

Coverage: A Phosphate Pretreatment Problem

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Flash rusting on production parts and inconsistent paint adhesion data on test panels treated with TT-C-490, Type-1 coatings (paint-based zinc phosphate coatings) prompted an investigation into the problem. Production parts were manufactured from an alloy steel with a Rockwell C hardness of around 45. Paint adhesion test panels were 1010 carbon steel with no thermal treatment. Coating weight, crystal structure and elemental X-ray analysis observations were made to understand the situation. The variations in coverage were documented for a variety of coatings.

Flash rusting and inconsistent paint adhesion are common problems associated with paint-based zinc phosphate pretreatments. These problems can often be traced to the "coverage" that is achieved during the pretreatment process. The normal coverage of a phosphate coating is assumed to be complete at the end of the spray or dip cycle, which can vary from one to ten minutes depending on the application technique. Furthermore, coverage is assumed to be complete based on a visual assessment of the uniformity in the gray color of the zinc phosphate coating. Most literature references state that a 2-4 void area can be expected, i.e., there may be some uncoated metal areas that are not completely covered with phosphate crystals. The bare areas are assumed to have some protection against premature rusting as a result of the final chromate rinse.

Visual examination of a paint-based zinc phosphate coating on alloy steel parts revealed a uniform gray color and coverage was assumed to be complete. A few months after phosphating, rusting was observed on the phosphated parts after removal from the protective packaging. Thus, a visual evaluation of coating uniformity did not provide an adequate assessment of coating quality. A visual examination of phosphated panels for paint testing also revealed a uniform gray color and again the coverage was assumed to be complete. Inconsistencies in paint ad-

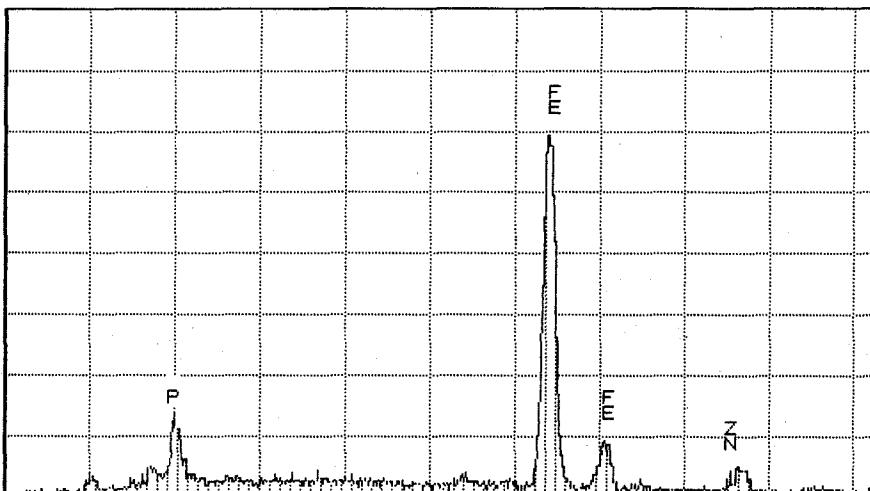


Fig. 1. Elemental X-ray analysis (above) and micrograph (right) of phosphate coating on alloy steel at 500 \times .

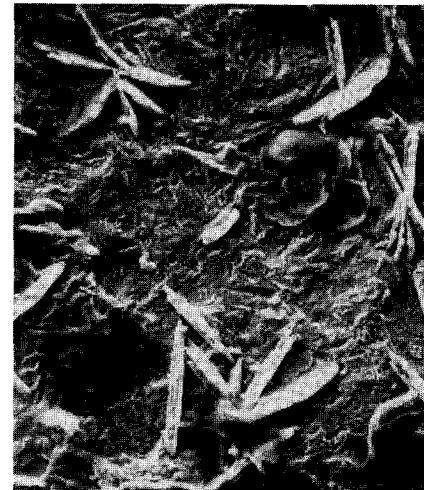
hesion data from the test panels resulted in a conclusion that the adhesion test must have been unreliable. It was assumed that all zinc phosphated panels for paint evaluation testing were the same.

FLASH RUSTING

Production parts with the zinc phosphate coating applied were obtained for testing. The parts were manufactured from an alloy steel and had a Rockwell C 45 hardness. The parts had been vapor degreased with trichloroethylene and were abrasive blasted prior to phosphating in a typical five-stage spray line. Sections were subjected to examination using the scanning electron microscope (SEM). Photographs and elemental X-ray analysis were used to document the results.

PHOSPHATED PANELS FOR PAINT ADHESION TESTING

Carbon steel panels with a commercial zinc phosphate coating conforming to TT-C-490, Type 1 were provided by a paint lab. The 4 x 12-inch



panels were coated using a proprietary formulation. Contact with the supplier revealed that these panels were no longer being supplied and that the chemicals used were no longer in stock (i.e., the chemical manufacturer had discontinued the product line). It was learned that two other companies were currently in the business of providing standard phosphated panels for paint testing. Contact with one company revealed that panels phosphated with two different chemicals were available: one chemical was similar to the discontinued product and the other chemical represented the newer phosphating formulations, which contain manganese

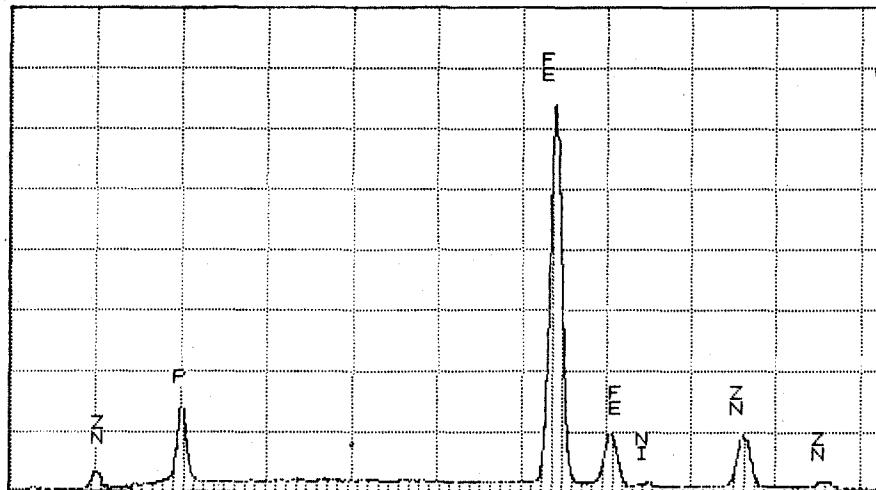


Fig. 2. Elemental X-ray analysis (left) and micrograph (right) of phosphate coating on carbon steel panels at 500 \times .

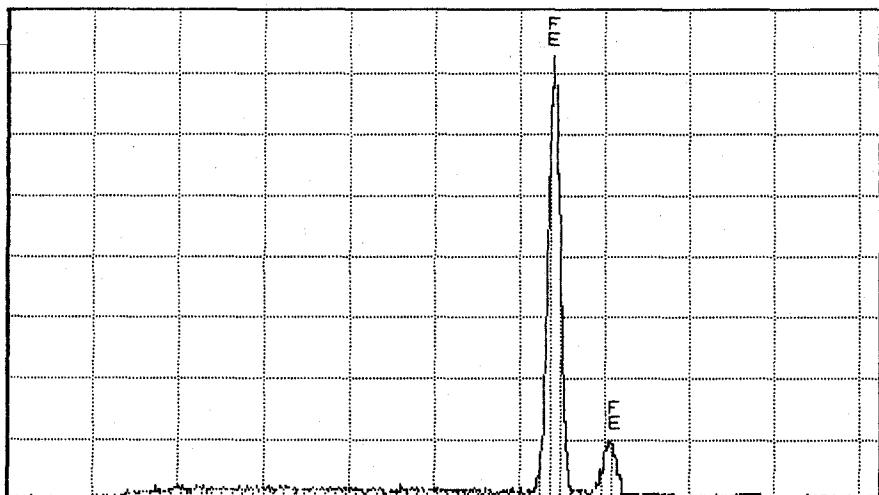


Fig. 3. Elemental X-ray analysis (left) and micrograph (right) between the crystals at 1000 \times .

as an additive. Panels coated with the new formulation were supplied to the automotive industry while panels coated with the older formulation were supplied to all the other organizations. The panel suppliers provided samples for testing. The panels were subjected to coating weight tests, SEM and elemental X-ray analysis.

RESULTS

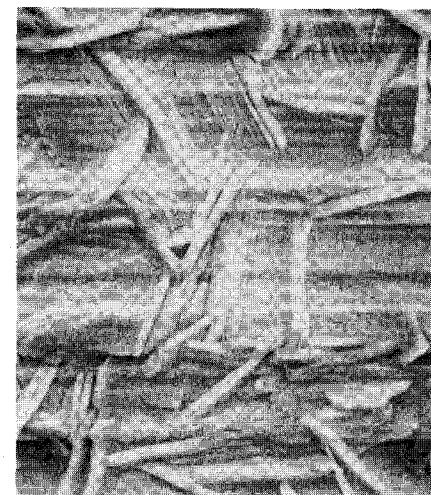
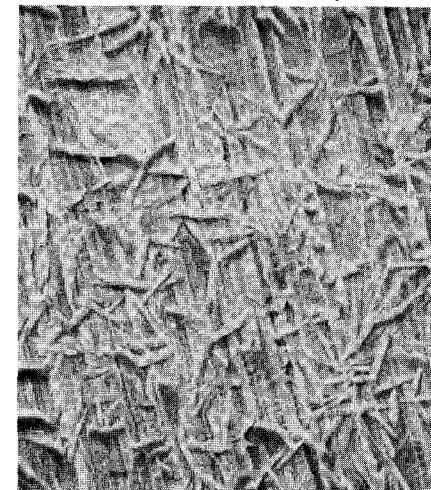
FLASH RUSTING

The elemental X-ray analysis and the micrograph of the spray phosphated alloy steel part is shown in Fig. 1. The coverage of the phosphate coating is only 10–30% of the surface, leaving 70–90% of the basis metal void of any phosphate coating. Further elemental X-ray analysis of the area between the crystals showed an iron peak and an oxygen peak indicating

some form of iron oxide coating may be present. Since no phosphate coating was present on most of the steel surfaces, the cause of the flash rusting is evident. A nonchromium rinse was used in the process and could have also contributed to the problem.

PANELS FOR PAINT ADHESION TESTING

Panels from the paint lab had an average coating weight of 254 milligrams per square foot (msf). This is within the 150–500 msf requirement per TT-C-490. The elemental X-ray analysis and SEM photograph at 500 \times of the phosphated surface is shown in Fig. 2. The crystals only cover about 60% of the metal surface, leaving approximately 40% of the surface void of phosphate coating. The elemental X-ray analysis in Fig. 2 made over the entire phosphated surface shows the



zinc, phosphorus and iron. Figure 3 shows an elemental X-ray analysis of an area between the crystals where only iron is present. Figure 4 is an elemental X-ray analysis of only the phosphate crystal. The zinc and phosphorus peaks are much higher and the iron peak is significantly lower compared to Fig. 2. Also evident is nickel, which is used as an accelerator in some phosphating solutions. The deep lines on the surface indicate that the panel may have been subjected to some type of grinding operation.

The test panel containing the phosphate coating similar to the discontinued product had an average coating weight of 220 msf. An SEM of the surface is shown in Fig. 5. At 500 \times it is evident that the light-colored crystals are about the same size as those in Fig. 2 but are more numerous, thus affecting better coverage even at a lower coating weight. Figure 6 shows that the

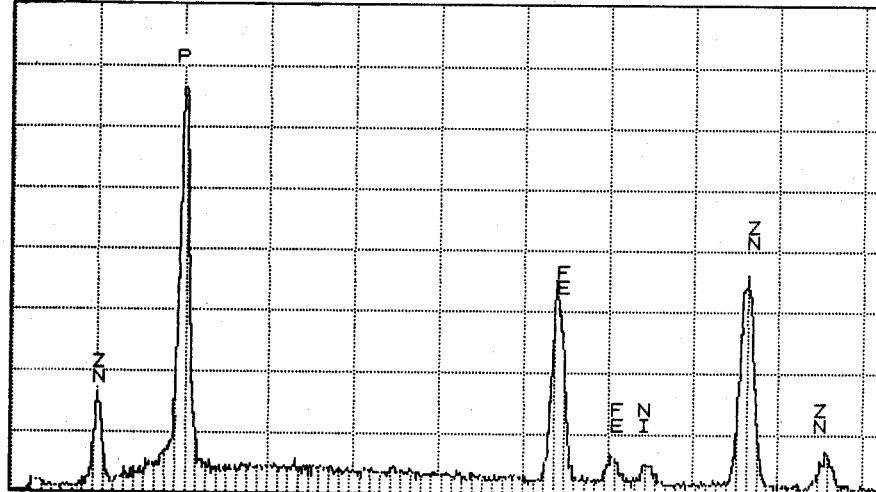


Fig. 4. Elemental X-ray analysis (left) and micrograph (right) of the phosphate crystal at 3000 \times .

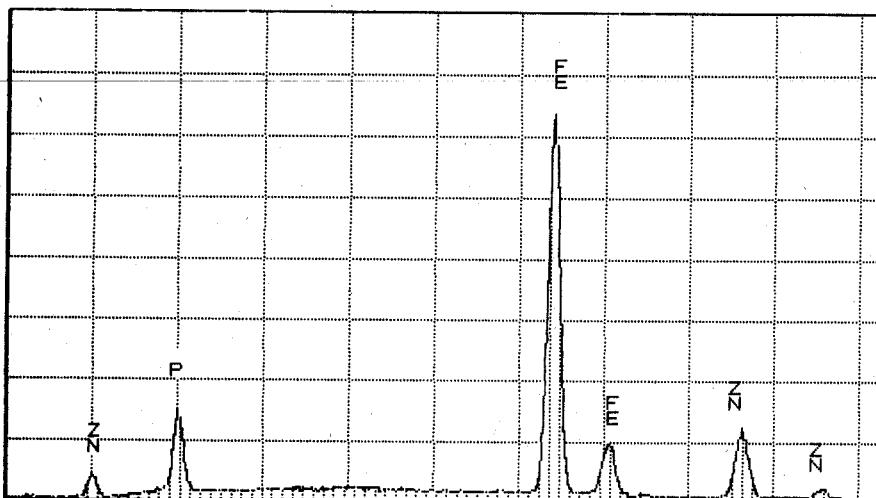
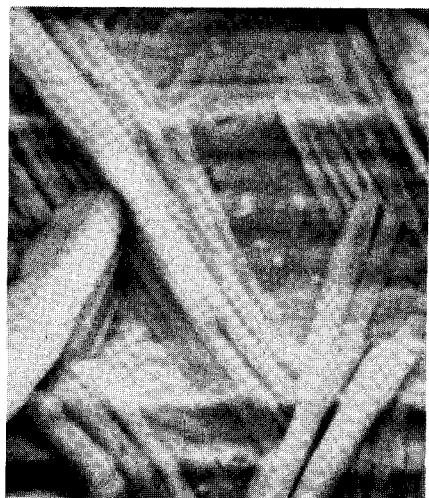
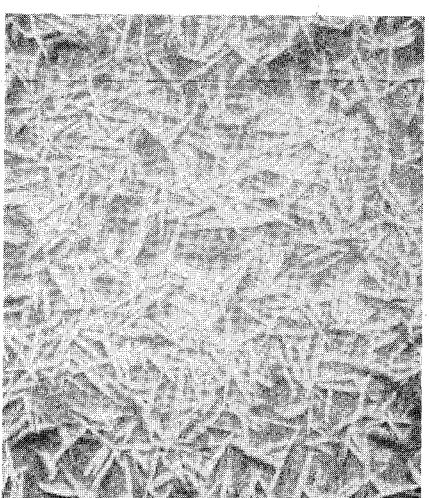


Fig. 5. Elemental X-ray analysis (left) and micrograph (right) of phosphate coating at 500 \times .



elemental X-ray analysis at 1000 \times picks up an area with a large amount of iron and some indications of the zinc phosphate coating. This suggests that the voids are very small. Figure 7 is an

elemental X-ray analysis of the phosphate crystal. The crystal structure and the small amount of nickel indicates that this solution provides a coating that is similar to the product that is no

longer available. No deep lines are evident on the surface indicating that the phosphate coating has completely covered any surface profile.

The test panel, containing manga-

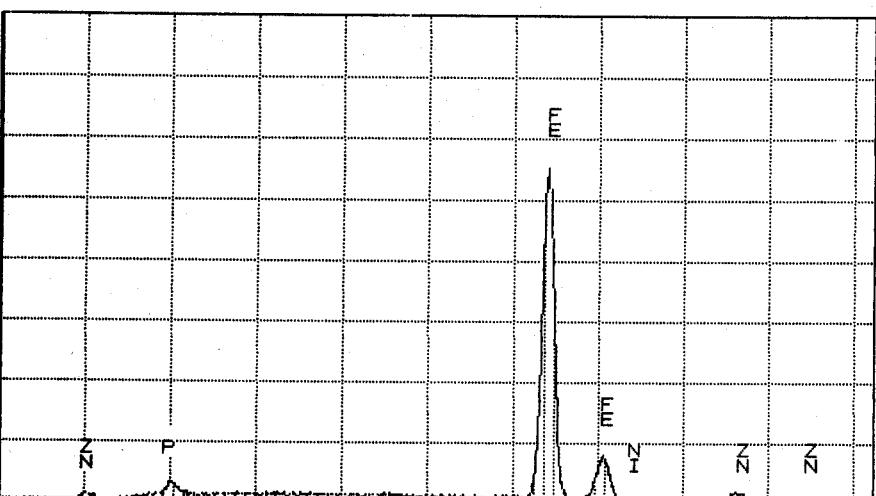
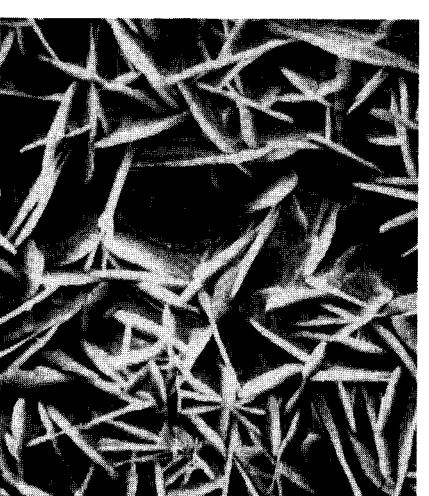


Fig. 6. Elemental X-ray analysis (left) and micrograph (right) between crystals at 1000 \times .



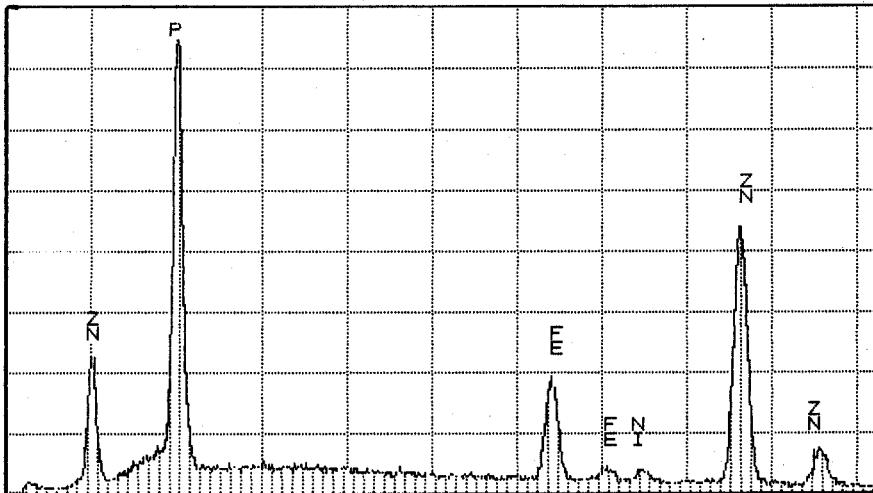


Fig. 7. Elemental X-ray analysis (left) and micrograph (right) of the phosphate crystal at 3000 \times .

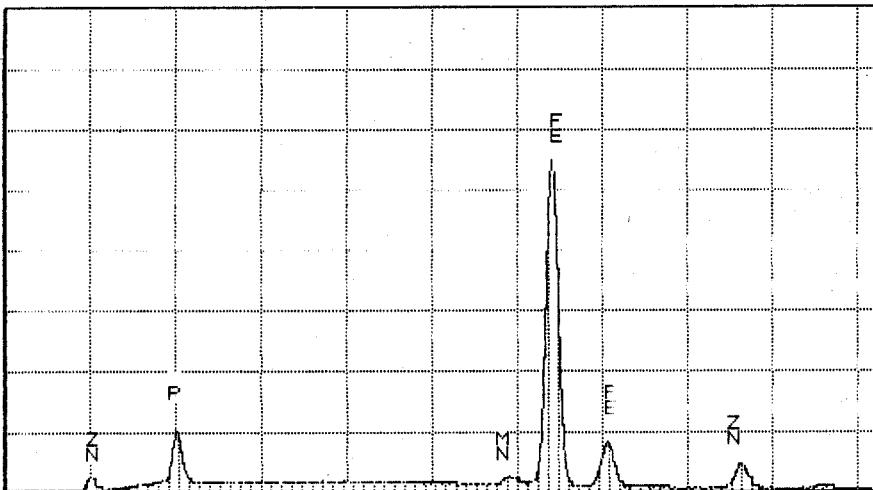
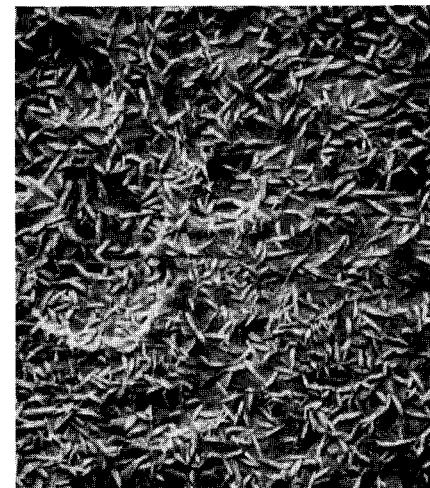
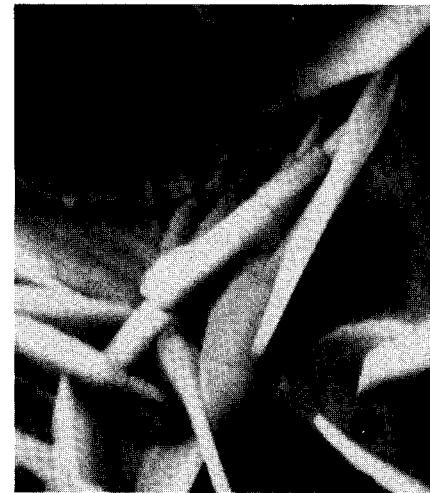


Fig. 8. Elemental X-ray analysis (left) and micrograph (right) of the phosphate coating at 500 \times .

nese in the zinc phosphate coating had an average coating weight of 172 msf. This complies with TT-C-490, Type-1 spray coatings but approaches the 150 msf minimum requirement. A micro-

graph of the surface is shown in Fig. 8. At 500 \times it is evident that the light-colored crystals are much smaller in size and much more numerous, thus affecting maximum coverage. Figure 9



shows that the elemental X-ray analysis at 2900 \times picks up an area with a large amount of iron and also some indications of the phosphate coating. This again suggests that the voids are

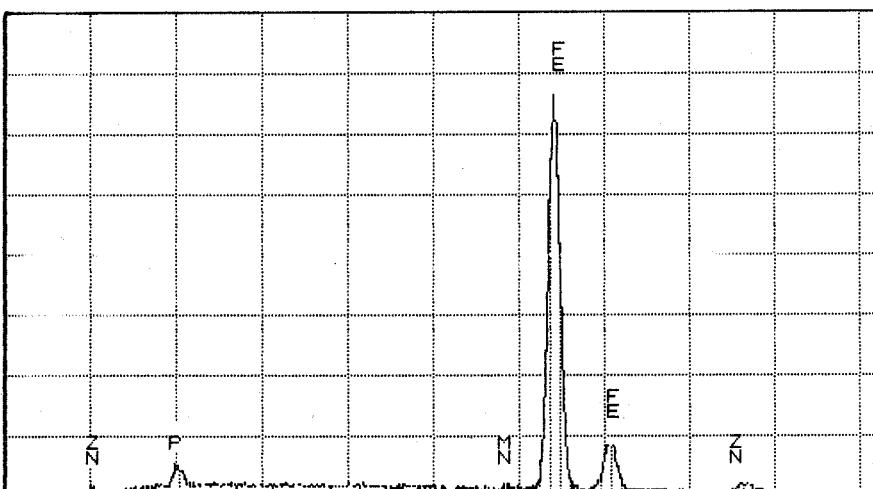
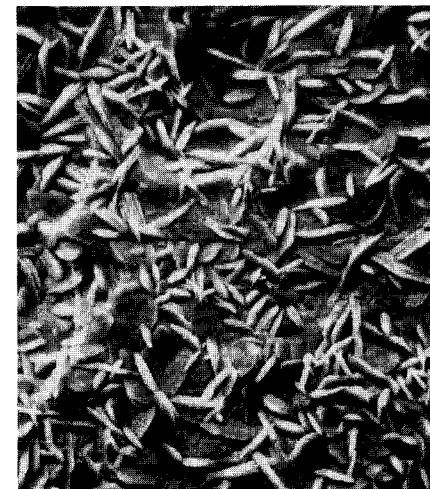


Fig. 9. Elemental X-ray analysis (left) and micrograph (right) between the crystals at 1000 \times .



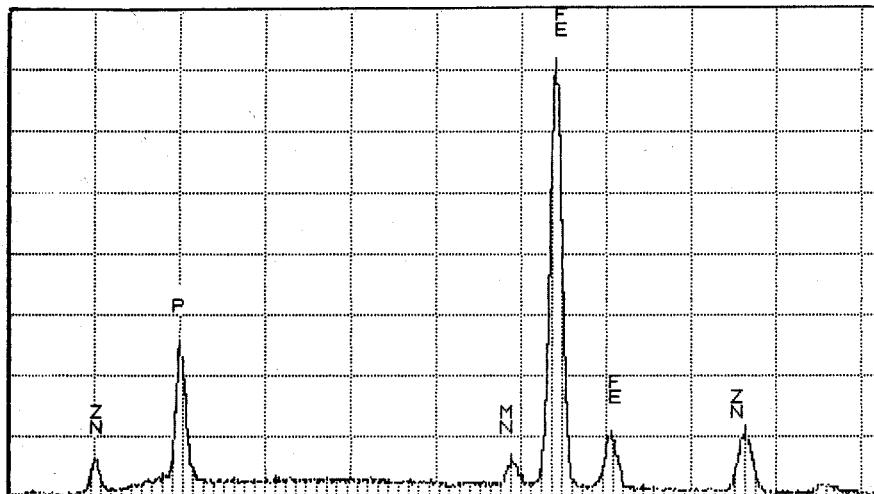


Fig. 10. Elemental X-ray analysis (left) and micrograph (right) of the phosphate crystal at 2900x.

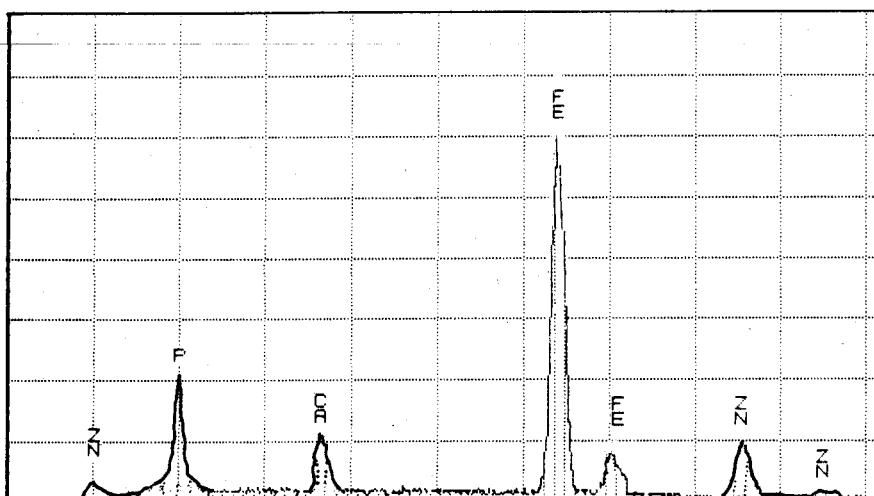
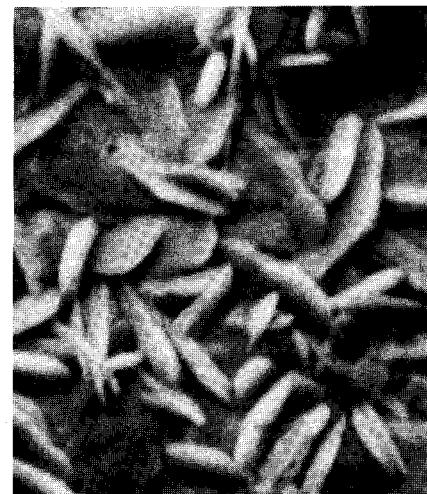
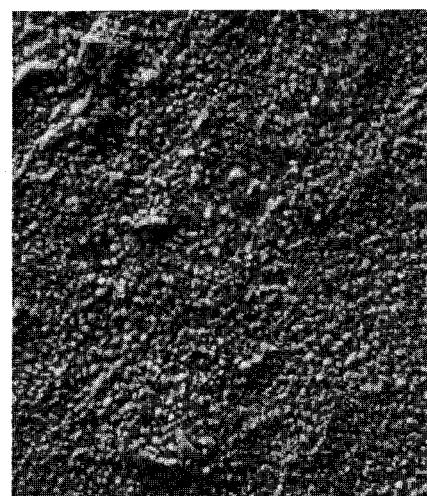


Fig. 11. Elemental X-ray analysis (left) and micrograph (right) of phosphate coating at 600x.



very small. Figure 10 is an elemental X-ray of the phosphate crystal. The crystal structure and the presence of manganese shows that manganese may act as a grain refiner as there are

significantly more and smaller phosphate crystals. It is also obvious that there is more iron in the phosphate crystal when manganese is used in the formulation.

OTHER OBSERVATIONS

Other observations on coverage include phosphate coatings formed with solutions containing calcium additions as a grain refiner. Figure 11 shows

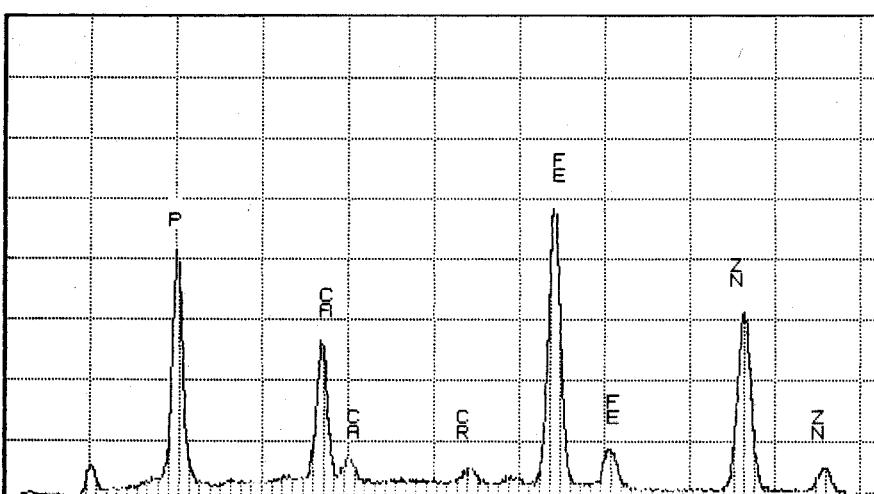
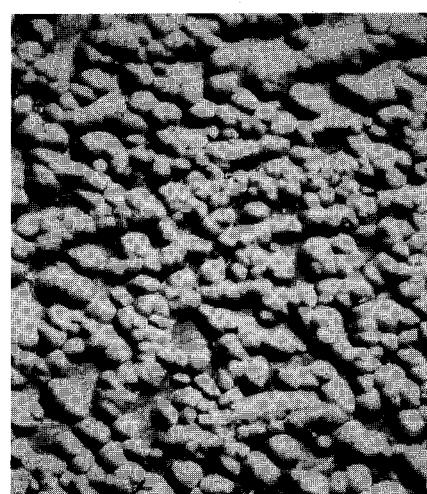


Fig. 12. Elemental X-ray analysis (left) and micrograph (right) of phosphate coating at 500x.



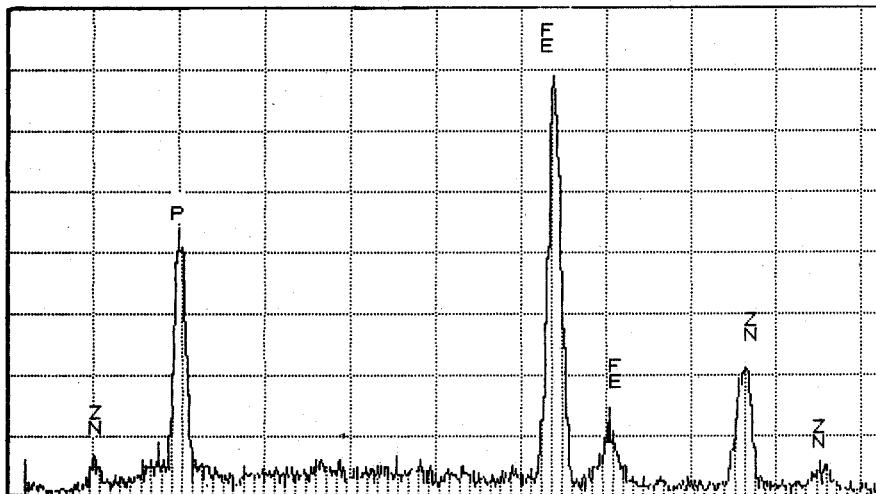


Fig. 13. Elemental X-ray analysis (left) and micrograph (right) of the phosphate coating at 500x.

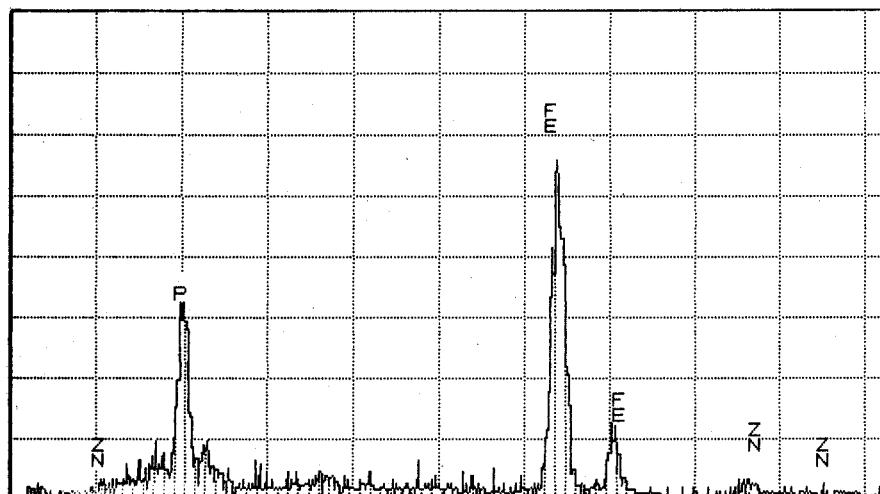
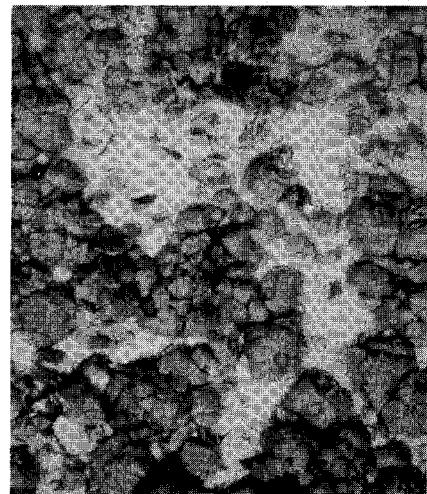


Fig. 14. Elemental X-ray analysis of the white deposits between the crystals.

good coverage and a very fine crystal structure obtained with a calcium-modified solution. Figure 12 shows the coating formed from a similar solution. The crystal size is much larger and a number of voids in the coating are obvious. Figure 13 shows a phosphate coating where the grain refiner was part of the alkaline cleaner formulation. Coverage with zinc phosphate crystals was not complete. The white areas between the zinc phosphate crystals were shown to be iron phosphate. Figure 14 shows the elemental X-ray analysis of the white deposits between the zinc phosphate crystals. Figure 15 shows poor coverage of a zinc phosphate coating on zinc plating along with the elemental X-ray analysis. Figure 16 shows the elemental X-ray analysis of the zinc phosphate crystal on the zinc-plated surface. Figure 17 is a photo and elemental X-ray analysis

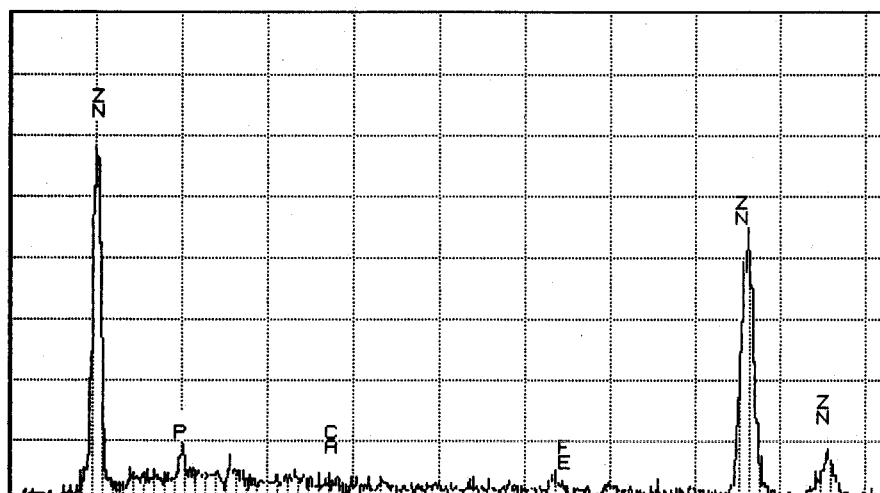
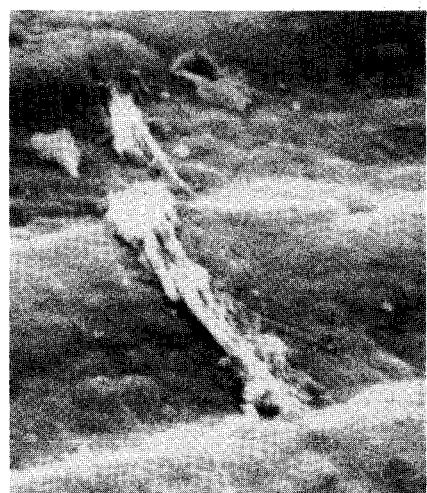


Fig. 15. Elemental X-ray analysis (left) and micrograph (right) of zinc phosphate on zinc plating at 700x. Coating thickness was 0.2-0.3 mil. No red rust appeared after 36 hours exposure to salt spray (ASTM B 117).



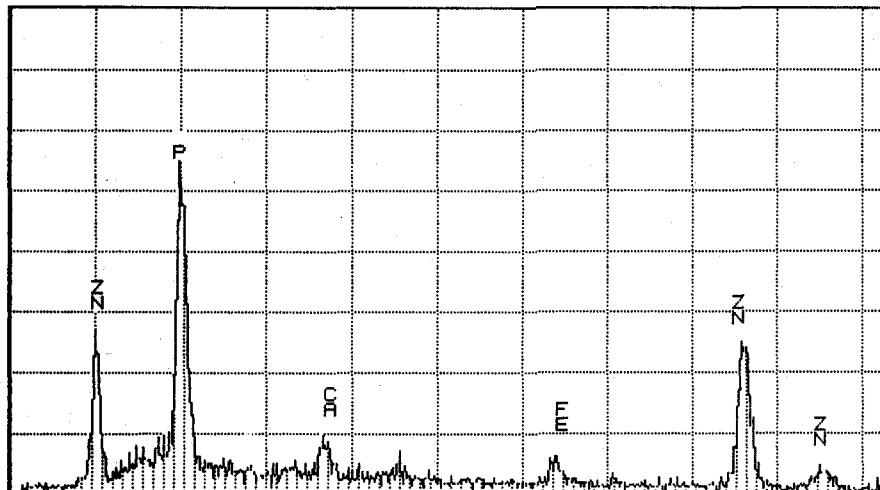


Fig. 16. Elemental analysis of the zinc phosphate crystal on zinc plating.

showing excellent coverage of zinc phosphate on a zinc-plated surface.

DISCUSSION

Flash rusting of phosphated surfaces that do not have good coverage is expected as bare areas in between the phosphate crystals would be susceptible to rusting. Since the chemical used for these parts was the same as for the panels shown in Figs. 5, 6 and 7, the variation in coverage is most likely due to the difference in the substrate material. Various references imply that heat-treated alloy steel may be more difficult to coat using standard phosphating procedures; however, the references do not distinguish between spray and immersion processes and it is known that heavy zinc coatings can be applied to heat-treated alloy steels by the immersion process. Discussions

of this phenomena with various experts suggests that spray phosphating may result in an oxidizing environment while immersion processing provides a reducing environment. This could also explain the presence of iron oxide between the phosphate crystals.

The variability of coverage and crystal size on paint adhesion test panels and other substrates needs to be addressed when qualifying the phosphate coating procedure. Variations in immersion versus spray operations, grain refinement, free acid/total acid, accelerator, temperature, etc. could result in significant changes in crystal structure and coverage. These variations may also effect data generated for adhesion and corrosion resistance of different paint coatings; for example, applying a low volatile organic compound (VOC) paint to a calcium-modified phosphate coating could re-

sult in adhesion problems as the more viscous paint may not wet and anchor to the very fine crystalline structure. The calcium-modified phosphate coating, however, could be an excellent substrate for a hot spray lacquer finish that has a high solvent composition. The manganese-modified zinc phosphate appears to promote more iron in the phosphate crystal. This could lead to better alkali resistance and be the preferred phosphate treatment for electrodeposited (E-coat) primer paints. The larger phosphate crystals with complete coverage could be the optimum phosphate pretreatment for most low-VOC primer applications.

CONCLUSION

The large variability in coverage can have a significant impact on flash rusting and the data generated as a result of painting "standard" phosphated panels. The coverage that is achieved during the application of paint-based phosphate coatings cannot be ascertained using the simple visual examination as stated in the specification. Phosphate crystal size and coverage along with coating weight should be documented on production parts as part of the preproduction process approval per TT-C-490. Knowing the extent of coverage on actual parts or standard panels is essential to proper process control. Only when proper process control is documented for the pretreatment can valid data be generated for subsequent finishes. Laboratories in the paint evaluation business should require an SEM photo and elemental X-ray analysis of the phosphate coating along with their standard panels. MF

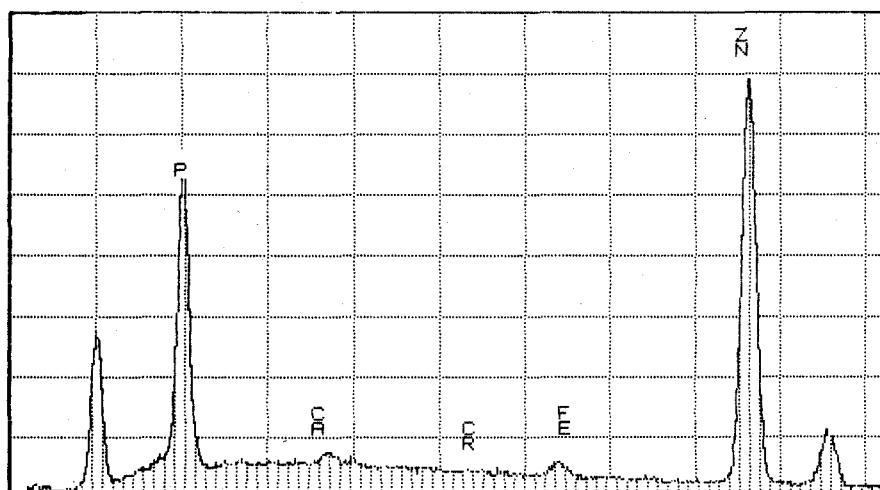
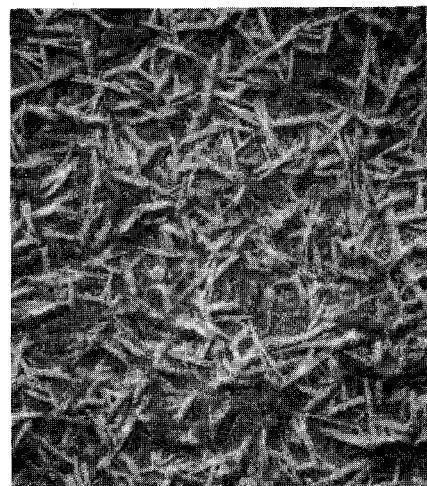


Fig. 17. Elemental X-ray analysis (left) and micrograph (right) of zinc phosphate on zinc plating at 500x.



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