PAINT ADHESION TO CHROMATED SURFACES.

BACKGROUND: Chromated surfaces come in numerous variations to improve corrosion resistance and adhesive bonding in a number of applications. A chromic acid rinse is specified for black oxide coatings. The chromic acid rinse neutralizes the residual alkali and leaves the surface with a slight acidic residue which can promote adhesion of organic paint coatings. Very few, if any, paints will adhere to surfaces with residual alkali chemicals. A chromic acid rinse on heavy phosphate coatings can improve the corrosion resistance of the coating and dilute the residual acid from the coated surface to improve paint adhesion. The chromate supplemental treatments on zinc and cadmium plating improve the corrosion resistance of the coatings and prevent the formation of non-functional or voluminous white corrosion products. The supplemental chromates on zinc and cadmium are also often used as a treatment to improve paint adhesion. The chromates on aluminum and magnesium are also used for both corrosion resistance and paint adhesion.

CONSIDERATIONS: Military specifications[1] in the past have stated that "aged chemical treatments may lose their ability to hold paint without visual signs of deterioration". It is therefore good practice to resurface treat within 18 hours of painting to insure uniformity of results. Not all Mil-C-5541 treatments are equally effective in promoting adhesion of paint to cadmium plate. Therefore, to ensure good adhesion to cadmium plated screws in aluminum structures, care should be taken to select a suitable, approved MIL-C-5541 manual treatment that will be effective on both the aluminum and the cadmium plated screws." While it is known today that supplemental treatments for cadmium are different from supplemental treatments on aluminum, the nature of the hydrous gel characteristic of all chromated coatings is essentially the same. They tend to dehydrate and shrink with time with no "visual signs of deterioration." The E revision of MIL-DTL-18264, dated 29 June 2015, paragraphs 3.5.1.7 and 3.5.1.8 requires chromated aluminum coatings be painted between 8 and 72 hours. Paragraph 3.5.1.7.1 also states that "paint will not adhere to a powdery surface of excessively treated magnesium or aluminum." Thus, prolonged treatment time (high coating weights) in the chromating bath can also be an adhesion factor. It is interesting to note that MIL-DTL-5541, the current specification for chromated aluminum, paragraph 6.12 suggests that the coated parts should be allowed to dry in accordance with the chemical manufacturer's recommendation. This implies that the drying properties of the individual chemical processes may vary based on the coating composition.

Technical papers can also be a source of information on paint adhesion to chromated surfaces. A thesis dissertation by Po-Nien Chen[2] on page 11 talks about the effects of aging on chromate conversion coatings. It is stated that no significant changes in coating chemistry was noted after 24 hours but more significant changes were noted with increased aging. Mr. Chen also noted that low and medium coating weights provided the best adhesion which confirms the statements in the military specifications. Another reference[3], states that "the painting takes place as soon as is practicable after chromating, invariably within 24 hours."

Baking the chromate conversion should not be done at temperatures above 140 degrees F to facilitate drying according to most guidelines. Those reports don't generally don't state a time so adhesion of paint is not predictable. Other reports state that baking chromates can occur at 250-400 degrees F for powder paint coating. Loss of water from the hydrous gel could cause separation at the chromate-powder coat interface. One option for powder coating could be to bake the chromate and dehydrate it before applying the powder coat. Depending on the water vapor permeability of the powder coating being applied, dehydration during curing maybe possible and not affect adhesion. It has not been shown what the condition of the chromate is after stripping a powder coating and then examining the condition of the chromate. Stripping a powder paint coating may likely strip the chromated zinc coating too. The best advice has been to skip the chromate after zinc plating and powder coat directly over the zinc. Again, the applicator/coater needs to know what processes are going to be performed after finishing to keep himself out of legal jeopardy.

DISCUSSION: It is well known that most chromate conversion coatings have the characteristics of a "hydrous gel." A good example of a hydrous gel is a bowl of Jello. If left in a refrigerator for a period of time, the Jello will begin to dehydrate and shrink in volume. Eventually, the hydrous gel begins to show the "mud flat cracking" pattern typical of dehydrated surfaces. See Figure 1. This shrinkage may also be referred to as "a network of microcracks" on the surface. See Figure 2. It is also known that paints tend to shrink during drying or curing. The normal shrinkage of epoxy coatings is in the 3-5% range. In essence, the secret of good paint adhesion to chromated surfaces is to match the shrinkage of the chromate with the shrinkage of the paint to minimize the residual stress at the interface between the chromate and the paint. Since humidity and temperature can vary from plant to plant and time to paint application can vary depending how the contractor is set up with his suppliers, the in-process times between chromating and paint application is entirely random without proper planning. Most platers don't paint and a lot of painters don't do pretreatment. Plated fasteners, for example, are done in bulk at a fastener manufacturer, then stored, and finally shipped to a manufacturer who is going to use the fastener in an assembly. This process could result in a time frame of possibly months. Painting over a chromate that is completely dried means there is severe stress at the chromate-paint interface as the paint shrinks after cure. The best advice is to paint the chromate in the 4 to 24 hour time frame after pretreatment. If there is no way to validate the time of pretreatment, it is recommended that the pretreatment be repeated and painted in the 4 to 24 hour time frame.

CONCLUSIONS: It is concluded that:

1. The optimum time to paint or get adhesion to a chromated surface is within 4 to 24 hours after the pretreatment is completed.
2. Temperature, humidity and time variables after pretreatment may affect the chromate and ultimately the optimum adhesion conditions. Retreatment may be required after prolonged exposure prior to painting.

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1. MIL-F-18264D dated 22 July 1965, page 58, paragraph 14. Note 40/
2. The effect of chromate on adhesion between epoxy coating and Aluminum substrate, Po-Nien Chen, Lehigh University, 1999.
3. The Corrosion Resistance and Paint Adhesion Properties of Chromate Conversion Coatings on Aluminum and Its Alloys, H.J. Allsop, J.B. Doble and V.C. McLoughlin, Technical Report 76063, 25 May 1976.

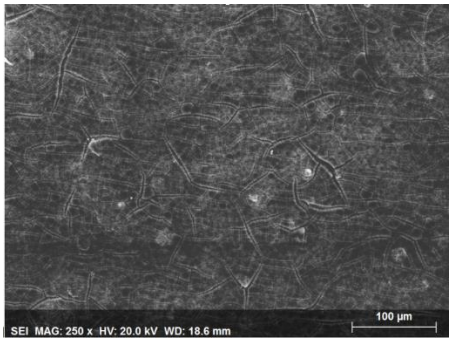

Figure 1. SEM photo of microcracks on a zinc plated and chromate treated surface. 250X.

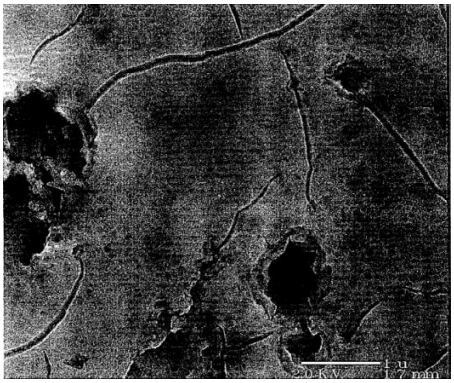

Figure 2. SEM photo of microcracks on a chromated aluminum surface. 20000X.