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Developing Hexavalent Chromate Free Coating Systems and Implementation Considerations Regarding the USAF T-38 Talon

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ABSTRACT

The United States Air Force (USAF) was tasked to remove carcinogenic chromium and chromate compounds, in particular hexavalent chromium, in order to prevent personnel exposure. The dominant sources of hexavalent chromium within the USAF were identified in aerospace primers and chromium plating. This drove the need to develop replacement coatings, which in turn drove the need to develop a standard to assure as good or better corrosion prevention for the outer mold line (OML) of aircraft. Through robust experimental protocol and disciplined scientific evaluation, Air Force Research Laboratory (AFRL) developed MIL-PRF-32239B to be utilized for the qualification of chromium free coating systems. It was established that the systems qualified through MIL-PRF-32239B must be used as stand-alone systems; the practice of mixing and matching suppliers for pretreatments, primers and coatings, as was the standard practice with hexavalent chromium systems, was no longer practical.

The T-38 "Talon" Program Office worked with scientists, logisticians, corrosion prevention subject matter experts, active duty corrosion prevention professionals and others to select the most practical solution to ensure protection for personnel as well as corrosion prevention for aircraft. The T-38 selected MIL-PRF-32239B System 4 and System 8. These systems will support the current fleet of trainer aircraft and welcome in the next generation of trainer aircraft with a common chromium free corrosion prevention system for the outer mold line. The T-38 is in the process of implementing the chromium free corrosion prevention system and looking forward to a successful replacement program.

1.0 INTRODUCTION

The T-38 is the premier fighter trainer for the USAF. The task to remove carcinogenic hexavalent chromium (Cr6+) from the outer mold line (OML) of the aircraft has been challenging from numerous perspectives. Hexavalent chromium compounds are carcinogenic. Reducing or eliminating hexavalent chromium from USAF weapon systems stems from a human health perspective. Qualified alternatives or replacement coating systems had to be developed. Specific testing protocol had to be established and validated; MIL-PRF-32239 was the result.

MIL-PRF-32239 designates hexavalent chromium free coating systems that have been tested and have passed qualification as specified therein. Hexavalent chromium free coating systems are required to demonstrate high durability for use in finishing (coating) aircraft exterior surfaces/OML. The coating system is comprised of a surface treatment (or pre-treatment), a primer, and a topcoat. MIL-PRF-32239 "Performance Specification Coating System, Advanced Performance, for Aerospace Applications" was released on 03 May 2007. An update, MIL-PRF-32239A, released 01 October 2014, enhanced the testing procedures and protocol for equivalent or improved hexavalent chromium free coating systems. The most current version, MIL-PRF-32239B, was released 29 April 2019. MIL-PRF-32239B defined the most up-to-date and specific evaluation protocol as well as pass/fail criteria for a coating system considered acceptable for use on United States Department of Defense (US DoD) aircraft.

The USAF Air Force Research Laboratory has performed testing to qualify coating systems; each separate system conforms to MIL-PRF-32239B specifications. Fundamental testing protocol and procedures are described as well as the evolution of the requirements driving modifications to the specification. Finally, hexavalent chromium replacement evaluation criteria for the OML of the USAF T-38 Talon is provided.

2.0 T-38 TALON

T-38 Talon was the first supersonic trainer, it was produced by Northrop Corporation (now Northrop Grumman) and was first utilized by the USAF in 1961. It has been relied upon to train pilots for more than 60 years. It is a two seat, dual engine supersonic jet; the instructor pilot mentors the student for various training and flight purposes. The Talon is a reliable and economic aircraft. Maintenance is performed regularly with oversight from the USAF T-38 Program Office. The T-38 Program Office is supported by numerous support contractors but is primarily engineered and managed organically by USAF personnel. This organic Aircraft Structural Integrity Program (ASIP) support is somewhat unique in the USAF to the T-38.

The T-38 has been in continuous service since 1961 and the need to ensure flight safety and airworthiness remains to 2034 and beyond. This has required numerous maintenance activities such as new wings and fuselage modifications. With these efforts, the trainer will meet necessary airworthiness requirements for the foreseeable future. The US Navy as well as NASA operate the T-38 for pilot training, pilot certification and flight test requirements. Additionally, numerous NATO countries utilize the T-38 as part of the Euro NATO Joint Jet Pilot Training program.

Specific to hexavalent chromium, the compound is found throughout the T-38 aircraft. Because the outer mold line (OML) of the T-38 is the area that see the vast majority of coating removal and reapplication, it is the primary focus regarding hexavalent chromium management. The OML is subject to coating removal and reapplication of paint on a recurring basis. The interval used to be approximately every eight years, now it is determined by time and ranking or inspection judgement of the condition of the coating system. For years aircraft were repainted on a time-based interval, however the USAF discovered that in general the aircraft were being painted more frequently than was needed. Since then, the USAF has adopted condition-based painting. The OML is evaluated and given a “score” or ranking from 1 to 5 where aircraft are repainted once they reach category five. When it is determined to be necessary to strip and repaint aircraft, the hexavalent chromium becomes a focus. The intention is to remove the coatings safely and properly dispose of the waste stream while minimizing exposure to personnel and the environmental impact.

3.0 HEXAVALENT CHROMIUM

Hexavalent chromium is chromium in the +6 oxidation state (Cr^{6+}). Hexavalent chromium has been used by the United States of America for corrosion prevention since World War II and particularly on US military equipment. Hexavalent chromium has high water solubility and therefore works effectively in paints, primers, etc. It leaches across the aluminium substrate and passivates the surface to create an effective oxidized layer that inhibits surface reactions and corrosion.[1] The tendency to use hexavalent chromium in corrosion prevention coating systems was the choice for decades. It is noted that there are other forms of chromium, including trivalent chromium. The emphasis of this paper is on replacing hexavalent chromium coatings on the OML of T-38 aircraft; this is primarily due to toxicity associated with hexavalent chromium.

3.1 Toxicity of Hexavalent Chromium

The dangers from hexavalent chromium compounds started to become recognized prior to 1991. Hexavalent chromium is a human carcinogen and is potentially responsible for several health conditions. The primary absorption route is through the lungs, however hexavalent chromium compounds may be absorbed through the eyes, nose, soft tissue in the mouth, and the skin. Due to the toxicity of the compound, the United States Air Force has been developing and implementing alternative coating systems that significantly reduce or eliminate the use of hexavalent chromium on the OML but still provide necessary corrosion prevention. This effectively reduces or eliminates personnel exposure to hexavalent chromium by removing it from USAF weapon systems where the greatest exposure occurs. In 2018, the United States Department of Labor, Occupational Safety and Health Administration (OSHA) reduced the Time Weighted Average (TWA) for an eight hour day exposure levels by two orders of magnitude or 100 times less permissible exposure levels. This shift in allowable exposure drove the TWA to $0.2\mu g/m^3$ for inhalable Cr^{6+} and drove the Short Term Exposure Limit (STEL) to $0.5\mu g/m^3$. STEL are for exposures less than 15 minutes. [2]

3.2 Hexavalent Chromium on T-38 Talon

The T-38 aircraft, like many USAF aircraft, was designed to use hexavalent chromium, in the form of strontium chromate, as an anticorrosive component of surface treatments and primers. The current corrosion prevention coating system on the T-38 aircraft is comprised of a pretreatment of either PreKote (an adhesion promoter that does not contain Cr^{6+}) or Alodine (a chromate conversion coating containing Cr^{6+}), a primer (MIL-PRF-23377, Type I Class C2, contains Cr^{6+}), and a topcoat (MIL-PRF-85285, does not contain Cr^{6+}). A notional depiction of this layered system is presenting in Figure 1.

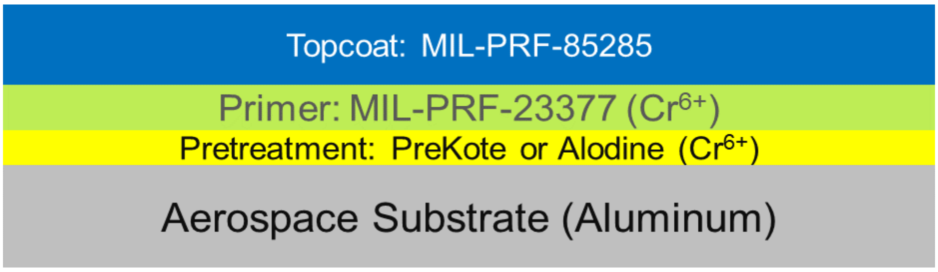

Figure 1: Notionally Typical Coating System Schematic with Hexavalent Chromium
(Note: "PreKote" is an adhesion promotor and does not contain chromium or other corrosion inhibitors)

3.3 Reducing Exposure to USAF T-38 Personnel

Given that most USAF aircraft have hexavalent chromium as part of their corrosion prevention coating systems, the USAF had to come up with a plan to protect personnel and prevent water and soil accumulation of hexavalent chromium in the environment. The easiest and immediate approach is to provide Personal Protective Equipment (PPE), however, there are far more effective controls. The hierarchy of controls from most effective (1st) to least effective (5th) are as follows:

- 1st : "Elimination" or physically remove the hazard
- 2nd: "Substitution" or replace the hazard
- 3rd: "Engineering Controls" or isolate personnel from the hazard
- 4th : "Administrative Controls" or alter the way people work and their exposures
- 5th : "Personal Protective Equipment" (PPE) or protect personnel with devices

PPE and Administrative controls are the easiest and quickest to implement but are also easily bypassed due to a variety of human factors. Engineering controls are often expensive yet effective at isolating personnel from the hazard. A problem arises as in this case when safety regulations change and render these controls obsolete, serious considerations must be given to invest in engineering upgrades or eliminate the hazard. Substitution and Elimination of the hazard with something less harmful or totally innocuous are by far the most effective controls. Therefore, the USAF elected to research and develop new products for replacing hexavalent chromium that would protect personnel from exposure and the environment, as well as provide necessary corrosion protection for aircraft.

Administrative controls and PPE are the easiest and quickest to implement. But eliminating the hazard and substituting the hazard with something not harmful are by far the most effective controls to utilize. Therefore, the USAF elected to research and develop new products for replacing hexavalent chromium that would protect personnel from exposure and the environment, as well as provide necessary corrosion protection for aircraft.

4.0 REPLACEMENT FOR HEXAVALENT CHROMIUM

The USAF had numerous requirements and challenges as they set out to develop suitable replacement products. The basic requirements were:

- Develop an easy "drop in replacement" for existing equipment and processes
- The products must be readily producible and widely available

- Stable technology that is reproducible to a standardized approach (MIL-PRF-32239B)

These basic requirements would make it such that individual units would be able to adapt to a new system with little to no interruption to their operations.

The primary challenges faced by these changes were mostly related to learning about available options and how those options may work with or against each other. The old coating system, as described in Figure 1, was relatively simple. A unit or base, in order to paint an aircraft, was able to use any pretreatment that met the conversion coating specification with any chromated primer that met the aerospace chromated primer specification, followed by the polyurethane topcoat that met specifications. Mixing and matching from one supplier or producer to another was suitable and common place because all of these combinations were based upon formula specifications that required a certain amount of hexavalent chromium in the pretreatment and in the primer. As coating engineers sought to mix-and-match chromium-free pretreatments with chromium-free primers, it was clear that different inhibitor systems could interact positively or negatively, depending upon their chemistry. Additionally, when "drop-in-replacement" testing sought to replace only the pretreatment or the primer but leave the other layer containing hexavalent chromium in the coating stack, again it became clear that hexavalent chromium did not perform well with many other corrosion inhibiting technologies. Beyond that, the "workhorse" test method to determine if there was sufficient corrosion resistance provided by a coating system, utilizing the typical "salt spray test," did not predict real world performance for partial chromium and fully non-chromium systems. The results could lead the researcher to false positive (i.e., it passed the salt spray test but failed in a flight test) or false negative (i.e., it failed the salt spray test but performed very well in the flight test). With so many unknowns, the Department needed to develop better methods for interrogating coatings. The creation of a performance specification with baseline requirements for non-chromium coatings as a complete coating system was necessary. [3]

4.1 Developing a Coating Specification for Aerospace Applications

Through the Society for Automotive Engineers (SAE) International, an Aerospace Material Specification (AMS) was available as a starting point; AMS3095A "Paint: High Gloss For Airline Exterior Systems" for commercial aircraft was a baseline for requirements. Some of the tests and pass/fail criteria in the AMS specification were only appropriate for commercial aircraft, such as tests focused on matching exact gloss coating colors and requirements for flexibility which were less stringent than military requirements. However, when requirements were compared between the AMS specification and the existing "mix-and-match" coatings that were currently on military aircraft, there were distinct differences between the two that necessitated the development of a military specification. This specification would qualify prescribed coating systems to be utilized on coating systems being used in the DoD. The requirements were compared, and a joint committee worked to finalize baseline acceptance criteria; and MIL-PRF-32239 "Coating System, Advanced Performance, for Aerospace Applications" was designated as the specification for which to qualify acceptable coating systems specific to military applications.

Prior to MIL-PRF-32239, the components of a coating stack-up could be mixed and matched from various product suppliers and vendors; Figure 1 shows the coating system. The new Performance Specification established the requirement for a coating system where each specific component worked together; the "mix-and-match" approach would no longer be effective. It was the goal for each MIL-PRF-32239 qualified systems to be: "as good or better" than the coating stack-ups that were actively in-use on USAF aircraft.

Testing on varying combinations of treatments, primers and coatings was initiated. There were some successes and some trials. The biggest challenges were questionable inconsistencies in salt spray results (re: false positive and false negative performance in salt spray testing versus real world corrosion degradation mechanisms). Therefore, a revision to MIL-PRF-32239 was developed then subsequently published on 1 October 2014. Numerous changes were introduced into the next version of the performance specification, MIL-PRF-32239A. One of the more insightful additions was to develop a standard test coupon. The coupon was simple yet elegant in its design; a schematic of the coupon is shown in Figure 2 (note: measurements are in inches).

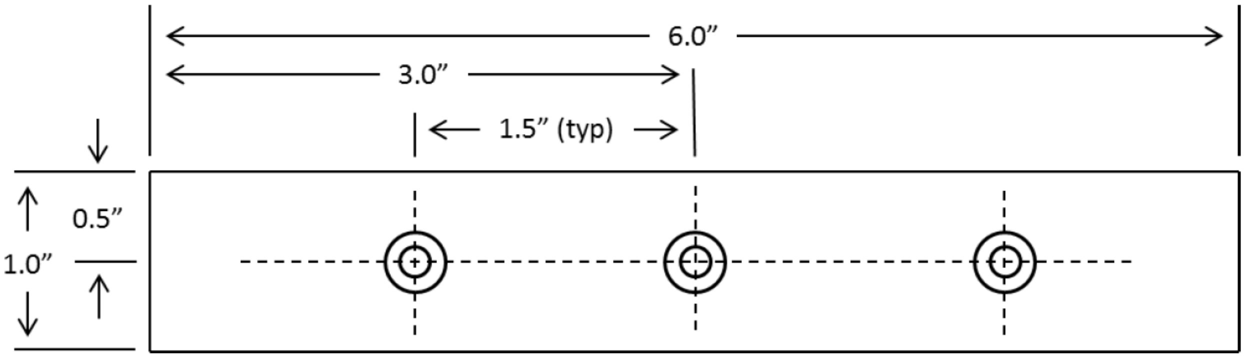

Figure 2: MIL-PRF-32239A Standard Test Coupon

Besides a consistent configuration, a host of specific preparation instructions guide test panel preparation. The following was quoted from MIL-PRF-32239A. [4]

> “Test procedure 4.6.19 shall use test panels manufactured as shown on Figure 2 (modified for this report) using 0.125 inch bare aluminum alloy conforming to AMS-QQ-A-250/4. Three holes shall be drilled and countersunk as shown to accommodate the dry installation of either a titanium fastener or cadmium plated steel fastener. The titanium fasteners shall be 10-24 × 5/8, Grade 2 with a 10-24 Grade 2 titanium nut. The cadmium plated steel fasteners shall be a NASM24693 screw with a 10-24 cadmium plated nut.” [4]

With the three-hole outdoor exposure galvanic corrosion sample, scribed and unscribed fasteners, and three panels per fastener type, the panel matrix was much larger. With this also came additional cost for vendors and the USAF to make and expose samples. With enough data collected, the engineering team at AFRL determined that the same amount of data could be collected by using half as many samples and scribing every alternate fastener. This reduced the number of panels required for testing, which in turn reduced the cost of panel generation, outdoor exposure, and evaluation time. Once this was completed, MIL-PRF-32239B was published on 29 April 2019. [4]

Figure 3 shows the test coupon configuration with the added holes. The following was quoted from MIL-PRF-32239B.

> “Test procedure 4.6.19 shall use test panels manufactured as shown on Figure 1 using 0.125 inch bare aluminum alloy conforming to SAE AMS 4037. Four holes shall be drilled and countersunk as shown to accommodate the dry installation of either a titanium fastener or cadmium plated steel fastener. The titanium fasteners shall be 10-24 × 5/8, Grade 2 with a 10-24 Grade 2 titanium nut. The cadmium plated steel fasteners shall be a NASM24693 screw with a 10-24 cadmium plated nut.” [5]

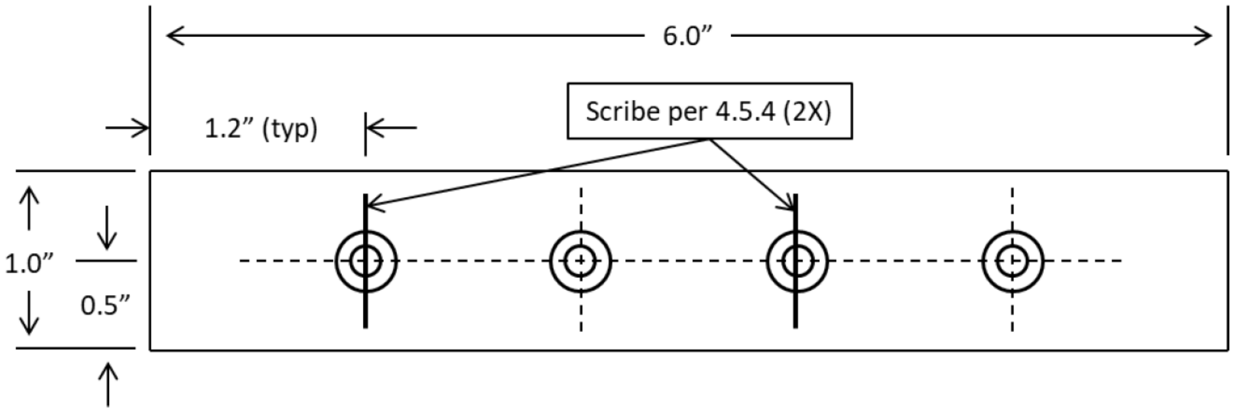

Figure 3: MIL-PRF-32239B Standard Test Coupon

4.1.1 Lessons Learned and Incorporated into MIL-PRF-32239B

During the development of MIL-PRF-32239B and the investigation of materials to be used as replacements for chromium based protections, it was learned that hexavalent chromium inhibitors are a robust and understood corrosion mitigation technology. Mixing and matching vendors and products is easy, reliable and yields little change in performance. However, eliminating hexavalent chromium does not generate a single class of materials. Non-chromium technologies are “group of technologies that do not include chromium.” Each and every non-chromium system is a separate technology of its own. [3]

Throughout the trials and tribulations of developing the performance specifications, there were several lessons learned that are shared here. These are presented in bulleted format for clarification purposes: [3]

- One cannot mix and match chromated inhibitor materials indiscriminately, mutual adhesion and compatibility characterization testing and evaluation is required
- Performance of each system in combination with others must be verified, even with small changes to the system
  - One MIL-PRF-85285 Type IV topcoat manufacturer versus another might matter
    - Performance specifications do not dictate chemistry
- Basic laboratory materials performance tests provide value
  - “Exposure effects” followed by flexibility testing is now incorporated into the new performance specification (MIL-PRF-32239B)
- ASTM B 117 Corrosion Resistance Test can give false positives and false negatives
  - B 117 laboratory testing passed, yet failed on wing during in-service testing
  - B 117 laboratory testing failed, yet passed outdoor exposure testing
  - Results showed good for in-service on small aircraft, but not good for in-service on large aircraft
    - Full characterization required
- Baseline corrosion resistance performance is better characterized with galvanic coupled corrosion testing, this was added to the performance specification.

Finally, there are a great many details involved in developing these performance specifications. Qualification and verification of each coating system is necessary for effective corrosion prevention.

4.2 Qualified Products via MIL-PRF-32239B

Utilizing the specific test protocol as developed by Air Force Research Lab (AFRL) and prescribed in MIL-PRF-32239B, the USAF has been able to test, monitor, evaluate and approve numerous systems that are free from hexavalent chromium. It is imperative to recognize that each of these systems must be used as a system. For example, that the pretreatment, primer and topcoat that belong to a given system must be used together as that system. Mixing and matching among the various systems is not appropriate and will likely cause coating system failure. These systems have been approved for the outer mold line (OML) of aircraft. However, the previous or existing chromated coating system needs to be removed; and as always surface preparation is key to successful any coating system. The layup for the new chromium free systems is depicted notionally in Figure 4. Comparison with Figure 1 shows that it is nearly identical to the previous chromated system at least in the layering onto the aluminium substrate. Table 1 shows the systems that have been approved by utilizing MIL-PRF-32239B as of the time this article was written.

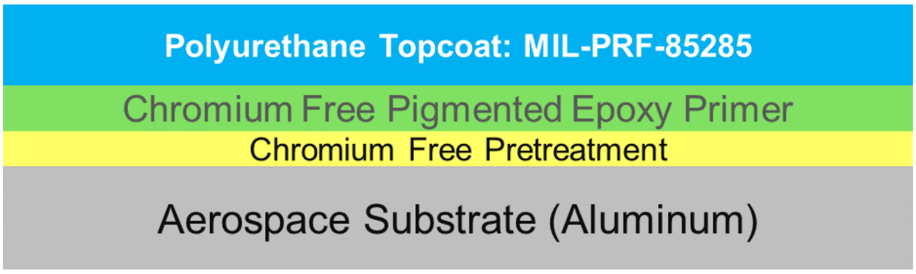

Figure 4: Chromium Free Coating System Notional Schematic

Table 1: Hexavalent Chromium Free Coating Systems Approved by MIL-PRF-32239B

System	Pretreatment – Chromate free	Primer – Chromate free	Topcoat
Coating System 1	PreKote®	AERODUR 2100	99GY001
Coating System 2	PreKote®	AERODUR 2100	AERODUR 5000
Coating System 3	AC-131	AERODUR 2100	AERODUR 5000
Coating System 4	DesoGel® EAP9	CA7236	CA9311
Coating System 5	AC-131	AERODUR 2118	CA9311
Coating System 6	AC-131	AERODUR 2118	AERODUR 5000
Coating System 7	PreKote®	AERODUR 2118	CA9311
Coating System 8	DesoGel® EAP9	CA7236	CA9800

5.0 A NON-CHROMIUM SYSTEM FOR THE T-38 TALON

The USAF had numerous drivers for omitting hexavalent chromium (Cr6+) from the OML of aircraft. These were heavily due to the risk to human health and environmental health due to the carcinogenic toxicity of the compound. This has driven mandates from the USAF. These include, but are not limited to:

- Undersecretary of Defense memorandum dated 08APR2009 stating to update technical data to authorize the use of qualified alternatives to chromated coatings, and document system specific Cr^{+6} risks. If technical data is not updated, there needs to be a very compelling reason why, and that reason should be certified by the aircraft system Program Executive Officer and the Air Force Corrosion Office as well as management.

- Air Force Instruction - AFI 63-101, paragraph 5.4.11.3.3 states - Prohibiting or strictly controlling the use of banned or restricted hazardous materials, such as hexavalent chromium and ozone depleting substances. The Chief Engineer does not introduce new operational or maintenance requirements for out-of- production Class I or Class II Ozone Depleting Substances unless approved or waived by SAF/AQ.

- Previous revisions of AFI 63-101 were more directive with respect to removing coatings that contain hexavalent chromium from aircraft.

The requirement to move away from chromium based corrosion prevention coatings was announced and responsibility for choosing a replacement system was delegated to the T-38 Program Office Corrosion Manager. Making decisions began by becoming familiar with MIL-PRF-32239B and reviewing a Background Paper on “Hexavalent Chromium Reduction In F-16 Outer Mold Line (OML) Stack-Up” written by Major Bradley Clark, dated July 2018. After reviewing these publications, the process of learning what would work best for the airframe took precedence. This led to the initial selection of System 2 (see Table 1 for details). The rationale for this choice was due to the knowledge that PreKote was already in use at all Air Education Training Command (AETC) bases, and that Aerodur 5000 topcoat, a MIL-PRF-85285 Type IV was compatible with the currently used topcoat, MIL-PRF-85285 Type I. Therefore, the product as well as procurement were established as well as familiarization with its application.

The choice of the non-chromated system was presented at the T-38 Corrosion Prevention Advisory Board (CPAB) in February 2020. The CPAB discussed and several highly relevant facts were brought to light by multiple members. The facts were multifaceted; the T-38 is the primary jet trainer for the USAF and as such shares facilities with other trainers at various bases. Additionally, the new training jet that was in procurement, would be using System 4. Therefore, logistically, it was prudent to select System 4 as the top choice because it is planned to be used on the T-7, the replacement trainer for the T-38. Adoption of System 4 would serve as a precursor to on boarding and maintaining the next generation jet trainer. After this decision was made it was realized that the topcoat for System 4 used a matte finish and the T-38, as well as other trainers, utilize a gloss finish topcoat. The question of compatibility of a matte finish versus a gloss finish for System 4 was presented to AFRL. The scientists at AFRL had already started the process of qualifying an additional non-chromium system for gloss topcoat; this system was modelled after System 4 with the topcoat changed to a gloss finish. Effective early 2023, System 8 was qualified to MIL-PRF-32229B. Referring to Table 1, System 4 is the same as System 8 with a different topcoat; the topcoat for System 8 is for the gloss finish used on the T-38 Talon. These factors resulted in the System 4 and System 8 from MIL-PRF-32239B as the final choices for the T-38 fleet.

The next challenge was to field the new system. This step is in process. The T-38 Program Office is working with AETC, individual units and field representatives. The following areas are the focus of implementation:

- Successful reduction and ultimate elimination of hazards and exposure to personnel

- Successful application and durability of robust coatings to control corrosion of the T-38 as well as other USAF trainer aircraft

- Appropriate training of personnel and demonstrations from suppliers

- Assuring availability of products in supply chain and ability to procure

Successfully transitioning to a hexavalent chromium free system will radically reduce the hazardous exposure of personnel. Training and adapting to new processes will assure successful coating application and maintenance. AETC has been working with the producers and suppliers of the various products for System 8 in efforts to assure timely delivery and availability of the new coating system products.

At the time of this writing, the plan is to begin with one field unit and establish training criteria and efficacy of applications. Once a robust approach has been developed and polished, the refined process will be transitioned to other bases in a timely manner.

The T-38 Program Office has assembled a team to implement this change. This requires cooperation across many groups including logistics, engineering, technicians, maintenance, supply, safety and environmental among others.

6.0 SUMMARY

Overall, AFRL has carefully and methodically engineered MIL-PRF-32239B to overcome the challenge of removing and replacing hexavalent chromium from coating systems for USAF aircraft. The T-38 was able to learn the specific challenges about this military specification and make informed decisions for replacement and implementation based on empirical data, logistics and efficacy. Ultimately, the decision was made to utilize MIL-PRF-32239B System 8. This system will likely be utilized by other USAF trainer aircraft. The move to the chromium free coating system, System 8, will be implemented in phases with the goal to be completed in as quick a time frame as proves manageable without significant interruption to mission capability.

7.0 RECOGNITION

The T-38 Corrosion Manager (the primary author) would like to extend sincere gratitude to Department of the Air Force personnel including Diane Buhrmaster (AFRL), Michael Spicer (AFRL, ret.), and Chad Hunter, Ph.D. (AFRL). Additionally, to Bradley Clark (F-16 USAF Reserves and T-38 Chief Engineer) who was instrumental in initiating the program for T-38. To SMSgt Bandele Howes (AETC), SMSgt Matthew Dowden (AFCPCO), Robert Madsen (AFCPCO) for their instruction and information that proved extraordinarily valuable towards implementation. And finally, to Vance Bowman (T-38 ASIP Manager), Travis Moulding (T-38 Engineer), Avery Cross (T-38 Engineer), Michael Blinn (T-38 Chief Engineer, ret.) the Air Force Corrosion Prevention Control Office, field unit Wing Corrosion Managers and all members of the T-38 CPAB for their patience, support and guidance through this challenge. Thank you kindly.

8.0 DISCLAIMER

The views expressed in this article are those of the author and coauthors and do not necessarily reflect the official policy or position of the United States Air Force Academy, the Air Force, the Department of Defense, or the U.S. Government.

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