Process Control For Phosphate Coating

A new military specification for phosphate coatings . . .

By JOSEPH T. MENKE
Chemical Engineer
U.S. Army
Rock Island, IL

In the past, paint-based zinc phosphate coating to Federal Specification TT-C-490, Revision C (March 85) required a minimum coating weight. Amendment 1 (June 87) to the C revision cited a limited coating weight range. Relief from the narrow coating weight requirement was provided in Amendment 2 (June 90). Recently, the D Revision was published and a new requirement has been added for process control, grain refinement.

The TT-C-490 document is somewhat different than most other military specifications. The document contains a distinct combination of cleaning methods for most metals, various types of phosphate coatings and paint application requirements. This combination creates some confusion, since most specifications address specific processes. In essence, the specification starts with a substrate material (steel, zinc, cadmium or aluminum) and prepares the surface for application of some supplemental coating such as paint, dry film lubricant or adhesive.

The specification has a requirement for preproduction process approval for the zinc phosphate coatings (Types I and V). Numerous observations have been made over the past two years as to the variety of coverage and crystal structures that can be obtained when applying Type I coatings.

Ever since the coating weight requirement was 300 mg per sq ft minimum, many applicators have provided coating weights in the 1,000 to 2,000 mg per sq ft range. After all, if a little bit is good, a whole lot must be better. And only one tank and one solution were necessary to meet the requirements of a heavy phosphate coating.

Unfortunately, this didn’t work when the Army switched to epoxy primers and urethane topcoats. The shrinkage of the epoxy upon curing left the phosphate/paint interface in shear stress.
1. X-RAY ANALYSIS of phosphate coating with poor coverage

2. FLAT PLATELETS and nodular structure

3. X-RAY ANALYSIS of phosphate coating formed on a machined surface

4. X-RAY ANALYSIS of phosphate coating on the ground surface

5. X-RAY ANALYSIS of the phosphate coating on a machined surface

6. X-RAY ANALYSIS of the phosphate coating on the as-formed surface

and articles exhibited poor adhesion in the field. As a result, subsequent specification revisions placed a maximum limit on the coating weight.

The approach that followed resulted in applicators reducing the phosphating time in an attempt to get the coating weight down. This
ended up producing coatings that met the coating weight requirement but did not provide complete coverage (Fig. 1). Accelerated corrosion testing revealed severe blistering of the paint coating over these pretreatments. The proper way to get the coating weight is to use a solution that is specifically formulated to provide the necessary crystal structure for proper paint-based coatings. Chemical suppliers know which of their products can provide this capability.

As applicators slowly changed to the proper chemicals for applying paint-based coatings, it was noted that coating weights still remained in the 600- to 900-mg-per-sq-ft range or that incomplete coverage was obtained on a majority of items. In addition, when panels and parts were submitted, there was a significant variation in the crystal structure and coverage.

Panels submitted along with a proposed procedure exhibited a mixture of flat platelets and nodules (Fig. 2). The
X-RAY ANALYSIS of the phosphate coating after exposure to a titanium grain refinement dip.

X-RAY ANALYSIS of the manganese modified phosphate coating applied using a spray technique. Processing temperature was approximately 145F using a calcium-modified zinc phosphating chemical. The actual part showed a mixed structure on the machined surface (Fig. 3) and another structure on the ground surface (Fig. 4). It was determined that different machining lubricants/coolants were used on the different surfaces and that the alkaline cleaner was not properly removing either contaminant prior to phosphating. Figure 5 shows a phosphate coating on a machined surface from a piece of four-inch tubing. Figure 6 shows the same coating on the as-formed tubing surface.

The installation and startup of a TT-C-490 solution was examined using SEM observations, x-ray analysis and coating weight tests. The solution studied was a calcium-modified zinc phosphate operated in the 130 to 150F range. Specimens were alkaline cleaned and subjected to the phosphating solutions at 130 to 153F. Other specimens were vapor degreased and abrasive blasted prior to phosphating at 130 and 153F for one minute. All the specimens showed a typical flat platelet structure when processed at 130F (Figs. 7 and 8). After processing at 153F, the alkaline cleaned specimens exhibited a nodular (Fig. 9) structure, while the abrasive blasted specimens still exhibited a flat platelet structure (Fig. 10). This shows that temperature and pretreatment can have an effect on the type of crystal structure that is obtained during phosphating.

Different parts that used a titanium
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grain refiner as a separate step after alkaline cleaning and prior to phosphating with a calcium-modified solution exhibited a flat platelet structure (Fig. 11). Other parts that were subjected to an alkaline cleaner that had a titanium salt in it also exhibited a flat platelet structure.

In this case, the applicator had no idea what was responsible for the fine grain structure. The material safety data sheet for the alkaline cleaner did not include a titanium salt in the formulation. Contact with the chemical supplier revealed that titanium salts were in the cleaner, but since the concentration was so small, the supplier was not required to include the chemical on the safety data sheet. This leaves the applicator in a position of not knowing what makes his process work.

A more recent product on the market is the manganese-modified zinc phosphate coating. It too is designed to give fine-grain coatings. Spray application results in a flat platelet structure (Fig. 12), while titanium salt grain refining and phosphating with this solution produces a nodular type crystal structure (Fig. 13). This is, in essence, the exact opposite of what is observed using the calcium-modified solution. This article covers only a few of the phosphating chemicals available from chemical suppliers.

During a recent failure analysis of rubber bonded to a zinc-plated surface that was phosphate coated, it was discovered that the adhesive manufacturer recommended a calcium-modified zinc phosphate with a coating weight of 150 to 300 mg per sq ft for optimum adhesion. Automotive manufacturers currently want a fine-grain zinc phosphate coating that has a high amount of iron phosphate in the coating to provide better chemical resistance to the conditions present when electrocoat paint is applied. Previously mentioned was the adhesion of epoxy paints over various phosphate coatings. These applications are typical for the way phosphate coatings are used today.

"Tailoring" is very much a part of today's phosphate coating technology, which will probably become even more sophisticated in the future. The TT-C-490 specification is only just beginning to recognize these aspects of the phosphate coating process. The applicator, the chemical supplier and the technical support people must work together even more in the future to meet the needs of the industry.

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