There was a defect of severe micro-flow mark lines in cathodic electrodeposited (CED) primer coating on car components. This problem was highlighted after final painting. This article describes the tests performed to determine the root cause of the defect. Tests included a surface profile of the CED coating and the determination of the microstructure and nickel content of the phosphate coating beneath the CED coating. The investigation identified the optimum concentration of nickel in the coating to refine phosphate grain size and create a unity crystal aspect ratio. It also found that the triple point junction of phosphate crystals determines the porosity to provide a uniform CED coating surface finish.

Root Cause Analysis

Defective CED primer-coated samples were collected from the automotive paint line. The coating thickness was measured and found to be at range of 25 to 28 μm, compared to the standard coating thickness of 18 to 20 μm recommended by the Japanese auto makers. It was thought that the flow mark lines might be caused by the higher coating thickness. But based on thorough investigations, the problem was not caused by a defect in the CED process parameters.

Investigations

CATHODIC ELECTRODEPOSITED PROCESS PARAMETERS

The waterborne colloidal and dispersive cationic epoxy resin ions are attracted to the electrode of the opposite polarity by the application of voltage where electrolysis of water and the deposition of resin ions take place simultaneously. The

CASE HISTORY

Prevention of Micro-Flow Marks in Cathodic Electrodeposited Primer Coating in Automotive Industries

TAPAN K. ROUT, PREETI P. SAHOO, AND DEEPAK DESPANDE, Research and Development Division, Tata Steel, Ltd.
cationic resin ions—R₃NH⁺ (R-alkyl or aromatic groups) are attracted and deposited at the cathode (car body). The following reactions take place at the electrodes:

\[ 4H₂O + 4e^- \rightarrow 4OH^- + 2H₂ \]  
(electrolysis of water at cathode)

\[ 4H^+ + 4e^- \rightarrow 2H₂ \]  
(2)

\[ R₃NH^+ + OH^- \rightarrow R₃N + H₂O \]  
(cathodic electrodeposition)

The deposition of resin ions depends on several factors, such as pH, solid concentration, conductivity, bath temperature, applied voltage, deposition time, and position of the car body. All the process parameters of CED for the present case were thoroughly checked and found to be according to specifications. This was confirmed by measuring the columbic yield, which is defined as “mg coating deposition/quantity of electricity passed.” The car body is suspended at equal distance from anodes to avoid any variation in coating deposition (Figure 2). In spite of that, the defect was observed, and it was difficult to correlate it to the painting line process parameters.

Analysis of Defect Samples

The primer coating was carefully removed from the defect locations and the surface beneath was subjected to scanning electron microscopy (SEM) and energy dispersive x-ray analysis (EDXA) to understand the phosphating process. It was observed that phosphate crystal sizes were not uniform and there were many voids in the coating surface. It was assumed that the voids might be caused by loss of phosphate coating during primer removal.

To ensure the phosphating process for superior CED primer coating finish, some coupon samples were tightly tagged along the car body. Two samples were removed from the car body after phosphating and another two samples were removed after primer coating. The surface profile of the primer coating was detected by stereo microscope; the graph of distance vs intensity was plotted by using metal power image analyzer software. It was observed that micro-flow mark lines on the car doors (left-hand and right-hand sides) after CED coating in the process line.

Micro-flow mark lines on the car doors (left-hand and right-hand sides) after CED coating in the process line.
that the intensities corresponding to the crest and trough of the surface fluctuated by ±30 units (Figure 3). This fluctuation indicated a poor surface finish. On phosphated samples, the phosphate crystal size and coating uniformity were studied by SEM at a magnification of 1,000X. The coating was not uniform, as shown in Figure 4. The porosity of the phosphate coating was determined per ASTM B7331 and found to be high, varying between 1.5 to 2.2%.

Coating elements were analyzed by EDXA. Peaks of zinc, manganese, and iron were observed, whereas nickel was found to be absent. Because the phosphate solution is tri-cationic with a nickel concentration between 400 and 600 ppm, its absence in the coating surface was not explained. The nickel concentration was determined in the coating surface using atomic absorption spectroscopy. The phosphate coating was dissolved in 10% sodium hydroxide (NaOH) at 80°C. It was found that the nickel concentration of the surface varied between 0.02 and 0.04%. It may be assumed that the nonuniformity in phosphate grain sizes may be due to lack of sufficient nickel in the coating surface.

**Problem Solution**

Experiments were carried out by increasing the nickel concentration in the bath from 400 to 1,200 ppm. A set of coupon samples was processed through the phosphating bath, followed by a CED bath. The phosphate coating uniformity and composition were observed using SEM and EDXA. Figure 5 shows the SEM results. Comparing Figure 5 with Figure 4, it can be observed that the grain sizes have been refined and the crystal aspect ratios approach approximate unity, indicating a spherical shape. The surface profile of the primer coating was mapped, showing that the intensities (crest to trough) varied in the range of ±8 units throughout the coating surface. The nickel concentration was determined in the phosphate coating and was found to vary between 0.8 and 1.3%. This concentration was sufficient to refine the grain size.

Comparing Figure 6 with Figure 3, it can be observed that the surface profile of the CED coating is uniform and the intensity of fluctuations was reduced from 30 to 8 units. This might be caused by the uniformity in the phosphate coating as a base for the primer coating. In this case, the porosity in the phosphate coating was judged by the triple-point junction of the crystals, which was found to vary between 0.1 and 0.5%. Uniform surface profile was correlated with this range of porosity in two ways: 1) the porosity may control the
uniformity of conductivity throughout the car body (cathode surface) during electrodeposition; therefore, the primer deposition from the applied voltage does not fluctuate much throughout the cathode body, and 2) primer covers all the crystals as well as pores in a uniform rate, so that there would be no abnormal coating thickness. But in the case of the phosphate coating, whose porosity varied between 1.5 and 2.2%, the primer deposition from the applied voltage took place abnormally, causing a nonuniform coating finish (Figure 3). The reason may be larger voids with respect to the phosphate coating, leading to variations in localized surface conductivity. This might have led to a variation in the deposition rate, thus creating micro-flow marks on the surface. The experimental results were correlated with the actual defects and showed that the micro-flow marks were caused by inferior phosphating.

Conclusions

1) A variation in primer coating thickness does not lead to micro-flow marks.  
2) Higher porosity and nonuniform crystal size leads to an abnormal surface profile of CED primer coating finish.  
3) A nickel concentration of 0.8 and 1.3% is suitable to refine phosphating grains.  
4) Porosity between 0.1 and 0.5% is suitable for a superior CED primer coating finish.  
5) Uniformly distributed spherical grains provide triple-point junction, which is required for a suitable CED primer coating finish.  
6) The fluctuation rate of surface profile intensity reduces from 30 to 8 units because of control grain sizes and porosity in the phosphate coating.

Reference


Bibliography

TAPAN K. ROUT is a senior manager at Tata Steel, Ltd., Research and Development Division, Jamshedpur, Jharkhanda, 831007, India. He has been working in the areas of corrosion and surface coatings for eight years. He has worked with various government and private organizations in India, including the regional Research Laboratory, Orissa; Imperial Chemical Industries, Mumbai; and Bhaba Atomic Research Centre, Mumbai. He received his Ph.D. in 2005 from Utkal University for his work on trapping radioactive and nonradioactive metal ions from liquid effluents during polymeric flocculation of sludge-forming solids.

PREETI P. SAHOO is a senior manager at Tata Steel, Ltd., Research and Development Division. He has an M.Tech. degree in metallurgy from the Indian Institute of Technology (2003).

DEEPAK DESPANDE is an application engineer in the Marketing & Sales Dept. at Tata Steel, Ltd. He has a B.S. degree in metallurgy.