# **PUSHING THE LIMITS ON VOCS:**

# High Performance Waterborne Acrylic Direct-To-Metal Coatings



by Laura Vielhauer, Leo Procopio, Mary Kate McCrea, and Bridget Dombroski

The Dow Chemical Company

One of the new norms of coating development and reformulation efforts is the drive to lower levels of volatile organic compounds (VOCs), often to meet increasingly strict regulations and specifications. Pushing VOCs to lower levels and performance to higher levels can also offer a more sustainable coatings solution for the end user. Lowering VOC while maintaining (or improving upon) high performance is often the goal when developing a new formulation, but the two objectives can be at odds with each other. For waterborne acrylic direct-to-metal (DTM) finishes and primers, a key challenge is to lower VOC while maintaining film hardness and good film formation. Hardness affects film properties such as block, tack, and dirt pickup resistance, while film formation is critical for latex DTM coatings because it strongly influences barrier properties, i.e., corrosion resistance. The industry is currently looking for acrylic resins which can be formulated below 50 g/L VOC, and yet have excellent hardness, corrosion resistance, and durability properties. The development of a new waterborne binder that offers this unique balance of properties in coatings for the protection of steel and other metals is described. Application testing results demonstrate how the unique composition and morphology of the latex polymer and proper formulating techniques are keys to gaining the desired performance balance. An evaluation of corrosion-resistant DTM finishes with VOC levels under 50 g/L is provided, including comparisons with currently available commercial technologies ranging in VOC levels from 200 g/L to under 50 g/L.

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### INTRODUCTION

Newer products in the paint and coatings industry have a lower impact on the environment without sacrificing performance properties, and in some cases the performance is improved over existing technology. The ways to create more sustainable coatings include formulating with lower emissions of hazardous air pollutants (HAPs) and volatile organic compounds (VOCs), or extending maintenance cycles by producing higher performing coatings that last longer with improved durability. Two common routes to lowering emissions are waterborne and high solids coatings. Among the choices of waterborne technologies, waterborne acrylic coatings have a large presence within the industrial maintenance market. A recent market study places waterborne acrylic latex coatings at approximately 24% by volume of the industrial maintenance market in the United States.<sup>1</sup> The only generic technology with a larger share than waterborne acrylic coatings is epoxy coatings, at approximately 35% (Figure 1).

Waterborne acrylic coatings are typically onecomponent, and are found in use mainly in light to medium duty service environments such as those described by the C1 through C3 categories within ISO 12944. Examples of typical uses in these categories include the protection of steel and concrete for applications such as bridges, railcars, and manufacturing and chemical plants. The performance of acrylic latex coatings has improved over the years, and today's versions have high gloss, corrosion resistance, and durability. Acrylics are a favorable choice due to their low VOC levels, low odor, low flammability concerns, and less hazardous disposal. The VOC levels of most waterborne acrylic primers and DTMs are below 250 g/L, with the latest generations formulated below 100 g/L. The decrease in VOC levels has been driven by regulatory limitations, such as the 100 g/L limit set for industrial maintenance coatings in the South Coast Air Quality Management District (SCAQMD) of southern California in 2007.2

Regulations are only becoming more rigorous, so resin suppliers and coatings manufacturers continue to push VOC levels to even lower values. For waterborne acrylics, some paint manufacturers are also selling products such as primers and DTM finishes into the architectural market, where different and lower VOC limits exist due to the use of the coatings by homeowners and DIYers. Acrylic technology has to overcome some significant challenges at lower VOC levels. Balancing properties related to hardness (such as tack, block resistance, and dirt pickup



**Figure 1**—Technology distribution by percent volume of industrial maintenance coatings used in the United States for the year 2010.'

resistance) while maintaining the good film formation necessary for the development of barrier properties is a key challenge in the design of a new acrylic latex polymer capable of these lower VOC levels.

This article describes the performance of a new acrylic latex polymer for primers and DTM finishes with VOC levels under 50 g/L. The low VOC target is in anticipation of future regulations for industrial coatings, as well as taking into consideration that DTM finishes are being promoted into the architectural market area, which has more limiting VOC regulations. The technology used in the polymer design also lends itself to high performance properties, including excellent durability and corrosion resistance. The performance of this new resin will be demonstrated through comparisons with commercial DTM gloss finishes that are available at various VOC levels.

#### **EXPERIMENTAL**

The acrylic latex polymer AC-1 was prepared by emulsion polymerization with a final weight solids of 48.5% and pH 9.0. AC-1 is a selfcrosslinking acrylic, made without the use of APEO surfactants, and has a minimum film formation temperature (MFFT) of 14°C. It was formulated for this study into a gloss white DTM finish at under 50 g/L VOC using 6% on polymer solids of dipropylene glycol n-butyl ether (DPnB) as coalescent. Table 1 shows the gloss white formulation DTM-1 used in this study. In other formulations, a nonvolatile coalescent (Optifilm Enhancer 400) was added at 1-2% (on polymer solids) to facilitate better film formation. Formulation DTM-2 is the same as DTM-1 except for an additional 1% of the nonvolatile coalescent, and formulation

Table 1—Gloss White Direct-to-Metal Formulation DTM-1

Ingredients	Weight (lb)
Grind:	
Water	60.00
Dispersant	7.43
Surfactant	4.00
Defoamer	1.00
Ammonia (28%)	2.00
Titanium dioxide	210.00
Grind for 30 minutes before adding:	
Water	20.00
Grind Sub-Total	304.43
Letdown:	
AC-1 Resin	527.79
Water	100.00
Ammonia (15%)	2.00
Add grind from above	
Surfactant	0.46
DPnB	15.36
Sodium nitrite (15%)	9.00
Water	22.57
Rheology modifier (ICI driver)	24.00
Rheology modifier (KU driver)	3.00
Total	1008.61
Paint properties	
Total volume	100.00 gal
PVC (%)	17.5
Volume solids (%)	36.0
Coalescent level (on polymer) (%)	6.0
VOC (calculated)	~50 g/L

DTM-3 has an additional 2% nonvolatile coalescent. The only pigment used in the formulations was titanium dioxide, at a pigment volume concentration (PVC) of 17.5%.

The experimental formulations (DTM-1, DTM-2, and DTM-3) were compared to three commercial DTM coatings, described in *Table* 2. The three coatings were supplied at various VOCs, as described in their technical data sheets as less than 50 g/L (COM-1), less than 100 g/L (COM-2), and less than 200 g/L (COM-3).

Panels for corrosion and humidity resistance testing were prepared using 4 in. x 12 in., 16-gauge abrasive-blasted hot rolled steel panels or smooth cold rolled steel panels. Blasted panels were abrasive blasted to a SSPC-SP 5 white metal finish with a 2.0 mil (50  $\mu$ m) profile (supplied by Custom Lab Specialties). Coatings were applied by drawdown to give a dry film thickness (DFT) of 3.0 mil (75  $\mu$ m). Panels were allowed to dry for one week at 21°C (70°F) /50% relative humidity (RH). Corrosion panels were scribed with a single vertical two-inch scribe prior to exposure. Accelerated corrosion resistance was tested according to ASTM B117. Humidity resistance was evaluated on cold rolled steel in a Cleveland condensation cabinet according to ASTM D4585.

Panels for gloss, gloss retention, hardness, tack, and dirt pickup resistance were prepared using 4 in. x 12 in. chromate-treated aluminum panels (supplied by ACT Laboratories). Coatings were applied by drawdown bar at approximately 3.0 mil (75 µm) DFT and allowed to dry for one week at 21°C (70°F)/50% RH prior to testing, except where noted below. Accelerated gloss retention was tested according to ASTM G154 in an ultraviolet (UV) light weathering cabinet and using UVA-340 bulbs. The panels were exposed to a repeating cycle consisting of eight-hour UV light exposure at 60°C (140°F, black panel temperature) and four hours of condensation exposure at 50°C (120°F). Panels were periodically removed from exposure to measure gloss and color. Konig hardness was measured according to ASTM D4366 using a TQC SP0500 pendulum hardness tester. Pencil hardness was evaluated according to ASTM D3363. Tack was measured using a Zapon tack test, consisting of placing a bent one-inch-wide metal strip on the coating, with a designated weight placed on top of the strip for 10 sec. After removal of the weight, if the strip tips over immediately, it is considered a pass. The highest weight (up to 500 g) is recorded where a passing grade is attained. Hardness and tack were evaluated at various dry times, for example, at one and seven days. Panels for dirt pickup resistance were exposed to UV-A light for 24 hr in an accelerated cabinet before the test was run, to allow the self-crosslinking mechanism to proceed. Dirt pickup resistance was tested by applying an aqueous brown iron oxide slurry on the panel surface and allowing it to dry at room temperature for four hours, followed by rinsing the panels with tap water and gently wiping the surface with cheesecloth. Y-reflectance values were measured before the dirt was applied and after it was removed. The change in Y-reflectance is used as a measure of dirt pickup resistance, with a number closer to zero being better.

Table 2-Description and Formulation Details of Commercially Available Controls

Paint #	COM-1	COM-2	COM-3
Description	Commercial Gloss White	Commercial Gloss White	Commercial Gloss White
	WB Acrylic DTM	WB Acrylic DTM	WB Acrylic DTM
VOC (g/L)	< 50	< 100	< 200
Volume solids (%)	35	40	38
pН	9.2	9.5	8.9



**Figure 2**—Different latex morphologies are possible technical approaches to balancing VOC levels and hardness properties.

Panels for block resistance and low temperature film formation (LTFF) were prepared by drawdown of the coatings onto a Leneta chart at approximately 1.0-2.0 mils DFT. The coatings were dried for either one or seven days at 21°C (70°F)/50% RH before evaluating block resistance. Block resistance was measured by cutting two 1.5 in. x 1.5 in. strips from the chart, laying two strips face-to-face forming a cross on a flat surface, and placing a #8 rubber stopper on the cross-section of the strips and a one-kilogram weight on top of the rubber stopper. Block resistance was evaluated: (1) after 30 min at 50°C (120°F), and (2) after 16 hr at room temperature. The following 0 to 10 scale was used to rate the coatings for tack and film damage: 10-no tack/perfect; 9-trace tack/ excellent; 8-slight tack/very good; 7-slight tack/ good; 6-moderate tack/good; 5-moderate tack/ fair; 4-severe tack, no seal/fair; 3-5-25% seal/ poor; 2-25-50% seal/poor; 1-50-75% seal/ poor; 0, complete seal/very poor. Low temperature film formation was evaluated by drying the coatings overnight in a constant temperature/humidity room at 4.5°C (40°F) and 40% RH. Panels were rated for cracking and other film defects. A pass denotes no cracking, and a failure denotes the formation of cracks across the film surface.

Adhesion was measured on smooth cold rolled steel (Q-Lab Type R-412 dull matte finish) and untreated aluminum (Q-Lab Type A-412) panels. Coatings were applied by drawdown to give approximately 2.0 mil (50 µm) DFT, and dried for one week before testing crosshatch tape adhesion according to ASTM D3359. Impact resistance and mandrel bend flexibility was evaluated on cold rolled steel panels prepared in the same manner as for the adhesion testing. For impact resistance, both direct and reverse impact were measured, and reported as the highest impact (units of in.-lb) which resulted in a pass with no film cracking. For mandrel bend, one-inch wide strips were cut from the panel, and bent over bars of varying diameter. The smallest diameter resulting in a pass (no cracking) is reported.

# **RESULTS AND DISCUSSION**

A good balance of hardness properties and film formation is a key challenge in achieving low VOC levels in acrylic coatings. Properties related to hardness such as block and print resistance, tack, and dirt pickup resistance are important in preventing damage to the coating and maintaining its aesthetics.

The quality of film formation is a major factor in the barrier properties of acrylic latex coatings. For a one-component acrylic DTM finish, such as the experimental formulation DTM-1 described in *Table* 1, prevention of corrosion is mainly through the barrier properties of the coating. Inhibitive pigments, such as zinc phosphate, typically have a detrimental effect on gloss, so are recommended for use in lower sheen coatings. Coalescing solvents, necessary for the film-formation process in latex polymers, are the main source of VOCs in a waterborne acrylic coating.

Simply removing coalescents from an existing formulation is not a feasible solution, as this would lead to poor film formation. Replacing volatile coalescents with a nonvolatile plasticizer is an option, but hardness properties are sacrificed because the plasticizer will remain in the film. The use of a softer polymer (i.e., a polymer with a lower glass transition temperature) is also an option, but again film hardness is sacrificed. A number of systems have been developed using latex polymers with complex morphologies, in which there is both a soft phase for aiding film formation and a hard phase to reinforce the film and minimize the impact on hardness. Some examples of the different morphologies, such as core-shell structures or blends of hard/soft latexes, are depicted in Figure 2. This approach can aid in getting to lower VOC, but careful design of the polymer and the coating formulation is necessary to ensure good film formation and barrier properties.

Achieving good film formation is a key factor to reaching the maximum corrosion resistance of acrylic latex DTM coatings. The new polymer AC-1 in the present study relies on a unique morphology to



Figure 3—SEM image of a latex-pigment composite particle.

achieve good film formation and hardness properties at low coalescent levels. In addition, to achieve the highest available performance in a DTM coating for other properties including corrosion resistance, gloss, and durability, another technology has been incorporated into the polymer design.

The binder technology of AC-1 relies on a novel interaction of the latex particles with the pigment particles, leading to the formation of latex-pigment composites. The use of latex-pigment composites has been described previously as a means to high performance in a waterborne acrylic DTM coating.<sup>3</sup> The composites are composed of pigment particles with a layer of latex particles adsorbed onto their surfaces. An image from a scanning electron microscope (SEM) shows an example of a composite particle in *Figure* 3.

To understand how the formation of the composites aids in the performance of the dry film, first consider how the film-formation mechanism affects the film structure in a pigmented coating using a conventional latex. Figure 4 shows a schematic of this film-formation process. Typically, a pigment dispersion is mixed with a latex dispersion to form the wet coating. In the wet state, the ideal situation is one where all polymer and pigment particles stay well separated. After a coating is applied, however, some agglomeration of pigment will usually occur as water and neutralizer evaporates from a drying film and particles become less stable towards agglomeration. As the particles pack together and coalescence of the polymer occurs, the final dry film will contain a certain level of pigment agglomerates. The pigment-pigment interfaces of the agglomerates can act as weak links in the barrier, allowing water and electrolytes through the film more easily and causing corrosion at the substrate surface. In addition, bare pigment particles will extend beyond the film surface, which then causes surface roughness and results in lower gloss.

In a coating based on the latex-pigment composites, a different process occurs, as depicted in Figure 5. The coating is made in the same manner, but during the mixing process, the latex particles begin to adsorb onto available pigment surfaces to form the composite particles. The layer of adsorbed latex acts as a spacer between pigment particles, and prevents agglomeration in the wet state and as the film is drying. This leads to fewer pigment-pigment agglomerates, as well as a more homogeneous distribution of pigment in the final film, and results in better barrier properties and corrosion resistance. In addition, because there are fewer bare pigment particles protruding from the film surface, the surface is more polymer-rich and smoother than in the conventional latex coating. This leads to higher gloss potential without a need to lower molecular weight of the polymer. It has also been shown previously that the formation of latex-pigment composites leads to better gloss retention under UV light exposure, and it has been suggested that this is due to a more homogeneous distribution of titanium dioxide, which can act as a UV absorber and prevent the UV light from penetrating too deeply into the polymer matrix.

In addition to the features mentioned above, polymer AC-1 has self-crosslinking functionality that facilitates better dirt pickup resistance than might typically be achieved in a low VOC coating. Light crosslinking of the polymer prevents dirt particles from sticking to the surface, and also aids in durability of the coating. Keeping in mind the three features of (1) unique latex polymer morphology, (2) formation of latex-pigment composites in a pigmented coating, and (3) self-crosslinking, the results of the evaluations and the comparison to commercially available DTM coatings are discussed below.

In this study, the new polymer AC-1 was formulated at VOC levels of under 50 g/L, and compared to commercial products formulated at levels ranging from 50 to 200 g/L. Table 3 shows results for two formulations based on AC-1. Both DTM-1 and DTM-2 contain 6% dipropylene glycol n-butyl ether as the volatile coalescent in essentially the same formulation, except that DTM-2 is formulated with an extra 1% of a nonvolatile coalescent. Both DTM-1 and DTM-2 were formulated with a rheology suitable for application by brush, roll, or spray. Gloss is similar to two of the three commercial products, with 60° gloss in the low 80s. The highest VOC commercial product, COM-3, had a slightly lower gloss by about 10 units. If the environmental condition in which a coating is applied is less than optimal, low temperature film formation is a critical property for a coating and is tested by drying the films at 40°F and 40% RH. Under these condi-







**Figure 5**—Film formation mechanism for a pigmented coating based on latexpigment composites.

Table 3–	<ul> <li>Comparison of</li> </ul>	Wet Coating and Dr	y Film Properties fo	or Experimental ar	nd Commercial DTM Coatings
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Paint #	DTM-1	DTM-2	COM-1	COM-2	COM-3
Description	Experimental DTM based on AC-1	Experimental DTM based on AC-1	Commercially available WB acrylic DTM	Commercially available WB acrylic DTM	Commercially available WB acrylic DTM
% Coalescent (on polymer solids)	6%	7%	not reported	not reported	not reported
VOC (g/L)	< 50	< 50	< 50	<100	< 200
Stormer viscosity (KU)	95	98	116	79	87
ICI viscosity (poise)	0.9	0.95	0.8	0.8	0.6
pН	9.2	9.3	9.2	9.5	8.9
Gloss (20°/60°)	58 / 81	59 / 82	65 / 84	57 / 83	35 / 73
LTFF (40°F/40% RH)	slight cracking	pass	fail	pass	fail
Konig hardness (sec)					
1 day	10.8	8.5	16.5	7.9	8.5
7 days	17.2	14.3	17.2	8.5	18.7
14 days	20.1	17.2	17.2	8.5	21.5
36 days	29.8	24.1	22.7	14.1	35.5
Pencil hardness					
1 day	6B	<6B	5B	6B	6B
7 days	5B	5B	4B	4B	4B
Zapon tack test (g)					
1 day	200	20	500	500	250
7 days	500	500	500	500	500

tions, COM-1 and COM-3 failed badly, with severe cracking. DTM-1 had some slight cracking at 40°F, but the results show that the small amount of nonvolatile coalescent in DTM-2 improves the film formation and passes the evaluation with no evidence of cracking.

Table 3 lists some of the hardness properties measured. The experimental formulations compare well to the commercial coatings in Konig and pencil hardness. The addition of the non-volatile coalescent in DTM-2 leads to a small sacrifice in both Konig and pencil hardness relative to DTM-1. The commercial









coatings have an advantage in tack after a short dry of one day, but all of the coatings performed well after seven days. DTM-2 has lower tack at one-day dry compared to DTM-1, due to the plasticizing effect of the extra nonvolatile coalescent. *Figures* 6 and 7 show the results of block resistance testing, after one- and seven-day dry times, respectively. Block tests comparing DTM-1 with the commercial products were carried out under both room temperature (21°C/16 hr) and oven (50°C/30 min) conditions.

The largest differences are observed for the one-day dry and oven condition, which is expected to be the most difficult situation. After a short dry time, the film may still contain some coalescent which can plasticize the film. The best block resistance under this condition was observed with DTM-1, and—perhaps surprisingly—the worst was for COM-3, the highest VOC (200 g/L) coating, and which is presumably based on a harder binder. However, harder binders require more coalescent, and if a coalescent with low volatility is used, it will remain in the film and make the film softer, which presumably occurred with COM-3. Under the other

test conditions, DTM-1 is equivalent to or slightly better than the commercial products.

Dirt pickup resistance is shown in Table 4. After a short exposure to UV light to allow the crosslinking to occur, the dirt pickup resistance of DTM-1 is better than the commercial coatings. Gloss retention on UV-A exposure is also observed to be significantly better than the three commercial products, and DTM-1 had excellent performance after more than 1000 hr of exposure. Gloss retention is aided by both the self-crosslinking technology and the formation of latex-pigment composites described above. Both DTM-1 and the 100 g/L COM-2 had good blister and rust resistance after 21 days in the Cleveland condensation cabinet, but the other two commercial coatings had some slight to moderate blistering and rusting. All of the coatings performed very well for impact resistance and flexibility. Adhesion on steel was good for all the coatings except the 50 g/L COM-1, which had significant adhesive failure. On aluminum, both COM-1 and the 100 g/L COM-2 did very poorly, but DTM-1 and COM-3 both had good adhesion on aluminum.



Paint #	DTM-1	COM-1	COM-2	COM-3		
Description	Experimental DTM based on AC-1	Commercially available WB acrylic DTM	Commercially available WB acrylic DTM	Commercially available WB acrylic DTM		
% Coalescent (on polymer solids)	6%	not reported	not reported	not reported		
VOC (g/L)	<50	<50	<100	<200		
Dirt pickup resistance						
Δ Y-reflectance	0.2	7.7	12.87	2.19		
% 60°Gloss retention (QUVA exposure)						
1130 hr	104%	48%	65%	17%		
Humidity resistance (Cleveland condensation cabinet, 21 days)						
Blistering	none	8F	none	6F		
Rusting	none	3G	none	1G		
Adhesion						
Cold rolled steel	4B	2B	5B	4B		
Aluminum	4B	0B	0B	5B		
Impact resistance (in./lb)						
Direct	>140	>140	>140	>140		
Reverse	>140	>140	>140	>140		
Mandrel bend flexibility	1/8 in.	1/8 in.	1/8 in.	1/8 in.		



Figure 8—Corrosion resistance on smooth cold rolled steel panels after 1000-hr ASTM B-117 salt spray exposure. Panels for COM-1 and COM-3 were stopped after 576-hr exposure.



Figure 9—Corrosion resistance on abrasive-blasted hot rolled steel panels after 1000-hr ASTM B-117 salt spray exposure. Panels for COM-1 and COM-3 were stopped after 576-hr exposure.

Results of corrosion testing are depicted in *Figures* 8 and 9, which show photographs of the panels after 1000-hr ASTM B-117 salt spray on smooth cold rolled steel and abrasive-blasted hot

rolled steel, respectively. For corrosion, all three of the experimental formulas were evaluated. As expected, results for DTM-1, DTM-2, and DTM-3 demonstrate that higher levels of coalescent help Figure 10—Summary of properties comparing DTM-1 and commercial DTM coatings.



with corrosion resistance due to the improvement in film formation. So, DTM-3, which contains 2% of the nonvolatile coalescent, outperformed both DTM-1 (0% nonvolatile coalescent) and DTM-2 (1% nonvolatile coalescent). All three coatings contain the same amount of volatile coalescent (6% DPnB), so they are each at 50 g/L VOC. The experimental coatings outperformed the commercial coatings, even those formulated at higher VOC. For COM-1 and COM-3, panels were removed from the testing after 576 hr because of the extreme failures at that point. The enhanced corrosion protection afforded by the experimental formulations is aided by the latexpigment composite technology described earlier.

A final comparison of the new polymer in 50 g/L gloss white direct-to-metal formulation DTM-1 with the three commercial controls is given in *Figure* 10. The spider chart shows a comparison of a number of important properties, and points lying closer to the outer ring of the plot are considered better. The new polymer has the best overall balance of properties. This includes the low-VOC capability of under 50 g/L, good gloss and gloss retention, excellent film formation as demonstrated by the low temperature film formation and good corrosion resistance, and good hardness-related properties such as block resistance and dirt pickup resistance.

## CONCLUSIONS

As VOC limits are pushed even lower, the goal of a high performing waterborne acrylic DTM coating under 50 g/L VOC is achieved through the combination of several novel technologies. First, through a careful design of the polymer composition and morphology, a binder that offers good film formation at low coalescent demand along with good hardness properties is possible. High performance in properties such as corrosion resistance, gloss, and gloss retention is facilitated by the formation of latex-pigment composites in pigmented formulations. The composites lead to better pigment distribution in the dry coating film, and boost performance when compared to conventional latexes. Finally, the selfcrosslinking functionality offers improved dirt pickup resistance, which is important at low VOC levels, as well as UV durability. The unique balance of low-VOC capability and high performance will facilitate use of the waterborne acrylic technology in light- and medium-duty service environments in both industrial and commercial architectural settings.

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#### **AUTHORS**

Laura Vielhauer, Leo Procopio, Mary Kate McCrea, and Bridget Dombroski, The Dow Chemical Company, Northeast Technology Center, 400 Arcola Rd., Collegeville, PA 19426; Ivielhauer@dow.com.