Autodeposition—The Environmental Advantage

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abstract
Autodeposition utilizes aqueous dispersions of polymer, pigment, and activators to coat metal. The process eliminates the need for a conventional conversion coating. The coating bath operates at room temperature and is chemical, rather than electrically activated. Autodeposition has a high coating transfer efficiency, energy use efficiency and eliminates volatile organic compounds.

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Volatile Organic Compounds
Water Borne Coatings
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Autodeposition is a unique, waterborne organic coating process which uses chemical reactions to achieve deposition of a quality finish on steel surfaces. The autodeposition process is simple in comparison to those for other corrosion-resistant coatings. Following conventional cleaning and rinsing stages, metal parts are immersed in a coating chemical bath where the deposition of pigment and resin particles takes place. The growth in thickness of the film is time dependent, with an initially rapid deposition rate followed by a decrease in growth limited by the diffusion of ions to the metal surface and "self-sealing" of the coating. A protective barrier film is formed wherever the coating bath makes contact with the metal workpiece.

A key advantage of the most modern autodeposition processes (PVDC-based coatings) is the zero VOC content of autodeposition coating chemicals. This presents a solution to meeting today's more demanding air quality requirements while still applying a highly protective finish. In addition, this autodeposition system employs no potentially toxic heavy metals and features a low (100°C) temperature cure, leading to energy savings as well as a reduction in waste disposal costs.

INTRODUCTION

While the autodeposition process was first utilized in the late 1970's, it has only been within the past few years that environmental improvements to the process have promoted large scale use. Today, autodeposition is used commercially to coat millions of square feet of steel weekly without the use of any solvent other than water.

Autodeposition has been described as "electroless electrodeposition" since the process appears similar to electrodeposition in some regards, although no electric current is introduced into the coating bath. However, bath compositions, mechanisms and controls are quite different. In contrast, electrodeposition uses an applied current to move electrically charged paint materials to an oppositely charged electrode (the workpiece). Autodeposition is the controlled destabilization of an anionically or negatively-charged latex polymer on ferrous surfaces by chemical means. Autodeposition and electrodeposition are similar in that:
The coating thickness obtained is proportional to the amount of time the metal surface is immersed in the coating bath.

- A "leveling" action occurs due to better deposition through thin films relative to thick films.
- Deposited films are resistant to water (or permeate) rinsing prior to cure.
- The coating thickness is uniform.

From an overall process viewpoint, a comparison of auto-deposition to a typical finishing sequence employing a zinc phosphate conversion coating followed by an organic finish (e.g., electropaint, solvent or waterborne immersion or spray, powder coating) to provide a high quality corrosion resistant film follows:

**ZINC PHOSPHATE + PAINT FINISHING SEQUENCE (TABLE 1)**

Cleaning is a critical operation in any finishing process. Heated alkaline cleaners are most commonly used to remove oils, lubricants, drawing compounds and any other organic or inorganic materials on the metal surface which can interfere with the adhesion of a subsequently applied paint. Spray cleaning is normally used to provide physical impingement as well as chemical action to remove soils. If the workpieces have closed or boxed sections which cannot be reached by a spray pattern, an immersion cleaner is often recommended, either by itself or in conjunction with a spray stage. The appearance of a "water-break free" surface is often used as a measure of adequate cleaning.

After cleaning and rinsing with water, a crystal-refining stage is normally used prior to a subsequent zinc phosphate. This stage contains an activating agent (e.g., titanium phosphate) in the form of small colloidal particles which adsorb onto the metal surface and assist in optimizing the grain size of the zinc phosphate crystals applied in the following stage. Microcrystalline zinc phosphates provide enhanced adhesion of paint and, by insulating the surface, greatly reduce the tendency for corrosion.

A phosphate coating is achieved by contacting the metal surface with a heated acidic solution of primary (soluble) zinc phosphate. As acid reacts with (etches) the metal, the resulting pH increase at the surface results in the formation of insoluble zinc phosphate crystals on the surface. Currently, bath compositions are available which contain additional divalent metals (e.g., managanese and nickel) which precipitate along with the zinc to produce multi-metal conversion coatings which impart superior adhesion and corrosion resistance to the finished product. The control of this type of processing solution normally requires monitoring of the free and total acid levels of the bath as well as maintenance of the zinc concentration and the amount of oxidizing
agent which may be added to the bath to minimize the formation of a hydrogen film on the metal surface.

The phosphate conversion coating stage is followed by a water rinse and, finally, a sealing rinse (usually based on chromic acid, although non-chromium products are available) which further enhance the adhesion and corrosion resistance of the finished product. The phosphate coating is then rinsed with deionized water (in the case of electropaint) or dried by passage of forced warm air. Complete drying is particularly important prior to the application of solvent-borne or powder coatings. The metal surface, after complete surface preparation and conversion, is now ready for painting.

The autodeposition process differs from the above cycle, most strikingly, by simultaneous pretreatment and coating of a metal workpiece. The typical autodeposition sequence consists of only six distinct operations.

TABLE 1

TYPICAL PROCESSING SEQUENCES

<table>
<thead>
<tr>
<th>AUTODEPOSITION</th>
<th>PHOSPHATE + PAINT</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Alkaline Clean (heated)</td>
<td>1. Alkaline Clean (heated)</td>
</tr>
<tr>
<td>2. Water Rinse</td>
<td>2. Water Rinse</td>
</tr>
<tr>
<td>3. Autodeposition (room temp.)</td>
<td>3. Crystal Refinement (heated?)</td>
</tr>
<tr>
<td>4. Water Rinse (room temp.)</td>
<td>4. Zinc Phosphate (heated)</td>
</tr>
<tr>
<td>5. Sealing Rinse</td>
<td>5. Water Rinse</td>
</tr>
<tr>
<td></td>
<td>7. Air Dry or D.I. Water Rinse</td>
</tr>
<tr>
<td></td>
<td>8. Paint</td>
</tr>
<tr>
<td></td>
<td>9. Cure</td>
</tr>
</tbody>
</table>
**AUTODEPOSITION SEQUENCE (TABLE 1):**

While the cleaning considerations for autodeposition are similar to those for phosphate and conventional coating, the remainder of the coating process is very different and much simpler. After cleaning and rinsing, the work is treated in the acidic autodeposition bath.

An autodeposition bath contains:

- A latex polymer (usually pigmented) dispersed in water
- A mineral acid (0.2 to 0.3 weight percent hydrofluoric acid)
- An iron salt (to aid in acceleration of the coating process)

When a metal object is immersed in the coating bath, a mild dissolution of the surface occurs. This results in the formation of positively-charged metal ions at the surface which destabilize the negatively-charged latex on the surface producing deposition.

The "latest generation" polymer currently employed for commercial autodeposition (called the "800 Series") is a high-molecular-weight polyvinylidene chloride material which provides superior tensile strength, impact strength and corrosion resistance. The viscosity of a coating bath made up with this material is low (< 5 cps) which enables application by simple immersion (conveyor line or indexing hoist) and by flow coat.

Control of the bath is accomplished simply by maintenance of the polymer solids, acid level (via conductivity) and a redox potential measurement, which specifies the relative amount of iron in the system.

The 800 Series polymers employed in autodeposition require zero organic solvents (or other volatile additives); hence, the atmospheric emissions (other than water) are essentially zero. Although bath solids can be varied over a wide range, current commercial operations range from 3 to 8 percent non-volatiles. This, again, represents a dramatic departure from typical paint applications where solids levels of 20 to 60 percent are common.

It is preferable to use deionized water to make up an autodeposition bath as well as to replace water lost by drag-out and by evaporation. Although there is no immediate harm in using local or "plant" water, constant evaporation of losses with water containing soluble salts will result in a build-up of those salts far in excess of those in the feed water supply. Increasingly higher conductivities can interfere with the autodeposition mechanism due to the presence of soluble ions which "protect" the latex polymer from reaction with metal cations.
AUTODEPOSITION COATING MECHANISM

Chemically, the autodeposition coating process is very simple. The mildly acidic bath reacts with an immersed steel part to produce positively charged iron ions at the surface of the workpiece. These cations react with the negatively-charged latex particles in the bath to form a deposit on the surface of the steel. The deposited wet film is adherent, yet porous, so that acid and iron ions can continue to diffuse and form additional coating. Since this process is diffusion controlled, coverage is quite uniform across the workpiece. Eventually, the wet film solids compact to the point where ionic diffusion can no longer occur and the reaction stops.

Table 2 shows the dry film thickness which can be obtained on test pieces at various immersion times from an autodeposition bath agitated at different rates. While film thickness increases with the time of immersion, an increase in fluid velocity will dramatically increase the thickness at a fixed immersion time.

<table>
<thead>
<tr>
<th>IMMERSION TIME (SECS.)</th>
<th>FILM THICKNESS (MILS)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>BATH FLUID VELOCITY</td>
</tr>
<tr>
<td></td>
<td>30 FT./MIN. 60 FT./MIN.</td>
</tr>
<tr>
<td>30</td>
<td>0.3 0.4</td>
</tr>
<tr>
<td>60</td>
<td>0.4 0.55</td>
</tr>
<tr>
<td>90</td>
<td>0.55 0.7</td>
</tr>
<tr>
<td>120</td>
<td>0.65 0.9</td>
</tr>
</tbody>
</table>

The autodeposition reaction is quite mild. It is observed that even when a bath is being used to process metal at a high rate, there is no measurable temperature increase due to chemical exothermic reactions. However, bath temperature increase resulting from heated parts entering the bath as well as ambient temperature can produce irregularities in the autodeposited paint film. Bath temperatures in excess of 80°F can result in the formation of small voids in the coating as a result of increased chemical reaction. Conversely, temperatures below 60°F will produce a lower film growth rate than that produced at the recommended operating range of 68 to 72°F. Heat exchanger coils should be used during steady operation to maintain close coating control but, unlike other coating systems which consume energy, there is no need to dissipate heat generated by the coating mechanism.
ABSENCE OF VOLATILE ORGANIC COMPOUNDS (VOC):

The new Clean Air Act Amendments enacted on November 15, 1990 have serious implications for the coatings industry. More restrictive standards promulgated by both the EPA and the individual states will greatly reduce the level of solvent emissions allowed. Non-compliance with the new regulations can lead to civil penalties as much as $25,000 per day per violation. Fines for falsification or omission of information can be as high as $250,000 for individuals and $500,000 for organizations. Penalties for a known release of a listed hazardous pollutant can reach $25,000 per day. Fines for violations in recordkeeping can be $5,000 per day.

The absence of volatile organic compounds or volatiles other than water from 800-Series autodeposition coatings presents a tremendous advantage to a metal finishing operation. In addition to enabling compliance to environmental regulations, the 100% aqueous systems have no flash point which eliminates the common paint shop fire hazard.

WHERE IT WETS-----IT COATS:

Few paint systems can be successfully applied to recessed areas of complicated parts. Conventional waterborne and solvent-borne immersion paint systems will wet most areas but suffer from the problem of solvent wash (i.e., during the curing of these materials, the water and solvent volatilized from the coating refluxes within any recessed section and washes most of the coating away). Electropaint will resist wash during the solvent evaporation step; however, electropaint cannot apply coating very far into an enclosed space due to electrical "caging" effects. Attempts to coat deeply recessed areas by increasing the applied voltage could lead to rupture of previously deposited exterior coatings.

Since autodeposition depends upon chemical rather than electrical energy, the bath will coat any area it can wet. For example, one can coat the interior of narrow tubular-style workpieces of extended length at a coating thickness nearly equal to that on the exterior surface.

FINAL SEALING RINSE:

When a coated surface is removed from an autodeposition bath and water rinsed, the coating is still permeable (i.e., the workpiece can be returned to the bath and coating growth will resume). This is believed due to the presence of iron (presumably as FeF₃) which is not bound to the negatively-charged latex particles. 800-Series films are processed through a final rinse tank containing a neutral salt which is capable of precipitating the iron and sealing the film. This greatly enhances the adhesion and corrosion resistance of the surface after cure.
CURING:

The cure schedule for 800-Series coatings is of low temperature and duration relative to conventional industrial finishes. Typical production convection oven parameters vary from 20 to 40 minutes at 200 to 230°F. Medium-intensity infrared ovens have also been commercially employed. Since the mechanism of film coalescence is simply water removal, these units are effective in rapidly heating the wet film and forcing evaporation. Commercial units vary in exposure times of 4 to 8 minutes and dramatically reduce line space.

It is also possible, with very thick workpieces (all sections 1/4 inch or greater) to utilize a technique known as "hot-water-cure (HWC)" wherein the part is immersed in an aqueous solution at 190 to 210°F for 90 to 120 seconds and then withdrawn. The term "HWC" is misleading in that the immersion serves only to quickly heat the piece. The actual "cure" (water removal) occurs when the part is withdrawn and allowed to dry for several minutes.

COATING PROPERTIES:

Table 3 shows the performance properties of 800-Series auto-deposited coatings. Of particular note is the excellent adhesion after any deformation combined with the hardness and durability of the film to resist chipping and marring. The corrosion resistance of these films is excellent.

**TABLE 3**

**AUTODEPOSITED 800-SERIES COATINGS**

*(CURED FILM PERFORMANCE)*

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Film Thickness (mils)</td>
<td>0.6 - 1.0</td>
</tr>
<tr>
<td>Pencil Hardness</td>
<td>4H - 5H+</td>
</tr>
<tr>
<td>Zero T-Bend</td>
<td>No Loss</td>
</tr>
<tr>
<td>Reverse Impact</td>
<td>160 Inch-Pounds (No Loss)</td>
</tr>
<tr>
<td>Gravelometer (chip resistance)</td>
<td>&gt;7+ (GM-9508-P)</td>
</tr>
<tr>
<td>Salt Spray Exposure</td>
<td>600 Hours</td>
</tr>
<tr>
<td>(≤ 3MM creep from scribe;</td>
<td></td>
</tr>
<tr>
<td>&lt; 5% face corrosion)</td>
<td></td>
</tr>
<tr>
<td>Cyclic Corrosion Test Exposure</td>
<td>&lt; 3MM Scribe Creep</td>
</tr>
<tr>
<td>Solvent Resistance</td>
<td>Very good</td>
</tr>
</tbody>
</table>
OTHER ADVANTAGES OF THE PROCESS:

A greatly reduced frequency of rack stripping is a bonus for users of autodeposition. In the case of racks constructed of "inert" materials, such as plastic (which will not react with the coating bath), the small amount of coating solution dragged out by surface tension is rinsed away by the first plant water stage. Steel racks will be coated (like the parts) but, after curing, the coating becomes resistant to the hot alkaline cleaners as well as the coating bath.

Since the rack is no longer susceptible to chemical attack, combined with the hydrophobic nature of the autodeposition coating, any clinging bath composition (which has a viscosity similar to water) drains rapidly back into the coating tank when the rack is raised. Any remaining material has a low solids content (i.e., 4 to 7%) and thus contributes very little to a loss of solids from the system. The racks show no measurable build-up of coating thickness, and most commercial autodeposition operations clean the racks at a rate of about once every three years. This results in savings of energy, chemicals, labor, and waste disposal costs usually involved in such an operation.

EQUIPMENT CONSIDERATIONS:

Mild steel is the normal material of construction for all tanks, piping, and related accessories for any autodeposition line. The coating tank is usually lined with any elastomeric material having resistance to mild acid as well as mechanical strength to prevent accidental damage from displaced parts or racks. It is also recommended that any rinse stages made up with deionized water be lined or constructed of corrosion-resistant material (e.g., plastics or stainless steel).

COATING BATH CONTROLS ARE:

- Total Solids (gravimetric measurement)
- Acid level (controlled by a conductivity measurement using a proprietary meter)
- A potentiometric measurement (usually automated) which by means of a millvolt reading describes the ratio of iron (III) to iron (II) in the bath.

Monitoring of these levels requires a small amount of laboratory equipment. The techniques are extremely simple and are readily learned by the line operator. Automated process control equipment is recommended for all cleaner and rinse stages, although manual acid/base titrations and/or a conductivity measurement can be used.