tests used in Phase II were chosen to evaluate the corrosive and etching effects of the solutions on different aircraft materials. The three candidate solutions tested in Phase II met all the requirements, except for Blue Gold, which failed sandwich corrosion at 100% concentration.

However, it should be noted that the sandwich corrosion test was not considered eliminatory. This was due to the fact that this test is usually used to determine the effect of candidate cleaners on parts or assemblies with faying surfaces, and at present, these type of parts are not immersion cleaned at Bombardier-Canadair.

Finally, Phase III was used to evaluate the effects of the three candidate degreasers on the corrosion protection of the inorganic finishes that follow surface cleaning. These tests simulated the surface preparation procedures that would be used prior to anodizing or conversion coating of aluminum alloys. The three candidates met the established criteria.

2.4 CONCLUSIONS AND RECOMMENDATIONS

From the seven aqueous degreasers evaluated, only three of them met all the performance criteria. These were Brulin 815GD, Daraclean 282 and Blue Gold.

Test results indicated that, when used as apecified and under laboratory conditions, these three aqueous degreasers did an acceptable job of removing the contaminants from the panels. Therefore, these cleaners were considered acceptable to be used in an immersion process with solution recirculation as substitutes for vapour degreasing with 1,1,1-trichloroethane at Bombardier-Canadair. This recommendation applied to all metallic detail parts, except for tubing and honeycomb.

At this stage, M&P Engineering recommended additional testing to determine the bath life and soil loading capacity of the cleaners, as well as a pilot-line evaluation to verify the performance of the selected cleaners under shop conditions.

3. PILOT LINE EVALUATION

One of the three aqueous degreasers recommended was selected at random for the pilot line evaluation. A 1670 U.S. gallon (6327 liters) tank was used to evaluate the aqueous degreaser in an immersion process with mechanical agitation followed by an immersion rinse.

The effects of various parameters on cleaning efficiency were investigated. Parameters studied were concentration, temperature, dwell time of the contaminant on the part, immersion time, racking techniques, bath life, soil loading capacity and foaming characteristics. The rating system used in the laboratory evaluation was used during the optimization of these parameters to establish the level of cleanliness.

Several different contaminants found in the shop floor at that time were used for the tests. These included forming lubricants and greases, inks, preservative oils, coolants, as well as drilling and honing oils. A list of these soils and their use is given in Table 11. A mixture of these contaminants was added to the degreasing solution at a rate of one liter a week. This was proportional to the equivalent amount of contamination that the vapour degreaser receives in a week.

Different types of parts were used in the evaluation, including extrusions, flat and contoured sheet metal parts, and machined parts. The results showed that, for the types of parts and the contaminants found at Bombardier-Canadair, the aqueous degreaser evaluated could clean parts to the required levels of cleanliness. It was concluded that it was feasible to implement aqueous degreasing to replace vapour degreasing at Canadair.

3.1 PROCEDURE

3.1.1 Phase I - Optimization of Parameters

A Design of Experiment (D.O.E.) technique was used in Phase I to determine the optimum values of immersion time, temperature and concentration that would meet both Manufacturing's and Engineering's requirements.

The three soils found to be more difficult to remove in the laboratory evaluation were selected for these tests. These were Sundraw 2020, Waylube 220 and Grease Cup No.3. Since Grease Cup No. 3 was no longer used in production it was replaced by Rustproof 1976, another stretch-forming grease.

Through statistical analysis it was determined that solution temperature was the most significant parameter, followed by immersion time and concentration, in that order. Therefore, it was decided to conduct the rest of the pilot line evaluation using 10 minutes immersion, 10% concentration (by volume), and a temperature of 170-180°F

3.1.2 Phase II - Verification of Parameters

The parameters optimized in Phase I were used to verify if the requirements for surface cleanliness prior plating, prior heat treatment and aging, and prior metal fabrication (ie. routing, drilling, etc) could be met. The verification was done using the most common contaminant left on the parts from the previous operation.

A] Cleaning Prior Metal Fabrication

For the purpose of this evaluation, metal fabrication included operations like deburring, routing, machining, drilling, forming and transportation. It was established that a cleanliness rating of 2 was required prior these operations for the operators to be able to handle the components safely, as well as to prevent contamination of the tools.

For all the contaminants used in those applications, parts of various types and sizes were degreased using the optimized parameters.

B] Cleaning Prior Plating

Tests were done on 4130 steel parts contaminated with VV-L-800 preservative oil, aqueous degreased, alkaline cleaned and then Cadmium plated.

C] Cleaning Prior Heat Treatment and Aging

Two sets of test pieces contaminated with Sunicut 154 were used to determine the level of cleanliness required prior heat treatment and aging. The first set consisted of strectch-formed aluminum skins. The skins were degreased and then aged at 250°F for 24 hours. The second set consisted of formed aluminum brackets, which were degreased and then heat treated at 920°F for 30 minutes. All parts were then visually inspected to determine if any scale had formed on the surface.

3.1.3 Phase III - Miscellaneous Parameters

This phase was used to evaluate the effects of racking technique on the cleaning efficiency of the degreaser. Bath life, soil loading capacity, and foaming characteristics were also evaluated.

A] Racking

Tests were done to determine the effects of racking technique on the cleaning efficiency of the degreaser. The tests compared the cleanliness rating obtained by aqueous degreasing to those obtained by vapour degreasing when cleaning typical loads of parts. It was concluded that for aqueous degreasing to be as effective as vapour degreasing, parts need to be separated. Racking systems should be designed so as to allow proper solution flow over the entire surface of the parts.

B] Bath Life and Soil Loading Capacity

Based on saturation tests done in the laboratory, the saturation point for this volume of degreasing solution was estimated to be around 3200 ppm of oil and grease. However, the theoretical saturation point does not necessarily correlate to the contamination level at which a degreaser becomes ineffective. After 6 months of pilot line evaluation, the degreasing solution was adjusted to 10% concentration, and for the next three months the rate of addition of the contaminants mixture was increased from one to four liters per week. The cleaning efficency of the solution was evaluated every week by cleaning typical 12-inch long aluminum "T" extrusions contaminated with Rustproof 1976.

C] Foaming Characteristics

Foaming has been a problem with some alkaline cleaners when they are aggressively agitated after additions of cleaner or water. Therefore, tests were done to determine if the degreasing solution would foam excessively when agitated aggressively for one hour. In each case, both the height of the foam and the time it took for the foam to settle were measured.

3.2 DISCUSSION OF RESULTS

Statistical analysis of the results from the D.O.E. indicated that temperature was the most significant parameter, followed by immersion time and concentration, in that order. Based on the statistical analysis and the cleanliness ratings obtained, the following parameters were selected:

Solution temperature:	170-180°F
Solution concentration:	8-12% (v/v)
Immersion time:	10 minutes
Racking:	Parts must be separated for effective cleaning

The verification of the optimized parameters showed that the soils identified in the shop could be removed after 10 minutes immersion in a degreasing solution at 8-12% concentration and 170-180°F.

A cleanliness rating of 2 or better was obtained prior plating, and the Cadmium plating obtained was smooth and free of defects. It should be noted that a rating of 1 was not required after aqueous degreasing because the alkaline cleaning step used prior plating was mandatory. In addition, although the components were allowed to dry off between aqueous degreasing and alkaline cleaning no flash corrosion was found on any of the parts. This was attributed to the fact the degreaser evaluated is formulated with a corrosion inhibitor.

Results of the degreasing tests prior heat treatment and aging showed that parts meeting a cleanliness rating of 2 had no scale on the surface. It was noted, however, that the skins meeting this rating sometimes had a powdery dust on them that was easily removed by wiping or by immersion in an alkaline cleaner.

The evaluation of the effects of racking on cleaning efficiency showed that parts in close contact with each other will not be properly cleaned in either the vapour or the aqueous degreaser. For example, vapour degreasing seemed slightly better for bundled extrusions. However, both methods cleaned equally well when parts were separated. It was also noted that the same parts are not cleaned as well when they are placed in baskets as when they are racked.

The tests to evaluate bath life and soil loading capacity were completed on a 9-month old solution. After 12 weeks of soil loading, the 10% solution still met cleaning efficiency requirements, although its performance was deteriorating. It was estimated that at this rate of contamination the solution should have a bath life of about 24 months.

Results of the tests done to evaluate foaming characteristics indicated that, for a fairly old solution, mechanical agitation did not cause any measurable amount of foaming. On the other hand, aggressive air agitation produced about 4 inches of foam, which took 23 minutes to settle. The results were almost the same for a new solution, although the fresh solution foamed faster than the old one, and it took a few more minutes for the foam to settle.

3.3 CONCLUSIONS AND RECOMMENDATIONS

After the pilot line evaluation, it was concluded that the degreasing solution tested could produce parts with a cleanliness rating of 2 or better if the following parameters were followed:

Solution temperature:	170-180°F
Solution concentration:	8-12% (v/v)
Immersion time:	10 minutes
Agitation:	Mechanical
Racking:	Parts must be separated for effective cleaning

Some rinsing parameters were also recommended to complement the above:

Rinsing temperature:	165-175°F
Agitation:	Mechanical
Rinsing time:	2-3 minutes

Based on this study, aqueous degreasing was approved at Bombardier-Canadair as replacement for vapour degreasing with TCA for metallic detail parts. The only exceptions were tubing and aluminum honeycomb.

Table 1: TEST SPECIMENS

	MATERIAL	SIZE	TEST
PHASE I	2024-T3 bare	3"x4"x0.020"	Cleaning Efficiency
PHASE II	2024-T3 bare	1"x2"x0.060"	Immersion Corrosion (ASTM F483, 7 days @ 140°F)
	2024-T3 clad		
	7075-T6 bare		
	7075-T6 clad		
	6061-T6 bare		
	6Al-4V Ti		
	321 S.S.		
	7075-T6 bare	2"x4"x0.040"	Sandwich Corrosion (BAC 5763)
	2024-T3 bare	1"x2"x0.060"	Metal Etching BAC 5763 (24 HRS @ Max. Operating Temperature)
	2024-T3 clad		
	4130 Steel		
	4130 Steel (Cadmium plated)		
	6Al-4V Ti		
	2024-T3 bare	1"x2"x0.060"	Intergranular Attack and End Grain Pitting (BAC 5763 & BSS 7219, 60 Minutes Immersion @ Operating Conditions)
	2024-T3 clad		
	7075-T6 bare		
	7075-T6 clad		
PHASE III	2024-T3 bare	3"x3"x0.040"	Weight of Anodic Coating (ASTM B137)
	2024-T3 bare	3"x10"x0.040"	Salt Spray Corrosion Resistance (ASTM B117)
	2024-T3 clad		
	6061-T6 bare		

Table 2: SOILS IDENTIFIED

NAME	USE
Shamrock HG Plus	NC Machining Coolant
Sunicut 154	Machining Oil
Thread Grinding Oil	Thread Cutting Oil
Sunicut 412	Drilling Oil
MB-30	Honing Oil
Blazocut Grindex 7804	Grinding Oil
WD-40	Penetrating Oil
VV-L-800	Rust Preventative Oil
Grease Cup No.3	Stretch-forming Grease
Sundraw 2020	Stretch-forming Lubricant
Waylube 220	Stretch-forming Lubricant
Mill Markings	Material Identification

Table 3: CANDIDATE DEGREASERS

NAME	MANUFACTURER
Axarel 52	DuPont
Blue Gold	Modern Chemicals
Brulin 815GD	Brulin Corporation
Daraclean 282	W.R. Grace
FX-9	Athans Chemicals
Ridoline 57	Parker+Amchem
Simple Green	Sunshine Makers
Turco 4215 NC-LT 1/	Turco

NOTES: 1/ Alkaline cleaner used as control

Table 4: RESULTS OF IMMERSION CORROSION PER ASTM F483 (7 DAYS @ 140°F)

SUBSTRATE MATERIAL	WEIGHT CHANGE (mg) 1/		
	Blue Gold (20%)	Brulin 815GD (15%)	Daraclean 282 (15%)
2024-T3 Bare	-0.8; -0.8; 0.0 (Avg: -0.5)	+0.8; +0.7; +0.3 (Avg: +0.6)	-0.5; -0.6; -0.4 (Avg: -0.5)
2024-T3 Clad	-0.8; -0.7; -0.5 (Avg: -0.7)	+0.5; +0.5; +0.5 (Avg: +0.5)	-0.4; 0.0; -0.3 (Avg: -0.2)
7075-T6 Bare	-0.8; -0.2; -0.2 (Avg: -0.4)	+0.9; -0.3; +0.1 (Avg: +0.2)	-0.6; -0.2; 0.0 (Avg: -0.2)
7075-T6 Clad	-1.0; -0.2; 0.0 (Avg: -0.4)	+1.1; 0.0; +1.1 (Avg: +0.7)	+0.7; 0.0; -0.1 (Avg: +0.2)
6061-T6 Bare	+0.4; +0.3; +0.3 (Avg: +0.3)	+1.2; +1.3; +0.9 (Avg: +1.1)	+0.3; +0.3; +0.4 (Avg: +0.3)
321 S.S.	+0.4; +0.3; +0.3 (Avg: +0.3)	+0.8; +0.9; +1.7 (Avg: +1.1)	+0.3; +0.3; +0.3 (Avg: +0.3)
6Al-4V Titanium	0.0; +0.2; +1.1 (Avg: +0.4)	+0.5; +1.2; +1.5 (Avg: +1.0)	+0.7; +0.6; +0.3 (Avg: +0.5)

NOTES: 1/ Limits for Aluminum alloys: ± 10 mg/24 hours
Limits for Titanium and S.S.: ± 5 mg/24 hours

Table 5: RESULTS OF METAL ETCHING PER BAC 5763 (24 HRS @ MAX. OPERATING TEMPERATURE)

SUBSTARATE MATERIAL	CLEANER CONC. (% VOL)	WEIGHT CHANGE (mg)		
		BLUE GOLD (160°F)	BRULIN 815GD (160°F)	DARACLEAN 282 (160°F)
2024-T3 Clad	10%	0.0; -0.3; 0.0 (Avg: -0.1)	-0.2; 0.0; 0.0 (Avg: -0.1)	-0.2; -0.1; -0.1 (Avg: -0.1)
	100%	-0.6; -0.5; -0.5 (Avg: -0.5)	0.0; -0.2; -0.2 (Avg: -0.1)	-0.3; -0.5; -0.5 (Avg: -0.4)
2024-T3 Bare	10%	-0.1; 0.0; -0.2 (Avg: -0.1)	0.0; 0.0; 0.0 (Avg: 0.0)	-0.2; -0.3; 0.0 (Avg: -0.2)
	100%	0.0; 0.0; -0.2 (Avg: -0.1)	0.0; 0.0; 0.0 (Avg: 0.0)	0.0; -0.2; 0.0 (Avg: -0.1)
4130 Steel	10%	-0.2; +0.2; +0.3 (Avg: +0.1)	-0.4; -0.7; -0.5 (Avg: 0.	+0.1; +0.1; 0.0 (Avg: +0.1)
	100%	-0.5; -0.5; -0.4 (Avg: -0.5)	-0.6; -0.5; -0.6 (Avg: -0.6)	0.0; 0.0; 0.0 (Avg: 0.0)
4130 Steel (Cadmium plated)	10%	-0.4; -0.6; -0.6 (Avg: -0.5)	-4.2; -3.9; -3.8 (Avg: -3.9)	+0.5; +0.7; +0.1 (Avg: +0.4)
	100%	-0.1; -0.1; 0.0 (Avg: -0.1)	-4.0; -4.1; -2.5 (Avg: -3.5)	+0.2; 0.0; 0.0 (Avg: +0.1)
6Al-4V Titanium	10%	+0.5; +0.4; +0.5 (Avg: +0.5)	+0.2; 0.0; +0.2 (Avg: +0.1)	-0.3; -0.3; -0.1 (Avg: -0.2)
	100%	+1.1; +0.6; +0.3 (Avg: +0.6)	+0.1; 0.0; 0.0 (Avg: 0.0)	-0.3; -0.3; +0.1 (Avg: -0.2)

NOTE: (a) Limits for Aluminum alloys: ±10 mg/24 hours; (b) Limits for 4130 Steel: ±30 mg/24 hours;
(c) Limits for Cadmium plated 4130 Steel: ±10 mg/24 hours;
(d) Limits for 6Al-4V Titanium: ±5 mg/24 hours

Table 6: COATING WEIGHTS PER ASTM B137

SUBSTRATE MATERIAL	SURFACE TREATMENT	COATING WEIGHT (mg/sq. ft.)		
		BLUE GOLD (16% @ 150°F)	BRULIN 815GD (15% @ 160°F)	DARACLEAN 282 (15% @ 160°F)
2024-T3 Bare	Chromic acid anodizing 1/	320, 322, 320 (Avg: 321)	317, 320, 321 (Avg: 319)	312, 319, 320 (Avg: 317)
2024-T3 Bare	Sulphuric acid anodizing 2/	1158, 1166, 1150 (Avg: 1158)	1155, 1164, 1181 (Avg: 1167)	1227, 1206, 1269 (Avg: 1234)

NOTES: 1/ Per MIL-C-8625 Type I, 2/ Per MIL-C-8625 Type II

Table 7: SOILS USED FOR PILOT LINE EVALUATION

NAME	USE
Shamrock HG Plus	NC machining coolant
Sunicut 154	Machining oil
Cindrol 4683	Stretch-forming lubricant
Sunicut 412	Drilling oil
MB-30	Honing oil
Blazocut Grindex 7804	Grinding oil
VV-L-800	Rust Preventative oil
Haughtodraw 7002	Stretch-forming lubricant
Rustproof 1976	Stretch-forming grease
Sundraw 2020	Stretch-forming lubricant
Waylube 220	Stretch-forming lubricant
Cerco XXX	Tube-forming lubricant
Polyglycol	Honeycomb machining
Sharpie Inc. No.30001	Identification ink

Table 8: CLEANING EFFICIENCY MATRIX FOR BLUE GOLD (Contaminant: Grease Cup No. 3)

IMMERSION TIME @ TEMPERATURE	CONCENTRATION (% VOL.)				
	4%	8%	12%	16%	20%
5 min. @ 140°F	5	5	4	3	3
5 min. @ 150°F	5	5	4	3	3
5 min. @ 160°F	5	5	3	3	3
10 min. @ 140°F	5	4	3	3	3
10 min. @ 150°F	4	4	3	3	3
10 min. @ 160°F	4	4	3	3	2
15 min. @ 140°F	4	4	4	3	2
15 min. @ 150°F	4	4	3	2	2
15 min. @ 160°F	4	3	3	2	2

Table 9: CLEANING EFFICIENCY MATRIX FOR BRULIN 815GD (Contaminant: Grease Cup No. 3)

IMMERSION TIME AT GIVEN TEMPERATURE	CONCENTRATION (% VOL)				
	3%	6%	9%	12%	15%
5 minutes @ 120°F	5	5	5	5	4
5 minutes @ 140°F	5	5	5	5	4
5 minutes @ 160°F	5	5	4	4	4
10 minutes @ 120°F	5	5	5	5	4
10 minutes @ 140°F	5	4	4	4	4
10 minutes @ 160°F	4	4	3	3	2
15 minutes @ 120°F	5	4	4	3	2
15 minutes @ 140°F	5	4	4	3	2
15 minutes @ 160°F	4	3	3	2	2

Table 10: CLEANING EFFICIENCY MATRIX FOR DARACLEAN 282 (Contaminant: Grease Cup No. 3)

IMMERSION TIME AT GIVEN TEMPERATURE	CONCENTRATION (% VOL)				
	3%	6%	9%	12%	15%
5 minutes @ 120°F	5	5	5	5	5
5 minutes @ 140°F	5	5	5	5	4
5 minutes @ 160°F	5	5	5	5	4
10 minutes @ 120°F	5	5	5	4	4
10 minutes @ 140°F	5	5	5	4	4
10 minutes @ 160°F	4	4	4	4	3
15 minutes @ 120°F	5	5	4	4	4
15 minutes @ 140°F	5	4	4	3	3
15 minutes @ 160°F	4	4	3	3	3

Cadmium substitution on aircraft

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SUMMARY

A Garteur (Group for Aeronautical Research and Technology in Europe) collaborative programme of research being undertaken to evaluate alternatives to cadmium plating for the corrosion protection of high strength steel aerospace components and fasteners is described. Coatings being investigated include electrodeposited zinc - nickel and zinc - cobalt - iron, ion vapour deposited and electrodeposited aluminium, metallic - ceramic deposits containing zinc and aluminium flakes and magnetron sputtered aluminium - magnesium coatings. The programme is examining both the corrosion resistance of the coatings and their galvanic compatibility with aluminium alloy airframe materials. The effects of coatings on fatigue life and susceptibility to hydrogen embrittlement are being determined. Physical properties including conductivity and lubricity are being studied, microstructure and resistance to aircraft fluids. The programme involves research in seven laboratories from the aerospace research institutes and the aircraft industry based in France, Germany, The Netherlands, Sweden and the United Kingdom.

1 INTRODUCTION

Cadmium plating is the preferred protective treatment for aerospace components and fasteners manufactured from steel. It offers a high general corrosion resistance, provides sacrificial protection if the coating is damaged and is galvanically compatible with aluminium alloys used in airframe structures. The high lubricity of cadmium plating makes it particularly attractive for fastener applications and for use on threaded parts. Although the electrodeposition of cadmium may result in the introduction of hydrogen into the steel substrate, effective heat treatments have been developed which eliminate the possible risk of hydrogen embrittlement in high strength steels.

The main disadvantage of cadmium plating is the toxicity of cadmium salts. Cadmium is considered to impose a serious environmental and health hazard during production, application and use. The toxic effects of cadmium can lead to damage of the kidneys, liver and lungs.

Cyanide containing baths are normally used for the electroplating of cadmium. The treatment of effluent from the plating process to reduce the level of cadmium in solution is an expensive process and one which will become more costly as the permissible level of cadmium is decreased. Compared with other industries the aerospace industry is in an exceptional position. The use of cadmium plating for general engineering purposes is no longer allowed under European Legislation but it may still be used for aerospace and military applications where there is no acceptable alternative. Member states of the European Union are seeking to widen the ban on the use of cadmium and it is likely that future directives may be extended to include the aerospace industry. It was against this background that an exploratory Garteur group was formed in 1993 to consider the setting up of a collaborative programme to evaluate alternatives to cadmium plating for use on aerospace components. A programme of work was agreed between the interested parties and an action group SM (AG17) "Cadmium Substitution in Aircraft" was formally set up. Research commenced on 1st January 1994 and is scheduled to finish on 31st December 1996.

This paper outlines the main objectives of the programme, the coatings being examined and the work plan. Some early results are presented.

2 PROGRAMME OBJECTIVES

The programme is primarily concerned with the testing and evaluation of selected coatings. The main objective is to identify alternatives to cadmium plating which may be applied to steel components and fasteners used in aircraft structures.

The various aims of the programme are as follows:-

- to select a range of coatings which are to be applied using environmentally compliant materials and processes
- to agree on the test specifications to be used
- to assess the performance of each coating
- to establish the technical, environmetal and economic aspects of each coating
- to complete the programme within a three year timescale

Paper presented at the 83rd Meeting of the AGARD SMP on "Environmentally Compliant Surface Treatments of Materials for Aerospace Applications", held in Florence, Italy, 4-5 September 1996, and published in R-816.

3 COATINGS EVALUATED

An important feature of cadmium plating is its ability to provide sacrificial protection if it becomes damaged in service. In considering the range of coatings which might be substituted for cadmium only coatings which would provide sacrificial protection were selected. Thus nickel plating which can provide a high level of corrosion protection was not chosen as the coating is more noble than steel and gives no protection once the coating is damaged. Details of the coatings being evaluated are given in table 1.

Table 1 Coatings being evaluated

Coating type	Method of coating
Zinc-cobalt-iron	Electrodeposition
Zinc-nickel	Electrodeposition
Metallic-ceramic consisting of aluminium particles in an inorganic matrix	Spray
Metallic-ceramic consisting of Al and Zn flakes in an inorganic matrix	Electrostatic spraying, dipping or spin coating
Aluminium	Electrodeposited from an organic bath
Aluminium	Physical vapour deposition
Aluminium - magnesium	Unbalanced magnetron sputtering
Cadmium	Electrodeposition

The coatings are either aluminium or zinc based and with the exception of the unbalanced magetron sputtered aluminium - magnesium coating are available commercially. Electrodeposited cadmium plating has been included in the programme as a reference.

4 WORK PROGRAMME

Each of the coatings listed in table 1 are being evaluated to determine their suitability for use on aerospace components. Hence in addition to properties such as corrosion resistance, lubricity, galvanic compatibility etc. the effect of coatings on fatigue strength, resistance to aircraft fluids and the risk of hydrogen embrittlement resulting from coating process are being investigated. The various tests currently being carried out are summarised in table 2.

In the first phase of the programme coatings were applied to 150mm x 100mm panels cut from 1mm thick 4130 steel sheet. These panels were used to evaluate the corrosion resistance of the coatings and properties such as paint adhesion and resistance to aircraft fluids. A series of fasteners were also coated to allow torque-tension and electrical conductivity measurements to be made. Fatigue specimens and hydrogen embrittlement test pieces were machined from 4130 steel bar heat treated to 1400 MPa and subsequently plated.

Table 2 Tests to evaluate substitute coatings

Coating characteristics (microstructure, adhesion etc.)	
Corrosion	General resistance
	Galvanic compatibility
	Hydrogen embrittlement
	Electrochemical studies
Torque-tension relationships for bolts and nuts	
Fatigue	Effect on fatigue strength
Resistance to aircraft chemicals	
Paint adhesion	
Repair	

4.1 Coating characteristics

Optical and scanning electron microscopy are being employed to determine the microstructure and surface roughness of the coatings. The adhesion and flexibility of coatings to the substrate are being measured using cross-cut tests.

4.2 Corrosion Resistance

Both accelerated and outdoor exposure tests are being used to compare the corrosion resistance of the various coatings with electrodeposited cadmium plating. Details of the tests being employed are given in table 3.

Table 3 Corrosion tests used to evaluate coatings

Test	Standard
Accelerated tests	
Exposure to continuous neutral salt fog	ASTM B117
Alternate immersion/emersion in dilute salt solution	Based on ASTM G44
Exposure to intermittent acidified salt fog	ASTM G85
Exposure to 100% humidity	ASTM D2247
Outdoor exposure sites	
DRA(Fraser) Portsmouth, UK	
NLR, (Noordoostpolder), The Netherlands	
Fokker, Schiphol, The Netherlands	

For all of the tests in table 3 the 150mm x 100mm test panels were employed. These were exposed both undamaged and with a scribe to expose the steel substrate. Evidence of corrosion products on the coating surface and time to red rust were recorded in each case. In addition some neutral salt spray tests and outdoor exposure trials are being conducted on samples consisting of aluminium blocks into which have been inserted coated fasteners. These experiments are intended to assess the galvanic compatibility between coatings and aerospace aluminium alloys.

4.3 Electrochemical measurements

A number of electrochemical techniques are being employed to study the corrosion behaviour of coated test panels. These include

- open circuit potential - time measurements
- linear polarisation sweeps
- galvanic corrosion current measurements

Data obtained from these measurements are being used to compare the barrier and sacrificial properties of different coating schemes and their long term compatibility with airframe alloys.

4.4 Hydrogen Embrittlement Studies

High strength steels are susceptible to hydrogen embrittlement. Electroplating processes such as cadmium plating are less than 100% efficient and some hydrogen will be evolved during deposition which may diffuse into the steel substrate. To reduce the risk of hydrogen embrittlement a post plating heat treatment is carried out on all steels with a strength greater than 1200 MPa. In the case of a steel part manufactured from a steel with a strength of 1850 MPa and electroplated with cadmium this would involve baking at 200°C for a minimum of 18 hours. In the current programme, tests are being conducted on coated steel specimens to identify potential hydrogen embrittlement problems. After coating the samples are de-embrittled in accordance with the plating specification or the coating suppliers instructions.

Two aspects of hydrogen embrittlement are being investigated. In the case of coatings prepared by electro-deposition, there is concern that the process itself may generate sufficient hydrogen to cause cracking under tensile loading. To investigate this sustained load testing and slow bend tests are being carried out on coated samples. A second consideration is the possible introduction of hydrogen into the steel substrate as a result of corrosion occurring on the coating. This is being studied using notched tensile specimens. These are loaded to 75% of the notched tensile strength after coating and are then subjected to alternate immersion in 3.5% sodium chloride solution until failure occurs. The performance of each of the coatings is being compared with cadmium plating.

4.5 Effect of coatings on fatigue

Surface treatments such as pickling, anodising and plating may have a detrimental effect on the fatigue life of aerospace components. Constant amplitude fatigue tests are in progress to determine the effects of the different coatings on the fatigue life of specimens machined from AISI 4340 steel tempered to give a tensile strength of 1400 MPa. Both smooth specimens and notched specimens are being used to give K_t (stress concentration) values of 1.0, 2.5 and 4.0. Tests are being conducted at a frequency of 185Hz and a stress ratio equal to 0.1.

4.6 Resistance to aircraft chemicals

Hydraulic fluids, aviation fuel, paint strippers and many of the other chemicals and liquids used on aircraft and in the maintenance of aircraft are potential corrosion hazards to the airframe structure. Immersion tests are being carried out to establish the degree to which coatings degrade when exposed to some of the more commonly used aircraft chemicals. The range of chemicals includes

- ethylene glycol
- aviation fuel
- butyl phosphate type hydraulic fluid
- alkaline based general purpose cleaner

4.7 Paint adhesion

The adhesion of conventional epoxy based primers to passivated coatings will be examined using a standard cross hatch test. In each case the primer will be applied to the complete coating scheme. For example in the case of the electrodeposited zinc - nickel and zinc - cobalt -iron coatings these will be passivated prior to painting.

4.8 Repair of coatings

Trials are in progress to examine the repair of coatings damaged in service. Brush plating techniques, for instance, are being evaluated as a method of replating areas on zinc - nickel electroplated parts. In some preliminary work bath plated test panels have been exposed to neutral salt fog and any corroded areas, after cleaning, reprotected by brush plating. The panels are then being further exposed to a salt fog environment. Repair methods for other coating systems will also be evaluated.

4.9 Torque - tension measurements

The low coefficient of friction of cadmium plating makes it an ideal coating for use on fasteners and threaded parts. Much of the torque used in tightening up a bolt is expended in overcoming the frictional constraints. Coatings with a high lubricity are therefore necessary if adequate preloads are to be achieved without the application of excessive torque levels. Another advantage obtained with cadmium plated fasteners is reproducible torque-tension characteristics. During the assembly of an aircraft, parts are often bolted into place and then removed for adjustment or modification. This process may be repeated a number of times and it is essential that there is no significant change in the torque-tension behaviour of the fasteners employed. In the current programme the effect of repeated tightening and untightening on the torque - tension behaviour of coated steel bolts and nuts is being determined.

5 PROGRESS

The programme is continuing to progress according to the original schedule. All the test panels, fasteners, fatigue and hydrogen embrittlement specimens have been plated and distributed to the partners. Accelerated corrosion tests are well advanced and data is being collated.

Three examples are presented here to illustrate the type of data being generated by the programme. Preliminary results obtained by one test laboratory using neutral salt spray testing are shown in table 4. Comparable tests are still in progress at other laboratories and will be analysed in detail at the completion of the programme.

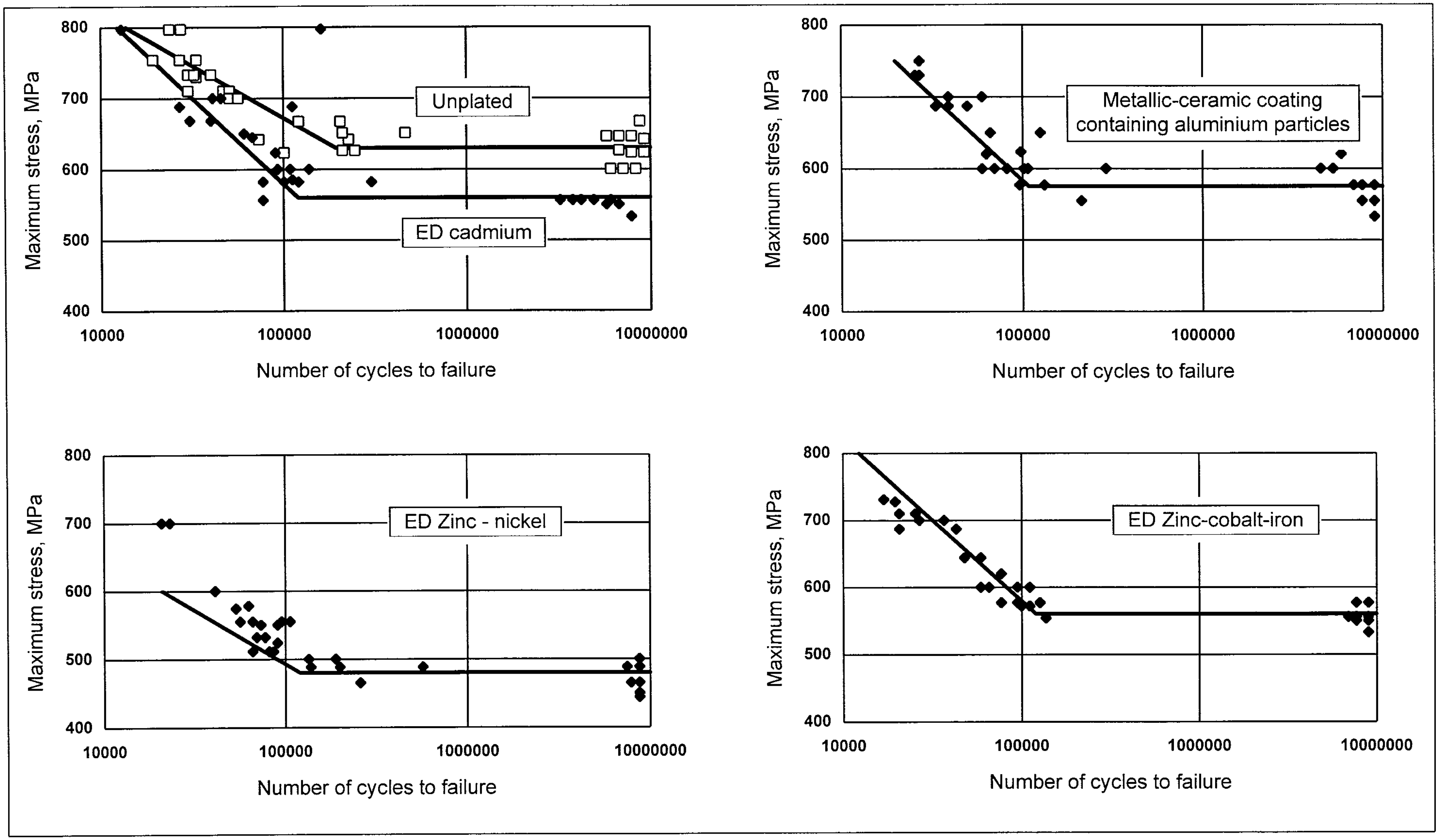

Fig.1 S-N fatigue curves showing the effects of coatings on fatigue life

Table 4 Neutral salt spray data - as plated undamaged panels

Coating	Time to red rust (hours)
ED zinc-cobalt-iron	310
ED zinc-nickel	440
Al metallic-ceramic coating	3020
Al-Zn metallic-ceramic coating	2056
ED aluminium	216
IVD aluminium	350
ED cadmium	740

Outdoor exposure trials are continuing at the three test sites. At the Schiphol site a selection of coated panels were placed on test in 1995. The appearance of the panels after 14 months exposure are summarised in table 5. Under these conditions rusting was detected in the scratch area of panels electroplated with zinc-nickel and on panels coated with a metallic-ceramic coating.

Table 5 Apearance of coated panels after 14 months outdoor exposure

Coating		Appearance in scratch
Passivated	ED Zn - Co -Fe	Discoloration + white rust some red rust
As plated	ED Zn - Co - Fe	White rust and dark areas along scratches
Passivated	ED Zn - Ni	Red rust
As plated	ED Zn - Ni	Red rust - spots of red rust outside scratch
Al metallic ceramic top coated		Red rust
Al metallic ceramic no top coat		Red rust
Al / Zn flake		Discoloration
Passivated	ED cadmium	Discoloration - dark in scratch
As plated	ED cadmium	Discoloration

Fatigue testing has been undertaken at three laboratories and some results are now available for cadmium plating, zinc-nickel, zinc-cobalt-iron and metallic-ceramic coatings applied to specimens with a Kt value of 2.5. Typical S-N curves are reproduced in fig. 1. Early results indicate that all the coatings examined so far including electrodeposited cadmium have a detrimental effect on fatigue life.

6 ENVIRONMENTAL AND ECONOMIC CONSIDERATIONS

In addition to the test programme, a survey is being undertaken to establish the environmental issues associated with each of the coatings being evaluated. Those issues which are being considered include

- the effects on employees involved in the assembly and maintenance of aerospace structures

- the effects on employees engaged in the application of coatings, processes etc.

- the effects on the environment - for example disposal of effluent, waste materials and the remnants of corroded coatings

Cost is another important issue. The perfect replacement for cadmium plating may at the end be too expensive. Estimates of plating costs are being sought from commercial coaters and finishers associated with the aerospace industry. To obtain some degree of uniformity across the industry, quotes for specified batches of fasteners and surface area of component are being requested. The aim is to be able to compare plating costs directly with electrodeposited cadmium.

7 CONCLUSIONS

A comprehensive test programme to evaluate a series of commercially available coatings as substitutes for cadmium plating has been started. The programme continues to run to schedule and testing will be complete in December 1996. The results obtained from the Garteur study will be used by the partners to recommend alternatives to cadmium plating for airframe applications and to identify areas where further testing and development may be needed.

R&D TO DEVELOP SUBSTITUTES FOR ELECTROPLATED HARD CHROME

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1. SUMMARY

Hexavalent chromium (CR^{+6}) is the ionic species used in the traditional electroplating of chromium for corrosion and wear resistance, referred to as electrolytic hard chromium (EHC). The resulting coating provides not only a hard wear resistive barrier, but also has lubricity making it ideal for hydraulic applications. Typical applications include landing gear components, flight control actuators, gun barrels, and turbine engine components. EHC plating is used for both rebuilding worn parts and as a protective coating by original equipment manufacturers.

The U.S. Environmental Protection Agency (EPA) has determined hexavalent chromium to be detrimental to health and the environment. Hexavelent chrome is known carcinogen, with some studies indicating a fifteen fold increase in instances of lung cancer among workers exposed to chrome plating operations. This substance is on the EPA list of 17 toxic compounds and is in the 33/55 program for reduction of hazardous materials. In January 1995, the EPA released new Clean Air Act rules to limit emissions from EHC operations. As a result, the Occupational, Safety and Health Administration (OSHA) is proposing to decrease the exposure limit from .1mg/m^3 to .005 mg/m^3. Reducing emissions to this new level will greatly increase the operating cost of EHC plating.

In addition to the environmental impact of EHC, reducing budgets and longer life-cycle requirements demand advanced coatings that will significantly reduce wear and expand the life of current systems. This has led to investigation of several alternative coatings and coating processes. Newly implemented processes will, necessarily, provide environmentally clean alternatives, improve component life, and reduce maintenance costs through the implementation of high performance coatings.

Electroplated chromium is used extensively to rebuild worn landing gear components, hydraulic actuator parts and many other components of present day weapon systems. Electroplated hard chromium has many excellent attributes which make it very attractive for use in high performance applications. It has generally good adhesion to steel substrates, is machinable, can be ground and polished and provides excellent wear and corrosion protection characteristics.

2. DISCUSSION

Chromium is electro-deposited from a water solution of chromic and sulfuric acids. Components are generally pre-processed prior to chrome plating by cleaning, degreasing and inspection, shot peening, masking and abrasive blasting. Prior to plating components are reverse current cleaned in the plating solution prior to plating. Subsequent to plating the components are again rinsed, cleaned and in the case of high strength steel are baked to prevent hydrogen embrittlement.

Significant costs are involved in making the chrome plating process safe from an occupational health hazard and in treating waste resulting from the processes involved.

Chromium electroplating replacement programs fall into several distinct categories. These include, the

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electro deposition of materials other than chromium as well as the electroless deposition of nickel; the spray up of chromium metal as well as other materials and alloys; the use of ion beam deposited metals as well as the use of non-metallic substitutes for chromium including, diamond like coatings; and high energy beam processes including, nitrogen implantation, laser cladding and electron beam deposition. Figure 1 lists some of the basic processes being investigated to replace electroplated hard chrome. The thermal spray processes have been and presently are now used in many production operations where they have replaced the conventional electroplating metal deposition processes. Of the thermal spray processes HVOF is perhaps the most widely used. Numerous HVOF coatings have been compared to chromium plating by spraying metal specimens and performing metallurgical tests (Ref 1). The results of the project indicated that several of the coatings tested exhibited excellent microhardness, galling and rubbing wear resistance. Also it was found that the coatings had good adhesion, fatigue and corrosion resisting properties. While coating thickness was easily controlled to between 8 and 12 mils, porosity was found in almost all of the coatings. Figure 2 is a listing of some of the tests that should be accomplished when comparing thermal spray coatings to electroplated chromium (Ref 5). The development of an engineering data package for electroplated chrome replacements needs to include testing at least three levels. These are; laboratory coupon and specimen testing, part or single component testing as well as sub and full scale component test and evaluation. Successful completion of the engineering data package should permit production trial runs and component service evaluation. Life cycle performance/cost analysis should determine whether whole sale chromium electroplate replacement makes good business sense (Ref 1). To replace electroplated chrome any desired substitute should have a set of desired characteristics (Ref 5). Figure 3, lists a few of the critical characteristics that should be considered. Substitute costs and environmental acceptably as well as performance are critical aspects to be evaluated. (Ref 3) Figure 4 depicts a flow diagram of generic, typical hard chrome plating process (Ref 2,5,6). The thermal spray processes have the potential to eliminate a number of the waste streams produced by electroplating and thus may be lower in cost and more environmentally acceptable (Ref 2,3,4,6). Figure 5 shows typical plating process (Ref 6) waste streams both with and without chrome recovery. Elimination of these waste streams from certain production processes could be good business practice.

3. CONCLUSION

Extensive and widely varying efforts are under way to find substitutes for electrodeposited chrome as well as to find acceptable alternatives to chrome itself. The most mature technology in the US today is the thermal spray process and specifically the HVOF process. Factors for HVOF are very favorable where cost, elimination of HAZTOX materials, waste streams and process water are concerned. Performance factors will vary widely depending upon the type of service required. Laboratory test results often provide conflicting data and information. In these instances then it is necessary to perform full up component test and evaluation to determine adequate performance.

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FIGURE 1

PROCESSES UNDER INVESTIGATION TO REPLACE ELECTROPLATED HARD CHROMIUM

- ELECTRO/ELECTROLESS DEPOSITION
  - NICKEL
  - Ni-W-B (AM PLATE)
  - TAKADA-W-SIC-N
- ION BEAM DEPOSITION, PVD AND CVD
  - T, N, (Ti-Al) N, CrN, Ta, W, N
  - DIAMOND LIKE COATINGS
  - Cr, Ni
- THERMAL SPRAY
  - HIGH VELOCITY OXY FUEL (HVOF), W-C, WC-Co, Cr, ETC
  - SPRAY CASTING (Cr, Ni, VERSALLOY 50, ETC)
  - D GUN, SUPER D GUN
- OTHER
  - RAIL GUN MAGNETIC POWDER SPRAY (ANY POWDER-MAGNETIC)
  - LASER DECOMPOSITION/DEPOSITION (Cr, Ni, CARBIDES, ETC)

FIGURE 2

METALLURGIAL TESTING PLAN

TEST	ASTM Method	Specimen Type	# of Specimens Per Condition	Total # of Specimens
Adhesion (heat quench/ Microstructural Evaluation	B571-84/E3-80 (1986)	Coupon	3	36
Tensile	E8-89	Tensile	6	72 (plus an additional 9 unplated)
Fatigue	E466-82	Fatique	8	96 (plus an additional 12 unplated)
Thickness/Microhardness/ Macrohardness	B487-85/B578-87/E18-89a	Coupon	2	24
Galling resistance	G98-91	Coupon Button	2 8	24 96
Taber wear	C501-84	Taber	5[a]	20
Rubbing wear (Crossed cylinder)	G83-90	Cylinder	6	72
Particle impingement	G76-83 (1989)	Coupon	2	24
Salt Fog	B117	Coupon	5	60
Adhesion (bend)	B571	Coupon	3	36

FIGURE 3

DESIRED CHARACTERISTICS OF A HARD CHROME SUBSTITUTE

Parameter	**Hard Chromium**
Plating rate	0.5 - 2.0 mils per hour
Maximum plating thickness	50 mils (typically 10-15 mils)
Metal turnover	"almost infinite"
Phosphorus by weight	NA
Bath operating temperature	55 - 60^{0}C
Melting point	1615^{0}C
Hardness as plated	900 - 1,000 Vickers
Maximum hardness after heat treatment	900 - 1,000 Vickers
Brightness	Bright
Neutral Salt Spay	20 - 100 hours to first corrosion spot
Taber abraser wear test index	4.7 grams for 10,000 cycles (1,000 gram load)

FIGURE 4

Flow Diagram of Hard Chrome Plating Process

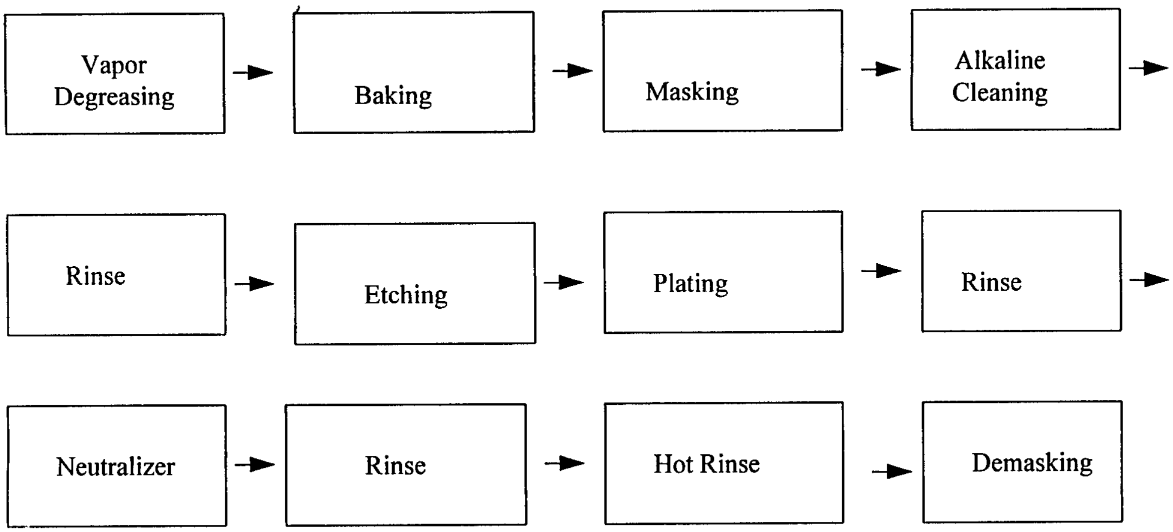

FIGURE 5

QUANTITATIVE COMPARISON OF WASTE GENERATION FROM HARD CHROME PLATING FOR SELECTED PARTS

Plating Process	Chromium Plating without Cr Recovery	Chromium Plating with Cr Recoery
Chemical stripping	93 lbs. Cr/year (dissolved Cr in spent stripping solution)	93 lbs. Cr/year (dissolved Cr in spent stripping solution)
Vapor degreasing	598 lbs/year (still bottoms)	598 lbs/year (still bottoms)
Masking and demasking	2,392 lbs/year (still bottoms)	2,392 lbs/year (still bottoms)
Chemical cleaning	325 gpy (spent acid and alkaline solutions)	325 gpy (spent acid and alkaline solutions)
Plating	150 lbs. Cr/yr (misc. losses)	150 lbs. Cr/yr (misc.losses)
Rinsing/scrubber	246 lbs. Cr/yr 1,000 gpd of rinse/scrubber water	33 lbs. Cr/yr 1,500 gpd of rinse/scrubber water
Neutralizer rinse	19 lbs Cr/yr 195 gal. of alkaline solution	19 lbs. Cr/yr 195 gal. of alkaline solution
Bath maintenance/disposal	14 lbs. Cr/yr (spent catholyte)	14 lbs. Cr/yr (spent catholyte)
Emissions to atmosphere	20 lbs. Cr/yr	20 lbs. Cr/yr
Energy use to heat solutions	657,000 KBTU/yr	657,000 KBTU/yr
Summary of significance	522 lbs. Cr/yr in wastewater and hazardous waste: 20 lbs. Cr/yr in air emisions. 520 gpy of spent solutions; 2,990 lbs/yr of still bottoms; and 365,000 gpy of rinse/scrubber water.	309 lbs. Cr in wastewater and hazardous waste 20 lbs. Cr/yr in air emissions; 520 gpy of spent solutions 2,990 lbs/yr of still bottoms; 365,000 gpy of rinse/scrubber water; and 183,000 gpy of rinse/scrubber water.

SOURCE: EPA/600/R/R-94/178-REF 6

Experiences in Maintenance and Overhaul of Military Aircraft

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Abstract

Corrosion as an unavoidable fact requires cost effective control measures. By these control measures aircraft life will be much higher in comparison with all the precaution done during the manufacturing of a/c. The main philosophy gained by the experiences of maintaining more than 5000 a/c is determined by: detection and removal of corrosion and followed renewal of the protective coating in the very early stages of corrosion. It has to be repeated in determined intervalls, based on the lessons learned over the years. A steady development of new coating systems: the elimination of toxic / hazardous chemicals, slower aging of the organic.

Protective coatings, the problems of how to get the higher chemical and mechanical resistant coatings removed, and the goal to collect all divergent properties under cost effective measuring are the guidelines for new development in the maintenance area regarding human and environmental protection.

Paper presented at the 83rd Meeting of the AGARD SMP on "Environmentally Compliant Surface Treatments of Materials for Aerospace Applications", held in Florence, Italy, 4-5 September 1996, and published in R-816.

Introduction

DASA Manching has maintained more than 5000 a/c in the past. Most of them military a/c with a planned service time of up to 40 years. Therefore structural condition is one of the most essential requirements for their airworthiness.

Depending on such an extremely long service time the protective treatments of a new a/c have to be controlled constantly. This includes the surface inspections in order, assess corrosion condition and coating aging. The increase of environmental influences requires non-interrupted detection regarding the material and structural properties.

Observing the surface of protected areas does not reveal problems beneath the protective layers. Based on that fact, a corrosion control concept is required.

I. Corrosion Control Concept

- Non-destructive inspections
- Visual inspections on bare metal substrates
- Corrosion removal
- Renewing the protective layers completely

Fig. 1

Shows the difference amongst the corrosion growth , the normal corrosion progress and the essential corrosion velocity caused by a consequently carried out corrosion control treatment programme. Normal corrosion untreated will progress by an exponential term up to that damage level where structural parts', class 1, airworthiness can not be guaranteed.

Dividing the progress time into determined intervalls, at which corrosion control treatment has to be performed, the new corrosion progress time starts after corrosion removal from a much lower level. The structural condition remains in a essential better condition. Comparing the amount of corrosion damage, on the term, the difference between the treated and non-treated vector locations are obvious.

Fig. 2

Essential for effective corrosion control treatment is the detectability of small corrosion spots as a just starting corrosion. Prone to corrosion are areas of production failures where poor or no adhesion occurs. Organic coatings are not closed for gas diffusion. Water in the gas phase may diffuse the coating system and condensation in the adhesion poor area is possible.

Together with oxigen and other environmental chemicals, an electrolyte may be created. Corrosion is programmed.

Under a topcoat, primer cracks are not detectable. Such cracks are equal to poor adhesion areas. System cracks are visible, but a repair by overspraying only closes the upper surface and will leave a cave where no adhesion occurs. In such cases the whole coating system must be renewed.

The general aging of organic coating systems causes a steadily growing embrittlement of the paint. Especially in areas where high movement or vibration works on fasteners and lap joint cracks become visible around fasteners and at edges. These are main areas prone to corrosion. Another doubtless fact is that corrosion, which blisters through the whole coating system, evolves to a damage level, where a repair is necessary in most cases.

Fig. 3

Shows a primer crack.

Fig. 4

Shows a coating system crack.

Fig. 5

Shows typical corrosion around the fasteners and metal edges.

Fig. 6

Shows corrosion which was detected much too late. A panel 8 mm thick is corroded through its entirety.

Fig. 7

Shows the interior surface of a TORNADO air intake before stripping. The corroded areas are marked.

Fig. 8

Shows much more corrosion than was found before stripping (there is no additional comment necessary).

II. Relations between Substrate Pretreatment and Coating Systems

In order to reduce corrosion progress protective coatings of different types are used.

Todays general coating systems are based on a chemical pretreatment followed by a 2-component primer with active corrosion protective pigments and a 1- or 2-component topcoat. Required features are: mechanical and chemical corrosion resistance, and additionally there is a long list of other essential properties. The aging component is close to the environmental conditions and is nearly not predictable. No laboratory investigations are able to forecast the change of features depending on the situation which cannot be simulated completely.

Fig. 9

Shows the rear bottom side of a F4 a/c with loose rivets. The dust from the dry stripping makes all the leaking oil visible. The picture may explain the importance of a high elasticity and, on the other hand, the reason why so many cracks occur around fasteners.

Fig. 10

Show a riveted lap joint where the rivet is wet assembled but without corrosion protection between the panels. Residues of Alodine without complete chemical reaction creates corrosion in this case.

If during overhaul the renewing of the complete coating system is required, we prefere a wash primer application. This philosophy includes all components which may have gaps and overlapping. Certain chemical liquids with cappilary flowing action / power pose problems to certain parts in that they tend to get into inaccessible areas where there is no way of removal.

This means a non-restricted repetition of paint removal independent to the dwelltime.

Fig. 11

Shows the correlation between the different hardness of media and substrate to the created compression stress.

Fig. 12

Was part of the laboratory tests regarding aluminium alloy 2024 T3 with specified pressure and media flow.

All that assumes the availability of precisely controlled blasting equipment. Another assumption is the knowledge of the substrate material and its thickness.

Fig. 13

Shows a substrate plan, where these details are colour-marked. Besides the process and equipment, a/c sealing will be as important as the paint removal avoided. Cleaning later will be very costly. By using hot glue, special masking tape and special covers that problem was solved.

Fig. 14

Shows part of sealed a/c fuselage.

Hot glue frames can be removed easily, because adhesion of the hot glue to a metal surface is good enough for blasting protection but not as strong as on other material surfaces.

The dry stripping facility was based on the trial results of 30 a/c stripped with test equipment. Prerequisites for the new facility were:

Fig. 15

Hangar size 25 x 25 x 8 m

Fig. 16

Hangar view exterior

Fig. 17

Hangar view interior

Fig. 18

Hangar ventilation with air exchange of 40 time p.h.

Fig. 19

Local evacuation with exhausting performance

Fig. 20

Floor recovery system vacu duct (Schlick)

Fig. 21

- Cyclon as pre-dust selectors
- Media cleaning and separating system
- Dust filters meeting the environmental requirements
- 4 electronically controlled pressure blasting machines
- Media hopper and refill station
- Dust collection system.

The hangar size allows a/c up to a size of A10 a/c and comparable. Depending on economic and conveniance of the operator the layout for a basic ventilation system was determined. In order to keep media flowing in the recovery circuit an air flow of 20 m/sec had to be installed. Volume and pressure of the air was adapted to the drag of the local evacuation devices.

The goal of that installation was to get 80-90 % of the blasting media directly picked up at the local blasting area. Together with the floor recovery system, 100 % collection of media will be performed.

The floor recovery system works like vacuum cleaner having arms which move in a floor channel. The working area can be controlled between two chosen points in order to avoid cleaning in areas where no blasting operations are done.
Media and paint dust cyclon filters and the cleaning system where very high separation is attained.

Cleaning blown out air is done by fine dust filters. Media and paint dust separated and collected in plastic bags, which are given to a special waste deposit. A comparison of the disposal costs shows:

DM 200.-	for dust deposit of 1 a/c dry stripped
DM 20,000.-	for deposit of the waste water of one a/c chemically stripped.

In the future the increase of chemical disposal costs will have grown to an uneconomical level. The chromate dust, as part of the primer, causes cancer if inhaled, not if touched.
Health requirements predict:

a. the general elimination of any material causing cancer

b. if it is possible to reduce the concentration to a dust level of 0.025 mg/m^3, personnel protection is required

c. „b“ will be allowed only as long as no alternative with lower danger exists.

The concentration level of point „a“ is lower than required at Manching plant.

We have stripped more than 150 a/c without problems.
Oldtimer cars and one oldtimer a/c (JU 52) have been stripped successfully, too.

IV. Corrosion Treatment

After stripping and corrosion detection, corrosion removal is carried out. The detection is done visually and by marking the corrosion spots. Small corrosion will be removed by glass bead blasting, in other cases sanding, milling and small nozzle blasting with aluminium oxide. A chemical corrosion treatment will create further corrosion, therefore this method is not allowed for the GAF.

V. Intermediate Coating

After paint removal some bare metal areas such as fasteners etc. are prone to corrosion during the overhaul time of the a/c. Therefore as a temporary measure we protect such areas with acrylic lacquer in aerosol spray form, which can be removed before paint renewing by acetone, thinner or degreasing solvent.

Protecting the bare surface can be avoided if the a/c are not placed outdoors and will be painted before next flight.

VI. Coating Systems

1. Actual Coating Materials

1.1 Specifications
1.2 Materials
1.3 Pretreatment
1.4 Coating materials / - systems

2. Future Coating Materials

2.1 Specifications
2.2 Materials
2.3 Developments of coating materials acc. to the increased environmental regulations
2.4 Quality improvements due to increased strains

1. Actual Coating Materials

1.1 National technical specifications, like e.g. MIL, TL, DTD are prescribed to a high extent for repair respectively general refurbishment in the military field.
With regard to multi-national objects comparable national specifications are considered.

1.2 Besides the known Al-alloys more and more plastic materials are used. There exists a high proportion of glass fibre reinforced plastics and to an increasing extent carbon fibre reinforced composite materials. Other materials are only used for special components.

1.3 Anodization with chromic acid represents the optimal pretreatment for a high proportion of the Al-alloys and it replaced the yellow chromating in many fields because it offers a better corrosion protection.
The above mentioned pretreatments remain nearly undamaged during the first dry stripping and they fulfill their entire function.

1.4 If a chemical pretreatment is not possible with regard to new aircrafts and refurbishment Wash Primer is still used as replacement in order to achieve a good adhesion and to improve the corrosion protection.

Actually, chromate-containing primers based on epoxy resins still dominate, above all with regard to new aircrafts.

However, chromate-free PUR- and EP-Primers are used on plastics.

The so-called One-Coat Paint (thermoplastic acrylate) is still used to a high extent as topcoat for the exterior painting. In former times it was directly applied on the chemical pretreatment or the Wash Primer.

In the interior field topcoats based on epoxy resins are mainly used, PUR-materials are used only to a small extent.

PUR-materials are prescribed for the exterior painting of some objects.

2. Future Coating Materials

2.1 New specifications e.g. for chromate-free primers, topcoats with a better weather resistance and similar, partly already exist respectively are being elaborated.

2.2 With regard to the materials there exists a trend towards plastics, EFA already reached approx. 70 %. New Al-alloys are also being tested.

With regard to the pretreatments one also tries to use no VI-valent chromic compounds. Various research projects are being executed.

2.3 If there exists a good chemical pretreatment on the Al-materials it is already possible to use chromate-free primers. There exists positive experience regarding the refurbishment of PHANTOM and TORNADO for approx. 8 years. The German components of the prototypes EFA also have chromate-free EP-Primer.

In the case of missing or inadequate pretreatment chromate-free primers still have obvious disadvantages. However, there exists an increasing international pressure to use no VI-valent Cr-compounds.

In the near future the solvent emissions also have to be drastically reduced. The development and practical testing of the so-called „Low VOC“ (**V**olatile **O**rganic **C**ompound) materials are being executed intensively.

This means that primers may contain max. 350 g/l and topcoats 420 g/l solvents when they are ready for processing.

The development of waterborne coating materials also made great progress. However, in the near future they will still fail in most cases due to the processing conditions.

Further polluants, e.g. Pb, Cd etc., are almost replaced completely.

2.4 The environmental strains steadily increased.

More intensive UV-strain together with greater chemical attacks cause a higher degradation of the surface protection.

Damage, like degradation of gloss, embrittlement, formation of hair cracking, loss of adhesion and similar, is observed.

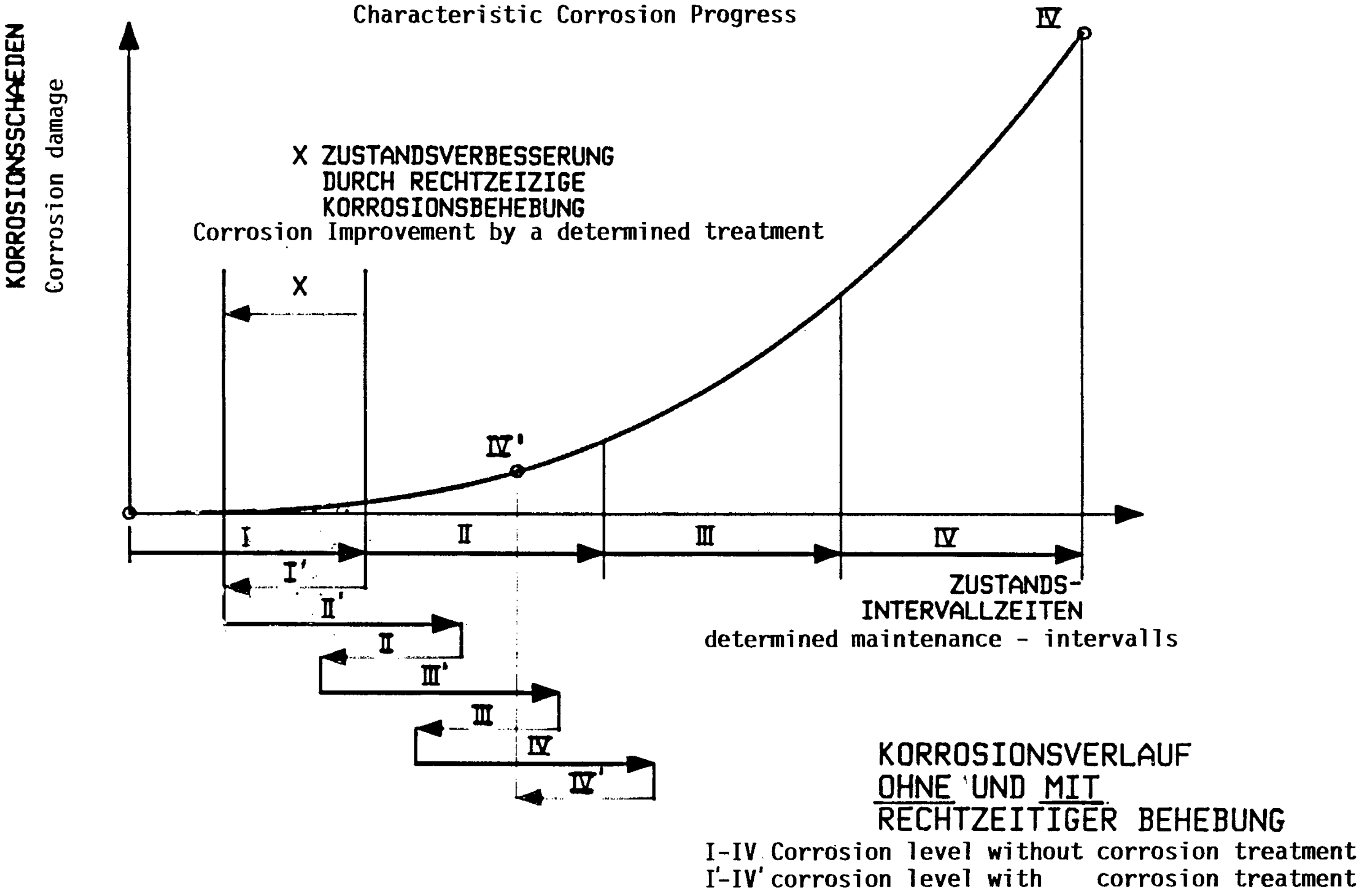
In order to compensate this damage new and more severe test methods were introduced showing now first results.

The paint stripping of military large-capacity aircrafts still is a problem. In this field wet paint stripping with ingredients like phenol and methylene chloride will be applied also in the future. Paint stripping materials being more beneficial to the environment and / or coating materials which can be stripped more easily are urgently required.

CORROSION-CONTROL

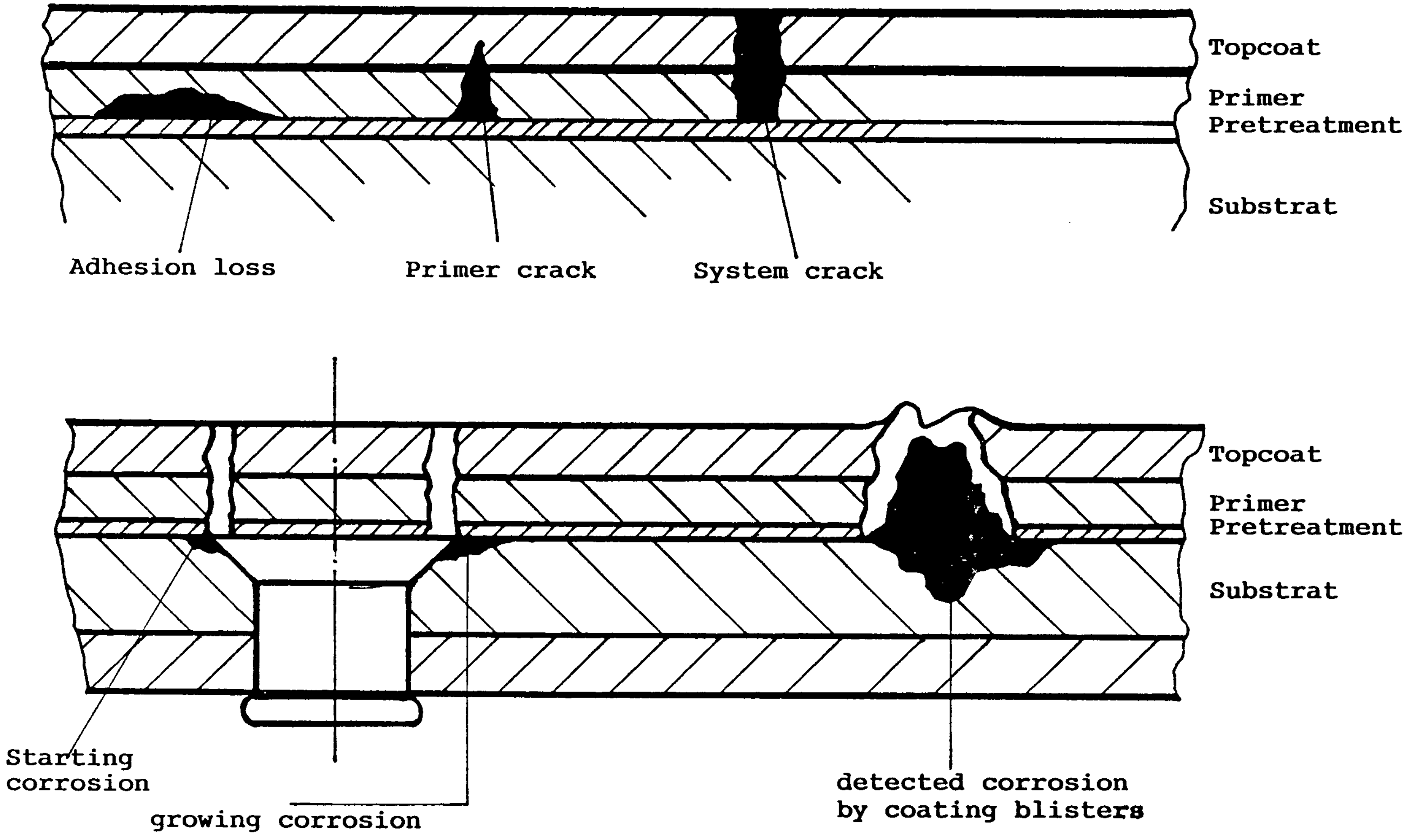
SCHADENSVERLAUF IN DER INSTANDHALTUNGSPHASE

Characteristic Corrosion Progress

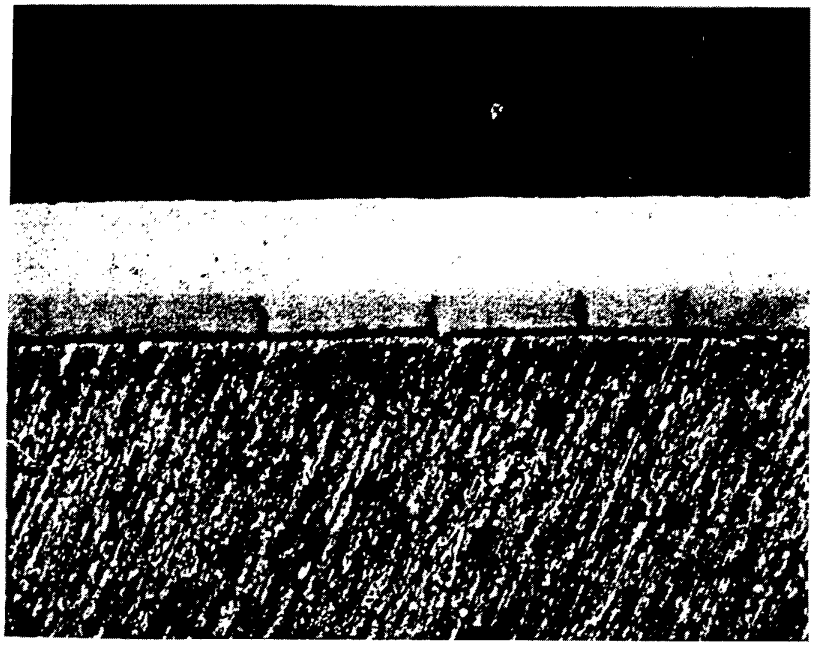


- Fig. 1 -

Corrosion detectability.

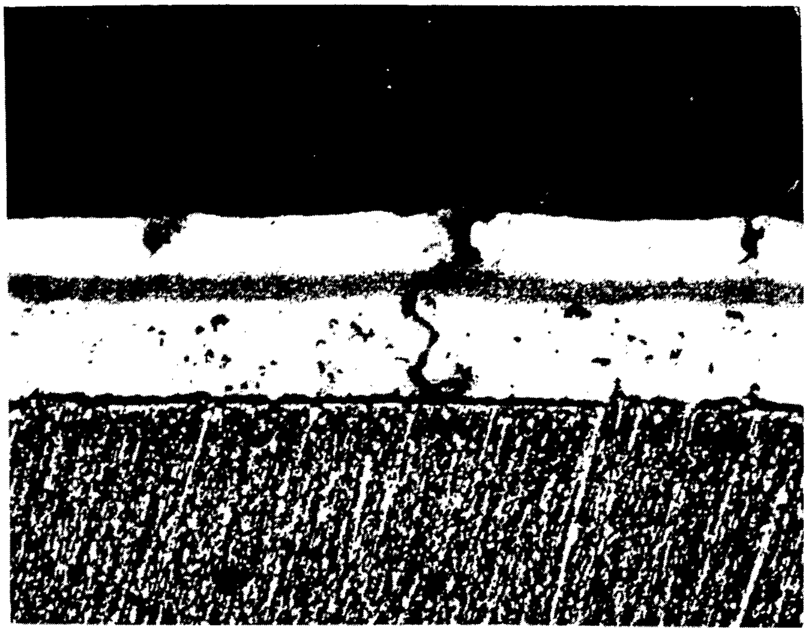


- Fig. 2 -



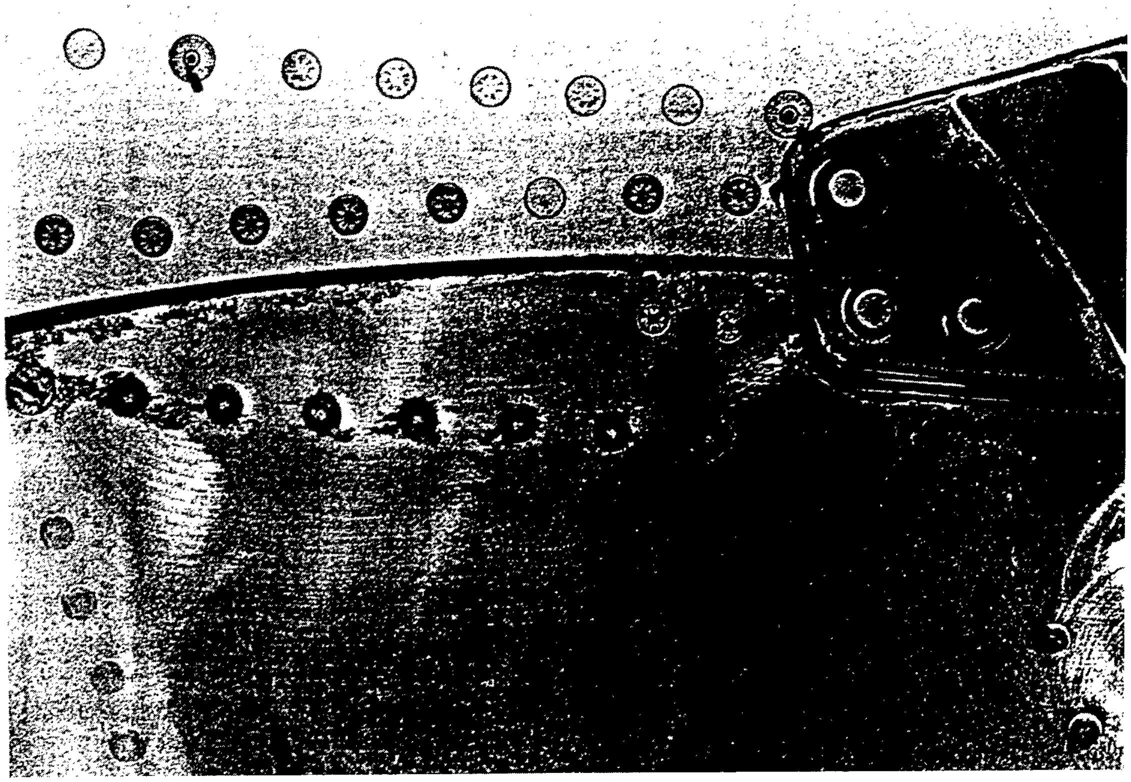
PRIMER CRACKS

- Fig. 3 -

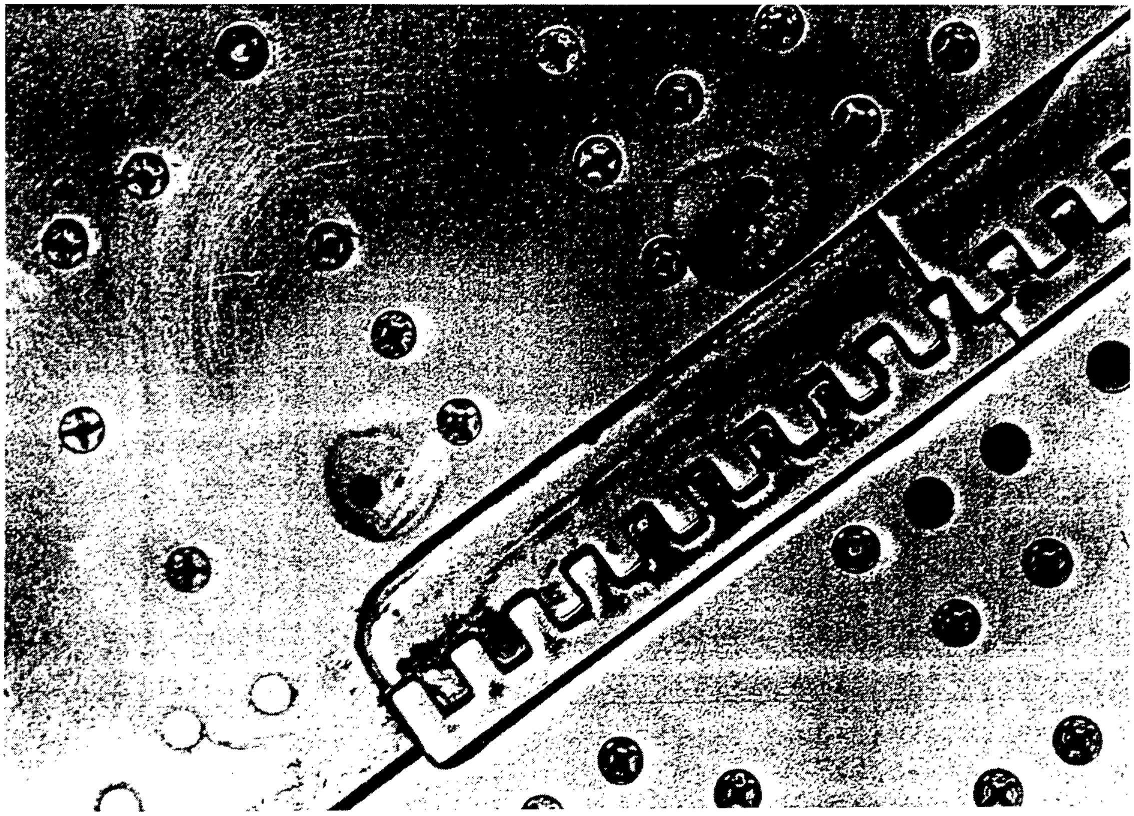


COATING - SYSTEM - CRACK

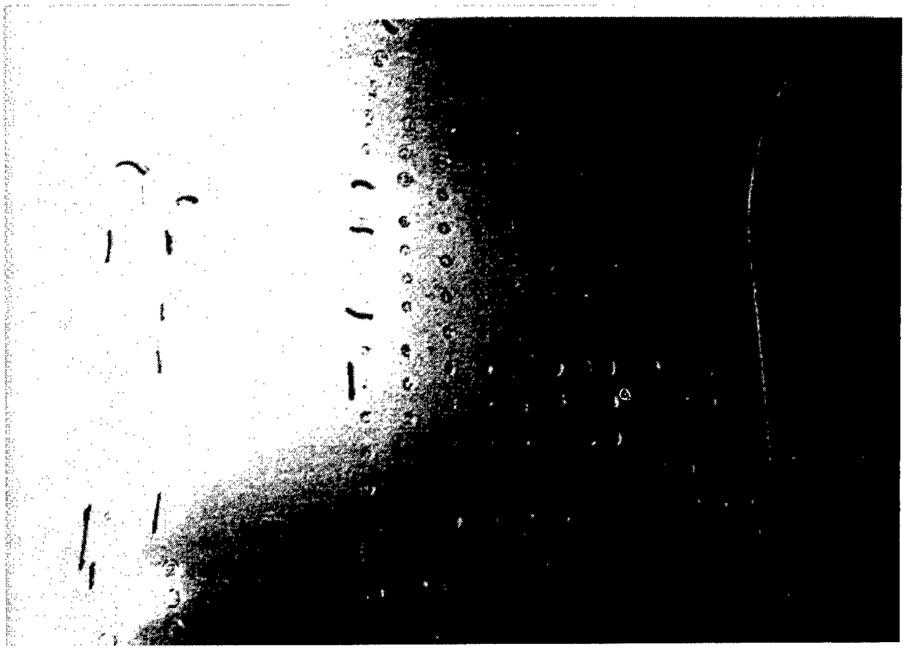
- Fig. 4 -



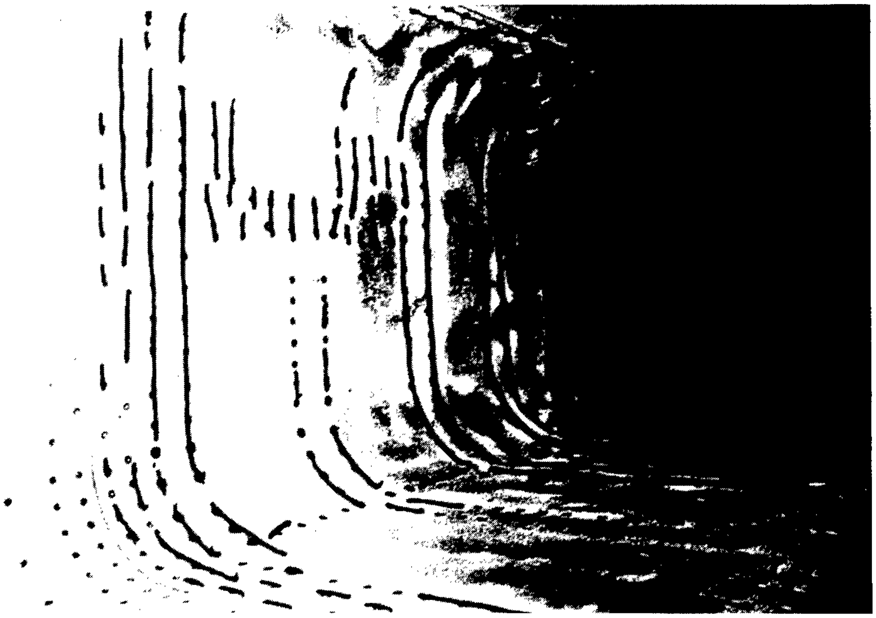
- Fig. 5 -



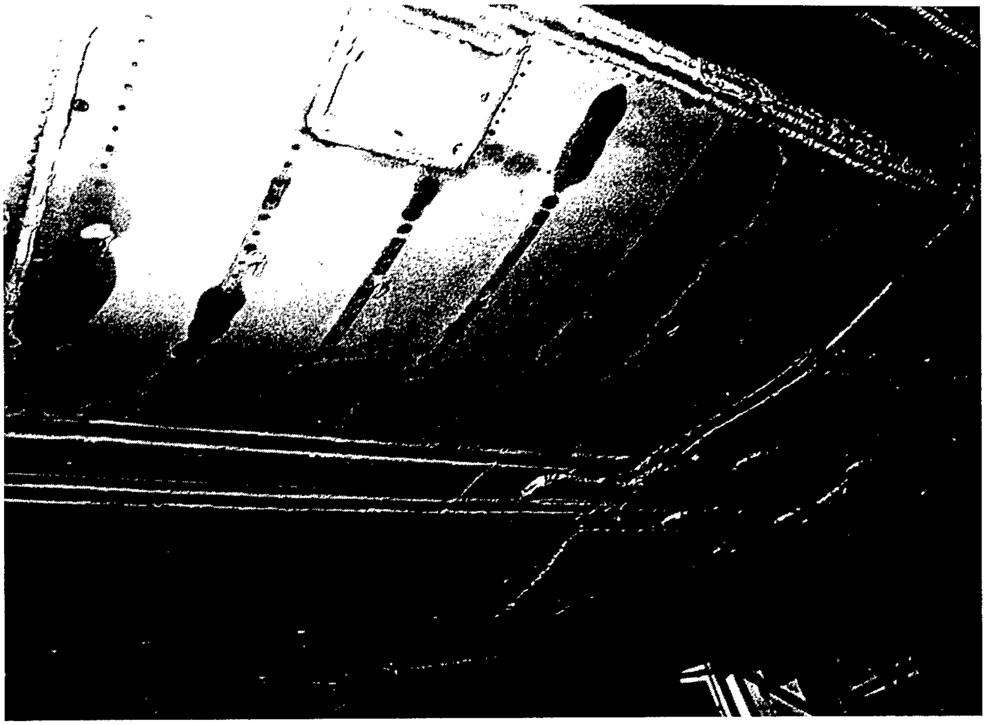
- Fig. 6 -



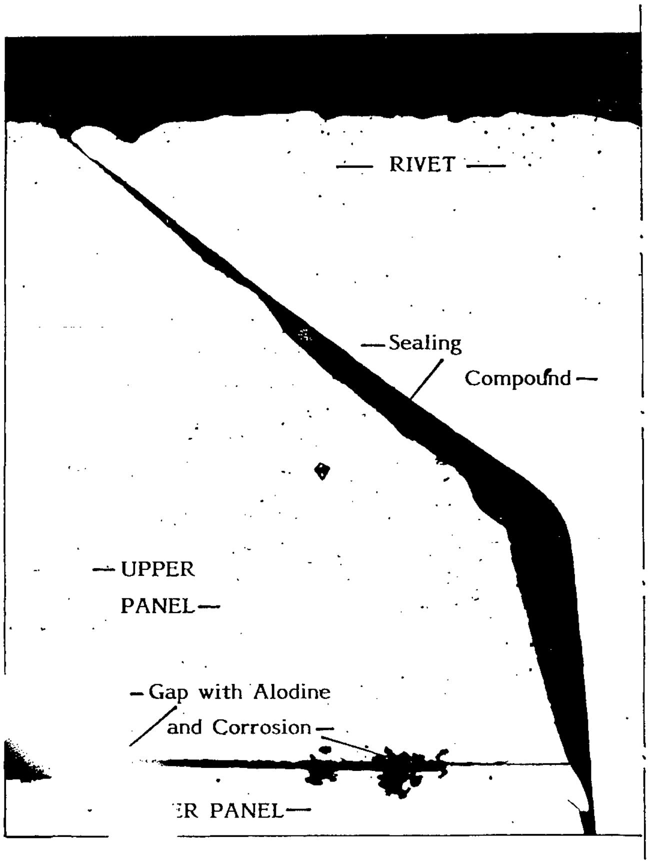
- Fig. 7 -



- Fig. 8 -



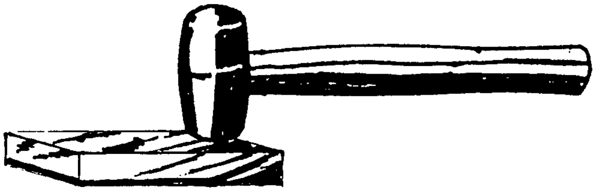
- Fig. 9 -


RIVET
Sealing Compound
UPPER PANEL
Gap with Alodine and Corrosion
ER PANEL

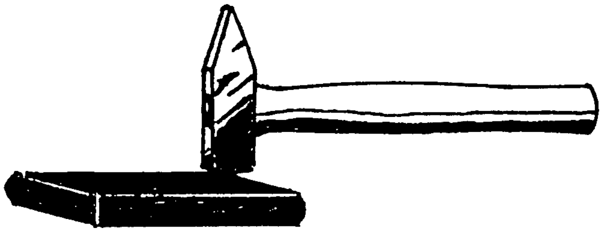
- Fig. 10 -

Compressive stress

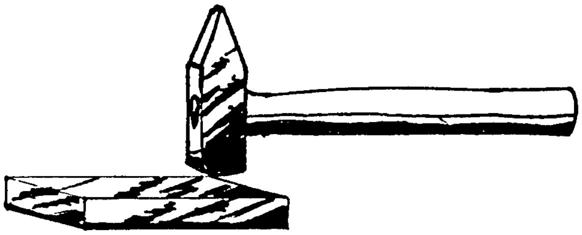
Correllation of the hardness between
blasting media and substrat material



Soft media to hard substrat

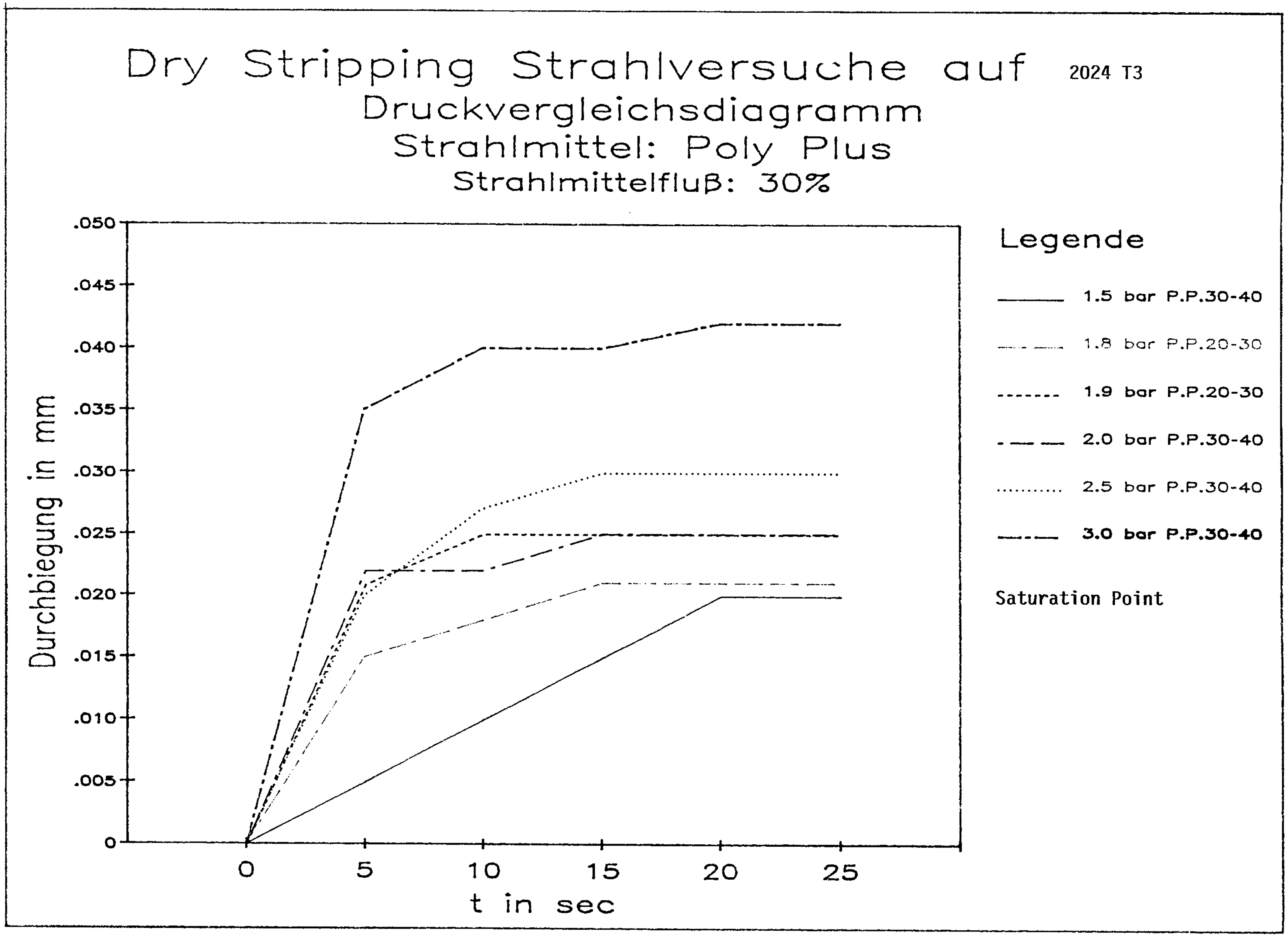


Hard media to soft substrat

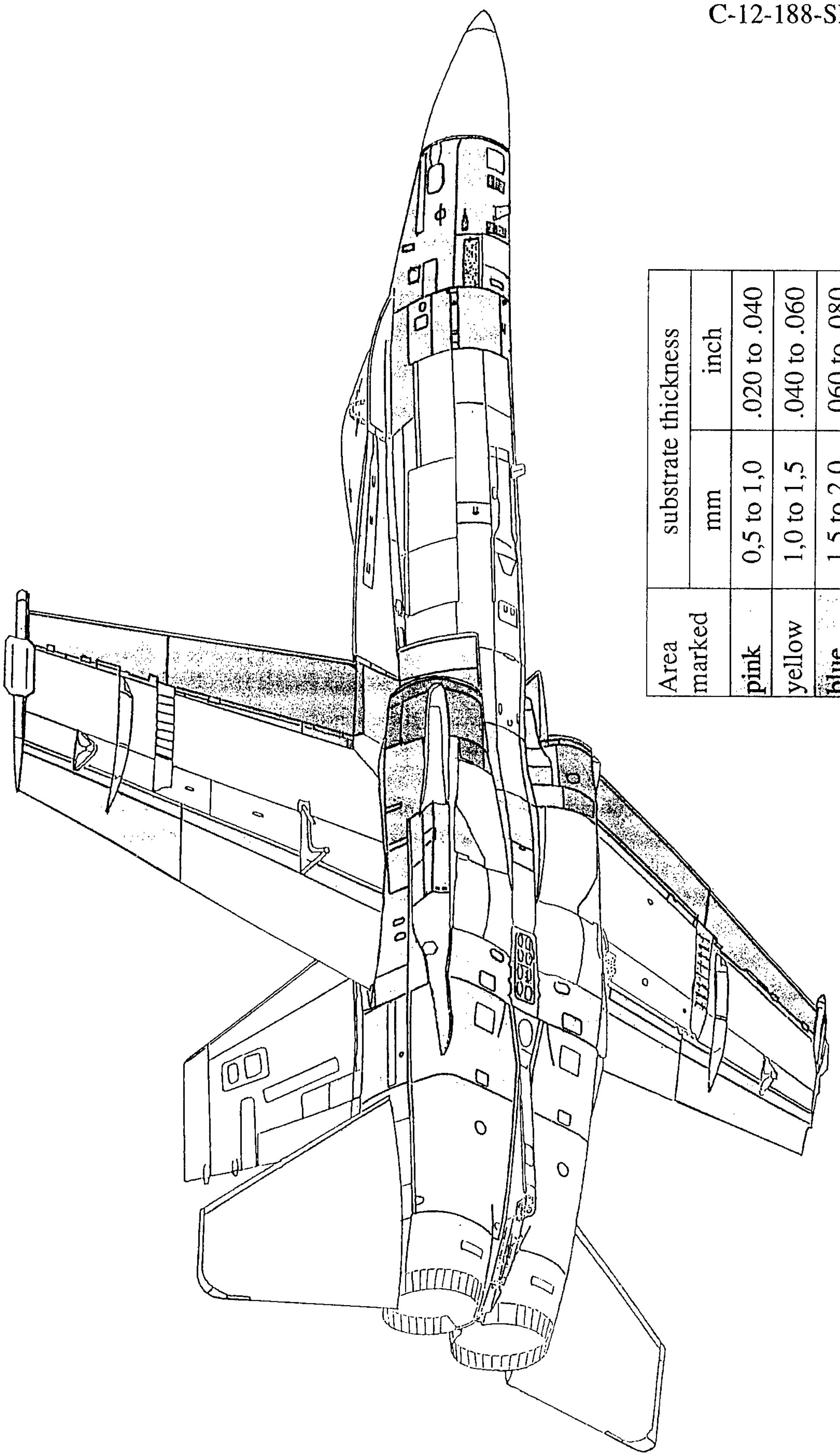


Hard media to hard substrat

- Fig. 11 -

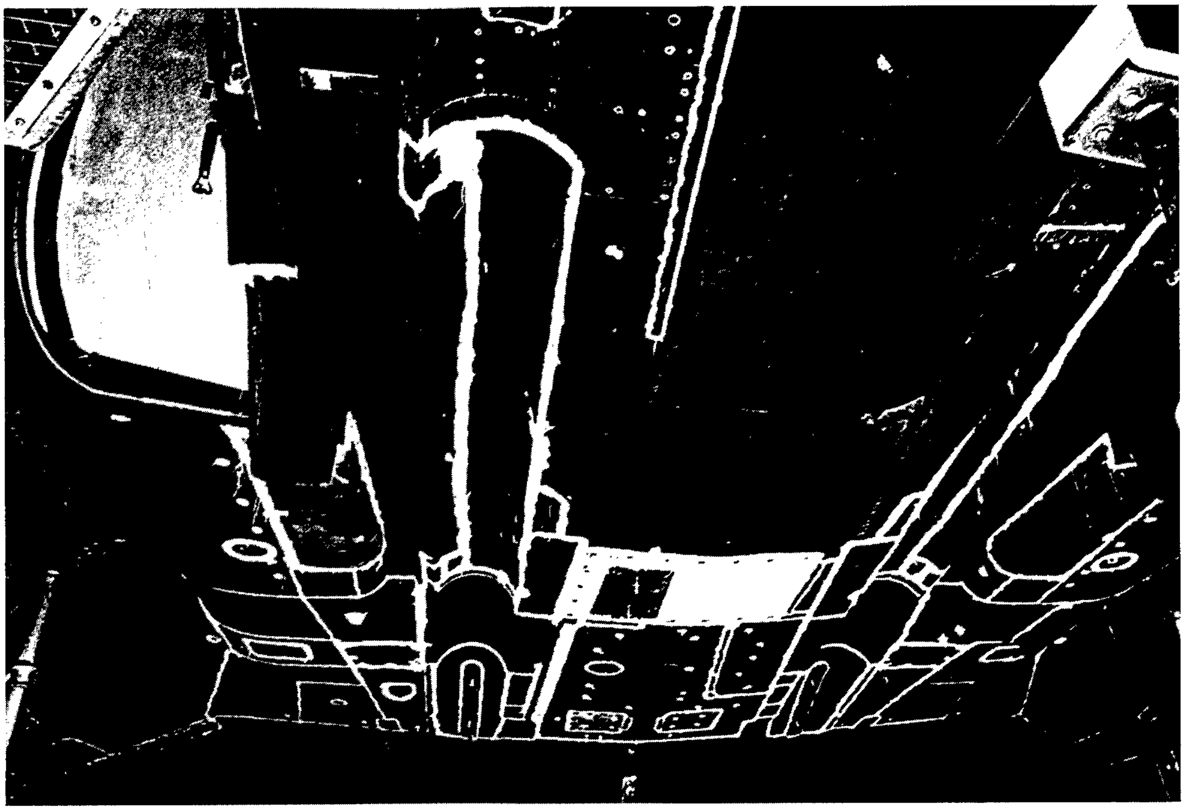

Dry Stripping Strahlversuche auf 2024 T3
Druckvergleichsdiagramm
Strahlmittel: Poly Plus
Strahlmittelfluß: 30%
Durchbiegung in mm
.050
.045
.040
.035
.030
.025
.020
.015
.010
.005
0
0
5
10
15
20
25
t in sec
Legende
1.5 bar P.P.30-40
1.8 bar P.P.20-30
1.9 bar P.P.20-30
2.0 bar P.P.30-40
2.5 bar P.P.30-40
3.0 bar P.P.30-40
Saturation Point

- Fig. 12 -

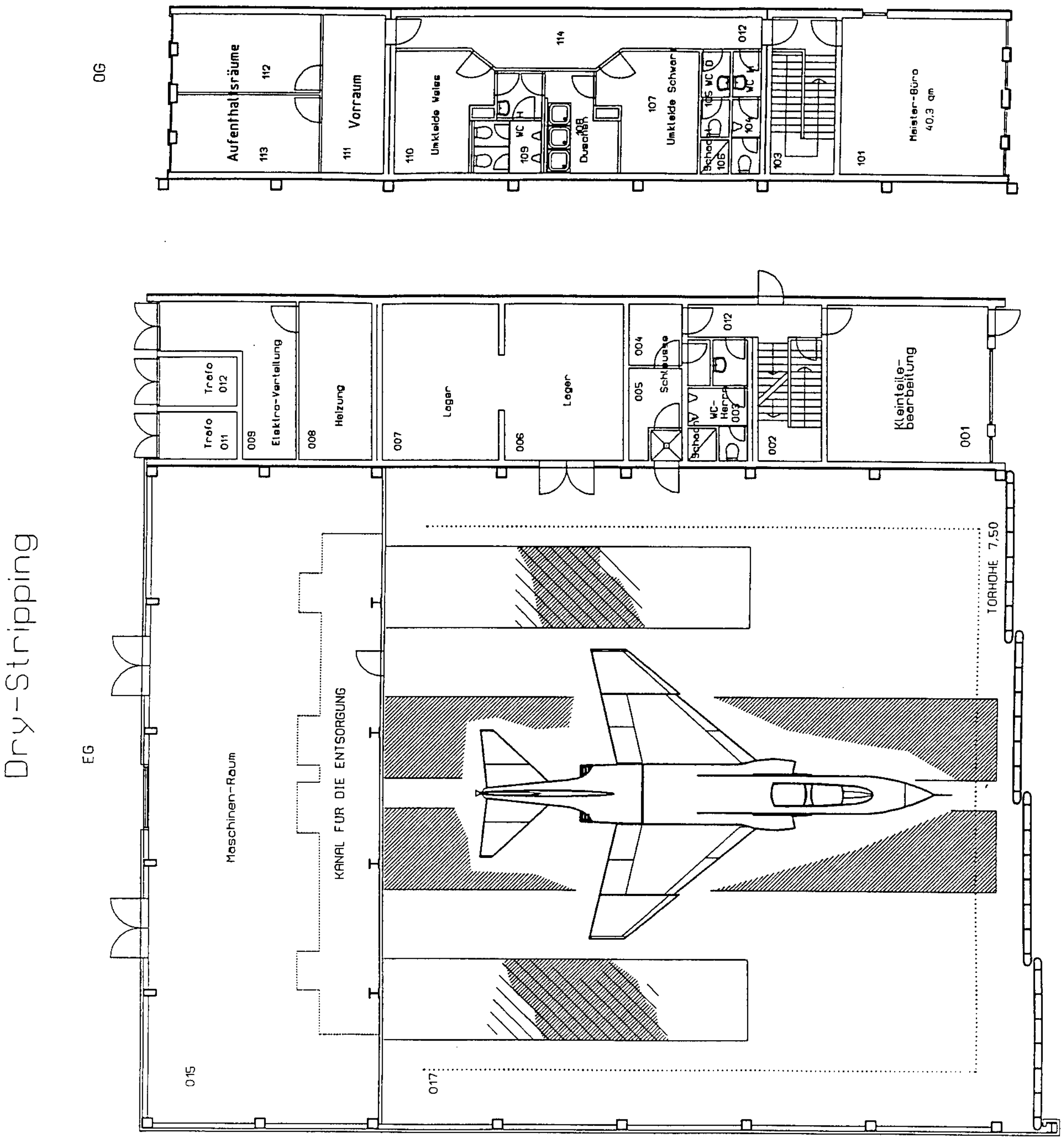


Area marked	substrate thickness	
	mm	inch
pink	0,5 to 1,0	.020 to .040
yellow	1,0 to 1,5	.040 to .060
blue	1,5 to 2,0	.060 to .080

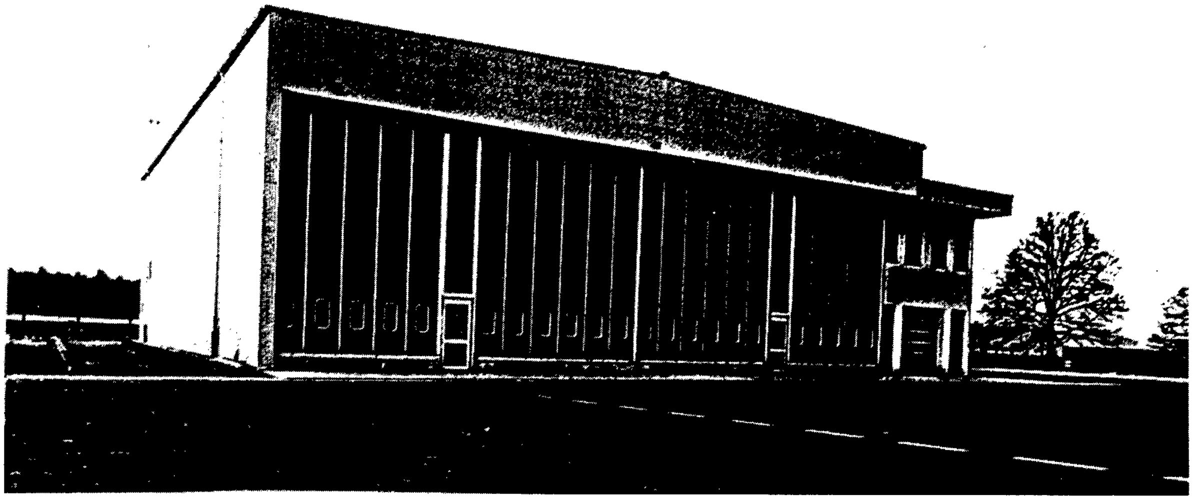
Fig. 3.2 Parameter and substrate plan for aluminium and steel on CF-18
(Sheet 4 of 4)



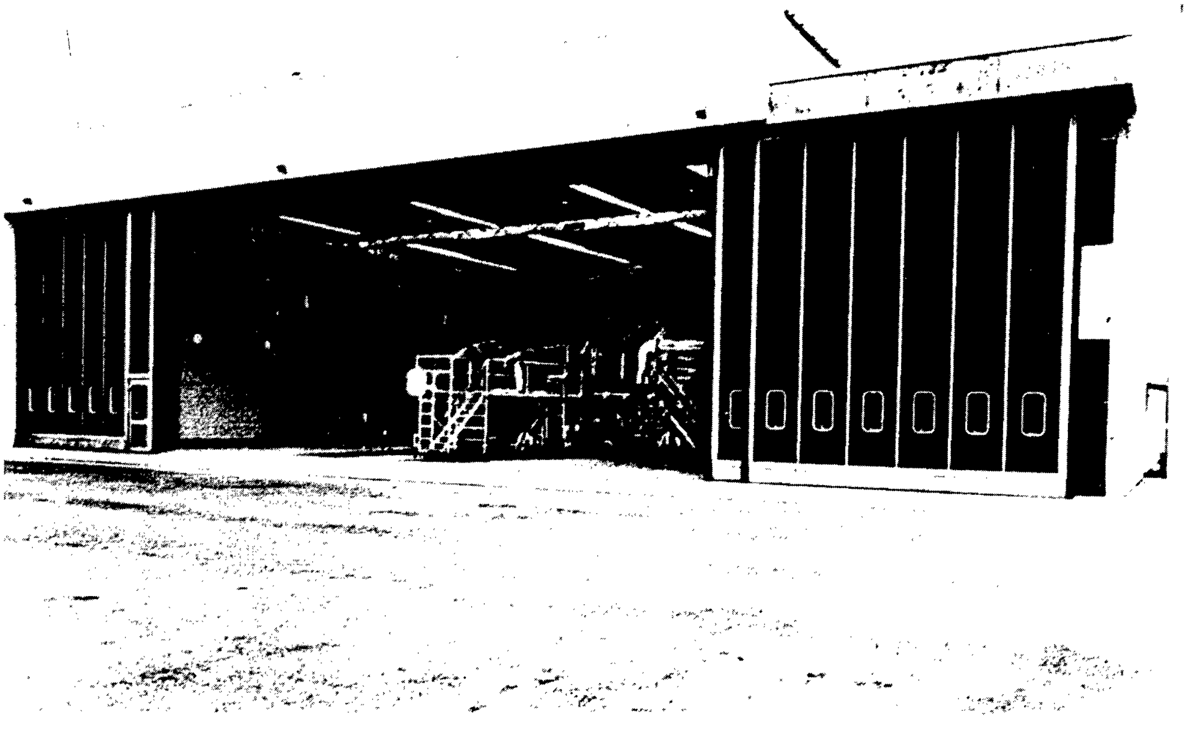
- Fig. 14 -


Dry-Stripping
EG
OG
Aufenthaltsräume
112
113
Vorraum
111
114
110
Umkleide Weiss
109
WC
108
Duschen
107
Umkleide Schwarz
105 WC D
WC H
104
Schacht
106
012
103
101
Meister-Büro
40,3 qm
Trafo
011
Trafo
012
009
Elektro-Verteilung
008
Heizung
007
Lager
006
Lager
004
005
Schleuse
012
WC-Herren
003
Schacht
002
001
Kleinteile-bearbeitung
015
Maschinen-Raum
KANAL FÜR DIE ENTSORGUNG
017
TORHÖHE 7,50

- Fig. 15 -



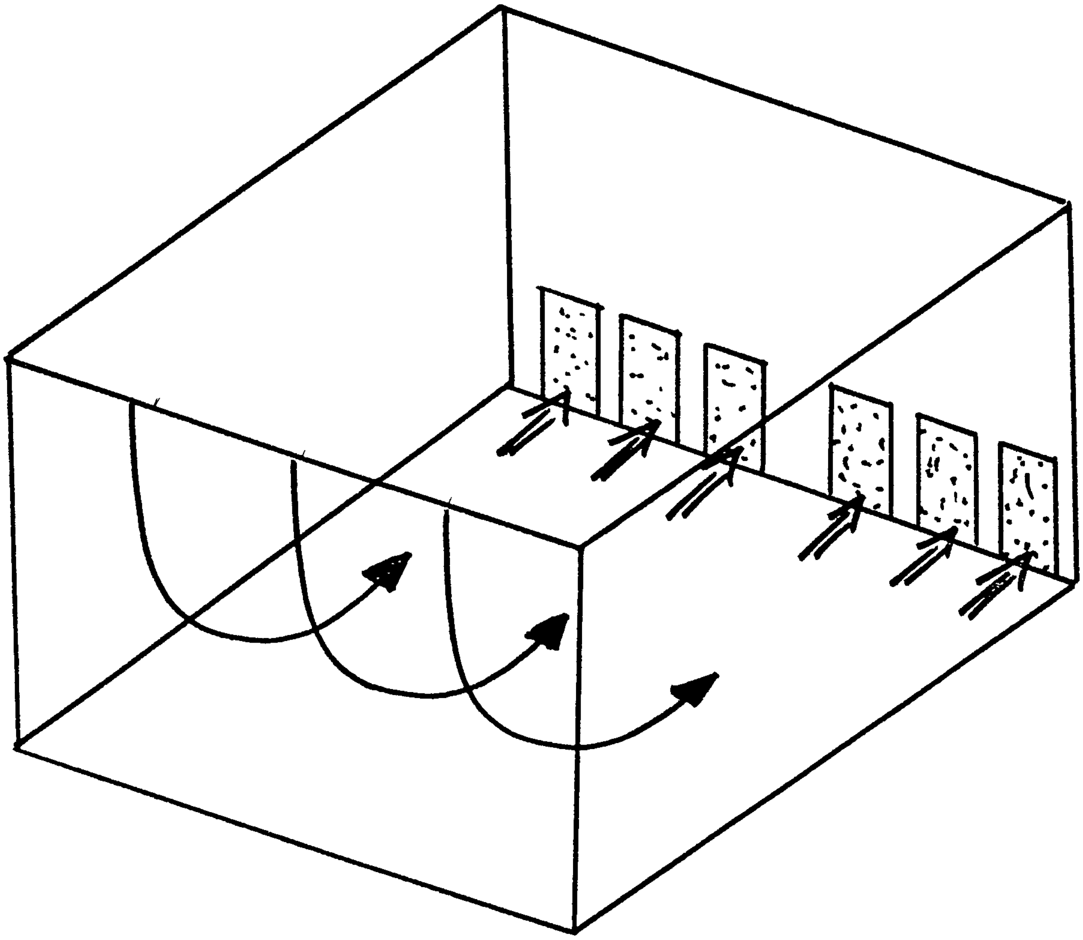
- Fig. 16 -



- Fig. 17 -

DRY - STRIPPING

AIR FLOW 160 000 m³ h



VOLUME

$V_H = 25 \times 25 \times 8 = 5000 \text{ m}^3$

TOTAL AIR FLOW

$160\ 000 + 40\ 000 = 200\ 000 \text{ m}^3 \text{ h}$

HANGAR LOCAL EVACUATION

$$V = \frac{VL}{A} = \frac{200\ 000}{25 \times 8 \times 3600} = 0.28 \text{ ms}$$

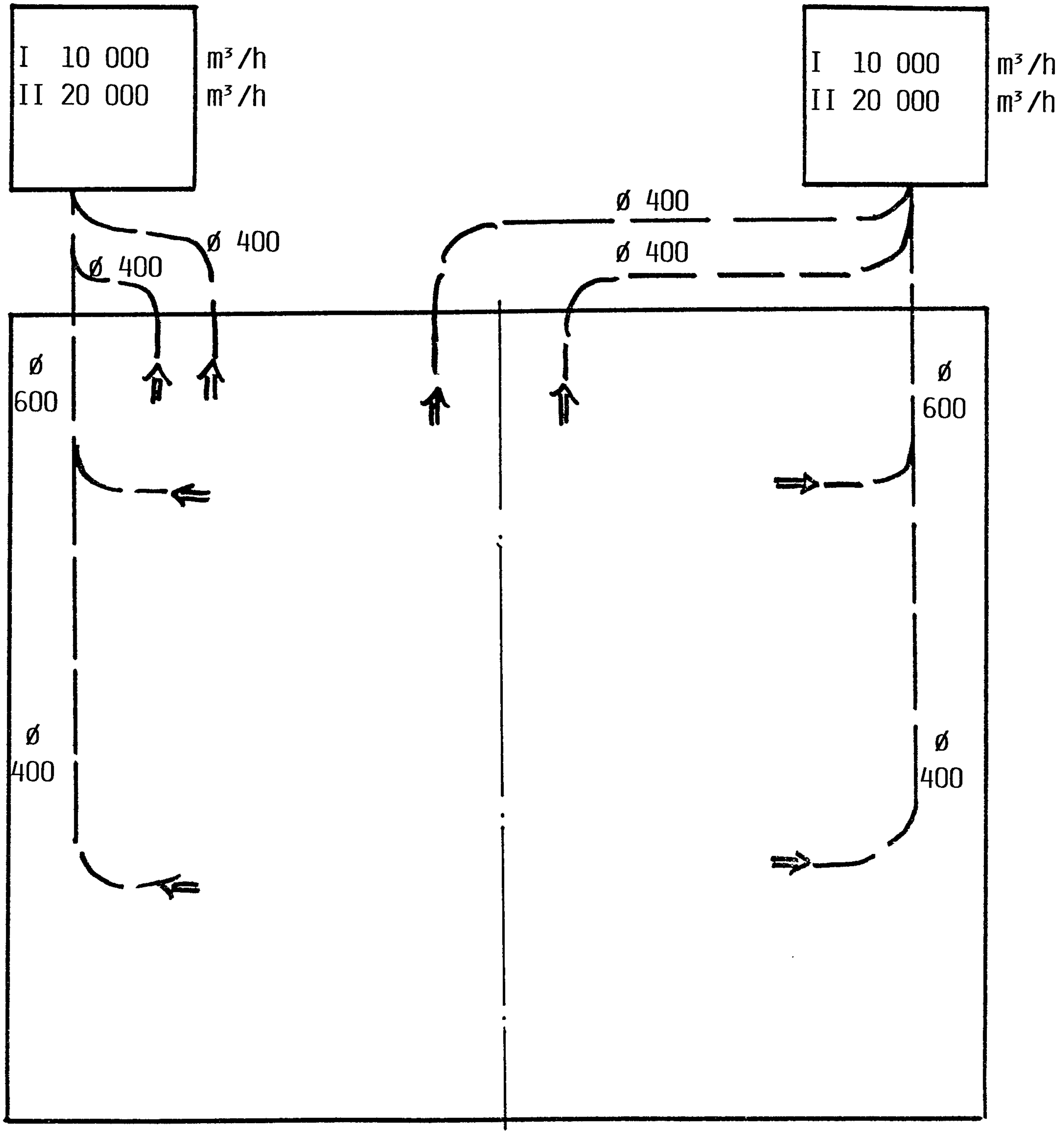
AIR EXCHANGE / h

$$\frac{V\ AIR}{V\ HANG} = \frac{200\ 000}{5\ 000} = \text{times/h}$$

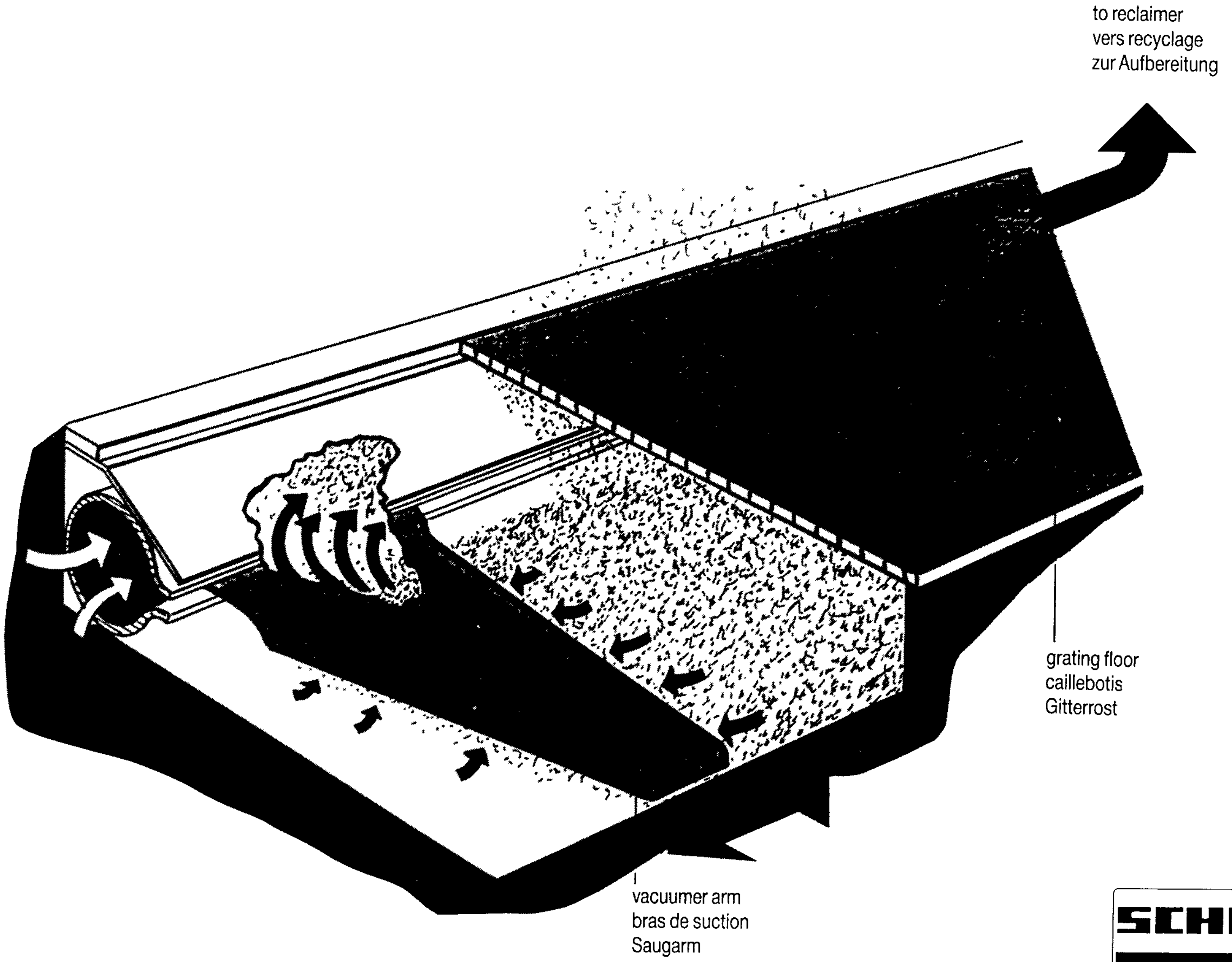
- Fig. 18 -

DRY - STRIPPING

LOCAL EVACUATION m³/h



- Fig. 19 -

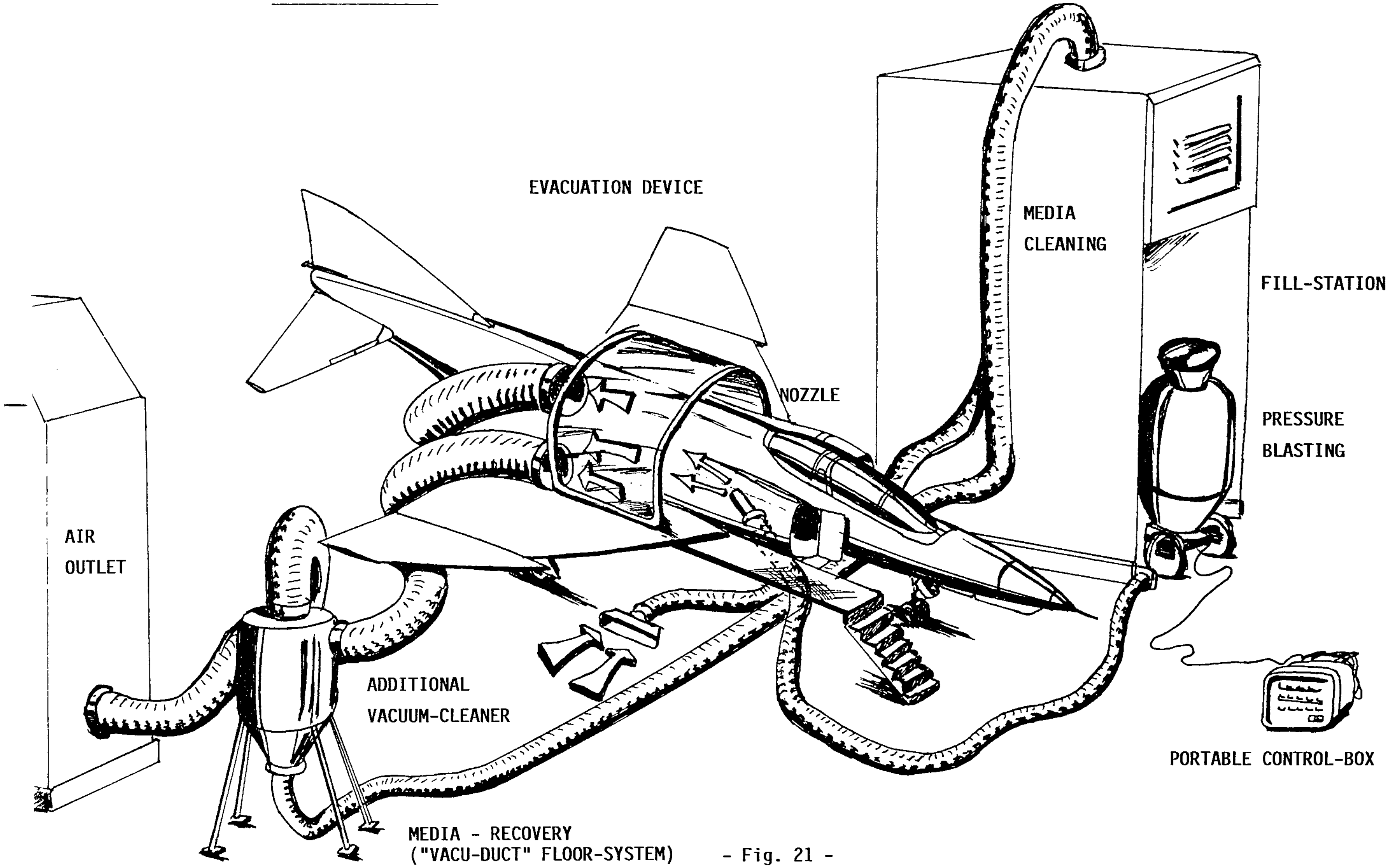


Detail drawing of the media recovery floor type VACUDUCT
Croquis détaillé du système de récupération de média type VACUDUCT
Detailzeichnung des Aufbereitungssystems VACUDUCT

- Fig. 20 -

DRY - STRIPPING - SYSTEM

LOCAL EVACUATION



- Fig. 21 -

QUALIFICATION OF CHROMATE-FREE PRIMERS FOR APPLICATION TO AIRCRAFT STRUCTURE

A.Higgins
Post Station 38
Avro International Aerospace
Chester Road
Woodford
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SUMMARY

Paint primers used on metallic aircraft structure are the major contributing element in the protection of the structure against corrosion. Qualification testing of primers for use on aircraft structure is therefore aimed at assessing if adequate service performance can be achieved.

All assessors use accelerated degradation testing based on long term immersion in fluids to which the aircraft structure will be subjected in service, thermal cycling, exposure to high humidity and various corrosion tests. Accelerated corrosion testing is the primary method used in most qualification specifications for assessing service life expectancy of the primed metallic surface. The variability of service conditions and the lack of precise data of service life to corrosion test performance make this assessment subjective.

The general performance of chromated primers in service can be used to compare respective accelerated corrosion test performance of alternative primers. Consideration needs to be given to the fact that chromated primers are capable of protecting structure for well past the airframe service life in most areas. This means that chromate-free alternatives with lower accelerated test performance could be considered for areas of the structure where the performance in service is assessed to be adequate.

The variation in approach to assessment and in the test methods used by different airframe manufacturers and those called up in national specifications needs to be rationalised and better defined if the primer manufacturers are to be able to provide the airframe industry with a suitable chromate-free alternative primer.

The assessment philosophy adopted by Avro International Aerospace is described.

LIST OF SYMBOLS AND TERMS

AECMA = European Association of Aerospace Industries

ASTM = American Society for the Testing of Materials

Avro = Avro International Aerospace (A Division of British Aerospace Regional Aircraft Limited)

BAe = British Aerospace plc

BS = British Standard from the British Standards Institute

DEF-STAN = UK Ministry of Defence Standard

DERD = UK Ministry of Defence Director General Engine Development

DRA = Defence Research Agency, UK Ministry of Defence

EN = European Standard (Euro Norme)

g/l = Grams per litre

ISO = International Organisation for Standardisation

OED = Owner of the Engineering Design

RH = Relative humidity

SAE = Society of Automotive Engineers Inc. (USA)

VOC = Volatile Organic Compounds

1 INTRODUCTION

Protection of aircraft metallic structure against corrosion in service is a primary aim of any aircraft OED. This is based on surface pre-treatments (eg Anodising or Alocrom/Alodine chromate conversion coating on aluminium alloys; aluminium, zinc or cadmium coatings on steel or titanium alloys; the use of sealants during build; and the application of corrosion inhibited epoxy or polyurethane primer to metallic surfaces. The primer is the most important contributor to the overall protection against corrosion in service. For some areas of structure which are not easily accessible for repainting (main interior surfaces of fuselage, wing, empennage etc) the primer will be required to protect the structure for the full service life of the aircraft, a period of 20 to 30 years.

The main corrosion inhibitors used in primers to achieve this are based on chromate salts (strontium, barium, zinc etc) which leach out sparingly soluble hexavalent chromate ions when subjected to moisture. Moisture containing small amounts of hexavalent chromate ions will passivate any exposed metallic surface it contacts by reacting with the metal to form a passive film of stable metal chromate. Aluminium in particular readily reacts in this way.

Leachable chromates in these primers also act as a potent biocide which prevents the growth of micro-organisms in liquid hydrocarbon fuels. (eg Cladosporium Resinae, a common fungi in middle distillate fuels commonly used in aircraft).

Leach rate controlled chromated epoxy primers have given excellent service performance but it has been recognised that hexavalent chromate ions present a health

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hazard and a lot of effort to develop alternative chromate-free primers has been made over the last decade.

Manufacturers of chromate-free primers guard their formulations carefully for commercial reasons and have not issued information on the type of inhibitors used or the corrosion protection mechanisms by which they function. The type of corrosion inhibitors considered as alternatives to chromate salts in primers is the subject of another paper in this Workshop (paper 8).

2 QUALIFICATION TESTING PROCEDURES

2.1 Overall requirement

To qualify for Avro acceptance a candidate chromate-free primer material will have to pass a series of qualification tests, as required by Avro material specification AVN 7-005, for three different production batches. Where possible European or UK national test methods are used, otherwise test methods called up in the Avro supply and inspection paint material specification AVN 7-001 are used. The tests are based on determining the following:

- Physical properties
- Film properties
- Fluids resistance
- Environmental exposure resistance
- On-line application appraisal

Any candidate primer, chromated or chromate-free would be required to pass the basic criteria for all these tests.

Chromate-free primers are however subject to different accelerated corrosion test pass requirements for reasons given in section 4.2. In addition the primer must be acceptable with regard to health and safety requirements for paint materials.

2.2 Physical properties

These are properties that characterise the material and are:

- Viscosity when mixed for application (BS EN 535)

- The weight/volume of the component parts (ISO 2811)

- The VOC content when mixed for application (BS 3900 part B2 or ASTM D2369)

- Pot life when mixed for application (AVN 7-001)

These properties when established will remain as tests required for the release of production batches of qualified material.

2.3 Film properties

These are properties that characterise the applied paint film and are:

- Drying time (ISO 1517)

- Force drying capability (AVN 7-001)

- Overcoating capability (to other qualified materials) (AVN 7-001)

- Flexibility of dried film (ISO 1519)

- Impact resistance of dried film (BS 3900 part 3)

- Hardness of dried film (ISO 1518)

- Adhesion (window) of dried film (Grade 0 ISO 2409)

- Impact resistance (Grade 2 BS 3900 part E3)

Of these, drying time, flexibility, hardness and adhesion testing are also required for release of production batches of qualified material.

2.4 Fluids resistance

The fluids used in immersion testing of primer by Avro and assessed by visual appearance (V), hardness to ISO 1518 (H), flexibility to ISO 1519 (F) or adhesion to ISO 2409 (A) are:

- Distilled water at 23±2°C for 14 days exposure. (Checks V, H (1200g) and A).

- 25% toluene + 75% trimethylpentane at 23±2°C for 2 hours (hrs) exposure. (Checks V and F).

- Lubricating oil to DERD 2487 (pyrolysed ester) at 23±2°C and at 70±2°C for 1000 hrs exposure. (Checks V and H (1200g)).

- Phosphate ester hydraulic fluid (Skydrol LD4) at 23±2°C and at 70±2°C for 1000 hrs exposure. (Checks V and H (1200g)).

- Mineral based hydraulic fluid to DEF-STAN 91-48 at 23±2°C and at 70±°C for 1000 hrs exposure. (Checks V and H (1200g)).

- Elsan toilet fluid at 23±2°C for 7 days exposure. (Checks V and H (1000g)).

- Fuel to DERD 2494 at 23±2°C for 7 days exposure. (Checks V and H (1000g)).

- De-icing fluids (SAE type 1) at 23±2°C for 7 days exposure. (Checks V and H (1000g)).

Of these, immersion testing in distilled water and phosphate ester hydraulic fluid are also required for release of production batches of qualified material.

2.5 Environmental exposure testing

The tests employed by Avro are as follows:

- Resistance to heat at 150±2°C for 100 hrs exposure. (Checks V and F carried out at 23±2°C).

- Resistance to thermal cycling. (15 cycles of):
- 24 hrs at 98 to 100% RH at 42 to 48°C temperature cycling every hour.
- 20 hrs at -23±2°C.
- 4 hrs at +23±2°C. (Checks V only at 23±2°C).

- Resistance to high humidity cyclic condensation to BS 3900 part F2 for 500 hrs. (Checks V and H (1200g).
- Resistance to filiform corrosion to Avro specification AVN 7-001 (Appendix I). Test comprises 1 hour exposure of scribed primed panel to hydrogen chloride vapour followed by 40 days at 40±2°C and 80 to 85% RH. (Checks V only).
- Resistance to continuous neutral salt spray to ASTM B117. Exposure time of test panel is 5000 hrs. (Checks V only).
- Biocidal and fungicidal properties. The test procedure for this is still to be defined and work on this is progressing at BAe Airbus Ltd. at Filton.

Of these, testing for resistance to high humidity cyclic condensation is also required for release of production batches of qualified material.

2.6 On-line application trials

These are simply trials in the Avro paint shops where the primer is sprayed under shop conditions on large structural test panels to determine if any particular application problems arise.

3 COMPARISON WITH OTHER SPECIFICATIONS

3.1 Other airframe manufacturers

All airframe manufactures have their own qualification procedures for primer paint and although tests and requirements are largely similar to those detailed for Avro qualification, there are differences eg.

Airbus Industrie TN 00/A.007.100012

Requirements not called for by AVN 7-005:

- Adhesion of sealant
- Alternate immersion corrosion testing to EN 3212 or BS EN 3212

The pass requirement for neutral salt spray (fog) testing is 3000 hrs exposure which differs from the Avro requirement of 5000 hrs. Another variation is that Airbus require the Skydrol immersion test panels to be prepared by acid pickling while Avro allow the panel to be chromic acid anodised. In other respects the the test requirements, test fluids, exposure times and temperatures are the same as used by Avro procedures.

North American OED's

Neither Boeing or McDonnell Douglas have published chromate free primer material specifications to replace BMS 10-11 and DMS 2143, respectively.

3.2 National standards

Europe

There are no national standards for chromate-free primers at present but a draft AECMA specification has been prepared. The latest version of this contains requirements not called for in AVN 7-005 these being:

- On individual component parts:

- Non-volatile matter
- Density
- Flash point

- On liquid mixed primer:

- Sedimentation rating
- Fineness of grind
- More complex drying time procedures

- On dried film:

- Colour
- Gloss
- Alternate immersion corrosion testing to EN 3212
- Corrosion test requirements for primer + topcoat are also included.

In addition, a ranking procedure is proposed with 5 types listed based on service performance required ie:

-01 Minimum requirements for use on "undemanding" aircraft. The corrosion test requirement for primer only, on pickled surfaces, is for 1000 hrs neutral salt spray (fog) ASTM B117 testing. Consideration is being given to reduce this requirement to 800 hrs.

-02 High corrosion resistance where aggressive fluid attack is not present. Corrosion test requirements for the primer only, on pickled surfaces, are 3000 hrs neutral salt spray (fog) to ASTM B117 and 1500 hrs alternate immersion. These tests are also required for primer plus topcoat with the addition of 1000 hrs filiform corrosion resistance.

Consideration is also being given to reducing these requirements to 800 hrs for ASTM B117 testing, 500 hrs for alternate immersion testing for primer and primer + topcoat and 500 hrs for filiform corrosion testing on primer + topcoat. In addition testing on painted Alocromed or chromic acid anodised (CAA) surfaces is proposed at the following exposure times:

- Primer on Alocromed surface:-
  ASTM B117 test = 1000 hrs
  Alternate immersion = 800 hrs

- Primer on CAA surface:-
  ASTM B117 test = 1500 hrs
  Alternate immersion = 1000 hrs

- Primer + topcoat on Alocromed surface:-
  ASTM B117 test = 1000 hrs
  Alternate immersion = 800 hrs
  Filiform corrosion = 800 hrs

- Primer + topcoat on CAA surface:-
  ASTM B117 test = 1500 hrs
  Alternate immersion = 1000 hrs
  Filiform corrosion = 1000 hrs

All of these different options represent a reduction in test performance requirement over the original proposals and to those required of currently qualified chromated primers.

-03 High corrosion resistance where the paint is subject to aggressive fluid attack. Corrosion test requirements are as for type -02 without any of the proposed reduced level of requirement.

-04 High corrosion and fluid resistance with surface tolerance. The test requirements are the same as type -03 but where the surface pretreatment of the test panels is by degreasing only.

-05 Intermediate corrosion and fluid resistance with surface tolerance. Corrosion test requirement is only specified for primer plus topcoat and is 1000 hrs filiform corrosion testing but where the surface pretreatment of the test panels is by degreasing only.

The AVN 7-005 requirements not included are:

- Force drying
- Resistance to any fluid immersion except for water and phosphate ester fluid. This latter fluid is specifically tri-n-butyl phosphate and not the more aggressive Skydrol LD4 used in Avro testing procedure.
- Filiform corrosion testing of primer coat

In addition there is a slight difference in the material used for the neutral salt spray (fog) ASTM B117 test panels. AVN 7-005 calls up 2014 alloy unclad annealed sheet while the draft AECMA calls up 2024-T3 alloy (solution treated and naturally aged) unclad sheet.

North America

The US Department of Defense are expected to incorporate requirements for chromate-free primer in MIL-P-23377 with reduced filiform corrosion pass requirement. Testing will also be allowed on aluminium alloy panels treated with chromate conversion coating (Alodine/Alocrom) in place of pickled surfaces.

4 FUNDAMENTALS OF ACCEPTANCE

4.1 General requirements

Clearly the physical properties, dry film properties, fluids resistance and feasibility of application described above are required of any primer, chromate-free or not. This is also true for most of the environmental resistance test requirements. The exceptions that can be considered are in relation to accelerated corrosion resistance requirements.

The airframe manufacturers have been asking the paint manufacturers for a chromate-free primer that matches the corrosion resistance performance of existing chromated primers. Some OED's simply wanted the performance to match their existing specification requirements of chromated primer. Others, including Avro, took the view that the chromate-free primer needed to match the actual corrosion resistance performance of chromated primers, which is not really reflected in the qualification tests called up in the various specifications. (See section 4.2.2).

These views are changing and the current opinions appear to favour the more realistic approach of specifying corrosion resistance requirements that would reflect adequate performance of the primer for the design life of the aircraft.

4.2 Corrosion resistance requirements

4.2.1 Corrosion test methods

a) Neutral salt spray (fog) test to ASTM B117

Continuous exposure to a fog of 5±1% pure sodium chloride solution in deionised water at 33.3 to 36.1°C at a pH of 6.5 to 7.2. Testing is carried out in purpose built corrosion resistant cabinets.

With this method the correlation between different test laboratories is usually good and it is the most widely used test procedure.

b) Alternate immersion test to AECMA EN 3212

Tests are carried out in a climate controlled chamber maintained at a temperature of 35±2°C and >80% RH.

The test solution consists of a buffered salt solution in deionised/distilled water made up from:
- 30g/l sodium chloride
- 0.19g/l disodium phosphate
- 1.25g/l boric acid

pH adjusted to 8±0.1 with 10% sodium carbonate aqueous solution. The solution is controlled by maintaining a constant level in the test piece container during the test cycle by the addition of deionised/distilled water. In addition the test solution is completely changed on the 2nd, 4th, 6th, 10th and every subsequent 10 days.

The material for the test panels is an unclad aluminium alloy, usually 2024 sheet, and this is sensitised to intergranular corrosion by solution treating at 495±2°C and quenching in boiling water.

The cycle time is 2 hrs full immersion in the test solution and 2 hrs out of the test solution, suspended above it.

With this method the correlation between different test laboratories is not as consistent as the ASTM B117 method. It is considered to be more aggressive than the ASTM B117 method, allowing shorter test exposure requirements but its use is mainly confined to European test laboratories.

c) Filiform corrosion test

Painted test panels are scribed horizontally and vertically to the base metal and exposed to the vapour of 32 to 34% hydrochloric acid in a closed container for 1 hr. The panels are then transferred to a climate controlled cabinet at a temperature of 40±2°C and RH of 80 to 85% for the test period.

This test is considered to be ancillary to the main accelerated corrosion tests but the correlation between different test laboratories is usually quite good.

d) Other accelerated corrosion tests

d1) Modified salt spray (fog) to ASTM G85

These are more aggressive test methods which use the same type of equipment as the ASTM B117 test but based on exposure to other types of fog atmosphere. The various atmospheres used are:-

a) Acetic acid/salt spray (fog) using 5±1% sodium chloride acidified to a pH of 3.2±0.1 with acetic acid. This is used by either continuous exposure at 33.3 to 36.1°C or intermittent exposure at 47.3 to 50.1°C with a cycle of 75 minutes fog exposure, 2 hrs dry air purge, 3¼ hrs soak at high RH (>80%).

b) Acetic acid/synthetic sea water spray (fog) by intermittent exposure. The cycle is 30 minute fog exposure and 90 minutes soak at high humidity (>90% RH). For paint coatings the recommended operating temperature is between 24 to 35°C at the users discretion.

c) Salt/sulphur dioxide spray (fog). This can use a 5% sodium chloride or synthetic sea water solution with sulphur dioxide gas introduced into the spray. The operating temperature is 33.3 to 36.1°C but the operating conditions (cyclic or continuous) are at the users discretion.

d2) Moben Prohesion test (2)

This is a system developed especially for testing paint coatings. It is an intermittent exposure test normally using a salt solution of 0.35% ammonium sulphate and 0.05% sodium chloride. The climate controlled cabinets used are capable of exposing test panels to salt spray (fog) and intermittent ventilation under controlled temperature and humidity conditions. The use of ultra violet light exposure during the ventilation period is also possible with this system.

None of these other test systems are currently in use for the qualification of aircraft primers but they offer potential for getting faster results compared to the ASTM B117 method. An intermittent method using the Prohesion system would probably be more consistent in terms of control than alternate immersion testing. The use of such a system using either neutral salt spray (fog) or the alternate immersion test salt solution as a spray (fog), at 35±2°C, cycling at 2 hrs fog exposure, 2 hrs high humidity (>80% RH) exposure, would give an interesting comparison with ASTM B117 and AECMA EN 3212 methods.

4.2.2 Comparative performance

The use of the corrosion test parameters currently set for qualification of chromated primers could not safely be used to qualify chromate-free primers. This is because correctly formulated chromated primers will perform significantly better than the pass requirements. For example the true neutral salt spray (fog) (ASTM B117) resistance of formulation controlled epoxy primer will be in excess of 8000 hrs for primer applied to unclad 2014-0 panels prepared by chromic/sulphuric acid pickling. This represents almost a full year of exposure and is clearly impractical to impose as a release test requirement. It is also never used as a qualification test for chromated primers.

At Avro (and the rest of BAe) the 3000 hr test requirement is acceptable for chromated primers because a special dry film release and qualification test is also used. This is a check on the leach rate of hexavalent chromate from a cured primer to the level shown in Figure 1. Control of this leach rate by proper formulation and manufacture of the primer materials is considered by BAe to be fundamental in assessing the primer performance in service and overrides the need to determine ultimate accelerated corrosion test performance.

A similar leach rate test on chromate-free primers is currently not an option and the major life performance assessment of these primers needs to rely on accelerated corrosion testing.

4.2.3 Corrosion test versus real life performance

a) Neutral salt spray (fog) test to ASTM B117

This is the only accelerated corrosion test that has been in use long enough to make any valid comparisons with life performance of primer materials. Even so, all that can be accurately deduced is that chromated epoxy primers giving 8000 hrs resistance to the ASTM B117 test will protect the majority of the primed structure for a period in excess of 30 years service in normal operating conditions.

Estimates of the general service life of a corrosion inhibited primer versus continuous neutral salt spray (fog) exposure (ASTM B117) test performance are difficult to make with absolute certainty. Nevertheless decisions on the requirement have to be made if the paint manufacturers are to be able to produce viable products. Personal estimates based on the experience with Avro RJ/BAe 146 and Hawker 125 aircraft performance are as stated in section 5.2.

b) Alternative immersion test to AECMA EN 3212

Because of the relatively short time that alternate immersion has been used for testing primer performance, the relationship to real life performance cannot be readily made. It should be possible to arrive at a real life value by comparison of the alternate immersion test life with that of continuous neutral salt spray (fog) (ASTM B117) test life of standard test panels and deriving a factor.

c) Filiform corrosion test

As mentioned earlier this test is ancillary to the other accelerated tests and is not normally used for predicting service life performance. The purpose of the test is to demonstrate permeability of the coating to corrosive vapours.

d) Other accelerated corrosion tests

The more aggressive accelerated corrosion tests described in section 4.2.1 d) could also have life factors determined by comparison with ASTM B117 performance. It is considered that most of these are not really suited for testing primer on aluminium alloy surfaces. The main exception being the intermittent exposure system based on the Moben Prohesion test cabinet using neutral sodium chloride or buffered sodium chloride as described in section 4.2.1 d).

Studies to obtain this type of comparative data has been carried out at DRA Farnborough and this work is presented in paper 8 in this workshop series.

A study by F.L.Haddleton and A.Higgins (1) in assessing the corrosion performance of surface treatments, including primer coating, on aluminium alloys gives a limited comparison of ASTM B117 testing and an intermittent cyclic test using a Moben Prohesion cabinet. The intermittent cycle used was based on ASTM G44 procedure being:

- 10 minutes exposure to 5% neutral salt spray fog at 35°C followed by ventilation of the fog and soaking for 50 minutes with no fog but with the cabinet maintained at low humidity (<50% RH) to promote drying.

A comparative chart reproduced from the paper of this study is shown in Table 1. This shows the comparative performance of ASTM B117 and this particular cyclic exposure on various aluminium alloys with various surface treatments. The indications were that the intermittent testing regime was more aggressive than ASTM B117 testing. The testing period of 3000 hrs was not really long enough to assess the life factor comparison between the two methods on primer coated panels.

5 AVRO QUALIFICATION ACCEPTANCE PHILOSOPHY

5.1 General requirements

Chromate-free primers for use by Avro will be required to pass all the physical properties, dry film properties, fluids resistance, filiform corrosion and feasibility of application required of chromated primers. If possible a leach rate control of the inhibition system will be imposed on chromate-free primers formulated to protect metal from corrosion. This is not likely to be available in the foreseeable future and the main qualification control will be based on neutral salt spray (fog) to ASTM B117 performance.

There will of course be areas of aircraft structure that are made of non-metallic composite and do not require corrosion protection. Primer used on these areas need not have corrosion inhibitors added but need to be included in chromate-free primer specifications. Care needs to be exercised when making decisions in the use of primer in such areas since most composite structures have metallic attachments, (fastener inserts, hinges etc) which will require corrosion protection.

Standard test panels used to assess the corrosion resistance of chromated primer will be used. (ie 2014-0 unclad alloy, surfaces prepared by chromic/sulphuric acid pickling only, primed surface cross scribed diagonally to bare metal after 7 days cure of applied primer).

In addition, any chromate-free primer used for the internal surfaces of fuel tanks will require to to be able to prevent the growth of bacteria or fungi at the fuel/water interfaces. Test procedures are still to be finalised. (See section 2.5).

5.2 Corrosion test requirements

Personal estimates of the general service life of a corrosion inhibited primer versus continuous neutral salt spray (fog) exposure (ASTM B117) test performance are:

ASTM B117 life	-	Estimated Service life
- 3000 hrs	-	10 to 15 years
- 5000 hrs	-	20 to 25 years
- 8000 hrs	-	30 to 40 years

Based on these figures it is considered that:

- Primers giving 3000 hrs ASTM B117 life could be used to protect against corrosion on all exterior metal surfaces but not interior surfaces. The reason for this is that exterior surfaces are readily visible for inspection, have topcoats giving extra protection to the primer, are regularly cleaned, and are usually repainted every 4 to 5 years.
- Primers giving 5000 hrs ASTM B117 life could be used to protect the interior and exterior surfaces for the design life.
- Primers giving 8000 hrs ASTM B117 life would protect the airframe well beyond normal design life.

For practical reasons it is improbable that any OED would countenance a mixed bag of primer types being used to paint metallic assemblies or even detail parts. Priming of resin fibre composite items with a different (non-standard) primer is usually possible since the metallic and composite manufacturing facilities are usually separate operations.

Based on all these considerations the chromate-free primers to be used on Avro aircraft will therefore be ranked in the following manner:

- Type 1

Requiring no resistance to neutral salt spray (fog) to ASTM B117, for use on resin-fibre laminate structure and for overcoating existing chromated primer or type 2 chromate-free primer on surfaces other than those of internal fuel tanks.

- Type 2

Requiring 5000 hrs neutral salt spray (fog) to ASTM B117 for use as per type 1 plus use on areas of metallic structure except for fuel tank internal surfaces.

- Type 3

Requiring 5000 hrs neutral salt spray (fog) to ASTM B117 and resistance to the growth of fungi or bacteria for use as per type 2 plus use on fuel tank internal surfaces.

It could be possible to use a type 2 primer for fuel tank applications if the fuel used was always treated with biocide (eg Biobor JF (3) or Kathon FP 1.5 (4)). This would require a major world-wide cooperative effort on the part of the aerospace fuel industry but is perfectly feasible.

6 CONCLUSIONS

There are no national material specification currently available to allow qualification of chromate-free primers, although a draft AECMA (European) specification is available.

There are significant differences in the qualification requirements of material specifications that are in use and with the draft AECMA specification. These mainly relate to accelerated corrosion test procedures and pass level requirements.

It is Avro's view that more work is needed to get accurate comparisons between the competing accelerated test procedures and until this is available, accelerated corrosion evaluation will rely on the long established continuous neutral salt spray (fog) ASTM B117 test procedure.

Of the other corrosion test procedures considered, intermittent neutral salt spray (fog) (Moben Prohesion) testing is preferred to the alternate immersion test. It should offer a faster result in terms of testing periods and give good reproducibility. The test procedure needs to be developed, defined and standardised in terms of:

- The test panel material.
- Panel preparation treatment. (eg use of intergranular corrosion sensitisation heat treatment, degreasing,pickling etc).
- The type of salt solution to be used.
- The testing cycle to be used.

Consideration could be given to the use of drying periods in the cycle to bring into play the effects of increasing concentration of salt solution on the surfaces as the water evaporates off. This would happen in real life exposure to a condensing salt laden environment. None of the currently specified accelerated tests, except for acetic acid/salt spray (section 4.2.1 d1) call for a drying period.

The possibility of introducing ultra-violet light exposure as part of the cycle could also be considered but is probably only relevant to topcoated primer.

Avro would still like to use a leach rate control test of the inhibitor system for chromate-free primers but recognise that at present this is not feasible.

Avro specification AVN 7-005 gives the primer manufacturers clear targets with regard to corrosion test requirements for chromate-free primers required for commercial aircraft. The requirements, based on continuous neutral salt spray (fog) ASTM B117 performance, should allow the development and introduction of chromate-free primers for application to aircraft structure and ensure adequate service performance.

7 REFERENCES

(1) F.L.Haddleton and A.Higgins, "Assessment of the corrosion performance of surface treated aluminium aerospace alloys". 3rd. International Aerospace Corrosion Control Symposium 15-17th March 1994. SP Conferences, London.

(2) Mebon Paints Ltd. Huthwaite, Nottinghamshire UK: Prohesion paint performance evaluation.

(3) Biobor JF microbiocide. Hammonds Fuel Additives Incorporated, P.O.Box 38114-407 Houston, Texas 77238-8114, USA.

(4) Kathon FP 1.5 microbiocide. Rohm & Haas (UK) Ltd. Lennig House, 2, Masons Avenue Croydon CR9 3NB, England. (+ Offices world-wide).

COMPARISON OF ACCELERATED CORROSION TEST METHODS

(Extracted data from reference 1)

Surface condition of test panel / Test panel material	Corrosion rating after 3000 hours exposure					
	Constant neutral 5% salt spray (fog) to ASTM B117			Intermittent neutral 5% salt spray (fog) + ventilation		
	A	B	C	A	B	C
Degreased only	1	8	7	0	9	6
Degreased and pickled	0	8	6	0	8	6
Degreased/pickled + Chromated epoxy primer (PR143)	10	10	10	10	10	10
Degreased/pickled + chromate-free epoxy primer (PR320)	10	10	10	9	9	9
Degreased/pickled + chromate-free inhibited epoxy primer (5805-1103)	9	10	10	8	9	9

Corrosion rating key											
%age of area corroded	>75	>56 <75	>41 <55	>31 <40	>21 <30	>11 <20	>7 <10	>4 <6	>2 <3	>0 <1	No Failure
Rating	0	1	2	3	4	5	6	7	8	9	10

Test panel coding "A" = 2024-T3 unclad aluminium alloy
"B" = 2024-T3 Alclad aluminium alloy
"C" = 8090-T81 unclad aluminium/lithium alloy

Intermittent cycle was :- 10 minutes salt fog exposure
50 minutes dry soak at <50% RH
Temperature at 35±2°C

TABLE 1

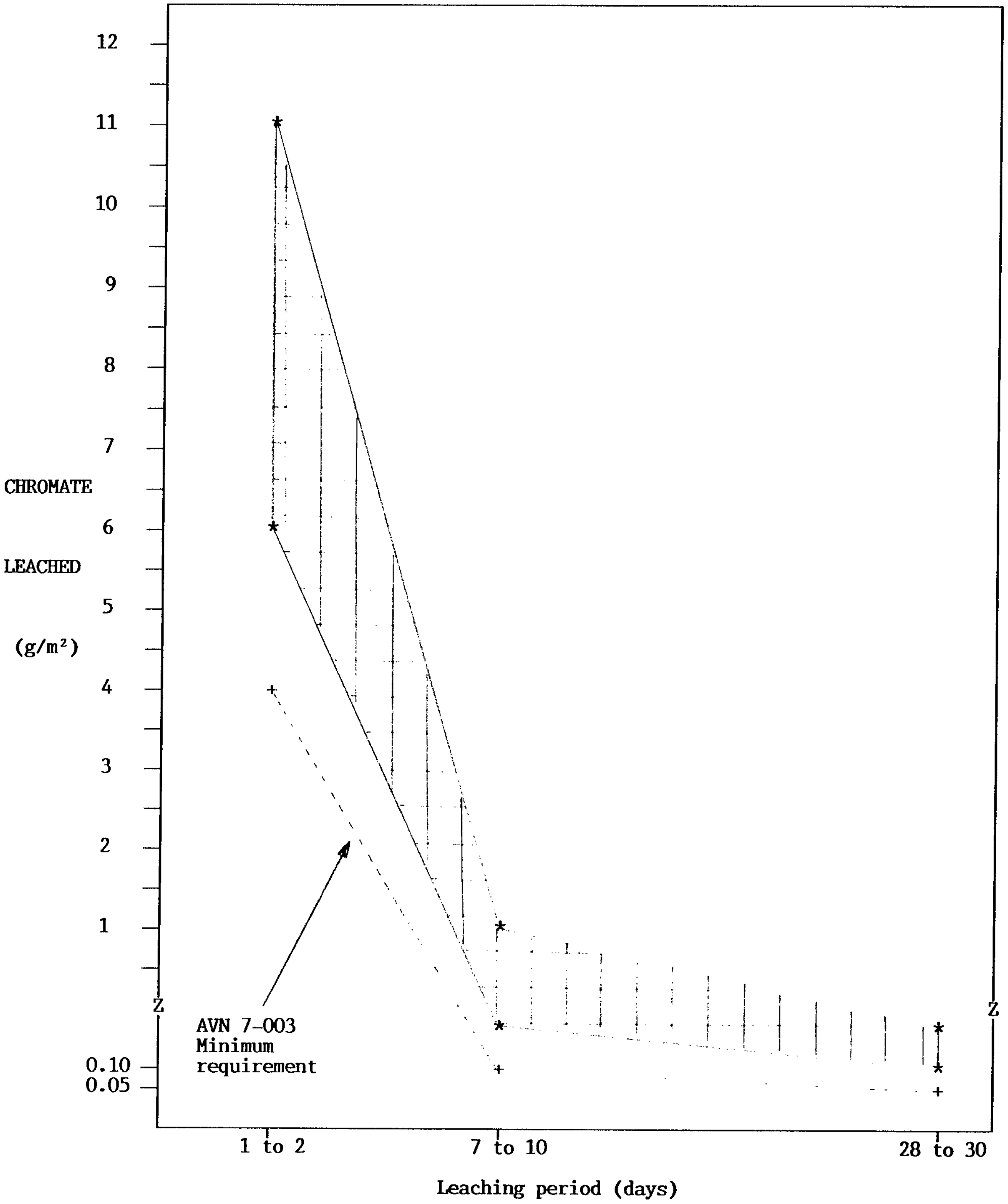

FIGURE 1 LEACH RATE OF CHROMATED EPOXY PRIMERS QUALIFIED TO AVN 7-003

Environmentally Compliant Electroplating Alternatives

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SUMMARY

The use of cadmium and chromium as electroplating metals continues to come under criticism from several directions. Both materials have been targeted by the USEPA for reduction / elimination. The toxicity of specific forms of both metals is widely known (reference 1) and efforts are underway to identify workable alternatives for both materials (references 2 and 3). This paper presents the methodology and results of tests performed to identify performance properties of select cadmium and chromium substitutes. These results and their interpretation are not to be inferred to be official US Navy policy.

LIST OF SYMBOLS

AISI	American Iron and Steel Institute
ASTM	American Society for Testing and Materials
HVOF	High Velocity Oxygenated Fuel
IVD	Ion Vapor Deposited
KSI	Thousands of pounds per square inch
NESHAP	National Emission Standards for Hazardous Air Pollutants
PEL	Permissible Exposure Limit
SERDP	Strategic Environmental Research and Development Program
TWA	Time Weighted Average (for single eight hour exposure)
USEPA	United States Environmental Protection Agency
USOSHA	United States Occupational Safety and Health Administration
UTS	Ultimate Tensile Strength

1 INTRODUCTION

Cadmium has long been regarded as the standard for corrosion resistant coatings (reference 3). Cadmium is easily plated from a cyanide-based solution; the solution chemistry is easily controlled and maintained. A cadmium plating solution typically possesses excellent covering power with minimal use of auxiliary anodes. Cadmium also possesses favorable anti-galling characteristics (reference 4). Cadmium is also the base coating for which the torque values of many joints has been determined. Despite all of its favorable properties, cadmium is overshadowed by the extreme toxicity of the plating solution and of the metal and its compounds..

In 1993, the USOSHA lowered the TWA PEL for workers exposed to cadmium to 5 micrograms per cubic meter of air. Prior to this action, the TWA PEL for cadmium was set at 100 micrograms per cubic meter. In some facilities, workers were required to don Tyvek suits and respirators in order to perform the task of cadmium plating. Turnaround time and worker performance were both degraded as a result of this new safety requirement.

Of equal importance to the search for cadmium alternatives is the search for hard chromium plating alternatives. In repair / overhaul facilities, chromium plating is used primarily for replacing metal that has been removed due to corrosion and / or wear damage. Normally, chromium plating displays excellent substrate adhesion and plating rates of 0.003 inches per hour are easily achievable. Other esoteric factors such as worker familiarity with the process and wide engineering acceptance combine to make chromium plating desirable as a repair coating. As with cadmium, chromium and its compounds are highly toxic.

The Clean Air Act Amendments of 1990 along with the USEPA's Top 17 List formed the first major assault on chromium. Shortly afterwards, the Aerospace Chromium NESHAP was enacted which further impacted on chromium emissions. Recently the USOSHA has indicated a desire to reduce the TWA PEL for chromium to an extent similar to that which cadmium was reduced. Studies performed indicate that compliance with USOSHA revised standards will be more difficult and quite expensive (reference 5).

The ultimate goal of the various projects that this paper relates is to identify the values of the critical properties of selected cadmium and chromium alternatives. The first section of the paper will focus on the cadmium alternatives while the second section will focus on chromium alternatives.

2. METHODS AND RESULTS

2.1 Cadmium Plating

Cadmium and hard chromium plating processes are extensively used in repair / overhaul facilities for refurbishment of aerospace components. To provide some indication of the extent of the problem associated with identifying a suitable replacement for cadmium , Figure 1 shows what percentage of metal finishing (electroplating) within a typical overhaul facility consists of cadmium plating.

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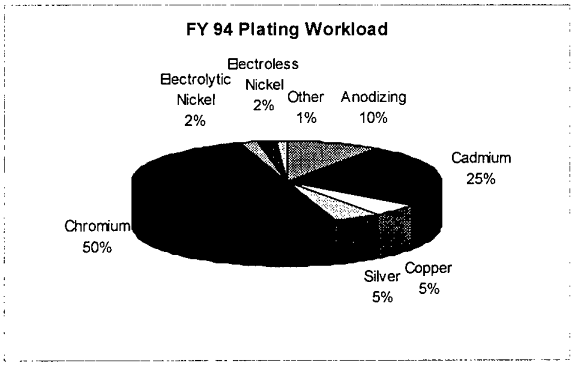

Figure 1 - Breakdown by type of electroplating work within a typical overhaul facility.

At this point, it is germane to mention that a physical vapor deposition process known as IVD-Aluminum has been in use for over a decade as a cadmium alternative on ultra-high strength landing gear steels (UTS > 200 ksi). This process has several technical and economic limitations that depreciate its worth as a cadmium alternative; nevertheless, the extent of its use mandates it receive just recognition. IVD -Al still remains the only widely approved cadmium substitute within the United States. For the purposes of the research this paper relates, IVD-Al was not selected for evaluation as a cadmium alternative (most of its critical performance values have already been determined).

Five specific properties have been identified for evaluation for the proposed cadmium alternatives. These five properties are as follows: 1) adhesion per ASTM B571, 2) corrosion resistance per ASTM B117 and G85, 3) hydrogen embrittlement resistance per ASTM F519, 4) torque / tension values of fasteners in joints, and 5) fatigue effects on substrate metal as evaluated by tension-tension and sheet flexure fatigue coupons.

Five coatings are proposed as cadmium alternatives. Each of these coatings will be evaluated for the five properties listed in the preceding paragraph. These five coatings consist of two competing brands of alkaline chemistry zinc/nickel, one type of acid chemistry zinc/nickel, tin/zinc and an aluminum-manganese molten salt bath. As of the time of the writing of this paper, approximately 65% of the test data has been gathered.

With any cadmium alternative, the first property of concern is that of corrosion resistance. A pass/fail criterion for corrosion resistance per ASTM B117 was established at 336 hours salt fog exposure with no evidence of red rust. This length of time is consistent with the standard established for cadmium plating. The following table presents the results of the salt fog testing:

Coating	**Time to Failure (hours)**
Tin / Zinc	573
Alkaline Zinc / Nickel #1	1893*
Alkaline Zinc / Nickel #2	340
Acid Zinc / Nickel	7968*

The times marked with asterisks indicate that there was no red rust noted when the test was terminated. On alkaline Zn/Ni #1 there was noted significant white corrosion product; the acid Zn/Ni displayed only isolated spots of white corrosion. Though not listed here, the cadmium controls far exceeded the 336 hour criterion. Values for the Al-Mn coating are to be determined at a later date.

The ASTM G85 acidified salt fog test only included coupons coated with the two competing alkaline Zn/Ni's, the Sn/Zn and the cadmium control. Within 189 hours, all coupons had failed (presence of red rust). The poorest performer in this test was the alkaline Zn/ Ni #2, which failed within one day of being placed within the test chamber. ASTM G85 is a very severe corrosion test that involves the bleed-in of a small amount of sulfur dioxide into the test chamber. An endurance of 300 hours without evidence of red rust is typically taken as the pass / fail criterion for the ASTM G85 test.

For the purposes of aerospace applications, the next most important performance criterion of any coating is any fatigue effects it imparts to the substrate. Presently, only the results of tension-tension fatigue testing are available; sheet flexure fatigue testing is ongoing. Specimens for tension-tension fatigue testing were manufactured from two separate lots of AISI 4340 steel (150 - 170 ksi UTS) and PH 13-8Mo stainless steel (175 - 195 ksi UTS). The tension-tension coupons are Goodman type, 4.000 +/- 0.002 inches long, 0.250 +/- 0.001inches in diameter in the center section. Figure 2 presents the baseline data for AISI 4340 steel heat treated to an ultimate tensile strength range of 150 - 170 ksi; Figure 3 presents the baseline data for PH13-8Mo stainless steel heat treated to an ultimate tensile strength of 175 - 195 ksi.

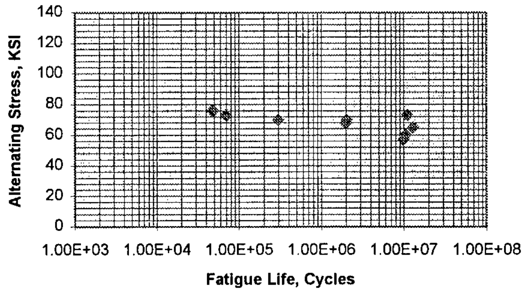

Figure 2 - Tension-tension fatigue test results of AISI 4340 steel baseline, 150 - 170 ksi UTS, K_t=1, stress ratio = 0.10.

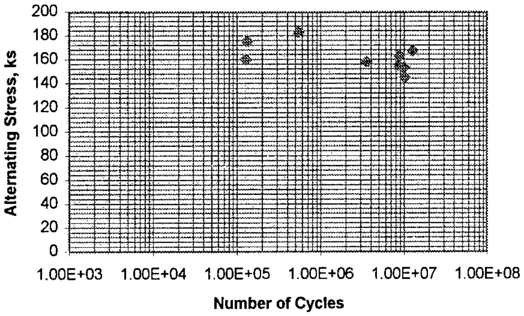

Figure 3 - Tension-tension fatigue test results of PH13-8Mo stainless steel baseline, 175 - 195 ksi UTS, K_t=1, stress ratio = 0.10.

For comparison, Figures 4 and 5 present the results of the same fatigue test performed on zinc/nickel and cadmium coated coupons.

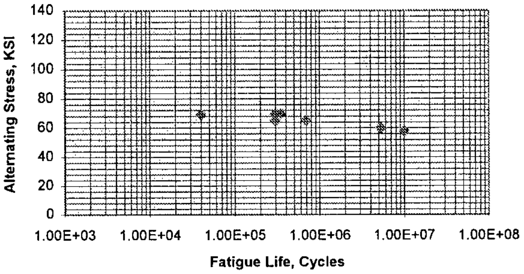

Figure 4 - Tension-tension fatigue test results of zinc/ nickel coated 4340 steel, 150 - 170 ksi UTS, K_t=1, stress ratio = 0.10.

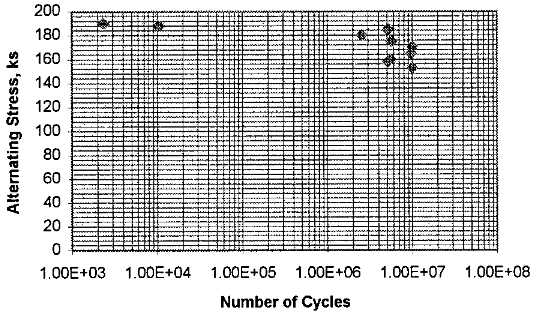

Figure 5 - Tension-tension fatigue test results of cadmium plated PH13-8Mo stainless steel, 175 - 195 ksi UTS, K_t=1, stress ratio = 0.10.

Figures 2 through 5 present data from non-shotpeened coupons. The data for the 4340 specimens is taken from reference 6; the data for the PH13-8Mo specimens is taken from reference 7. The test data shows a reduction in the fatigue life of the substrate as a result of the application of the zinc/nickel coating (approximately 5%). The test results of the cadmium plated coupons shows a minor increase in the fatigue life of the substrate over baseline data.

Adhesion testing of each coating revealed no unexpected failures. The acid zinc / nickel plating is very sensitive to current density. In high current density areas, the nickel content of the coating rises and the coating becomes more brittle. This brittleness results in failure of the coating in bend tests.

Torque-tension testing for fastener applications is presently ongoing. Test results should be available by early October, 1996.

Zinc / nickel plating baths have been implemented within the United States as cadmium alternatives in numerous locations. Perhaps the earliest identification of a plateable zinc / nickel coating is found in reference 8. The chemistry of this early effort is acidic in nature; it is also probably the most thoroughly "prototyped" of any of the baths. In use, however, the acid solution has many limitations. Foremost among these is the very narrow operating window for the plating properties of the bath. Operating temperatures between 70 and 78 degrees Fahrenheit, a zinc to nickel anode ratio of 3:1, current density of 15 - 20 amps per square foot - this all combines to make the acid zinc / nickel plating bath user unfriendly. Additionally, the use of auxiliary anodes to plate into recesses and inner dimensions is mandatory. Because of these technical limitations, the next effort will be to prototype the alkaline zinc / nickel #1, which possesses more favorable plating properties.

Up to this point, relatively little has been said regarding the aluminum-manganese molten salt bath. Testing of the coating's properties lags the testing of the other cadmium alternatives by several months. Also, the fundamental design of a 10 gallon plating bath is still being developed. The chemistry of the solution requires that it be isolated from all water and maintained at an operating temperature of 400°F.

2.2 Chromium Plating

Electroless nickel, thermal spray and physical vapor deposition (PVD) have been identified as the most likely avenues on which to find a suitable substitute for hard chromium electroplating. Electroless nickel (8% and 10% P) is presently being used with varying success on some components. HVOF WC has also met with success as a chromium alternative on certain components. Some service experience has also been gained in the use of PVD coatings.

Electroplated chromium possesses many unique properties that are not found in other coatings. Engineers are quite familiar with chromium's low coefficient of friction and hardness; platers prefer chromium because of its excellent adhesion, machinability and plateability. The following list identifies those coatings/processes offered as alternatives to hard chromium:

Electroless Nickel - 2-4% Phosphorus
8% Phosphorus
10% Phosphorus
Nanocrystalline Diamond impregnated
PVD - Chromium Nitride
Chromium
Thermal Spray:
Super D-Gun - 2040A Tungsten Carbide
Hybrid Plasma Spray - Tungsten Carbide
HVOF - Triballoy 400
Triballoy 800
Tungsten Carbide - Cobalt (83-17)
Chromium Carbide
Nickel - Chromium
Nickel-Tungsten-Boron electroplating

Extensive service experience has been garnered using either 8% or 10% phosphorus electroless nickel as a hard chromium alternative. This substitution has been successful, but not without difficulty. The 8% P plating is limited in its build-up ability (≤ 0.005 inches) due to a tendency for cracking and deadhesion from the substrate in greater thicknesses. In service, this cracking can be extremely detrimental leading to pitting corrosion of the substrate occurring beneath the coating. During overhaul procedures, the delamination of the plating can result in costly re-processing. Use of a 10% P bath allows for greater build-up without concern over adhesion or in-service cracking. The higher phosphorus bath also possesses greater corrosion resistance, though lower hardness.

Early in the testing it became apparent that the wear characteristics of most of the coatings equaled or exceeded those of chromium. Concerns remain that the tungsten carbide coatings may actually be "too hard" - that is, those coatings may detrimentally wear (sliding wear) into mating components and seals to the extent of causing the mating hardware to be repaired or scrapped. Service experience has shown that this can indeed occur but that the detrimental wear on mating components can by alleviated by coating both wearing surfaces with the tungsten carbide coating.

Another aspect of wear of concern is galling. Chromium is often used to coat the small hardware of larger assemblies that requires frequent installation/ removal. Service implementation of tungsten carbide for this application found that severe galling resulted from its use. A detrimental result was also obtained when using a PVD coating; in this instance, the coating delaminated from the substrate.

One property not often considered when considering chromium alternatives is the corrosion resistance of the coating. Actually, what is meant is how well the coating protects the substrate. As chromium is deposited thicker, it forms a more effective barrier to substrate corrosion. What emerged as an area of concern is that all the thermal spray and PVD coatings showed poor corrosion resistance for thicknesses less than 0.005 inches. The WC thermal spray coatings suffered failure (defined as rust undercutting and blistering the coating) in 216 hours; PVD chromium nitride flaked and delaminated in less than 24 hours. Service experience with the same WC thermal spray (actually applied with the Super D- gun process) does not record such delaminating failures in service; in fact, general corrosion of WC - coated components is not reported to be problematic.

Corrosion experience with chromium plating records that chromium plating pits but seldom delaminates. History also reveals that the single most significant driver for repair of chromium - plated components is the pitting corrosion occurring in the substrate after moisture has infiltrated through the plating.

As is the case with alternatives to cadmium plating, the single most critical factor for a chromium alternative is effect on substrate fatigue life. The same tension-tension fatigue test coupons are used for a "quick look" at how a particular coating affects the substrate fatigue life.

Fatigue testing of alternative coatings for chromium was carried out on substrates of AISI 4340 steel and PH13-8Mo stainless steel. Figure 6 presents fatigue test data from the baseline coupon testing of PH13-8Mo stainless steel.

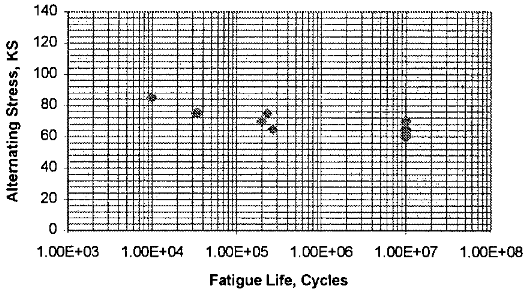

Figure 6 - Tension-tension fatigue test results of baseline PH13-8Mo stainless steel, 175 - 195 ksi UTS, shot peened to MIL-S-13165 standards.

Figure 7 presents the results of the fatigue test on a Super D-gun 2040A tungsten carbide coated set of coupons.

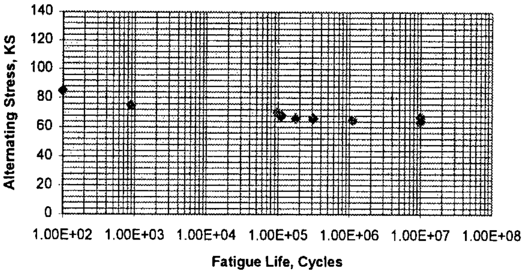

Figure 7 - Tension-tension fatigue test results of 0.005 inches thick Super D-gun 2040A tungsten carbide on PH13-8Mo stainless steel substrate, 175 - 195 ksi UTS, shot peened.

The condition of the test for the data from Figures 6 and 7 is a K_t=1 and a stress ratio = 0.1. Notched specimens were also prepared (K_t=3.0) but it was discovered that the thermal spray coatings did not cover into the notched area. A comparison of the data from the two tests shows a minor reduction in the fatigue life of the substrate as a result of coating with the tungsten carbide.

A quick look at other thermal spray coatings in addition to the Super D-gun application shows that all the thermal spray processes appear to carry similar substrate fatigue effects. The test data from the reference 6 and 7 programs is not complete so a final comment on how the various processes compare is yet to be made. In the meantime, some turbine engine driveshafts are being successfully coated with HVOF WC in lieu of hard chromium plating.

Another type of fatigue test performed on coated coupons is the R.R. Moore rotating beam. This test was used as a screening test for further evaluation of proposed chromium alternatives (i.e., it is less expensive than the tension-tension testing). If a coating showed a drastic fatigue life reduction under R.R. Moore testing, then that coating was discontinued from further evaluation. One such coating that failed the R.R. Moore screening was the nickel/tungsten/boron electrodeposit. The R.R. Moore specimens were all cut from 4340 steel heat treated to 150 - 170 ksi UTS. Test conditions established R= -1.0, K_t=1. Figure 8 provides the baseline plot for the unnotched, non shot peened test specimens.

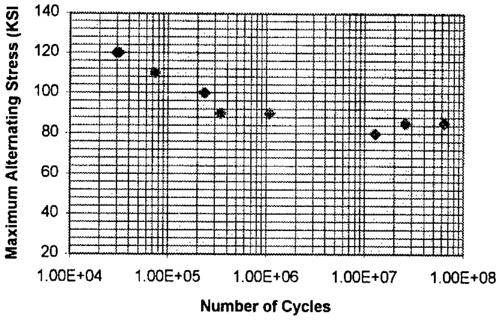

Figure 8 - R.R. Moore fatigue test results of 4340 baseline material.

Figure 9 shows the results of the fatigue test on the Ni/W/B coated specimens. As is evidenced from the test data, a reduction in the fatigue life of the substrate of approximately 50% has occurred. This degree of fatigue life reduction is unacceptable for a coating to be used on fatigue sensitive aerospace components.

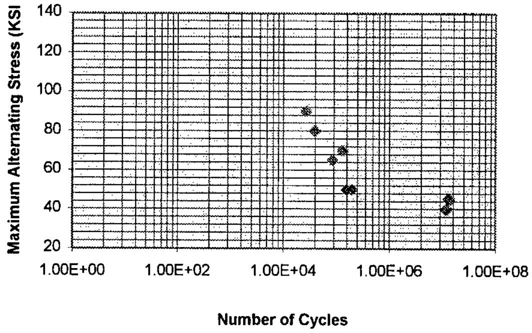

Figure 9 - R.R. Moore fatigue test data for nickel / tungsten / boron electrodeposited coating.

2.3 Economics

The economics of alternative plating processing has yet to be fully evaluated. With effective control of emissions and effluent, cadmium plating is still less expensive to perform than IVD-Al or zinc/nickel plating. On a per part basis, it costs four times the amount to IVD coat as opposed to cadmium plate (\$40.21 versus \$166.25); most of this amount is tied up in labor. Accurate numbers for zinc/nickel are not available, but it is anticipated that the operating cost of zinc/nickel plating will be 1.0 - 1.2 times the cost of cadmium plating.

The economics of chromium alternatives are less well known. Reference 9 provides a good discussion of what savings/costs are anticipated for switching from chromium to less hazardous alternatives.

3. DISCUSSION OF RESULTS

The single most critical performance criteria for any alternative coating in aerospace applications is its effect on the fatigue life of the substrate. This of course assumes that the coating fulfills its primary function of corrosion or wear resistance. Much of the attention of the testing is consequently focused on fatigue properties, not all of the available data being published in this paper. It is well known that hard chromium plating reduces the fatigue life of the substrate (references 10 and 11) so any possible replacement must be no more detrimental than hard chromium. It is unlikely that any coating that reduces the fatigue life of the substrate more than 5% will receive general acceptance within the aerospace community.

The search for an effective cadmium plating replacement is still ongoing. The alkaline zinc/nickel process #1 is considered to be the leading candidate at this point. A 450 gallon production tank will be operational early this fall. Two areas to be monitored closely are operational costs and ease of operation. Early optimism regarding the acid zinc/ nickel has ended in disappointment due to the service performance of the plating bath. Despite its successful track record, the IVD-Al process remains costly (relative to wet processing) and will probably not grow beyond its present share of the workload. It is too early in the development stage to predict the future of the aluminum-manganese molten salt bath; unless less exotic environmental controls are designed, it is unlikely that the process will see widespread commercial acceptance.

Initially thought to be a low-cost substitute for hard chromium, electroless nickel has been disappointing in service implementation. Similar to the problems encountered with the acid zinc / nickel process, electroless nickel has experienced problems with process consistency and ease of use.

Coatings applied by HVOF or Super D-gun processing appear to be the most desirable candidates for chromium replacement. These thermal spray processes offer the potential for heavy build-up (up to 0.012 inches) of a coating, thus closely matching one critical performance criterion of hard chromium plating. HVOF processing is actually preferred because it is possible to purchase the equipment and establish work cells within individual facilities; the Super D-gun process is a proprietary process. Two issues of concern with thermal spray processes are its machinability (for the cermet coatings) and the inability of thermal spray processing to coat inside dimensions.

One major drawback to PVD processing is its extremely high initial investment cost ($1 to $4 million); this cost makes the process unsuitable for facilities desiring to retrofit or upgrade. While PVD technology shows some promise for reduction of the use of hard chromium plating, experience reveals that the application must be within the process' and the coating's performance parameters. PVD coatings may be limited to only those applications of relatively low contact loading. Also, it is important that a coating process be capable of heavy build-up for the purposes of refurbishment. The only PVD process that offers the potential for such metal thickness build-up is electron beam - PVD.

With both cadmium and chromium replacements, there is concern over the use of nickel. USEPA identified nickel as a hazardous material whose usage must be reduced. To date, no tighter USEPA or USOSHA regulations have been proposed. As more data regarding the toxicity of nickel is gathered the future might reveal the same drivers acting to reduce / eliminate nickel that are presently at work against cadmium and chromium.

4. CONCLUSIONS

The downselect process for identifying both a cadmium and chromium replacement is ongoing. For repair / overhaul facilities, it is imperative that alternative processes be reliable and user-friendly; this is critical despite what outstanding performance characteristics make the coating appealing. What is apparent from the testing and evaluation that has been performed is that it is unlikely that either cadmium or chromium will be replaced by a single coating. The coating and application process will likely be determined by assessing each individual component and its performance requirements. Economics also plays a significant role in determining what processes are used in aviation maintenance. The next twelve months will result in a great deal of information being analyzed concerning what alternative coatings are best used in specific situations. In the meantime, zinc/nickel and IVD - Al are being used on a limited basis as cadmium replacements while electroless nickel and Super D-gun (or HVOF) tungsten carbide are being used as chromium replacements.

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14. Abstract

Traditional surface treatments for aerospace materials are becoming unacceptable due to pressures exerted by national and international environmental and health organizations.

In recent years, research and development efforts in environmentally compliant surface treatments for cleaning, surface preparation, coating and electroplating have resulted in new or modified materials and processes for the aerospace community.

The conclusions of the AGARD SMP Workshop held in September 1996 stated that continued research and development efforts are required in order to successfully develop and implement new environmentally compliant surface treatments for aerospace applications.

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