ABSTRACT

Autodeposition coatings are thin, highly corrosion resistant organic coatings that are deposited in a chemical reaction with a metal surface. Because the autodeposition process deposits a coating only on metallic surfaces, coating of just the metal portion of metal-plastic or metal-rubber assemblies is possible. The overall autodeposition process includes stages of clean, water rinse, coat, reaction rinse, and cure. The use of a reaction rinse after the autodeposition stage is unique among coating processes and allows new properties to be introduced to the coating before curing.

This paper will briefly review the general chemistry of autodeposition, and then focus on how corrosion performance and physical characteristics of a recently developed epoxy-acrylic autodeposition coating are designed into the product and how the autodeposition process controls these properties. The role of the organic polymer and the reaction rinse in all the properties will be discussed. In general, physical properties, such as flexibility, hardness, UV durability, and chemical resistance are affected by the polymer design. On the other hand, corrosion properties are largely conferred by the chemistry of the reaction rinse.

INTRODUCTION

Autodeposition is a unique waterborne process used to coat cleaned, fabricated steel parts with an organic paint film. What differentiates autodeposition from other coating processes is that it depends on chemical reactions to achieve deposition. Since its introduction to the market in 1975, the autodeposition process has been employed throughout the world to apply a high-quality, functional finish to a wide variety of metal components. Over the years, the autodeposition product offerings have grown and matured. Today, such coatings are available in acrylic, polyvinylidene chloride (PVDC) and epoxy-based polymers. The most recent introduction to this family of coatings is a thermoset epoxy-based coating available for use as a single coat or as a primer.

MECHANISM OF AUTODEPOSITION

The autodeposition process consists of a mildly acidic bath that contains a negatively charged (anionic) polymer dispersion, ferric fluoride, and DI water. The bath solids are normally between 3% and 6% by weight. The bath viscosity is close to that of water with little or no organic solvents in the coating bath. The mildly acidic and oxidizing bath liberates a small amount of iron from the immersed steel parts resulting in a locally high concentration of ferrous ions at the surface of the steel. These positively charged ferrous ions interact with the negatively charged polymer dispersion particles causing destabilization and a coating to deposit on the surface of the steel parts. The newly deposited organic film is adherent yet remains quite porous. This allows the iron dissolution to continue as active materials diffuse through the newly deposited film and continue to etch the surface of the metal.

Iron Dissolution Reaction

\[2 \text{FeF}_3 + \text{Fe}^0 \rightarrow 3 \text{Fe}^{2+} + 6 \text{F}^-\]

Deposition Reaction

\[\text{Fe}^{2+} + (\text{anionic particle}) \rightarrow \text{Fe(anionic particle)}\]
(stable dispersion) (coagulates)

Coating thickness is controlled by diffusion of Fe\(^{2+}\) and Fe\(^{3+}\) ions through the deposited polymer layer, and thus depends on reactant concentration, time and temperature of exposure to the paint bath. Initially, the deposition rate is quite rapid, but slows down as the film increases in thickness and it is “self-limiting”. This provides a very uniform coating thickness even on parts with complex geometries.

The autodeposited wet film can be thought of as a tightly adherent “wet sponge”, which can be water rinsed immediately after leaving the bath with virtually no coating rinse-off. The process has low drag-out losses since the low viscosity autodeposition bath has only 3-6% solids. Low drag-out means a shorter rinse stage and greatly reduced demand on waste treatment. The wet film after autodeposition is porous and not yet coalesced. This open pore space allows chemistry in a subsequent reaction rinse stage to permeate the “wet sponge”. The scanning electron micrograph (SEM) in Figure 1 shows a tight, uniform autodeposited wet film before coalescence and curing. In this particular example the average particle size of the polymer dispersion is approximately
150 nm. The pore space available for Fe-ion permeation and reaction rinse penetration is also readily visible.

Figure 1. SEM of Autodeposited Wet Film

AUTODEPOSITION PROCESS SEQUENCE

Process configurations in commercial use with autodeposition coatings include: programmable hoist, indexing, and conveyor lines. A typical eight-stage process sequence is shown below in Figure 2, along with nominal temperature ranges for each stage:

Stage 1 - Alkaline Spray Clean (160-200 °F)
Stage 2 - Alkaline Immersion Clean (160-200 °F)
Stage 3 - Tap Water Rinse (70-100 °F)
Stage 4 - DI Water Rinse (65-80 °F)
Stage 5 - Autodeposition (72 °F)
Stage 6 - Tap Water Rinse (72 °F)
Stage 7 - Reaction Rinse (70-140 °F)
Stage 8 - Curing Oven (Technology Dependant)

Figure 2. Example of 8-Stage Hoist Line

The autodeposition process does not require a chemical conversion coating stage prior to paint application. Additionally, no heavy metals are used throughout the process. The elimination of conversion coating stages leads to considerable savings in required floor space, energy, and operating costs, as well as the total elimination of toxic metals from the painting process.

UNIQUE FEATURES OF AUTODEPOSITION

INFINITE THROWPOWER

The first unique feature of autodeposition is the ability to produce a very uniform film over the entire surface of the work piece, even on complex part geometries and in difficult-to-reach areas. The low viscosity bath allows the coating dispersion to flow into and around the most complex shapes for complete coverage. Unlike coating processes that require an electric charge to deposit the coating (i.e., where electrical energy is required to “throw” the coating into recessed areas), autodeposition will uniformly coat tubular, assembled, or intricate-design areas as shown in Figure 3. In this case the tube was approximately six feet long, three inches in diameter, and the coating had to flow into the tube via a 3/8 inch bolt hole at each end. The dry film thickness (DFT) on the outside of the part was 18 µm, while the interior was coated with 13-15 µm.

Figure 3. Cut-Away of Tubular Part

This infinite throwpower feature is important since, under highly corrosive automotive driving conditions, the first point for corrosion is usually the unprotected surface inside tubular frames and box sections such as doors and fenders. Typical cathodic electrodeposition (CED), powder, or spray coatings do not protect these hidden areas. Standard zinc or iron phosphate pretreatment provides short-term protection, but without a paint layer to prevent its dissolution, corrosion will rapidly begin.

EDGE COVERAGE

The second most common site for corrosion is on sharp edges of components. Epoxy-acrylic autodeposition coatings provide a very high degree of edge coverage. This feature is readily seen in Figure 4, where an OEM manufactured L-shaped part with a carefully machined burr on the front, horizontal edge was...
primed, topcoated, and subjected to 168-744 hr of neutral salt spray, NSS, (ASTM B-117). In Figure 4, are compared in a stack from bottom to top: autodeposited coating (ACC® 915/E2 + topcoat), cathodic epoxy E-coat over iron phosphate + topcoat, one-, and two-layers of TGIC polyester powder coating. Increasing rust on the burr edge is seen in this series of coatings. A detailed cross-section of the same autodeposited coating over a razor blade is seen in Figure 5. The coating has thinned slightly, but remains intact across the razor edge.

Figure 4. Edge Coverage on Burr after 168-744 hr of ASTM B-117 Neutral Salt Spray.

Figure 5. Edge Coverage over Razor Blade.

Any coating must fulfill a multitude of seemingly contradictory requirements. A smooth surface and good leveling require a lower molecular weight polymer component that can flow during cure. On the other hand, good edge coverage requires exactly the opposite for minimal flow away from the sharp edge. The excellent edge coverage is designed into the autodeposition coating. These contradictory requirements can be met by designing a polymer dispersion containing both low and high molecular weight components. Figure 6 compares the gel permeation chromatograms (GPC) of a typical low molecular weight epoxy prepolymer used in a 100% epoxy coating and the epoxy-acrylic hybrid polymer (labeled mini-emulsion) in an autodeposition coating (ACC® 915). The wider distribution of molecular weight, and especially the high molecular weight tail (see left side of the GPC trace), gives an optimized performance in both leveling and edge protection.9

Figure 6. GPC traces showing wide molecular weight distribution in an autodeposition polymer.

HARDNESS AND FLEXIBILITY

Similar to leveling and edge coverage, hardness and flexibility tend to be diametrically opposed. A perfect automotive coating would be exceedingly hard, mar resistant, and yet flexible to enable post-forming operations or to survive dents without cracking. The flexibility of any paint system depends on the entire system: substrate, pretreatment, and paint layers. The least flexible components in the system will contribute to failure. For any paint system applied over a crystalline zinc phosphate, the pretreatment is often a brittle point, and, therefore, any paint applied over it can suffer. A highly crosslinked paint will also degrade the coating system flexibility. Figure 7 compares an autodeposition coating vs. CED applied over zinc phosphate. Both panels were subjected to increasing force reverse impacts from right to left (20, 40, 80, 120, 160 in-lbs), and the damaged coatings then subjected to 72 hr of salt spray. The corrosion indicates the extent of the damage down to the substrate. Because the autodeposition coating has no crystalline pretreatment layer beneath the paint, the flexibility can be controlled by the polymer matrix itself. The mixture of high and lower molecular weight polymers and moderate level of crosslinking in the coating also helps promote the combination of hardness and flexibility. The coating shown in Figures 7 and 8 has a pencil hardness of 2-3H.

Figure 7. Reverse Impact followed by 72 hr ASTM B-117 Neutral Salt Spray (160, 120, 80, 40, 20 in-lbs). Autodeposition ACC® 915 (upper), CED/Zn-phosphate (lower).
Figure 8 compares the flexibility as measured by a T-Bend test. The coating on the right is a commercial CED over zinc phosphate, while the autodeposition coating is on the left. The CED paint has flaked off the CRS substrate and fails a 4-T bend test, while the autodeposition coating continues to have good adhesion passing 3-T and it survives even a 1-T test.

Figure 8. T-Bend Test. Autodeposition ACC® 915 (left) passes 3-T, CED (right) fails 4-T.

This much higher flexibility allows post-forming or crimping of prepainted parts, which saves cost in manufacturing and touch-up repaint. Figure 9 shows a photomicrograph of CED compared to an autodeposition coating. The CED coating (left) is completely cracked across the outside of the crimped edge. The autodeposited film, on the other hand, shows no such cracking, and was deemed superior by the customer. It allowed the part to be painted and post-formed, greatly reducing the overall cost of manufacture.

Figure 9. Crimp Test. CED over zinc phosphate (left) compared to autodeposition, ACC® 915 (right).

THERMAL STABILITY

Many painted parts in automotive use are exposed to high temperatures during use. However, the majority of specification testing occurs on panels or parts that have never been exposed to thermal excursions or cycling. Thermal stability of a paint system is dependent on the pretreatment as well as the paint itself. Above 200 °C a zinc phosphate pretreatment will start to lose water of hydration, thereby changing the crystalline structure and weakening adhesion at the pretreatment-paint interface. The paint itself can also be thermally degraded or certain components volatilized under high heat. Thermal degradation of the paint is obviously very paint specific, but typical problems are further loss of coalescing solvent, blocking agent from the crosslinker, or polyethylene oxide degradation. Table 1 shows the change in dry film thickness (DFT) and 60° gloss readings of autodeposited and CED coatings after heat aging. Both the DFT and gloss of the CED coating decreased quite dramatically after 24 hr at 204 °C followed by 504 hr of NSS. These property changes are most likely related to differences in the polymer chemistry of the two paint systems, specifically to the loss of volatile components in the paint film. The 40% loss of film build for the CED coating indicates that the coating continues to change upon heat aging. The <5% DFT loss in the autodeposition coating indicates that there is very little additional weight loss of volatiles after it was initially cured.

<table>
<thead>
<tr>
<th>Paint System</th>
<th>Initial DFT (µm)</th>
<th>Final DFT (µm)</th>
<th>Initial 60° Gloss</th>
<th>Final 60° Gloss</th>
</tr>
</thead>
<tbody>
<tr>
<td>ACC® 915</td>
<td>24</td>
<td>22</td>
<td>35-45</td>
<td>36</td>
</tr>
<tr>
<td>CED/Zn-Phos</td>
<td>27</td>
<td>16</td>
<td>55-60</td>
<td>10-15</td>
</tr>
</tbody>
</table>

Table 1. CRS panels coated and aged for 24 hr at 204 °C followed by 504 hr NSS. Initial and final readings.

Figure 10 shows the GM 9540P cyclic corrosion performance after heat aging at 200 °C for 24 hrs of the autodeposition coating vs. CED from three different suppliers over zinc phosphate. Three of the four paint systems still show fairly good performance with severe blistering on one CED. When the heat aging is increased to 24 hr at 230 °C, complete destruction of the zinc phosphate layer and the subsequent CED paint layer is observed, Figure 11. Under both of these heat aging studies, the autodeposition coating still shows good paint adhesion, and the creep from scribe is unchanged from a non-heat aged panel. The better thermal stability of the autodeposition coating is due to the absence of a zinc phosphate layer and any other organic or inorganic species in the coating that thermally dehydrate or chemically degrade.

Figure 10. Heat Soak (24 hr @ 200 °C) followed by GM 9540P (40 Cycles). Autodeposition ACC® 915 (far left), CED/Zn-phosphate (3 different manufacturers, middle-left, middle-right, and far right).
Figure 11. Heat Soak (16 hr @ 230 °C) followed by GM 9540P (40 Cycles). Autodeposition ACC® 915 (far left), CED/Zn-phosphate (3 different manufacturers, middle-left, middle-right, far right).

UV STABILITY

UV stability is a relative term. No aromatic epoxy coating can be considered UV stable compared to acrylic or polyurethane coatings designed for extended outdoor exposure. However, CED coatings are routinely used in applications requiring only limited UV stability, or as a primer under UV stable topcoats. In these applications the UV reactivity of the CED coating is tolerated. However, it can be the limiting factor in UV stability of the entire paint system, and improvements would be greatly appreciated. Figure 12 shows the result of Xenon-Weatherometer (WOM) testing of two different CED manufacturers compared to an autodeposition epoxy-acrylic coating. The loss of gloss is almost complete for the epoxy-based CED coatings after 90 kJ. Loss of gloss for the autodeposition coating occurs at a much slower rate for either low DFT (15 µm) or standard DFT (20-25 µm). Eventually, both coatings experience a total loss of gloss as neither is truly UV stable.

Figure 12. Xenon WOM Testing. Gloss reading initially and after 27.5 and 90 kJ exposure.

The increased UV stability of the epoxy-acrylic autodeposition coating is due to several polymer features. Typical CED polymers are crosslinked with blocked aromatic isocyanates, whereas the autodeposition polymer is crosslinked by aliphatic isocyanate functionality. The aliphatic crosslinker is not UV active, and so the crosslinks remain stable to UV exposure. In addition, the acrylic portion of the epoxy-acrylic autodeposition polymer is UV stable, and so the UV reactive epoxy polymer is diluted in the total matrix.

REQUIRED DRY FILM THICKNESS

Most paint systems are designed around an optimal DFT. Typically for CED paint this is specified by automotive OEMs to be around 1 mil (25 µm). The corrosion behavior of many paints fall off rapidly as the DFT decreases. However, for the epoxy-acrylic autodeposition coating the corrosion performance is remarkably stable down to 12-15 µm DFT, Figure 13. This is approximately half of the normal coating thickness. The reason for this behavior is still being evaluated. However, it is believed that at lower DFT the coating cures with less internal stress and the reaction rinse better penetrates the polymer film to react with the metal substrate. The importance of the reaction rinse in corrosion protection is addressed in the next section.

Figure 13. Graph Comparing Corrosion Performance at Low and High DFT, Autodeposition vs. CED coatings.

EFFECT OF REACTION RINSE

The reaction rinse plays an important role in autodeposition. The reaction rinse is the final stage in the autodeposition process. The reaction rinse can be varied to optimize the overall autodeposition coating properties. A common reaction rinse is a dilute phosphate ion containing solution (E3 reaction rinse). The exact chemistry that the reaction rinse effects on the metal substrate surface and the specific interaction of the reaction rinse on the bulk polymer coating is not fully understood. Nonetheless, it is very apparent that the reaction rinse permeates through the wet autodeposited paint film, and reaches the substrate surface where it reacts to form a visible and protective layer. Cross-sectioning of autodeposition films treated with the phosphate-based E3 reaction rinse, followed by SEM/EDX showed that phosphate remains evenly distributed throughout the depth of the coating, presumably in the form of iron phosphate. In Figure 14 the thin, iridescent layer produced by this reaction rinse on the substrate surface is clearly visible (right) when
compared to an untreated CRS panel (left). The treated panel was prepared by autodepositing a coating on a clean CRS panel, rinsing it in water, and immersing it in the reaction rinse for 60 seconds at 54 °C. The wet, uncured film was then removed by gently washing with methyl isobutyl ketone. The inorganic layer produced by the reaction rinse remained on the CRS surface.

**Figure 14.** Photograph of Bare CRS and CRS after Autodeposition, Reaction Rinse Treatment, and Removal of the Uncured Paint Film.

If this surface is analyzed by scanning electron microscopy (SEM), the surface morphology can be more clearly seen. In Figure 15 the surface is distinctly rougher and entirely covered by a dense iron phosphate layer. The composition of this layer depends on the reaction rinse chemistry employed. In the case of the phosphate-based E3 reaction rinse it is a modified iron phosphate. In the case of the E2 reaction rinse, it is a zirconium-mixed metal oxide.

**Figure 15.** SEM Photomicrograph of CRS after Autodeposition, Reaction Rinse Treatment, and Removal of the Uncured Paint Film.

GENERAL PERFORMANCE LEVEL

Over the years, finishers throughout the world have conducted extensive testing of autodeposition coatings. Panels and parts coated under standard conditions and tested against various automotive and general industry specifications find them to be well suited for many applications in the automotive and general industrial markets. Table 2 provides an overview of the commercial epoxy-acrylic autodeposition coating performance when applied over cold-rolled steel panels.

The standard coating film thickness employed for autodeposition applications is 0.6-1.0 mils (15-25 µm). The results in Table 2 show that autodeposition coatings provide excellent adhesion and corrosion resistance when applied directly to metal without a phosphate pretreatment. In addition, autodeposition coatings demonstrate excellent mechanical properties including flexibility, hardness and impact resistance while providing excellent moisture and chemical resistance. No softening or change in appearance of the coating is observed on exposure to unleaded gasoline, diesel fuel, transmission fluid, engine oil, or engine coolant.

The epoxy-based coating is quite hard (2H - 3H) ASTM D3363 pencil hardness, yet remain very flexible, passing a conical mandrel test, T-bend test (1-2T), and reverse impact (up to 160 in-lbs) when tested with the zirconium salt-based E2 reaction rinse. The epoxy-acrylic coating also maintains this flexibility and impact resistance after exposure to high temperatures. For example, after 2 hours at 400 °F, this coating still shows excellent adhesion and no change in reverse impact resistance. The properties provided by autodeposition coatings clearly demonstrate the suitability for many conventional automotive parts and general industrial applications.

<table>
<thead>
<tr>
<th>Test</th>
<th>ACC® 915</th>
</tr>
</thead>
<tbody>
<tr>
<td>Film Thickness</td>
<td>0.6 – 1.0 mil</td>
</tr>
<tr>
<td>Cross Hatch Adhesion (ASTM D 3359-95)</td>
<td>No Failure, 5B</td>
</tr>
<tr>
<td>Pencil Hardness</td>
<td>2H – 3H</td>
</tr>
<tr>
<td>Gloss @ 60º</td>
<td>40 - 80</td>
</tr>
<tr>
<td>Reverse Impact</td>
<td>&gt; 80 in-lb</td>
</tr>
<tr>
<td>Mandrel Bend, 10 Rating (GM 9503P)</td>
<td>Pass</td>
</tr>
<tr>
<td>Stone Chip (~30ºC)</td>
<td>Pass</td>
</tr>
<tr>
<td>Water Immersion (240 hrs)</td>
<td>Pass</td>
</tr>
<tr>
<td>GM 9540P 40 Cycles (3 mm Max. Creep)</td>
<td>Pass</td>
</tr>
<tr>
<td>SAE J2334 40 Cycles (3 mm Max. Creep)</td>
<td>Pass</td>
</tr>
<tr>
<td>Salt Spray, 504 hr (3 mm Max. Creep)</td>
<td>Pass</td>
</tr>
<tr>
<td>Thermal Stability</td>
<td>&gt; 425 °F</td>
</tr>
<tr>
<td>Cure Temperature</td>
<td>350 – 400 °F</td>
</tr>
<tr>
<td>VOC (EPA Method 24)</td>
<td>&lt;0.2 lbs/gal (HAPS compliant)</td>
</tr>
<tr>
<td>ELV, RoHS, and WEEE compliant</td>
<td>Free of Ba, Cd, Cr, Hg, Ni, Pb, and Zn</td>
</tr>
</tbody>
</table>

**Table 2. General Properties of ACC® 915**
CONCLUSION

Autodeposition coatings have demonstrated cost-effectiveness and high-performance in the world market with a proven record over 25 years. They are successfully used in both automotive and general industry markets to apply a high-quality, functional finish to metal components. The most recent introduction to this family of coatings is the ACC® 900 Series of thermoset epoxy-acrylic based coatings suitable for use as a stand-alone coating or as a primer. ACC® 900 series epoxy-acrylic autodeposition coatings provide higher temperature stability and a heavy metal-free finishing system for reduced environmental impact. Additionally, it maintains the core advantages provided by autodeposition yielding very uniform coating thickness even on parts with complex geometries and on the inside of tubular components. The family of autodeposition coatings is capable of providing a good mix of performance and aesthetic properties available to a wide range of finishing applications.

ACKNOWLEDGMENTS

The author wishes to thank Bashir Ahmed, John McGee, Danielle Kapp, Roman Skikun, Chris Weller, Donna Calhoun, Oscar Roberto, and Kevin Woock of Henkel Corporation and Andreas Taden of Henkel KGaA for their contributions, test data, and review of this paper.

REFERENCES


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DEFINITIONS, ACRONYMS, ABBREVIATIONS

ACC®: ACC® and Autophoretic® are registered trademark of Henkel KGaA for autodeposition coatings and chemicals. ACC® 915 is Henkel’s commercial epoxy-acrylic autodeposition coating product. ACC® 915/E2 is the combination of ACC® 915 autodeposition coating with the E2 reaction rinse (zirconium-based). ACC® 915/E3 is the same coating used with the E3 reaction rinse (phosphate-based).

CED: Cathodic Electro-Deposition
DFT: Dry Film Thickness of the coating
GPC: Gel Permeation Chromatography
NSS: Neutral Salt Spray (ASTM B-117)
SEM: Scanning Electron Microscopy
WOM: Weatherometer