

NEXT GENERATION OF Aircraft Coatings Systems

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The current generation of aircraft coatings had its basis in the polymer technologies of the 1970s and the use of chromate-based metal pretreatments and primers. There have been some incremental improvements in the epoxy and polyamide oligomers used in the primers as well as the isocyanates and flexible polyols used in topcoats, plus increases in the volume solids of the coatings to continue minimally meeting environmental requirements, but no truly new technologies have been developed and applied to aircraft coatings since that time. However, because of increasing economic and environmental pressures, this situation will soon change. Also, the U.S. Air Force is seeking a coating system that will have an ultimate lifetime of 30 years for maintenance cost control and fleet sustainability. The first change in the present coatings system will be in the pretreatments plus primers that currently constitute the metal protection system for the high strength Al alloys used for aircraft. For military aircraft, these alloys will continue to be Al 2024 T-3 and Al 7075-T6, heat-treated metals that have phase-separated regions rich in reactive metals such as Cu, Mg, and Zn. There are several new technologies now under consideration for such metal protection including conductive polymers as primers without Cr-based metal pretreatments, sol-gel based pretreatments and primers, plasma polymer metal pretreatments, and organo-modified aluminum oxide particles. Each of these technologies has shown some promise for Cr replacement, but each presently has a weakness that needs to be corrected for immediate usage. For the topcoat system, fluorinated polyols and improved use of UV-absorbers and light stabilizers will probably be the first changes implemented, with ceramer and other new crosslinking systems the most likely next polymer matrix candidates. The target for the entire coatings system is to have drastically improved wet-adhesion due to a covalently bonded system that has a gradient in composition that goes continuously from metal to metal oxide to mixed metal oxide/organic polymer to high-performance UV-stable organic polymer. The materials cost for such a system may be quite high, but the maintenance cost savings will much more than offset these costs.

INTRODUCTION

The three primary reasons for painting military aircraft are survivability (visual appearance, infrared signature), corrosion protection, and appearance (including weatherability as well as abrasion and chemical resistance), while civilian and commercial aircraft use coatings for corrosion protection, airline identification, and appearance. The coating film on aircraft protects the metal and composite components of aircraft from their environment, since many components are designed and fabricated for structural reasons from materials that are not very resistant to atmospheric exposure. As aircraft coatings systems evolved, by the 1960s and 1970s, the predominant requirements were chemical and fluid resistance, corrosion resistance, exterior durability, and ambient cure. There are also coatings used over the plastics and metal substrates on the interior of aircraft, but this paper addresses only the high performance exterior coatings used on aircraft.

CURRENT COATINGS SYSTEMS

The current aircraft coatings systems are based mainly on a chromate pretreatment to an aerospace Al alloy surface, a chromated epoxy-polyamide primer, and a urethane topcoat based on a two-component isocyanate-flexible polyol system.¹ A schematic of such a coating system, which is used by the military, is given in Figure 1. Sometimes a tiecoat is used between the primer and the topcoat. The corrosion protection of this system depends on both the chromated pretreatment and the chromate pigment used in the primer. The relatively current specifications for common military and commercial aircraft coatings are discussed in several references.²⁻³ The Department of Defense (DoD) specification number for its common gray topcoat is MIL-C-85285; and the specification number for the solvent primer is MIL-P-23377. The coatings are usually applied by electrostatic assisted spray coating methods. The OEM business for commercial aircraft is dominated world-wide by Boeing and Airbus, and both seem to have fairly similar specifications for OEM usage. References in this paper will be predominantly from Boeing. Military usages and specifications are more diverse, and this paper will utilize U.S. DoD information pertaining to U.S. Air Force and Navy aircraft.

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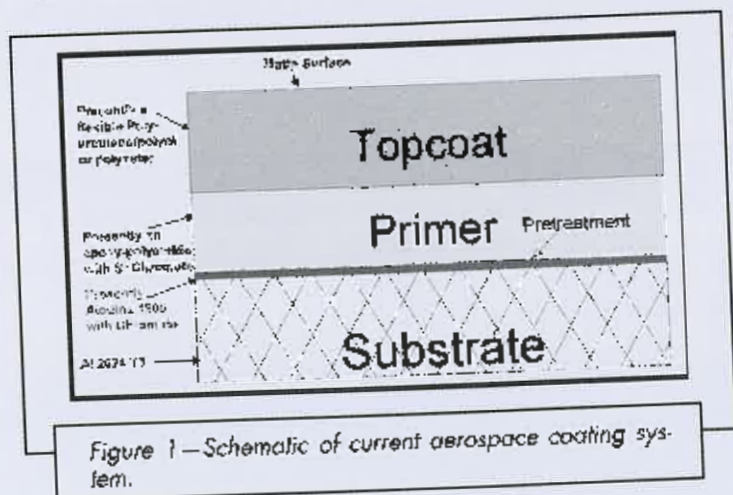


Figure 1—Schematic of current aerospace coating system.

The specifications for the military and commercial coatings are quite similar, but the flight usage and refinish practices of commercial and military aircraft are very different. Military aircraft spend up to 95% of their time on the ground, where a primary threat to performance is corrosion, while commercial aircraft spend up to 30% of their time in flight; the primary threat to performance is probably structural fatigue. A discussion of corrosion threats in commercial aircraft was given in a recent article.¹

NEEDS IN NEXT GENERATION MILITARY FINISHES

The needs of the U.S. Air Force (USAF) are for much increased service life protection against corrosion and increased durability in the topcoat. For the next generation of USAF coatings, all materials must be environmentally benign (i.e., chromate-free pretreatment and primer), with a 40-year corrosion protective (pretreatment + primer) system, and a minimum of eight years of topcoat durability with mission strippability as needed. Maintenance costs for the USAF fleet in 1997 were \$800 million. The annual cost of corrosion maintenance per aircraft is escalating at a rate of 36%.⁵ The primary aircraft for which these new coatings will be used are the aging KC-135, KC-141, and C-5 tanker and transport aircraft of the USAF fleet.

Enhanced Durability—Minimum Maintenance

These requirements given represent an extraordinary increase in performance requirements from those presently in use and are even more demanding in that there must be chromate-free corrosion protection.

There will be a need for the extraordinary lifetime of pretreatment + primer structure, and for the topcoat, a cleanable durable system is demanded.⁶ The goals of these requirements are increased fleet readiness, risk reduction, and drastically reduced maintenance costs. This will mean that the coating must have drastically improved exterior durability, as well as cleanability in field use. It should not be soiled easily by lubrication fluids or other hazards of normal use. The optical properties should be tailorable to mission requirements—this most often will require a matte, camouflage appearance. This last requirement has been difficult to achieve simultaneously with true cleanability.⁷

Strippability

The topcoat system should be strippable in existing Air Logistic

Centers (ALCs) using environmentally acceptable materials and methods. The primer-pretreatment system should not be affected by topcoat removal and should be recoatable in the field or at ALCs as needed.

Compliance with Volatile Organic Compound Emission Regulations

In new military and commercial coatings, VOC compliance will be an important issue, but definitely not a new issue. There has been ongoing work to reduce VOC emissions in all classes of coatings, including those for aircraft, since the 1960s, and a drastic improvement in VOC reductions has occurred in this period.⁸ In aircraft coatings, most of the VOC reduction has occurred through the use of high-solids, two-component systems for primers and topcoats as well as some use of waterborne (W/B) systems for primers. These developments will continue. The most difficult improvements to achieve will be in obtaining the proper rheological properties of new topcoats that provide enhanced exterior durability and fluid resistance. The very systems that can provide these properties, such as fluorocarbon containing oligomers/polymers, require very strong solvents and have not been amenable for use in W/B systems. The restrictions of ambient cure at high crosslinking levels for fluid resistance also provide a considerable challenge for VOC reduction.

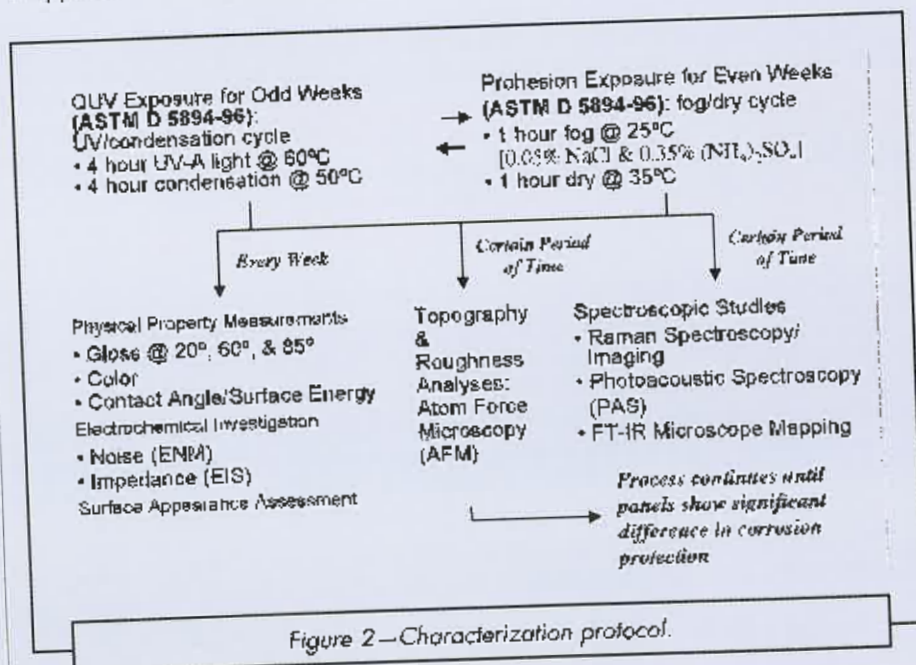


Figure 2—Characterization protocol.

NEEDS IN NEXT GENERATION COMMERCIAL COATINGS SYSTEMS

Exterior Coatings

The primary requirements for exterior aircraft finishes will be durability and cleanliness in field use, including gloss, color, and other decorative attributes. The system should be field recoatable and repairable and have low maintenance costs. As long, high altitude flights become more common and more aircraft are spending a considerable amount of time at altitudes that give UV exposure at shorter wavelengths than at ground level, improved UV durability will be required in topcoats. Improved and modified ultraviolet absorbers (UVAs) will need to be tuned to a wider band of UV (at higher altitudes, the pertinent UV wavelengths are from 290-400, rather than the 320-400, nm region at sea level.) Also, improved hindered amine light stabilizers (HALS) will be needed to provide improved coatings photostability, and all pigments utilized in topcoats must have outstanding UV stability and a total lack of oxidative photocatalytic tendencies.⁹⁻¹¹

Primers

The (primer + pretreatment) system should be environmentally benign and provide up to 10 years of corrosion protection. Therefore, much like the military systems, a chrome-free system is required. The newer generations of commercial aircraft will have extensive use of composites and newer, more corrosion-resistant alloys for the aircraft structure and skin, and so the threat of corrosion will not be as great as that for older military aircraft.

Refinishing and Strippability

The refinishing and strippability requirements of the next generation finishes will be much like those of the military. The systems should be strippable with environmentally benign materials and use recoat systems that provide the same gloss and color retention as the OGM finishes.

Compliance to Volatile Organic Compound Emission Regulations

The comments concerning VOC compliance issues in future military aircraft apply as well to commercial aircraft coatings. In commercial aircraft

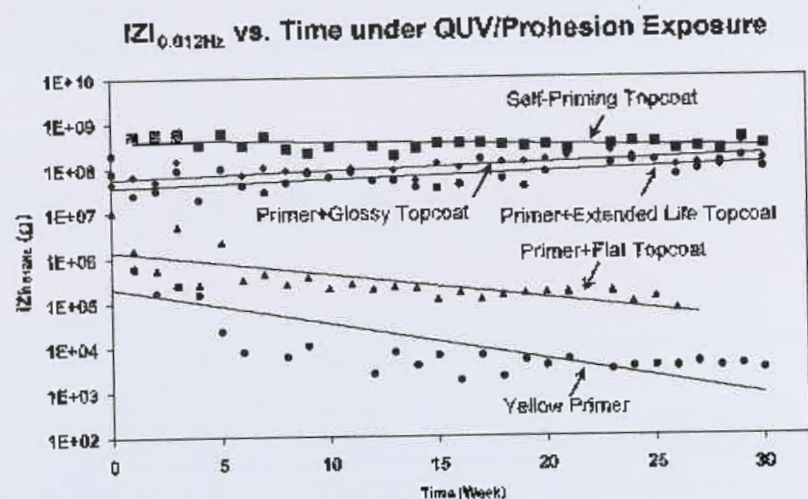


Figure 3— $|Z|$ vs. exposure time for several military coatings.

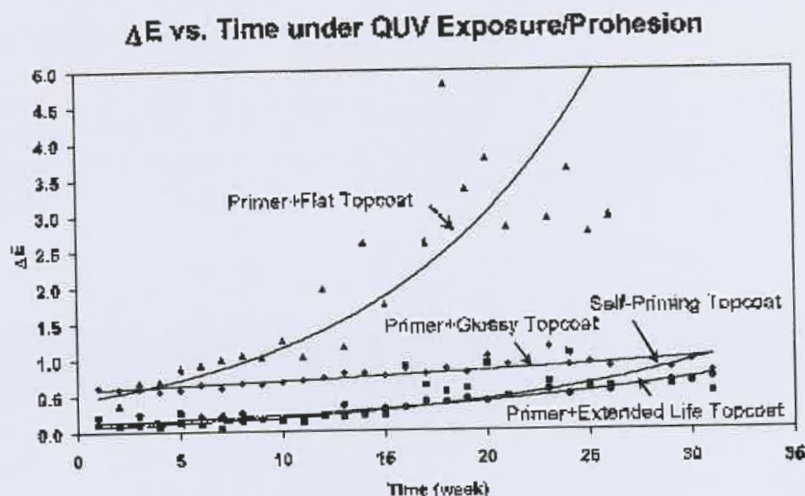


Figure 4— ΔE vs. time for the same coatings as shown in Figure 3.

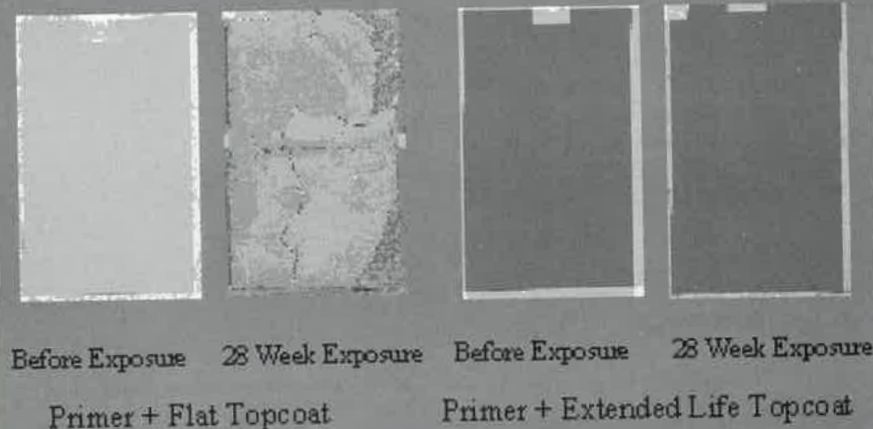
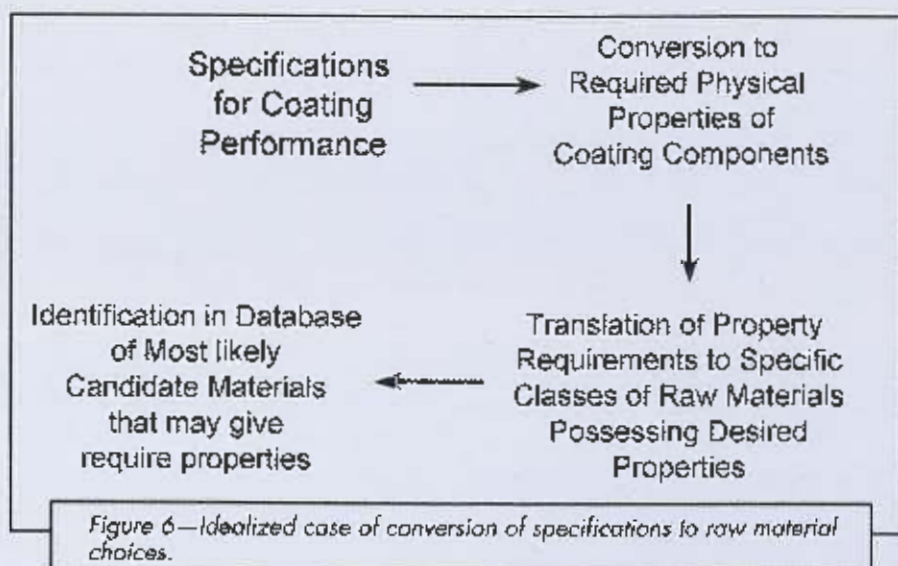


Figure 5—Photos of fluorocarbon-based coating vs. standard after exposure.



usage of coatings, local regulations will have to be considered very carefully as there is a large variation from site-to-site in such rules. In the U.S., for example, the rules for VOC emissions are most severe in southern California, and perhaps the least severe in North Dakota.

NEW MEASUREMENT TECHNOLOGIES FOR AIRCRAFT COATING DEVELOPMENT

There have been many new measurement and characterization techniques developed for the testing of coatings which are being utilized in the development and study of aircraft coatings and metal pretreatments. Many of these have been developed in the area of corrosion characterization and polymer surface analysis. New methods have also been developed, or are in development, directed towards *in situ* sensors of corrosion under coatings as applied to aircraft metal substrates.

New Developments in Corrosion Measurement Methods in Coated Systems

Considerable effort has been expended by scientific instrument developers in making the use of electrochemical techniques easier and more accurate. This holds true especially for electrochemical impedance spectroscopy (EIS),¹² electrochemical noise methods (ENM),¹³ and dynamic polarization methods. There have been considerable improvements in the instrumentation for the routine use of such measurements, especially in the computer methods for controlling the experiments and data acquisition and analysis.

Also, equipment for local (measurements made in a scanning, mapping mode at a resolution of $\sim 1\mu\text{m}$) characterization of electrochemical properties has been introduced and shown to be extremely useful in studying performance of coatings systems in providing corrosion

protection to damaged areas in coatings. Two methods, the scanning vibrating electrode technique (SVET), first introduced for corrosion studies by Isaacs and co-workers,¹⁴ and local EIS (LEIS), most recently studied by Taylor and his co-workers,^{15,16} have been shown to be quite useful in such measurements. A recent paper from this laboratory discusses these methods.¹⁷ Also useful in coatings studies is the use of scanning Kelvin probe force microscopy,^{18,19} as well as other scanning electrochemical microscopies.

In situ Corrosion Sensors

There has been much work done on developing *in situ* sensors of corrosion under coatings, especially in the area of EIS testing. A recent article²⁰ discusses one such system, and other workers are pursuing similar studies based on EIS²¹ and ENM techniques.²²

New Developments in Coatings Durability Characterization and Lifetime Prediction

A recent symposium reviewed current efforts in durability characterization and lifetime prediction in organic coatings.²³ Much work has been expended utilizing surface analysis methods for this purpose²⁴ as well as micro-FTIR and micro-FT-Raman techniques.²⁵

NEW POLYMER SYSTEMS AND ADDITIVES FOR AIRCRAFT COATINGS

Fluorocarbon-Based Polymers

The development of polyurethane topcoats based on fluorocarbon-

Sol-Gel Coatings Chemistries

- Two approaches
 - “Thin Film”
 - Metal oxide films with organic coupling agents
 - Adhesion and corrosion protection
 - Functions similar to present conversion coatings
 - “Hybrid coatings”
 - Organic/inorganic network polymers
 - Flexibility for incorporating corrosion protection schemes
 - Enhanced mechanical performance
- Progress
 - Non-Cr sol-gel + Cr-primer system passes salt fog
 - Non-chromated sol-gel/primer system fails salt fog
 - RT cure, low acid system formulated
 - Hybrid systems are improving

Figure 7—General description of sol-gel chemistries.

“Thin Film” Sol-Gel Coating Status

- Boegel-EP provides excellent primer adhesion
 - RT cure, low acid system formulated
 - Surfactant improves visual appearance
 - No impact on adhesion
- Non-Cr primers perform poorly on non-Cr conversion coatings
- Investigating methods of encapsulation or incorporation of inhibitors
 - inhibitor materials alters sol-gel film formation
 - solubility of non-Cr inhibitors not optimized

Figure 8—Sol-gel coatings status.

based polyols²⁶ and exterior-grade isocyanate oligomers is the current, most promising route to increased durability. These systems have extremely good UV and moisture resistance and have the potential of giving topcoats with lifetimes greater than 10 years. The exposure protocol used to study the system is described in Figure 2.

Some recent data on a military topcoat of this type examined under this exposure protocol is shown in Figures 3-4. The corrosion performance as the low frequency impedance modulus, $|Z|$, data for this topcoat over a standard chromate pigmented epoxy primer (e.g., MIL-P-23377) is given in Figure 3. Figure 4 gives color data for the same systems and Figure 5 shows a photo of the panels of the ELI fluorocarbon versus the standard coating. These systems have shown little change in either their appearance or corrosion protection behavior over considerable exposure time and show much promise as a future military system.

Ceramics and Other Mixed Organic/Inorganic Systems

The use of ceramic precursors together with standard coating polymer systems has shown promise in leading to enhanced durability and barrier performance in coatings systems for aircraft. The usefulness of these materials is being studied for this purpose.²⁷

New Developments in UV-Stabilization Additives

References 9 and 23 discuss the state-of-the-art in UVAs and HALS for improved resistance to photodegradation in coatings.

Expert Systems Use for New Coating Design

Recently, the USAF has been sponsoring work on the development of advanced coating design methods for the development of new, cleanable, durable topcoats and aircraft primers.²⁸ The original emphasis of this project was properly incorporating C/PVC prediction methods into the formulation process. This work has been extended in recent studies.²⁹ Figure 6 shows a flow chart of the coatings design software currently under development.

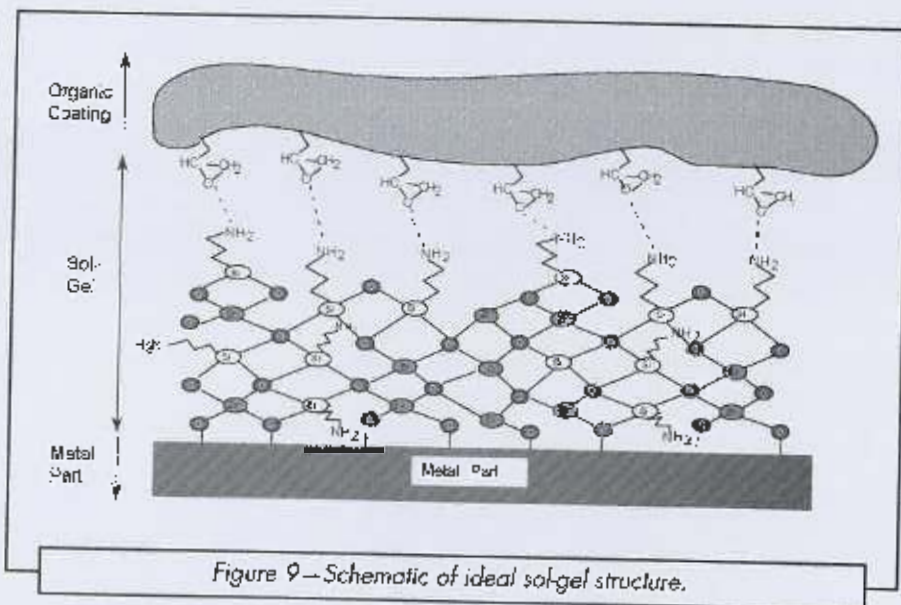


Figure 9—Schematic of ideal sol-gel structure.

CHROMATE-FREE CORROSION PROTECTION IN AIRCRAFT COATINGS

Specific Aerospace Alloy Issues—Al 2024 and Al 7075

The main driver of new coatings development at this time is the need to find a system that provides corrosion protection better than or equal to the present chromate pigmented primer + chromate-based pretreatment. This has been the focus of both basic³⁰ and applied research.³¹ The problems are exacerbated by the facts that the primary alloys used in the military air fleet and much of the commercial fleet

are Al 2024 and Al 7075. Both are especially corrosion prone because they are heat-treated Cu/Mg rich alloys which have phase-separated intermetallic compounds that cannot be coated with materials which require curing temperatures exceeding 180°F. Chromate species of some sort are the only current option for effective corrosion protection for these common aerospace alloys.³²

Sol-Gel Systems

Work done in a DARPA (Defense Advanced Research Projects Agency) Project led by Boeing has been examining sol-gel type materials for chromate-

E-Coat Bulk Phase (20-30 μm)

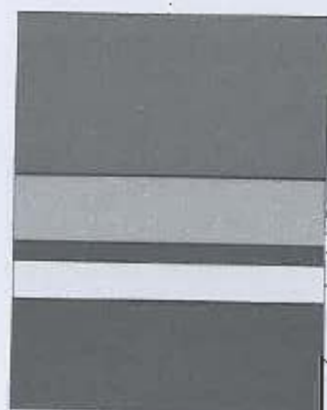


Figure 10—Schematic of plasma polymer-based pretreatment coating system.

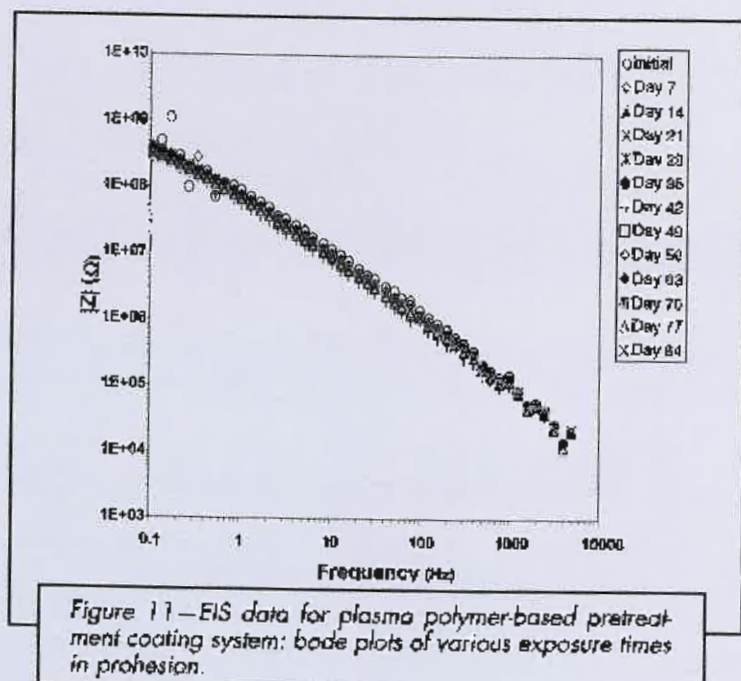
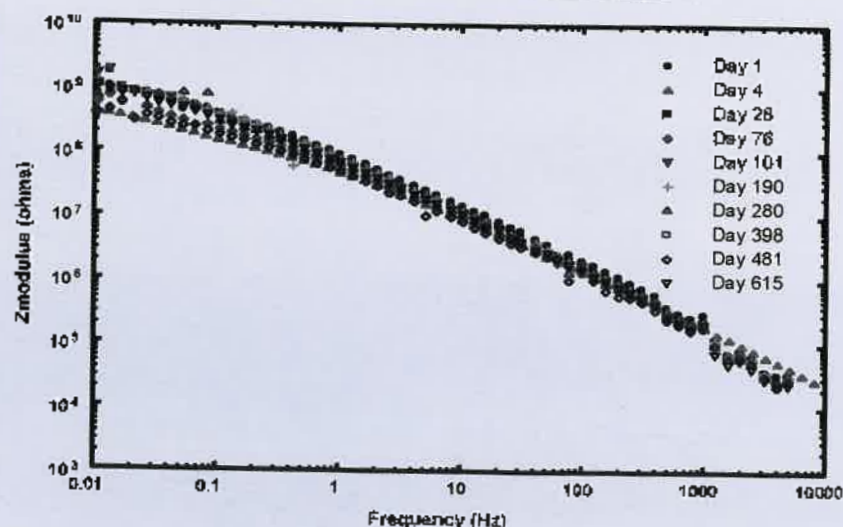
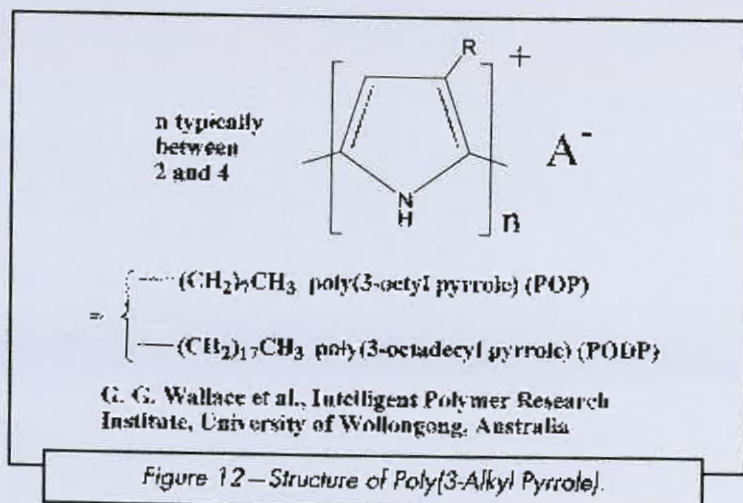


Figure 11—EIS data for plasma polymer-based pretreatment coating system: bode plots of various exposure times in Prohesion.



free protection of Al 2024 T-3. This work has not succeeded in totally matching the performance of chromate pretreatment (Aludine™) or chromate-pigmented primers, but it is hoped that further improvements of the sol-gel precursors that are under study will yield the desired performance.³³ Figures 7-9 are generic descriptions of the process and current status. The goals of the sol-gel process are to generate a chemically bonded structure that undergoes a controllable gradient in chemical properties from inorganic metal oxide at the surface through an inorganic oxide formed in a sol-gel process through a mixed inorganic/organic structure to the purely organic structure of a primer coating. A schematic of this ideal structure is given in Figure 9.

Plasma Pretreatment

A possible strategy for protection 2024 and 7075 based on plasma polymer films plus an electrodeposition primer has been considered in recent studies.³⁴ This continues work begun by Yasuda in studies of the plasma polymer pretreatment of steel.³⁵ These studies have shown that by cleaning the surface of Al 2024 T-3 first with an alkaline cleaner and then plasma-treating the metal in a cold cathodic plasma, with O_2 to further clean the surface and then forming a plasma polymer film based trimethyl silane as the monomer gas, by a subsequent coating with a cathodic electrodeposition primer one can get corrosion protection exceeding chromate pretreatments or chromate pigmented primers. A schematic of this structure for an aircraft alloy substrate is given in Figure 10. The performance of such a system has been studied by standard salt fog and ProhesionTM exposure cabinet testing followed by visual ranking as well as by immersion and Prohesion exposure with ENM and EIS testing. Examples of these electrochemical data are given in Figure 11. The data shown in Figure 11 is for a 2024 T-3 sample with a plasma polymer pretreatment and a chromate-free electrodeposition primer measured by EIS during Prohesion exposure. A similar experiment with a chromated epoxy primer over an alkaline washed 2024 T-3 panel gave failure ($|Z| < 10^6 \text{ ohm/cm}^2$) after several weeks.

Conductive Polymers

Another strategy for non-chromate based corrosion is the consideration of conductive polymers. These materials

have received considerable attention for providing chromate-like corrosion control, including corrosion protection in damaged areas, as primer coatings for metals without the need for pretreatments.^{36,37} This work has recently been extended to aircraft metal alloys³⁸ and recent work of our lab shows considerable promise in this area.³⁹ One such polymer under consideration is poly(3-octyl pyrrole) whose structure is given in Figure 12.

Figure 13 shows the remarkable stability in immersion in dilute Harrison's solution of the corrosion protection of this material as a primer with a standard urethane topcoat over Al 2024 T-3 as measured by EIS. Figure 14 shows an optical micrograph of this system after 615 days.

SUMMARY and CONCLUSIONS

New aircraft coating systems will provide enhanced and environmentally compliant ways to increase outdoor durability and corrosion protection. New polymers and the improved use of UVAs and HALS will drive the enhanced durability of aircraft topcoat systems for both military and commercial use. However, future aircraft coatings will change most in the way in which they provide corrosion protection. Even though there is no current system available to replace chromate-based pretreatments and primers, there is much work in progress indicating that chrome-free systems for aircraft alloys will be available in the near future. Among the top candidate strategies currently being considered are sol-gel based systems, plasma polymer pretreatments, and conductive polymers. The most immediate beneficiaries of these new coatings systems will be military air fleets and aging commercial aircraft.

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Figure 14—Optical micrograph of Polyurethane/POP/Al 2024-T3-615 days.

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