Waterborne Direct-to-Metal Coatings: Enduring Solutions in Corrosion Protection

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Corrosion is a process where a refined metal, such as aluminum or iron or alloys such as steel, undergoes degradation. In scientific terms, corrosion is an electrochemical process leading to oxidation of the metal and returning it to its natural state, such as iron being converted to iron oxides.

Electrochemical reactions eat away at the underlying metal substrate, sometimes degrading it to such an extent that it creates aesthetic, mechanical, or structural failures.

The economic impact of corrosion is enormous. In a recent report, corrosion was estimated to cost the global economy more than $2.5 trillion annually, or approximately 3.4% of global gross domestic product (GDP).[1] Preventing corrosion is clearly an important goal, and paints and coatings play an important role in this never-ending battle.

Coatings applied to metal substrates can have a variety of purposes, including the enhancement of aesthetics such as gloss and color, or various functional purposes such as thermal insulation, sound dampening, or antimicrobial properties.

However, in many cases the most important role of a coating on a metal substrate is protection of the metal surface from the environmental effects that lead to corrosion. Waterborne direct-to-metal (DTM) coatings are just one category of coatings designed to protect metal substrates.

We begin by considering the science behind the corrosion process and the methods by which a coating can prevent corrosion. Then we will examine what is meant by direct-to-metal and how the term “DTM coating” is typically discussed in the industry, followed by a description of one-component (1K) DTM coatings based on acrylic latex polymers, which are the most common type of waterborne DTM coatings. We will also discuss principles of formulating waterborne acrylic DTMs for maximum performance over metal substrates. Finally, we will present a two-part, roundtable Q&A, where industry experts discuss the current trends and technology advances.

In a recent report, corrosion was estimated to cost the global economy more than $2.5 trillion annually, or approximately 3.4% of global gross domestic product (GDP).[1]

THE SCIENCE OF CORROSION

For corrosion to occur, four basic elements of an electrochemical cell must be present, as shown in *Figure 1*. The first element is a thermodynamically unstable metal (the anode) that will undergo oxidation (i.e., the base metal gives up electrons and is converted to the corresponding metal cations). In *Figure 1*, the anode is zinc, which oxidizes to form Zn^{+2} ions. The electrons travel via the second element, a metallic conductive pathway, to an electron acceptor. The cathode is the third necessary element, where the electrons take part in a reduction reaction.

In *Figure 1*, electrons travel to the iron cathode, where oxygen, water and electrons combine to generate hydroxyl ions. The metal cations formed at the anode, and hydroxyl anions formed at the cathode, need a medium that allows ion movement. That medium, an electrolyte, is the fourth element to complete an electrochemical cell. In its simplest form, an electrolyte is a polar solvent such as water containing some soluble salts. In the presence of an electrolyte, the cations can move towards the cathode and the anions can move towards the anode. Corrosion products, such as zinc hydroxide shown in *Figure 1*, will form as the two ions form a salt and precipitate from solution.

In the case of dissimilar metals, such as zinc and iron in *Figure 1*, the galvanic series (shown in *Figure 2*) dictates which metal acts as the anode and corrodes, and which metal acts as the cathode and is protected from corrosion. Zinc is more active than iron, and when in electrical contact, zinc will act as the anode and will preferentially corrode.

FIGURE 1—Electrochemical Corrosion Cell Showing the Four Elements Needed for Corrosion and Reactions Occurring at the Anode and Cathode.

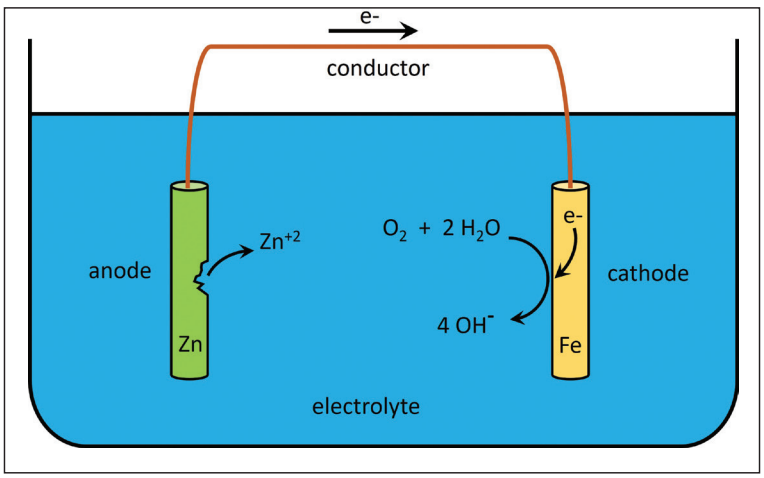
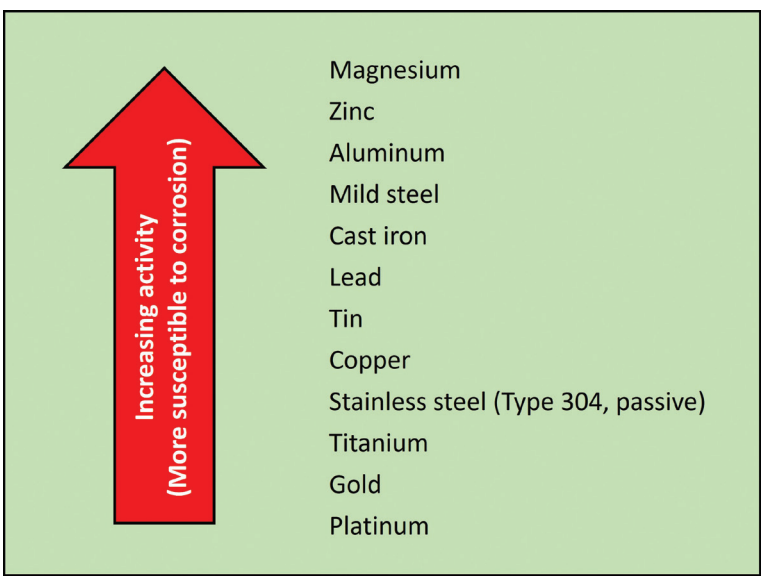


FIGURE 2—Galvanic Series in Seawater.



One might ask, "Why does a piece of steel (an iron alloy) corrode if it is by itself and not in contact with another metal?" It will undergo corrosion because it is heterogeneous in nature; that is, there are domains within the steel structure that have slight differences in electrochemical potential. This slight difference is enough to allow one domain within the steel to act as the anode and another to act as the cathode as seen in *Figure 3*.

Mild or low-carbon steel is a very common material used in manufacturing and construction and corrodes quite readily if not protected. The corrosion products are iron oxides and hydroxides, commonly referred to as rust. Three types of coatings can be used to protect steel and other metals from corrosion—sacrificial, inhibitive, and barrier.[2]

A sacrificial coating works by making itself the anode and sacrificing itself for the metal substrate. A sacrificial coating is formulated with a high level of metal particles, such as zinc dust, which in the dry film are in electrical contact with each other and the metal substrate. If the metal particles are a more active metal than the substrate, they will act as the anode in a corrosion cell and sacrificially corrode and protect the substrate (i.e., the cathode). When a piece of steel is coated with a zinc-rich primer, the zinc particles sacrificially protect the steel substrate. These types of primers are often used in heavy duty service environments, such as in industrial maintenance applications, and are very effective at protecting steel from corrosion.

An inhibitive coating interferes with the corrosion process by introducing chemical species that interact with the metal surface. Inhibitive primers typically contain pigments that are slightly soluble, and once solubilized in the presence of water, can create a passivating layer that disrupts the electrochemical reactions at the anode or cathode. This type of inorganic pigment is often called a reactive, inhibitive, or anticorrosive pigment, and an example is basic zinc phosphate. Various organic corrosion inhibitors may also be used in formulating metal primers. Primers containing inorganic and organic corrosion inhibitors can be very effective at protecting metals from corrosion, and waterborne, solventborne and high-solids versions based on various resin technologies (e.g., epoxies, alkyds, etc.) are available.

Both sacrificial and inhibitive coatings must be in direct contact with the metal surface to provide effective protection. A barrier coating, on the other hand, can be the first layer in contact with the metal, or can be a subsequent layer on top of a primer. Barrier coatings disrupt the corrosion process by preventing either the fuel for the cathodic reaction (water and oxygen, or other chemicals) or the electrolyte from coming into contact with the substrate. Most coatings provide some barrier properties to a coating system, but their effectiveness will depend on factors that influence permeability to water and electrolyte, such as polymer hydrophobicity and coating porosity.

DEFINING DIRECT-TO-METAL (DTM) COATINGS

Many applications utilize coatings that are applied to metal substrates. Protective coatings used in marine and industrial maintenance settings, transportation finishes (auto, rail, and aerospace), coil coatings, and factory-applied general metal finishes are often applied to steel, aluminum, or other metal surfaces.

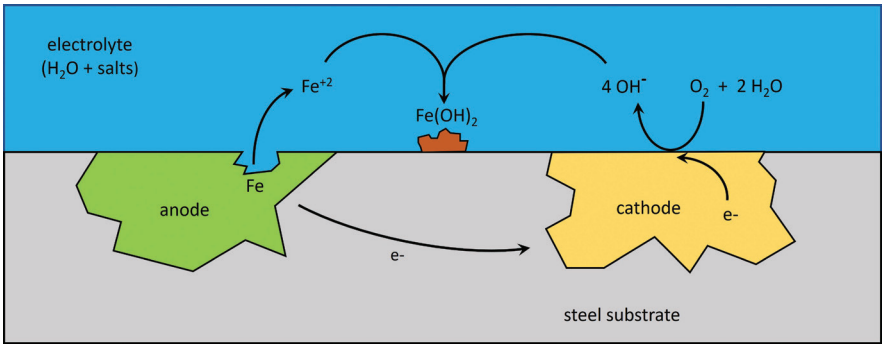
Metal finishes are often applied in multicoat systems with two or three coats. In these systems, the first coat is a primer designed to provide corrosion protection, typically through sacrificial or inhibitive properties, and adhesion to the substrate. Topcoats are designed to primarily provide the aesthetics (color, gloss) and durability, but they can also contribute to the overall corrosion resistance through their barrier properties.

Direct-to-metal coating, or DTM coating, is a term that is often used but sometimes poorly defined in the coatings industry. Primers for metal are, of course, applied directly to the metal surface. DTM coatings, however, are typically designed to handle the functions of both primer and topcoat in a single coating, by providing the adhesion and corrosion resistance of the primer, and the aesthetics and durability of the topcoat.[3]

DTM coatings are often applied in a single coat, and thus allow reduction of the number of layers in a traditional two- or three-coat system. Reducing the number of layers can also result in manufacturing efficiencies (e.g., time) and cost savings (e.g., labor), as well as simplifying inventories by decreasing the number of different coatings that must be stocked. DTM coatings can also be applied as both primer and topcoat, essentially providing a self-priming, multicoat system relying on only a single coating formulation.

Offered in many different varieties, DTM coatings are supplied in waterborne, solventborne, high-solids, and powder form, and span a broad range of polymer chemistries, including acrylic, alkyd, epoxy, polyurethane, and hybrid technologies. Waterborne DTM coatings in particular are frequently used over metal substrates in light-to-medium-duty service environments. The most common waterborne DTM coatings are one-component coatings based on acrylic and acrylic-styrene latex polymers, but other available 1K systems are based on water-reducible alkyds, alkyd dispersions, and polyurethane dispersions (PUDs). Two-component (2K) waterborne DTM coatings are often based on epoxy emulsions crosslinked with either carboxyl-functional acrylics or amine-based hardeners, or PUDs crosslinked with polyisocyanates.

FIGURE 3—Depiction of the Corrosion Process for Steel.



WATERBORNE ACRYLIC DTM COATINGS

The most common waterborne DTM coatings are based on acrylic and acrylic-styrene latex polymers. Waterborne acrylic DTM coatings have been available since the 1960s but became more popular in the 1980s especially for use in light- and medium-duty industrial maintenance settings, when versions with improved corrosion resistance were introduced to the U.S. market.

Since then, steady technical advances in polymer design and coating formulation have led to significant improvements in properties such as corrosion resistance, adhesion, exterior durability and volatile organic compound (VOC) levels.[4]

Today, waterborne acrylic DTM coatings are successfully used in a variety of applications such as freight rail cars (e.g., auto carriers, boxcars), electrical boxes, metal shelving, and racking. DTM coatings can also protect structural steel in industrial maintenance (e.g., storage tanks, buildings, bridges), commercial and residential architectural (e.g., interior steel beams, doors) settings, and many factory-applied general metal finishing applications (e.g., auto parts, propane tanks, etc.).

Benefits of waterborne acrylic DTM coatings include their ease of use (application and clean-up), low toxicity, non-flammability, and low VOC levels. In addition, most acrylic DTM coatings are 1K and have the advantage of no mixing ratios or pot-life limitations. Although 2K versions that offer films with higher crosslink density are available, 1K acrylic DTMs are most prevalent.

For 1K DTM coatings requiring some polymer crosslinking to improve chemical/solvent resistance or exterior durability, self-crosslinking 1K acrylic polymers are used. The available 1K self-crosslinking technologies usually provide a lower-density crosslinking compared to a 2K system, but when coupled with an initially high-molecular-weight acrylic, can result in fairly robust chemical and solvent resistance.[4,5]

Waterborne acrylic DTM coatings typically protect metal substrates from corrosion due to their barrier properties, but in some cases are formulated with anticorrosive pigments or corrosion inhibitors to also provide inhibitive protection. Because the anticorrosive pigments usually have a negative impact on film gloss due to their large particle size, acrylic DTM coatings at gloss and semigloss sheens are typically formulated without the pigments and must rely primarily on their barrier properties to provide corrosion protection.

In many situations, waterborne acrylic DTM coatings are applied in one or more coats directly to steel, aluminum, or galvanized steel substrates. However, in cases where greater corrosion protection or adhesion is required, they might be used as a topcoat over an acrylic inhibitive primer or a primer of another technology, such as a zinc-rich primer.

In addition, for field-applied situations, many waterborne acrylic DTM coatings are recommended for application over properly primed drywall, concrete or wood substrates. This versatility allows painting applicators to use the acrylic DTM coating for metal and adjacent surfaces of other substrates where appropriate.

FORMULATING WATERBORNE ACRYLIC DTM COATINGS

Formulating any coating is a complicated process that involves choosing the right combination of ingredients to yield a coating with all the required performance properties. Making choices that optimize one property can often lead to a tradeoff in another. Fortunately, for waterborne acrylic DTM coatings, many of these formulating effects are well-known, and some general rules can be applied towards preparing new formulations.[6,7] A generic formulation for a gloss white DTM coating based on a waterborne acrylic latex is shown in *Table 1* and will be used to discuss some of the basic principles for formulating a high-performance DTM coating.

Because the resin is such a large portion of a coating formulation, one of the keys to maximizing performance is to start with a good binder that is designed for DTM applications. Commercially available acrylic latex polymers

TABLE 1—Formulation for a Waterborne Gloss White DTM Coating Based on an Acrylic Latex Polymer.

MATERIAL	POUNDS	GALLONS
Grind		
Water	80.00	9.60
Dispersant (42%)	7.50	0.85
Surfactant	4.00	0.50
Defoamer	4.00	0.50
Ammonia (28%)	2.00	0.27
TiO_2	215.00	6.44
Letdown		
Acrylic Latex Polymer (49%)	530.00	61.63
Water	115.50	13.87
Ammonia (15%)	2.00	0.27
Deaerator/Defoamer	10.00	1.20
Coalescent	15.60	2.06
Coalescent (No VOC Coalescent)	5.20	0.65
Sodium Nitrite, Flash-Rust Additive (15%)	9.00	1.00
HEUR Rheology Modifier (ICI thickener)	7.00	0.81
HEUR Rheology Modifier (KU thickener)	3.00	0.35
Totals	1009.80	100.00
Properties (levels without additives)		
PVC (%)	18.0	
Volume Solids (%)	35.6	
Weight Solids (%)	47.0	
Density (lb/gal)	10.1	
Coalescent (% on Polymer Solids)	8.0	
VOC (g/L)	45	
pH	approx. 9.0	

recommended for DTM coatings vary in glass transition temperature (T_g) from as high as 60° C to below 0° C. The choice of polymer T_g will affect not only the achievable VOC level, but also properties related to film hardness, such as block, print, scratch, and dirt-pickup resistance. The formulation in *Table 1* has a VOC under 50 g/L, so the acrylic polymer used in that formula should have a T_g or minimum film formation temperature (MFFT) of approximately 15° C or below to ensure adequate film formation.

The quality of film formation is one of the most important features to optimize for a waterborne acrylic latex DTM coating, as it has a direct correlation with barrier properties and corrosion resistance.[8] Poor film formation can occur if a latex is not formulated with enough coalescent to effectively lower the MFFT of the coating below the drying temperature, or if the application temperature is too low. When the quality of film formation is poor, microscopic channels and voids can be present in the film, resulting in a more porous film through which water and electrolyte can more easily reach the metal substrate.

The formulation in *Table 1* has a total of approximately 8% coalescent on polymer solids, which would be needed to maximize corrosion resistance for the 15 °C T_g polymer. To maintain the VOC level below 50 g/L, about 2% of the coalescent would need to be a non-volatile coalescent or plasticizer that does not contribute to VOC. For any resin, the proper level of coalescent to optimize corrosion resistance can be determined through a coalescent ladder experiment.

Using the proper level of coalescent is obviously important in maximizing the performance of an acrylic latex. Due to VOC regulations and customer preference, VOC levels of high-performance waterborne acrylic DTMs have been falling for the past 15 years. First, resins were designed for under 100 g/L when South Coast Air Quality Management District (SCAQMD) regulations dictated that level for industrial maintenance coatings in 2007, and more recently, achievable VOC levels have dropped to under 50 g/L and below.[5,9–13]

The success in many of these developments was realizing the low-VOC levels while maintaining hardness properties such as block and dirt-pickup resistance. Balancing VOC and hardness is often accomplished by using complex internal latex morphologies (e.g., core-shell or other multistage morphologies) and self-crosslinking.[9,10]

Acrylic latex polymers designed for DTM coatings tend to have very hydrophobic backbones. In addition to proper coalescence and good film formation, the hydrophobic backbone assists in providing good water and corrosion resistance. A more hydrophobic polymer will be a more effective barrier to water and electrolyte, and thus aid in corrosion resistance.[13,14]

Hydrophobic acrylate and methacrylate monomers, such as 2-ethylhexylacrylate (2-EHA) and butylmethacrylate (BMA), can be used in DTM binders to increase polymer hydrophobicity. Many DTM binders are acrylic copolymers also containing styrene because styrene aids in polymer hydrophobicity. Even so, high styrene levels tend to hurt exterior weathering, so styrene levels need to be moderated to provide resins with excellent gloss and color resistance.[6]

Today's 1K waterborne acrylic DTMs can provide superb adhesion, corrosion resistance, and exterior durability.

Adhesion of a waterborne acrylic polymer to a metal substrate is typically driven by manipulating molecular weight and using copolymerized acid-functional monomers, such as acrylic and methacrylic acid. Bare steel, and especially aluminum and galvanized steel, can be difficult for acrylic resins to adhere to, particularly if the level of acid-functional monomer is low. For this reason, many acrylic DTM binders have higher acid numbers compared to latexes used in architectural applications. Lower molecular weight can also help with adhesion (and gloss) but can have a detrimental effect on exterior durability and solvent resistance. Copolymerizable phosphate-functional acrylate monomers have also been reported to assist with not only metal adhesion but also corrosion resistance.[15,16]

After the resin (and of course, water), pigments are typically the next largest ingredient by volume in a waterborne DTM coating formulation. The formulation in *Table 1* contains titanium dioxide (TiO_2) at 18% pigment volume concentration (PVC), which would be a typical amount for a gloss or semigloss white DTM coating with good hiding. In general, acrylic DTM coatings have better corrosion resistance when formulated at lower PVC levels. As PVC increases, films tend to have more porosity, and thus barrier properties and corrosion resistance are decreased.

Extender pigments can be used to lower sheen levels, but corrosion resistance should be expected to suffer compared to a high-gloss formulation due to increased PVC. Commercially available acrylic DTM binders can often achieve 60° gloss of 80+ units in gloss white formulations such as shown in *Table 1*. As sheen is lowered and PVC increased by adding extender pigments, the formulator also has the option to add anticorrosive pigments to help with corrosion resistance through an inhibitive mechanism. Because they tend to have large particle sizes, anticorrosive pigments will usually lower gloss, and therefore are typically not able to be used in gloss DTM coatings but are suitable for lower sheens.

A variety of effective anticorrosive pigments are available for use in waterborne acrylic DTM coatings. In addition to basic zinc phosphate, there are many varieties including orthophosphates, polyphosphates, phosphosilicates, and borosilicates, among others. The trend, particularly in Europe, is towards the use of zinc-free versions to avoid regulatory labeling.

One thing that most anticorrosive pigments have in common is the ability to destabilize latex polymers due to the presence of soluble multivalent ions (e.g., Zn^{+2}). Destabilization could lead to grit formation or even gelation in the worst case, so formulations should always be tested for shear and heat age stability prior to scale-up and commercialization. Minor stability issues can often be solved by adding low levels of nonionic surfactants that provide steric stabilization to the latex.

The pigment dispersion impacts not only properties of the wet paint such as viscosity and stability, but also many final film properties such as gloss, color, and corrosion resistance. Better

dispersion of pigments and proper stabilization to prevent re-agglomeration in the wet state, improves the barrier properties of a DTM coating. Optimizing pigment dispersion can be accomplished through proper selection of pigment dispersants or use of latex-binder technology that forms latex-pigment composites.

When designing a DTM formulation, care should be taken as it relates to both the type and level of pigment dispersant. Although the pigment dispersant is typically a small portion of the coating formulation as shown in *Table 1*, it can have an outsized effect on water sensitivity because it is a water-soluble material. Dispersants are low-molecular-weight oligomers, often containing carboxylic acid-functionality. Hydrophobic copolymer dispersants are typically better for corrosion resistance compared to hydrophilic and polyacid dispersants due to their lower acid levels and reduced negative effect on water resistance of the final film. Recent work has shown that amino alcohols can be used as a co-dispersant in acrylic DTM formulations with improvements in corrosion and early water resistance.[17]

Another technology that has been used to provide improved pigment dispersion, both in the wet paint and the dry film, is based on latex polymers that interact with the pigments to form latex-pigment composites in the wet coating.[5,10,12,18,19] The composites are formed during the paint formulation process and consist of latex particles adsorbed onto the pigment particles. The latex particles act as spacers to keep the pigments from re-agglomerating in the wet state, and space out the pigments more evenly in the dry film. The improved dispersion of pigment in the dry film leads to greatly improved barrier properties (corrosion resistance) compared to a standard latex.

In addition to pigment dispersants, the type and level of other additives should be chosen to minimize water sensitivity. Wetting surfactants are required to aid in pigment wetting during the dispersion process, as well as to lower surface tension and help with substrate wetting. However, too much surfactant can hurt water sensitivity and therefore corrosion resistance.

Defoamers typically don't affect water sensitivity very much, but proper defoaming is essential for DTM coatings. Any pinholes or trapped bubbles due to foam are weak points in the barrier properties of the coating. It can be shown that poor defoaming leads to worse corrosion resistance. In the formulation in *Table 1*, a defoamer in the pigment grind is used to prevent foam generation during processing, and an effective defoamer or deaerator is also used to prevent foam generation during application. Deaerators can be effective at preventing microfoam, which is often generated during airless spraying of waterborne coatings. Of course, many waterborne DTM coatings are applied by airless or air-assisted airless spray, so prevention of both macrofoam and microfoam is required.

Rheology modifiers are another key additive that can affect corrosion resistance. As with dispersants and wetting surfactants, rheology modifiers used in waterborne coatings are typically water-soluble molecules and will affect water sensitivity. For acrylic DTM coatings, hydrophobically modified ethoxylated urethane (HEUR) associative rheology modifiers are usually safe choices. HEUR rheology modifiers tend to have less effect on water sensitivity and corrosion resistance compared to alkali-soluble emulsions (ASE) and hydrophobically modified alkali-soluble emulsions (HASE). While HEUR rheology modifiers are nonionic, ASE and HASE have carboxylic acid functionality in their backbone.[20]

Associative thickeners such as HEURs also tend to provide a more homogeneous film structure compared to thickeners that function through a volume exclusion mechanism, such as ASE and hydroxyethyl cellulose (HEC). *Table 1* shows the use of two different HEURs to provide a rheology for brushing application. The choice of specific rheology modifiers will depend on the type of application method and other performance requirements such as sag resistance or flow and leveling. For example, if formulating for a spray-applied DTM coating, the formulator might choose a HEUR designed for low shear rate viscosity to provide good sag resistance and leave out the high-shear-rate thickener to improve atomization.

The last additive to be discussed is the flash-rust additive. Flash rust is corrosion that occurs while the wet coating is in contact with the steel. In the absence of a flash-rust additive, a waterborne coating will typically cause corrosion to occur as the film is drying, leading to either a rust-colored tarnishing or spots of rust appearing on the dried film.

In *Table 1*, the flash-rust additive is sodium nitrite, added as a 15% aqueous solution. Sodium nitrite is a common and very effective flash-rust additive. It is typically added as an aqueous solution, at an approximate level of 1–2 lbs of sodium nitrite per 100 gallons of coating. Organic amines such as dimethylaminoethanol (DMAE) are also effective as flash-rust additives. Commercial flash-rust additives are also available that typically contain combinations of sodium nitrite and organic amines or are based on other salts such as phosphates, borates or organic carboxylates. Maintaining a pH above 9.0 also helps deter flash rust.

CONCLUSIONS

Waterborne direct-to-metal coatings are currently used in a multitude of applications to protect steel and other metals from corrosion. DTM coatings are unique because they are designed to provide the performance of both primers (adhesion and corrosion resistance) and topcoats (aesthetics and durability) in a single coating. They allow simplification of coatings systems and can save time and money for applicators and end-users.

Many varieties of waterborne DTM coatings exist, with those based on waterborne acrylic technology being the most prevalent. Waterborne acrylic DTM coatings have changed with the demands of the coatings industry, consistently moving to higher performance and lower VOCs, and driven by innovations in raw material product development (resins, pigments and additives) and formulation.

Their story spans the past 60 years, but today's 1K waterborne acrylic DTMs can provide superb adhesion, corrosion resistance, and exterior durability. Together with other waterborne technologies such as epoxies, alkyds and polyurethanes, waterborne DTM coatings will no doubt be around for many more years to help us solve many of the difficult problems posed by corrosion.

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ROUNDTABLE Q&A ON WATERBORNE DTM COATINGS, PART I

The industry experts providing comments include:

- **Mark Langille, Ph.D.**—Customer applications specialist, Paints & Coatings, at ANGUS Chemical Company
- **Anthony Gichuhi, Ph.D.**—Paints & Coatings R&D director at ICL Phosphate Specialty
- **Sudhir Ananthachar**—Technical manager (Coatings) Crosslinkers BL at Evonik Corporation
- **Andrew Thorn**—Industry manager for Coatings at Heubach Group
- **Joey Ruiz, Ph.D.**—Principal scientist at Solvay
- **Claire Reynier**—Global marketing manager for Industrial Coatings at Arkema
- **Ivan Tyre**—Senior applications chemist at Alberdingk Boley
- **Gregory Monaghan**—Applications manager at Specialty Polymers
- **Chris LeFever**—R&D Technical manager at Engineered Polymer Solutions (EPS)
- **Chuck Jones, Ph.D.**—Technical manager, Resins for Industrial Coatings at BASF
- **Ronald Brashear**—Marine and Protective Coatings End-Use manager, North America, at BYK USA Inc.
- **Kiran Baikerikar, Ph.D.**—Associate R&D director for Industrial Coatings at Dow
- **Matthew Padaon**—Lead technical specialist for Industrial Coatings at Dow

In the first of this two-part Q&A, *CoatingsTech* asked several industry experts for their views on waterborne direct-to-metal (DTM) coatings. Topics included important trends driving their development efforts and recent products that they have introduced. They also talk about some of the key benefits and disadvantages of waterborne technologies for metal coatings, and some misconceptions about waterborne DTMs that exist in the market. Their opinions on some of the challenges remaining for this category of coatings are also described, as well as some sage advice for formulators attempting to create new waterborne DTM

coating products. Part II of this Q&A will appear in the August-September issue of *CoatingsTech*.

Participants in the Q&A roundtable discussion include industry experts from several raw material suppliers involved in the production of a range materials used in waterborne DTM coatings, including resins, additives, and corrosion inhibitors.

What do you see as the key market trends that are driving R&D/ innovation efforts for waterborne direct-to-metal (DTM) coatings and the raw materials used in their formulation?

Langille (Angus): In addition to continuous efforts to further improve protection performance, environmental, health, and safety (EH&S) considerations are always top of mind when transitioning from solvent-based to water-based coatings. Performance is paramount, but so is adhering to both current and future EH&S trends. We see many formulators and raw material suppliers looking to eliminate the use of hazardous materials in their products, which is driving innovation to not only make better waterborne DTM products, but to do so while simultaneously improving their EH&S profile. Even the most recent supply chain disruptions have spurred innovation efforts around the evaluation of alternative available chemistries.

Gichuhi (ICL): The key market trends are regulatory, human and environmental safety, and paint labeling concerns. VOC-emission reduction remains a strong push and customers are willing to improve their brands by claiming low or zero VOC. There is also a slow shift towards heavy metal-free anticorrosive pigments, especially those with the dead-fish/dead-tree labeling that lead to the classification of the final paint. Zinc-free has been and continues to be a push in Europe for a number of years since zinc oxide or zinc phosphate pigments trigger the dead-tree/dead-fish labels. The daunting target of 1,000 hours of salt spray at 50 microns (2 mils) can be achieved in many cases with pretreated steel vs. bare cold rolled steel. DTM coatings perform well in C1 to C3 environments (ISO 12944) but have a long way to go to achieve C5 (onshore exterior environments and industrial areas with high humidity and aggressive atmospheres) or CX (extreme industrial areas, offshore areas, and high salt exposure).

Ananthachar (Evonik): Faster return to service is a key driver for coatings development as downtime for an asset often equates to money lost. Reduced formulation complexity and the desire for systems that are easier to manufacture also guide our development of raw materials. The use of materials with friendly EH&S profiles and the elimination of raw materials of concern are key concerns when developing most coatings today, including waterborne DTMs. VOC regulations (in the Far East especially), the mandate to convert from solvent to waterborne systems in China and Korea, and proactive steps taken by major economies to reduce carbon footprint are also very important factors.

Thorn (Heubach): End customers are always looking to get better coating properties at a lower film thickness. These properties can include color development, weather resistance, light fastness, heat resistance, corrosion resistance, and coverage, to name a few. Ease of application is always a bonus, as well as a reduction in the number of coats. Formulating environmentally friendly coatings is definitely important. Choosing additives from renewable resources or from materials with a low carbon footprint is definitely a plus.

Ruiz (Solvay): The key market driver for efforts directed at waterborne direct-to-metal (DTM) coatings is primarily sustainability. The move to waterborne technologies reduces and ultimately removes VOCs to comply with increasingly stricter regulations for these coating systems. By definition, DTM coatings often start as a single-coat system of about 50 microns (2 mils). For some coating applications, good binder systems exist that can be used to formulate coatings that achieve the performance of solventborne counterparts. In cases where labor costs are high, this single-coat approach is more applicable as it presents a more cost-effective solution. Mono-coat systems are definitely more convenient to apply on-site; however there is a balance between cost and performance. In general, using thinner coat systems is a trend moving forward as it will save costs.

Reynier (Arkema): Sustainability and high performance are still the driving factors in polymer development for these applications today. In coating markets, these factors are linked. When we speak of sustainability, we include of course the reduction of VOC emissions, but also the fact that we will avoid toxic compounds and the fact that coatings will increase the service life of steel structures.

Another approach to sustainability is to reduce the number of coating layers applied. Traditionally, anticorrosive protection is achieved using at least two layers; the primer and the topcoat. Principal

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–Mark Langille, Ph.D., ANGUS Chemical Company

requirements for a primer include adhesion, corrosion resistance and water resistance (barrier properties). The topcoat's main properties are exterior UV durability, dirt resistance, chemical resistance, and appearance (color and gloss). The development of binders capable of use in single-coat DTM coating applications can, in certain situations, enhance sustainability.

Tyre (Alberdingk Boley): Lowering VOC content is still a factor driving most formulation development. Other sustainability trends affecting DTM coatings include the use of heavy metal-free anticorrosives and the incorporation of renewable content via plant-based monomers versus petroleum based. Designing products with better adhesion profiles to difficult substrates and better oil resistance are also important targets.

Monaghan (Specialty Polymers): In addition to the desire for low-VOC formulations, we find companies looking for higher-performance waterborne coatings with a better balance of adhesion and corrosion resistance. These benefits have to be delivered in a polymer with a cost similar to existing technology polymers. If required properties can be achieved without using multiple additives used for corrosion or UV protection, this would simplify the formulation and reduce compatibility problems.

LeFever (EPS): The regulatory environment is what I see as the primary driver of the technology. There seems to be a broader adoption of VOC regulations across the country, and different jurisdictions are requiring the sale or use of lower-VOC coating products. Some of these jurisdictions are in areas that have historically permitted the use of higher-VOC solventborne products. Another driver is the increased demand for high throughput in coatings applications. High throughput requires faster dry times for immediate storage and faster return-to-service times.

Jones (BASF): Waterborne DTM performance continues to be a key driver. End-users desire DTM formulations that can achieve longer corrosion resistance (e.g., for a C3 environment, ISO 12944) with thinner applications (< 2 mil) and lower VOC levels (< 50 g/L). At the same time, innovation for raw materials and technologies that are less hazardous for the applicators and the environment is increasingly important. Raw materials from renewable feedstocks are actively being evaluated for waterborne DTM coatings.

Brashear (BYK): From my perspective the most visible trends driving R&D and innovation in waterborne DTM coatings are:

- Regulatory/VOC restrictions: Environmental regulations and VOC restrictions have long been a driving factor in continued development of waterborne technologies in the coating market. Depending on one's geographical location, VOC restrictions for coatings systems could range from > 400 g/L to as little as 100 g/L VOC.
- Safety/exposure/clean-up concerns of solvent-based systems also contribute to the greater acceptance of waterborne DTM coatings. Coatings manufacturers are ultimately looking to deliver safer products to end-users. There are even positive "social implications" for offering products that are deemed to be greener/safer for the environment and end-users.
- Performance: Advancements in waterborne binder technologies have allowed the performance of waterborne DTM systems to equal or in some cases exceed that of their solventborne counterparts.
- Portfolio management: Companies with broader geographic supply footprints are more likely to produce coatings that meet the most stringent requirement in their respective geographies. For example, a coating producer that has a waterborne DTM coating that is 100 g/L capable and offers equal performance to a higher-VOC solventborne system might consider consolidating its smaller-volume product offering to the waterborne system to maximize operational efficiencies.

Padaon (Dow): China is leading the way when it comes to conversion from solventborne to waterborne systems. Regulations and sustainability are big drivers in many parts of the world. However, in North America, various formulators and manufacturers are opting for sustainable solutions in the absence of stringent and enforced regulations. Formulators that have a global footprint want to harmonize their product portfolio across regions due to a push for more sustainable products. In North America, local formulators are seeing the trends in China and Europe and proactively preferring sustainable solutions to stay ahead of the game. Many formulators and applicators are expecting that the United States will have more stringent VOC regulation in coming years. Also, when sustainability is discussed, the scope is not just limited to a switch from solventborne to waterborne systems, but also encompasses the replacement of materials of concern, such as alkylphenol ethoxylate (APEO) surfactants and certain classes of biocides.

We are continuously working on the next generation of waterborne acrylic DTM binders, looking for advances in corrosion, adhesion, hardness, low VOC, appearance, exterior durability, and ease of use. The advances that happened during the last couple years were geared toward development of a water-based binder that demonstrates formulation robustness and can be very forgiving to different additives used as ingredients across a spectrum of formulation spaces.

"Waterborne DTM paints can have better exterior gloss retention and can have better impact resistance than solvent-based DTM paints, which can lose gloss or embrittle with age. It is also generally possible to get faster drying and lower VOC products with waterborne DTMs."

–Gregory Monaghan, Specialty Polymers

What are the advantages/disadvantages of waterborne DTM coatings compared to their solventborne and high-solids counterparts, and are there specific applications that are more suitable for waterborne DTM coatings? Are there segments currently using solventborne coatings that should consider waterborne DTM coatings? Are there places where waterborne DTM coatings should not be used?

Ruiz (Solvay): One of the key challenges of waterborne DTM coatings is drying time as compared to solvent-based and high-solids counterparts. In addition, early water resistance is another challenge that needs to be addressed. Marine coatings are predominately solvent-based systems due to the harsh environment. There could be a potential water-based conversion in this application with a water-based epoxy system. It may not necessarily be as a DTM application, but rather a 2- or 3-coat system to replace the solvent-based system. Current investigations are exploring all the different waterborne epoxy options together with emulsion-type hardeners.

Monaghan (Specialty Polymers): It is a perception that solvent-based products are superior to waterborne paints and this bias sometimes prevents development and qualification of waterborne products with equal performance. Since they are much less hazardous to use than solventborne DTM paints and are much easier to clean up, the water-based DTMs are the perfect choice for DIY painters. They also find extensive use for light duty industrial and shop primers. We have not been recommending the waterborne DTM coatings for corrosive environments such as marine settings, but we have found that the waterborne DTM coatings can have better exterior durability than the solvent-based DTM paints. Waterborne DTM paints can have better exterior gloss retention and can have better impact resistance than solvent-based DTM paints, which can lose gloss or embrittle with age. It is also generally possible to get faster drying and lower VOC products with waterborne DTMs.

Brashear (BYK): Advancements in waterborne binder technology are outpacing those for solventborne alternatives. Waterborne DTM coatings are advantaged because they are less toxic, lower VOCs are more easily achieved, and they offer fast return to service (elimination of the primer coat). Waterborne coatings are easy to apply and clean up and offer greater sustainability when factoring in disposal costs associated with solventborne coatings. Disadvantages include more restrictive application conditions (i.e., they are more sensitive to lower temperature and high humidity conditions), flash-rusting concerns, substrate wetting, shelf-life stability, and increased additive demand.

Waterborne DTM systems are best suited for ISO-12944 service environments of C1 to C3, and typically encompass a wide range of light and general industrial maintenance coatings for "noncritical" service environments. There also appears to be a growing trend to use waterborne systems for insulative coatings. It is highly recommended that waterborne DTMs are not used in service environments exceeding C3 as defined by ISO-12944, and nonaqueous systems (solventborne, high solids, and solvent-free) are recommended for critical and/or immersion service environments.

Thorn (Heubach): Due to the higher surface tension of water, more care must be taken when choosing additives for waterborne DTM systems. Balancing the interfacial tension becomes more complex when formulating waterborne DTM systems. Storage and application of waterborne DTMs at low temperatures can also be a problem due to potential freezing. Heated spray application equipment can be utilized when spraying in cold environments, but there could still be incompatibilities between the coating and the metal, due to a reduction in the metal temperature. This could result in poor film appearance and color development. Application of waterborne DTMs in high humidity environments (> 85% relative humidity) can also result in poor film appearance and color development.

Langille (Angus): The broader use of waterborne DTM coatings is limited by their performance. However, recent advances in resin technology and an improved understanding of additive and ingredient selection have made waterborne DTM coatings more accessible than ever before. Formulators can now consider replacing many types of light-duty solventborne coatings with waterborne DTM coatings without major loss of performance. This change can yield time and cost savings while also positively contributing to organizational sustainability goals.

Jones (BASF): The biggest advantage for waterborne DTM coatings is their ability to provide good appearance (high gloss) and protection at lower VOC levels than their solventborne counterparts. The disadvantage for waterborne DTM coatings is that they are unable to meet the long-term corrosion resistance of their counterparts. Solventborne technology is still needed for protection in ISO 12944 environments of C4 and above for DTM applications. Waterborne DTM coatings are not suitable for environments with high salinity (near a coastline or offshore applications).

Tyre (Alberdingk Boley): Advantages include less odor compared to solvent-based coatings. Acrylic DTMs have a reduced tendency to yellow, and as a class are more flexible over time due to their limited oxidative cure. In addition, polymers with higher molecular weight can be supplied while maintaining higher solids levels. One disadvantage is that waterborne DTMs will not attain as high gloss or distinctiveness of image as solventborne coatings. Waterborne coatings are also less forgiving on application due to the impact of humidity, heat, and open time constraints. Waterborne coatings are more difficult to apply in the automotive OEM market, with investments needed for spray equipment and ovens.

Padaon (Dow): Waterborne DTM coatings are easier to work with and apply in comparison to solventborne and high-solids technology, while delivering lower VOC. Relative to solventborne technology, waterborne coatings allow formulators and end-users to decrease the use of hazardous solvents; in return, lower VOC levels are achieved, leading to increased safety conditions in the workplace and improved air quality. Waterborne DTM coatings can also enable the reduction of coating layers (e.g., going to one coat from two coats) to further simplify the application process and reduce waste. High-solids coatings facilitate high performance while contributing relatively low VOC levels, but not always to the level provided by waterborne systems. In addition, high-solids coatings typically come with a high cost-in-use (due to premium pricing of the materials), and higher viscosity, resulting in the need for specialized equipment to effectively process and apply these systems.

General industrial finishes utilized for steel building materials (such as I-beams and metal fixtures) and specialized machinery often leverage solventborne alkyd technology for their fast-dry capability, their ability to adhere to contaminated surfaces, and their high-gloss potential; these are properties often achieved through this relatively low-cost technology. Many advancements have been made by raw material suppliers to match these performance benefits through a waterborne DTM offset, giving end-users an opportunity to reduce the workplace hazards that come with solventborne alkyd coatings, all while maintaining coating performance.

Baikerikar (Dow): Water-based binders (considering all available waterborne chemistries/technologies) can be used in almost all applications where environmentally friendly and sustainable solutions are required. However, the environmental conditions (temperature, humidity) at the time of application need to be carefully considered when assessing the viability of waterborne DTMs, due to their strong influence on final performance. For instance, high humidity can prolong dry time, and low temperature can lead to film cracking of a coating with an unoptimized coalescent package. As a result, uncontrollable environmental conditions must be considered prior to working with waterborne DTM coatings. In addition, applications that require continuous exposure or immersion to aggressive chemicals can also present a challenge for waterborne DTM coatings.

Gichuhi (ICL): Solvent-based paints contain VOCs and hazardous air pollutants (HAPs) that contribute to air pollution and cause numerous adverse health effects, including eye and skin irritation, and central nervous system effects. Although high-solids solvent-based paints (> 60% solids) will have lower VOCs and better corrosion performance, the conditions during their application will have a major impact on their drying time. The higher viscosity of high-solids coatings can be extremely thick and difficult to apply.

LeFever (EPS): Waterborne DTM coatings offer several advantages, such as exterior durability, when compared to legacy alkyds. They also deliver gloss and color retention, while providing comparable corrosion performance. In light-to-medium-duty industrial applications, waterborne systems can achieve required performance levels and offer ease of cleanup and reduced exposure to potentially hazardous materials. By using waterborne products, the hazards associated with handling solventborne coatings, like flammability risk and exposure to solvent vapor, are substantially reduced. Waterborne products are also more convenient for use in facilities that don't have VOC reclamation systems. To varying degrees, most industrial segments are evaluating a shift from solventborne to waterborne systems. There are still applications where waterborne coatings present a challenge, like marine environments or applications involving water immersion or requiring a very high degree of chemical resistance.

Ananthachar (Evonik): An advantage of waterborne DTM coatings is they require less complex application methods. Waterborne DTMs can be applied using standard conventional or airless spray systems, while many high-solids coatings require plural component spray. Applications using waterborne DTMs are limited mostly to C3 corrosive environments today, but the advancement of technology in waterborne systems like waterborne HYBRIDUR® Acrylic-Urethane resins and Acrylic-Epoxy Hybrid resins and the introduction of the next generation of waterborne epoxy curing agents, such as Anquamine® 469, is enabling conversion from solventborne coatings to waterborne systems in important markets like container coatings in Asia.

What are some recent products that you've introduced to the market for waterborne DTM coatings, and what are their main benefits versus existing products?

Monaghan (Specialty Polymers): We have developed a line of styrene acrylic polymers modified with epoxy, giving improved corrosion, adhesion and very good exterior durability. The first polymer in this line was RAYKOTE® 2020 that was introduced in 2018. This polymer can be formulated into DTM paints at under 100 g/L VOC. Since that time, we have developed new polymers using that platform, introducing variants that have self-crosslinking or higher glass transition temperature (T_g).

LeFever (EPS): The latest polymer from Engineered Polymer Solutions for DTM coatings is EPS® 2580. It can be formulated at < 50 g/L VOC and can be used in numerous industrial applications. The primary coatings segments for EPS 2580 include rail, industrial maintenance, and general industrial applications. EPS 2580 provides exceptional thin-film corrosion resistance. The corrosion performance approaches that of competitive solventborne resins. Additionally, this product offers rapid hardness development and early hot-block resistance.

Langille (Angus): The technical team at ANGUS has recently looked at how to optimize waterborne acrylic DTM coatings with amino alcohol dispersants, and while many formulators are familiar with AMP-95™, our studies have identified that DMAMP-80™ can offer exceptional improvements to gloss, contrast ratio, weatherability and corrosion resistance. The greater hydrophobicity and higher volatility of DMAMP-80 as compared to AMP-95 makes it a particularly good fit for low-VOC waterborne industrial coatings. ANGUS is also in the final stages of the initial registration process with the U.S. Environmental Protection Agency for a new-to-world tertiary amine molecule that has shown outstanding ability to improve corrosion resistance in waterborne metal coatings.

Tyre (Alberdingk Boley): Our most recent development for the metal coatings market is ALBERDINGK® AC 2433, which delivers superior wet adhesion and corrosion resistance properties at an attractive price-performance ratio. It is suitable for DTM and primer applications and can be formulated at < 50 g/L.

Padaon (Dow): The quest to get lower and lower VOC has put pressure on resin manufacturers to select monomers, raw materials and processes that contribute very minimally to total VOC. Because resin is such a large component of any coating and affects so many coating properties, many advancements depend on improvements in the design of the resin system. For example, advancements in 1K waterborne acrylic DTMs have included more hydrophobic binders that facilitate coatings with greater corrosion resistance and binders with complex latex morphologies that allow good hardness properties at low-VOC content. These advancements are driven by end-user needs for improvements in these properties. In particular, a need for low-VOC waterborne acrylic DTM finishes below 50 g/L with good hardness (related to properties such as block, tack, dirt-pickup resistance) has been expressed by the industry, and Dow has responded with several products to meet that goal, including MAINCOTE™ 4950 and MAINCOTE 5045.

Dow has most recently introduced MAINCOTE 5045, which facilitates DTM coatings below 25 g/L VOC while demonstrating industry-best corrosion resistance, adhesion and durability. MAINCOTE 5045 is the latest in our product line of DTM binders that utilizes the AVANSE™ resin technology, which changes the way in which latex and pigment particles interact, resulting in an optimal film morphology that enhances barrier properties. Another key development addressing needs in the DTM coatings market is the MAINCOTE Acrylic-Epoxy Hybrid (AEH) technology. The MAINCOTE AEH emulsions are acrylic latex particles imbibed with epoxy-functional resin and can be crosslinked in a 2K coating with either waterborne amine hardeners or carboxyl-functional acrylic latexes such as MAINCOTE AE-58 and AE-610. The choice of crosslinker allows a range of performance. In our additive portfolio, TAMOL™ 2028 dispersant was recently introduced for better dispersion of organic pigments and improved corrosion.

"Jet-milled and easy-to-disperse pigments are a mainstay for waterborne DTMs particularly in cases where high gloss is desired."
–Anthony Gichuhi, Ph.D., ICL Phosphate Specialty

Gichuhi (ICL): Recent products for the waterborne DTM market include liquid flash-rust inhibitors and liquid post-addable corrosion inhibitors (HALOX® 570 LS). In the DTM roof coating segment, we recently introduced a heavy metal-free anticorrosive pigment based on hydroxyapatite (tricalcium phosphate) that also improved the dirt-pickup resistance of white and colored elastomeric acrylic roof coatings and increased the solar reflectivity and emissivity of the coating. HALOX CW-314 allows coaters to apply a corrosion-resistant DTM and saves on labor by eliminating the primer layer altogether. Jet-milled and easy-to-disperse pigments are a mainstay for waterborne DTMs particularly in cases where high gloss is desired.

Reynier (Arkema): Arkema has also introduced a new waterborne product, SYNAQUA® 9511 acrylic emulsion polyol, specifically designed for 2-pack industrial coatings for plastic and metal. This new resin offers a range of performance attributes typically found in solventborne polymers, including good hardness, adhesion, toughness (balanced with flexibility), gloss, weatherability, and fast drying. It is suitable for monocoat systems for plastic and glass substrates as well as topcoats for metal application in 2K or 1K stoving applications.

Brashear (BYK): One disadvantage of waterborne coatings systems is that they often require greater use of additives to achieve acceptable levels of performance. During the past few years, BYK has begun to highlight its more recent waterborne-additive portfolio developments more proactively. This is particularly true when looking at wetting and dispersing additives.

Many wetting and dispersing additives on the market do an excellent job of effectively allowing high pigment loading and reduced mill-base viscosities in waterborne systems, but this often comes with the cost of negative impact on the film and barrier properties of the system. Corrosion resistance and moisture resistance often suffer due to increased hydrophilicity in the cured film from the wetting/dispersing additives. DISPERBYK-2080 and DISPERBYK-2081 were introduced in the market a few years ago to address this problem. Both work on the principle of increasing hydrophobicity as the coating cures, and by increasing the hydrophobicity of the cured system we have seen tangible improvements in film and barrier properties such as early moisture, stain, and corrosion resistance properties. Continued advancements have led to the more recent commercialization of DISPERBYK-2018 and DISPERBYK-2019.

Defoaming is also a critical component when considering the impact on film and barrier properties. BYK-1789 is a recent development addressing the defoaming/deaeration demands of airless spray applied waterborne systems. The combination of hydrophobic particles and unique polymer structure yields a highly compatible defoamer that exhibits exceptional performance in eliminating both macro and micro foam.

Jones (BASF): BASF has recently introduced ACRONAL® PRO 770 NA into the waterborne DTM coatings market. It is low-VOC capable (< 50 g/L) and offers superior corrosion protection with good early water and humidity resistance. It also has good adhesion to various metal substrates. It is an APEO- and zinc-free acrylic dispersion designed for 1K waterborne formulations, with recommended applications that include DTM protective coatings, interior/exterior industrial and institutional maintenance, as well as interior/exterior general industrial coatings.

Ananthachar (Evonik): We are aware of emerging trends in Asia to move away from solventborne technologies and have several initiatives underway to address the emerging trend. Our best current recommendation for a waterborne epoxy curing agent in a DTM coating is ANQUAMINE 419, a modified aliphatic amine supplied at 60% solids in water and methoxypropanol. Intended for use with waterborne solid epoxy dispersions in two-component, ambient-cure waterborne epoxy coatings, it delivers excellent corrosion and adhesion properties in anticorrosive primers, white-gloss DTM coatings and clear coats. We are pleased to introduce the next generation waterborne curing agent ANUQAMINE 469 for the container coatings market.

Thorn (Heubach): Most recently we have introduced our HEUCOTINT™ W Line. This is our waterborne, APE-free, VOC-free point-of-sale line of colorants for the market. It was designed to be compatible with waterborne architectural coatings, EIFS, stucco, waterborne wood stains, and light industrial waterborne coatings. We have also added a complementary line of liquid flash rust/in-can rust preventatives to our line of HEUCOPHOS®/HEUCORIN® anticorrosives. Included in this line is our HEUCOFLASH™ LQ1, which is a nitrite-based chemistry. The HEUCOFLASH LQ1 contains a lower level of nitrites compared to commonly used, competitive flash-rust inhibitors. Our HEUCOFLASH LQ2 is totally nitrite-free. We have also seen improvements when using the HEUCOFLASH LQ2 in waterborne systems applied over weld seams.

Ruiz (Solvay): Our Sipomer® line of products is intended to promote adhesion to a variety of substrates. Sipomer PAM monomers, including Sipomer PAM-600, promote adhesion to a number of metallic substrates thereby improving corrosion inhibition of the coating. These monomers, when incorporated into the resin polymer, also exhibit improved film properties such as gloss and color acceptance in the final coating.

In addition, we recently introduced an innovative emulsifier, Reactsurf® 0092, for waterborne epoxy systems. Waterborne industrial coatings formulated with Reactsurf 0092 demonstrate excellent corrosion resistance, superior adhesion, and other key performance indicators equivalent to solvent-based coatings, but with the added sustainability benefit of very low levels of VOCs. ❊

PART II OF THIS Q&A WILL APPEAR IN THE AUGUST-SEPTEMBER ISSUE OF *COATINGSTECH*.

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