Next Generation of Aircraft Coatings Systems

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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, fireline 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 1940s and 1950s, the predominant requirements were chemical and fluid resistance, corrosion resistance, exterior durability, and ambient cure. There are also coatings used over the plastic 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-fusable polyol system. A schematic of such a coating system, which is used by the military, is given in Figure 1. Sometimes a topcoat is used between the primer and the topcoat. The corrosion protection of this system depends on both the chromated pretreatment and the primer. The relatively current specifications for common military and commercial aircraft coatings are discussed in several references. 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-53277. 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 predominately from Boeing. Military usage and specifications are more diverse, and this paper will utilize U.S. DoD information pertaining to U.S. Air Force and Navy aircraft.
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., chrome-free pretreat-
ment and primer), with a 40-year corrosion protective (pretreatment + primer) system, and a minimum of 8 years of topcoat durability with mission stripability as needed. Maintenance cost for the USAF fleet in 1997 were $407 million. The annual cost of corrosion maintenance per aircraft is escalating at a rate of 36%. 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 that there must be chrome-free corrosion protection.

Topcoat Primer Pretreatment

Figure 1—Schematic of current aerospace coating system.

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 1980s, and a drastic improvement in VOC reductions has occurred in this period. 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 the 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 external durability and fluid resistance. The very systems that can provide those properties, such as fluorocarbon containing oligomers/matpolymers, require very strong solvents and have not been amenable for use in W/B systems as the restrictions of ambient cure at high crosslinking levels for fluid resistance also provide a considerable challenge for VOC reduction.

Compliance with 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 2—Characterization protocol.

Figure 3—[Z] vs. exposure time for several military coatings.

Figure 4—AE vs. time under QUV Exposure/Prohesion

Figure 5—Phases of RustAAC/5T-based coating vs. standard after exposure.
The specifications for the military and commercial coatings are quite similar, but the flight usage and reusability 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 93% of their time in flight; the primary threat to performance is probably structural fatigue. A dissertation of threats to commercial aircraft was given in a recent article.

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NEEDS IN NEXT GENERATION COMMERCIAL COATINGS SYSTEMS

Exterior Coatings

The primary requirements for exterior aircraft finishes will be the durability and deatability in field use, including gloss, color, and other decorative attributes. The system should be field reproducible, replaceable and have few maintenance costs. As long, high altitude flights become more common and more aircraft are spending a considerable amount of time at high altitudes, low out exposure at higher wavelengths (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 penetrating UV wavelengths are from 290-400, rather than the 280-400, nm region at sea level). Also, improved handed dim light stabilizers (HLS) will be needed to provide improved coatings durability, and all pigments utilized in topcoats must have outstanding UV stability and a total lack of oxidative photodegradation tendencies.†

Primers

The (pretreatment + primer) 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 Stripability

The refinishing and stripability requirements of the next generation finish will be much like those of the military. The systems should be strippable with environmentally benign materials and use rework systems that provide the same gloss and color retention as the OEM 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.
usage of coatings, local regulations will have to be considered very carefully as there is a large demand from sites-to-site in such areas. 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 DESIGN

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 polymeric 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.

**Sol-Gel Coatings Chemistry**

- Two approaches
  - Thin Film
  - Thick Film
- Metal oxide films with inorganic coating agents
- Surface and electronic properties
- Functionality similar to metal coatings
- Organic-Inorganic hybrids
- Stability for long-term protection

**Properties**

- Non-Cr system pass salt fog test
- Non-chromating phosphate system pass salt fog test
- Resistant to low acid etching
- Non-Cr systems are improving

**Figure 7—General description of sol-gel chemistries.**

**“Thin Film” Sol-Gel Coating Status**

- Boeigal-EP provides excellent primer adhesion
- CRT cure, low acid system formulated
- Surface improves visual appearance
- No impact on adhesion
- Non-Cr primers perform poorly on non-Cr conversion coatings
- Investigating methods of encapsulation or incorporation of inhibitor
- Alumina sol in a gel film formation
- Solubility of non-Chromiums not optimized

**Figure 8—Sol-gel coatings status.**

**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), electrochemical noise methods (ENM), and dynamic polarization methods. These have been considerable improvements in the instrumentation for the routine use of such measurements, especially in the new 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 ~5μm 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), and its derivative for corrosion studies by Issacs and co-workers,19 and local EIS (LEIS), most recently studied by Taylor and his co-workers,20,21 have been shown to be quite useful in such measurements. A recent paper from this laboratory discusses these methods.22 Also useful in coatings studies is the use of scanning Kelvin probe microscopy,23,24 as well as other scanning electrochemical microscopes.

**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 article discusses such systems, and other workers are pursuing similar studies based on EIS and ENM techniques.

**New Developments in Coatings Durability Characterization and Lifetime Prediction**

A recent symposium reviewed current efforts in durability characterization and lifetime prediction in organic/inorganic systems. The work has been expended utilizing surface analysis and data for this purpose as well as micro-FIR and micro-FTIR-Raman techniques.

**New Polymer Systems and Additives for Aircraft Coatings**

**Fluorocarbon-Based Polymers**

The development of polyurethane topcoats based on fluorocarbon-based polyols25 and exterior-grade acrylate 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 30 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 and 4. The corrosion performance as the low frequency impedance modulus, Z" data for this topcoat over a standard chrome-pigmented epoxy primer (e.g., MIL-P-5277) 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 ELT 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 polymeric 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.

**New Developments in UV- Cured Coating Additives**

References 9 and 23 discuss the state-of-the-art in UVAs and HAJS 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. The original emphasis of this project was properly incorporating CPVC prediction methods into the formulation process. This work has been extended in recent studies. Figure 6 shows a flow chart of the coatings design software currently under development.

**Figure 9—Schematic of ideal sol-gel structure.**

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

<table>
<thead>
<tr>
<th>E-Coat Bulk Phase (20-30 μm)</th>
<th>Plasma Polymer</th>
</tr>
</thead>
<tbody>
<tr>
<td>50 nm</td>
<td>New Surface State</td>
</tr>
<tr>
<td>Oxide</td>
<td>Aluminum Alloy</td>
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</tbody>
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Usage of coatings, local regulations will have to be considered very carefully as there is a large variety of 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 even more so in Northern Dakota.

**NEW MEASUREMENT TECHNOLOGIES FOR AIRCRAFT COATING DESIGN**

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- **Two approaches**
  - Thin Film
    - Metal oxide films with organic coating agents
    - Adhesion and degradation protected surface functions similar to present conversion coatings
  - Hybrid coatings
    - Organoceramics, network polymers
    - Porosity by introducing protection considered hybrid schemes for enhanced mechanical performance
- **Process**
  - In situ sol-gel Co-deposit system passes salt fog
  - Non-chromated alloy/substrate system passes salt fog
  - RT cure, low acid system formulated
  - Hybrid systems are improving

**New Developments in Corrosion Measurement Methods in Coated Systems**

Considerable effort has been expended by scientific instrument developers in making the use of electrochemical measurement techniques easier and more accurate. This holds true especially for electrochemical impedance spectroscopy (EIS), electrochemical noise methods (ENM), 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.

**New Polymer Systems and Additives for Aircraft Coatings**

- **Fluorocarbon-Based Polymers**
  - The development of polyurethane topcoats based on fluorocarbon-based polyol and exterior-grade saturated 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.
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- **Ceramics and Other Mixed Organic/Inorganic Systems**
  - The use of ceramic precursors together with polymeric 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.

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**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, and aircraft primer. The original emphasis of this project was properly incorporating CPVC prediction methods into the formulation process. Work has been extended in recent studies, Figure 6 shows a flow chart of the coatings design software currently used in testing.
free protection of Al 2024 T-3. This work has not succeeded in fully matching the performance of chromate pretreatment (Alodine®) 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.9,12,14,15 Figure 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 phase to the purely organic structure of a primer coating. A schematic of this ideal structure is given in Figure 9.

**Summary and Conclusions**

New aircraft coating systems will provide enhanced and environmentally compliant ways to increase outdoor durability and corrosion protection. New, high-performance aerospace coatings demonstrate this improved use of UVAs and HALS to provide the enhanced durability of aircraft topcoats for both military and commercial use. However, existing aircraft coatings can be expected to change to some extent 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 chromate-free systems for aircraft alloys will be available in the future. Among the top candidate strategies currently being considered are sol-gel based systems, plasma polymer film precursors, and conductive polymer cathodic protection systems. The use of these new coating systems will be militarily significant and enable aging, commercial aircraft.

**Acknowledgments**

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### References

5. Taken from a briefing presented by Dr. O. Tofel of USAF Research Laboratory, Coating Technology Information Office, WPAFB, OH, 1995. AERMAT.
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**Conductive Polymers**

Another strategy for non-chromate barrier coatings is the consideration of conductive polymers. These materials have received considerable attention for providing chromate-like corrosion control, including protection against corrosion in damaged areas, as primer coatings for metals without a need for pretreatments.25,26 This work has recently been extended to aircraft metallic alloys27 and shows considerable promise in this area.28 One such polymer under consideration is polysulfonylethylene (PSE) whose structure is given in Figure 10. Figure 11 shows the remarkable stability in immersion in chloride and 550°F (232°C) solution of this material as a primer, with a standard useable life of over Al 2024 T-3 as monitored 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 compatible coatings to increase outdoor durability and corrosion protection. New developments in UV and HALS will drive the enhanced durability of aircraft topcoat systems for both military and commercial use. However, existing aircraft topcoats will change 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 chromate-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 coatings, and chromate-like polyphosphazene, and conductive polymers. The most immediate candidates of these new coating systems will be military and future and commercial aircraft.

**ACKNOWLEDGMENTS**

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**Reference**


**Figure 13—1ZI vs. frequency at various times: polyurethane/PPO/Al 2024 T-3.**

**Figure 14—Optical micrograph of Polycarbonate/PPO/Al 2024 T-3 615 days.**

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**Note:** The document contains scientific and technical content related to aircraft coatings and polymers, including descriptions of materials, processes, and applications. It references various studies and patents, and mentions ongoing research and development efforts. The text is structured to provide a comprehensive overview of the state of the art in this field, highlighting both challenges and recent advancements. The references at the end of the page cite relevant research papers and patents, providing a basis for the discussed technologies and their applications in the aerospace industry.
Novel Coatings From Soybean Oil
Phosphate Ester Polylols

Bin Zhong, Chirag Shaw, Maruf Rahim, and John Massingill*—Coatings Research Institute/ Eastern Michigan University

INTRODUCTION

Soybean oil (SBO) is the most readily available and one of the lowest-cost vegetable oils in the world. It consists of triglycerides of a mixture of fatty acids formed by the reaction of glycerine and three fatty acid molecules. Epoxidized soybean oil (ESBO, Figure 1) is the result of the oxidation of soybean oil with hydrogen peroxide and either acetic or formic acid. According to the ratio of double bonds converted to epoxy groups, one can get partially epoxidized soybean oils such as 1/3, 1/2, 2/3, and fully epoxidized 3/3 ESBO. Both soybean oil and ESBO are industrially available in large volume at low price. In recent years, there has been a decline in the coating market share of soybean oil alkyls due to growth of latex paints that have lower VOC, low odor, improved properties, and ease of cleanup. Most recently, the higher VOC of alkyls has been a major problem. Improvement in adhesion and corrosion resistance along with reduced VOC and reduced cost would make industrial alkyls more viable. Some envisioned soybean derivatives have the potential to improve adhesion, resist corrosion, and reduce VOCs and the cost of coatings.

In our group’s earlier work, ESBO had been directly incorporated into air-dry alkyl systems as a reactive diluent and in a cationic UV-cure system as an additional epoxy component. There were adhesion problems in the UV-cured coatings with or without ESBO. In this work, the technology of epoxy phosphate esters was employed to reduce the VOCs of industrial alkyl coatings and improve adhesion. It was found before that a phosphate ester group made organic resins dispersible in water so one could produce waterborne alkyl coatings with lower VOC and excellent physical properties. The phosphate ester group was also found to increase the adhesion to metal substrates by reaction with the metal, thus providing a strong chemical bond between the coating polymeric and the metal. This metal-phosphate bond is more resistant to displacement by water than the normal coating group bonded to metal substrates and contributed to improvements in corrosion resistance of the coatings as well. This technology can be traced back to the late 1970s. Martin claimed water-thinnable epoxy phosphate esters

![Figure 1—Epoxidized soybean oil](image-url)