

Characterization of Zirconium Oxide-Based Pretreatment Coatings

Part 1 – Variability in Coating Deposition on Different Metal Substrates

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ABSTRACT

One of the key coating layers that inhibits corrosion on modern automobiles is the pretreatment film. This layer, which is typically a tri-cationic zinc phosphate material, provides both corrosion protection and enhanced paint adhesion to the base metal. Recent tightening of environmental regulations has made the use of this coating more difficult. In response to these pressures, pretreatment suppliers have been developing a new generation of metal pretreatments based on zirconium oxide.

Characterization of these new materials is challenging as the zirconium oxide-based coatings are over ten times thinner than the current zinc phosphate coatings. Methods that are currently employed for studying zinc phosphate films such as coating weight determination by weighing, and scanning electron microscopy-energy dispersive x-ray spectroscopy (SEM-EDS) are not sensitive enough to fully characterize these materials. Therefore, we have employed a combination of surface analysis (Auger electron spectroscopy) and x-ray fluorescence to obtain a more detailed characterization of the zirconium oxide-based pretreatment coatings. These methods allow for an assessment of the variability in coating composition as a function of key parameters such as metal substrate and process variations.

Relatively thick, uniform coatings were found on galvanized substrates while significantly thinner coatings were observed on cold rolled steel (CRS) and aluminum (AL). The coatings formed on CRS and AL had significantly more variability than those deposited on galvanized steel. Coating bath contaminants also affected the coating thickness and corrosion performance on CRS and AL more than they did on galvanized steel.

INTRODUCTION

Automotive pretreatment systems consist of three primary steps – cleaning the vehicle of oils and dirt from the body construction process, deposition of a pretreatment layer (traditionally zinc phosphate), and rinsing of the vehicle body of pretreatment chemicals. These steps require up to 12 stages in the process, resulting in a significant amount of chemical, water, and energy usage. The purpose of the pretreatment layer, although very thin, is to provide a consistent surface to which the rest of the paint system can adhere. It also converts the metal surface to a consistent, relatively inert material that is less susceptible to chemical attack than untreated metal.

Although zinc phosphate has been the standard automotive pretreatment for many years, automotive manufacturers and their suppliers continue to develop alternative materials that will reduce waste streams and complexity from the manufacturing process. One of the issues with the current zinc phosphate process is that metal is etched during residence in the phosphate bath resulting in a significant amount of metallic sludge. The resulting sludge is a waste stream that is regularly removed and landfilled. The process also takes place at elevated temperature requiring heat input for the deposition of the zinc phosphate to occur.

An alternative to zinc phosphate is zirconium oxide coatings which has recently been in development by pretreatment suppliers and OEM's^{1,2}. The zirconium oxide process results in little to no sludge production and the coating deposits at a significantly lower temperature than zinc phosphate. The result is a shorter pretreatment process with significantly less waste generation. Below is a diagram showing the differences in the two pretreatment processes.

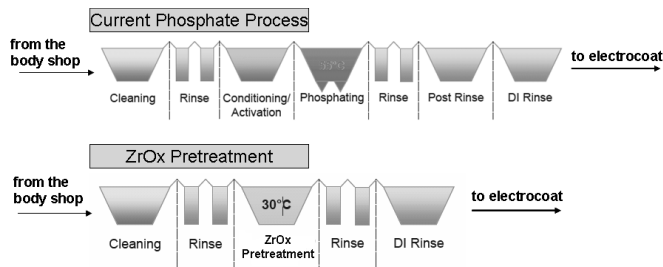


Figure 1. Comparison of pretreatment process layouts.

While there are significant chemical, water, energy, and waste-reduction benefits in the use of zirconium oxide coatings, customers require that the performance of the coating be equivalent or better than that of zinc phosphate coatings. Initial screening tests show that corrosion performance is comparable to zinc phosphate when the zirconium oxide coating is properly applied³. However, little information exists of the affects of processing variability on coating performance.

A major challenge for the development and testing of zirconium oxide coatings is the difficulty in characterizing the pretreatment films that get deposited. The zirconium oxide film is an amorphous layer that is about one tenth of the thickness of the crystalline zinc phosphate coatings that it is designed to replace. These properties make detection and quantification of the zirconium oxide coating difficult, both visually and with instrumentation. The following paper discusses the characterization of the zirconium oxide coating on a variety of substrates and the performance of the coating compared to zinc phosphate.

RESULTS AND DISCUSSION

CHARACTERIZATION METHODS

Coating weight measurements The most common pretreatment characterization method is determination of the coating weight. In fact, coating weight has been incorporated into pretreatment specifications by OEM's and suppliers. Coating weight is usually measured by the weigh-strip-weigh method where a panel of known surface area is weighed before and after chemically stripping the coating from the panel. Unfortunately, accurate coating weights are difficult to measure for zirconium oxide films by this method as they are significantly thinner and thus contain much less mass than zinc phosphate films.

Scanning electron microscopy-energy dispersive x-ray spectroscopy (SEM-EDS) The second most common method for characterizing zinc phosphate coatings is SEM-EDS. This method produces high resolution, high depth of focus images of the coating surface which are used to measure crystal shape, size, and distribution from zinc phosphate films. In addition, the electrons used to probe the sample cause elements in the solid to emit characteristic x-rays that can be used to generate elemental maps or to obtain elemental composition

information. These x-rays emanate from a depth of approximately 1 μ m into the solid which is comparable to the coating thickness of zinc phosphate films.

An example of the coating variability that can be observed with SEM-EDS is shown in Figure 2. The top image is from an area with a well formed zinc phosphate coating. The film is composed of a dense collection of small, uniformly shaped crystals. An example of poor phosphate growth is shown in the bottom image. Only a few large, irregularly shaped crystals formed in this region.

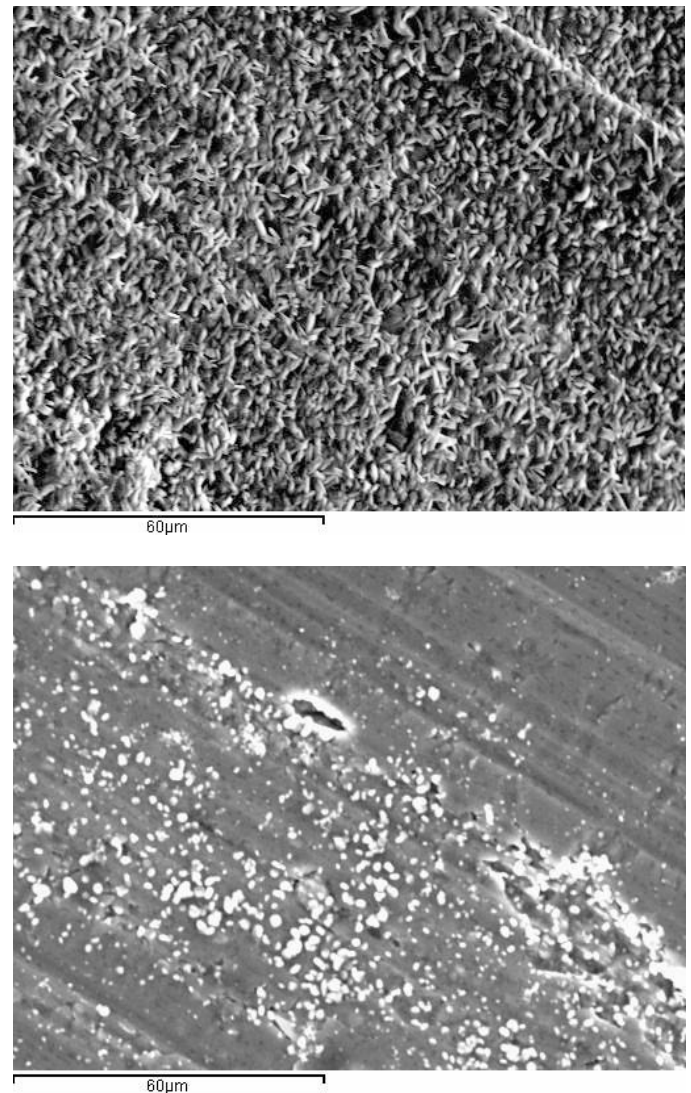


Figure 2. These are secondary electron images from a zinc phosphate coating on aluminum from an area with a good coating (top) and a poor coating (bottom).

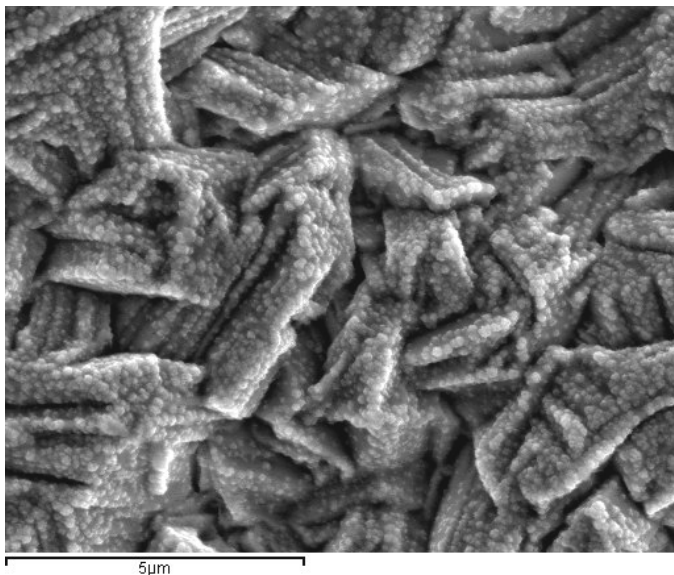


Figure 3. This is a secondary electron image of the zirconium oxide coating on electrogalvanized steel.

SEM-EDS is less useful for characterizing zirconium oxide films as they are amorphous and do not exhibit much texture. The lack of texture results in secondary electron images showing significantly less contrast than zinc phosphate coatings. Consequently, panels need to be examined at high magnification to see contrast in the images (see Figure 3). Note that the magnification of the zirconium oxide film in Figure 3 is ten times greater than the magnification of the zinc phosphate film in Figure 2. In addition, the coating is so thin that only trace amounts of film elements are visible in the EDS x-ray spectrum. This is illustrated in Figure 4 (top) which is an EDS spectrum from a zirconium oxide coating on CRS. Only small amounts of zirconium from the film are visible. In contrast, the EDS spectrum from a typical zinc phosphate film on CRS (Figure 4, bottom) shows strong signals from the film components, phosphorus, zinc, and iron. This coating is so thick that even minor elements, manganese, and nickel are visible in the spectrum.

These issues make it very difficult to see changes in the zirconium oxide coating that occur as a result of process variability using SEM-EDS.

X-ray photoelectron spectroscopy (XPS)

Characterization of coatings in the thickness range of these zirconium oxide films requires surface sensitive analysis techniques to get the required sensitivity. One of the most popular surface analysis methods is XPS which uses a monochromatic x-ray beam to probe the surface of a solid. The x-rays cause the solid to emit characteristic electrons that are used to identify and quantify the elements that are present. These electrons can only escape from the outer 1-5 nm of the surface making the technique surface sensitive. However, the x-rays can only be focused onto a relatively large area (~50 μm or larger) which prevents this method from being used to probe point-to-point variability in the

coating. Results assume that the coating is uniform in composition over the analysis area of this technique.

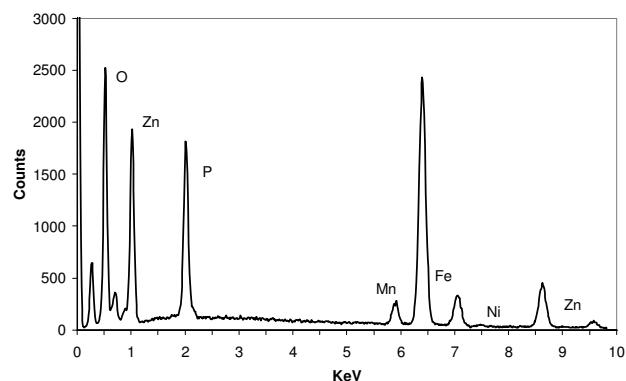
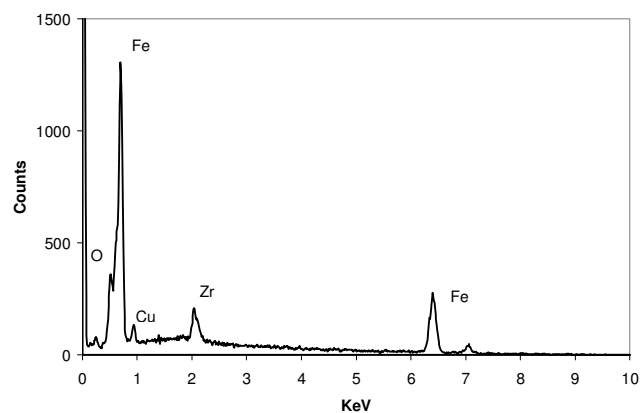


Figure 4. These are EDS spectra of the zirconium oxide (top) and zinc phosphate (bottom) pretreatment coatings on CRS.

Auger electron spectroscopy (AES) Another popular surface analysis method is AES which uses a focused electron beam to probe the sample. The electron beam causes the solid to emit characteristic electrons that are used to identify and quantify the elements that are present. These characteristic electrons can only escape from the outer 1-5 nm of the surface making the method surface sensitive. With a focused electron beam as a probe, AES can provide images, elemental maps, and examine localized areas similar to SEM-EDS.

Thin film characterization by either XPS or AES is aided by combining either measurement technique with ion sputtering, typically with inert gas ions such as argon. The sputtering process removes a thin layer of material from the surface revealing subsurface layers for analysis. Elemental changes as a function of depth can be followed, and film thickness is proportional to the sputter time to which the specimen is exposed. Careful calibration is required as sputter gun parameters such as incident angle, beam energy etc. can have a drastic affect on the effective sputter rate. Also, different materials exhibit large differences in sputter rates.