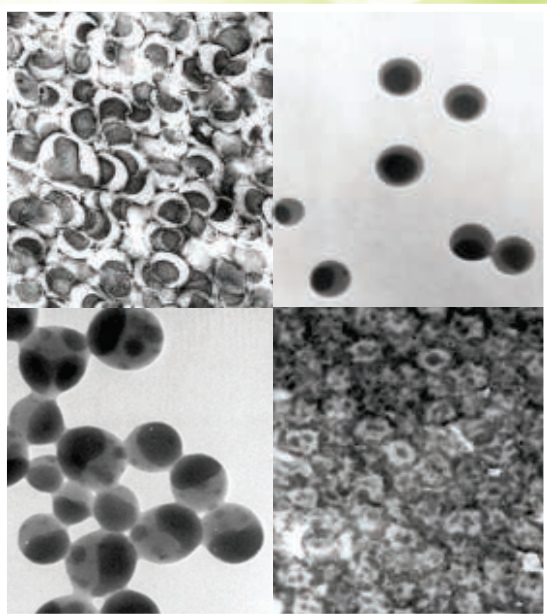


NOVEL MULTI-PHASE ACRYLICS

FOR HIGH PERFORMANCE COATINGS



By **Ivan Tyre** and **Terri Carson**
Alberdingk Boley

For the past few decades, coatings chemists have been responsible for developing high performance coatings while complying with tightening environmental restrictions, particularly the reduction of volatile organic compound (VOC) content. With the initial restrictions in the early 1990s, a chemist could potentially pull out “extra” solvents such as propylene glycol which enhanced freeze/thaw, flow and leveling, and open time, and reduced the levels of coalescing aids used to lower the minimum film formation temperature (MFFT) of the coatings based on very hard polymers with glass transition temperatures (T_g) in the 40–60°C range. As restrictions became even tighter, a strategy employed (and, in some cases, a very effective one) was the blending of soft and hard single phase resins. Care had to be taken with this approach, as film formation with two distinct polymer particles of varied size and MFFT did not always impart desired properties. Clear, haze-free films were not guaranteed¹ and block resistance properties were subject to the ratio and size of the hard polymer to soft particle.²

With the advent of computer-controlled reaction vessels, the production of multi-phase particles that have both a soft segment for film formation at lower VOC, along with improved elasticity, and a harder portion for property enhancements such as block and dirt pick-up resistance, is possible. This article does not intend to describe the fine details of manufacturing these resins, but presents a simplified schematic view along with a description of possible morphologies.

POLYMERIZATION SCHEME AND MORPHOLOGY

Figure 1 displays a simplified polymerization of a single phase emulsion. In the pre-emulsion type process, water, surfactant, and the monomer mix are fed over a period of time, and an initiator is added to begin the polymerization. The feed rate is typically held constant with a continuous “similar” composition created throughout the polymer particle. Multi-phase polymerization approaches can be very different. They include feed schemes such as sequential, gradient, and step-gradient-step types. Figure 2 shows a sequential process that includes feeding at least two different monomeric composi-

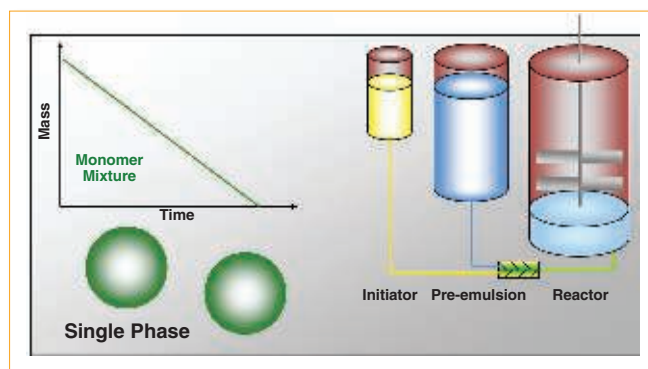


Figure 1—Polymerization of single phase particles.

(Above) AFM images showing multi-phase particles. Photos courtesy of Alberdingk Boley Inc.

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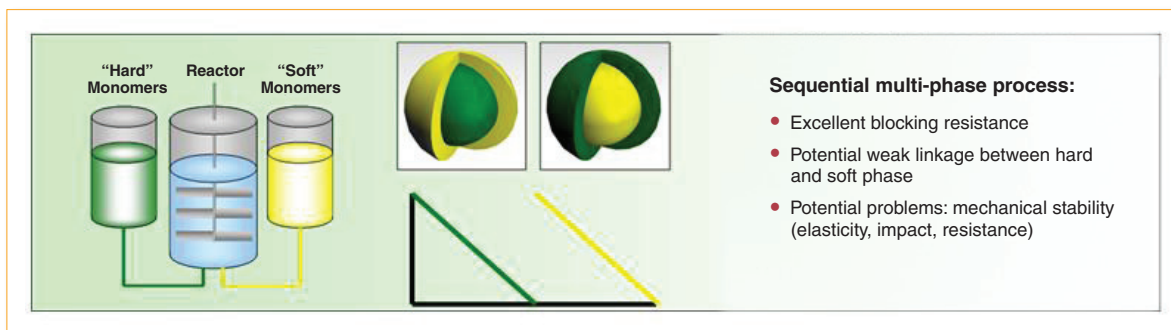


Figure 2—Multi-phase sequential polymerization process.

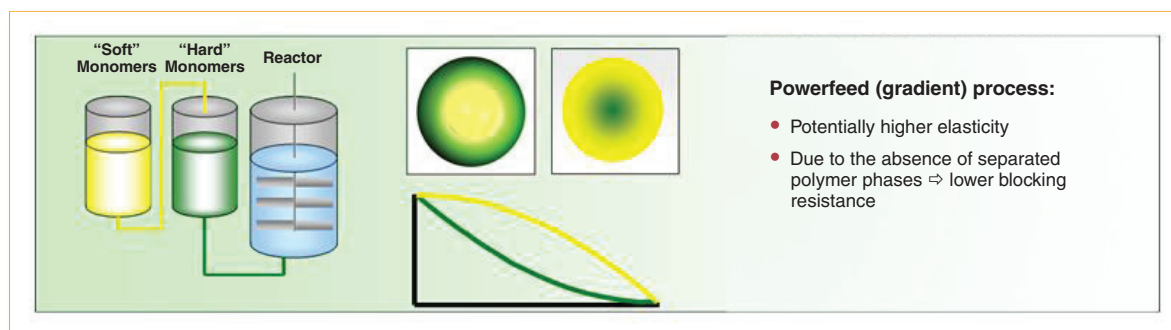


Figure 3—Multi-phase gradient process.

tions into a reaction vessel. The basis here is that one portion (e.g., the soft phase composition) of the polymer is fully reacted prior to the addition of the second (harder phase), which will graft or surround the first. If the reaction is successfully controlled, one could create a particle which will exhibit excellent block resistance but with potential detrimental issues including poor mechanical stability due to weak inter-polymer linkages between soft and hard phases. *Figure 3* shows the gradient process that contributes to stronger inter-polymer linkages since the phases will be “blended,” but block resistance could potentially suffer. *Figure 4* shows a morphing of both sequential and gradient type processes. The process begins with a feeding of “hard” mix during the first segment and then, at some specified point, a second feed is begun which overlaps the first, creating a smooth transition from hard to soft phases, and is completed with the remainder of the “soft” mixture. This scheme is the most ideal for producing multi-phase dispersions with very good block resistance, elasticity, and mechanical stability.

Given these processes, it is apparent that differing morphology is possible, driven by thermodynamic and kinetic principles. Descriptions of morphology types include “core-shell,” “inverted core-shell,” “raspberry,” or complete phase separation (*Figure 5*).³ *Figure 6* shows an atomic force microscopy (AFM) 3-D image of the surface profile of a typical single phase versus a multi-phase emulsion. The surface irregularity of the multi-phase emulsion with high “hills” can contribute to the potential block resistance performance if those segments are made up of the “hard” material.

It should be noted that both single phase and multi-phase emulsion processes are much more complex than

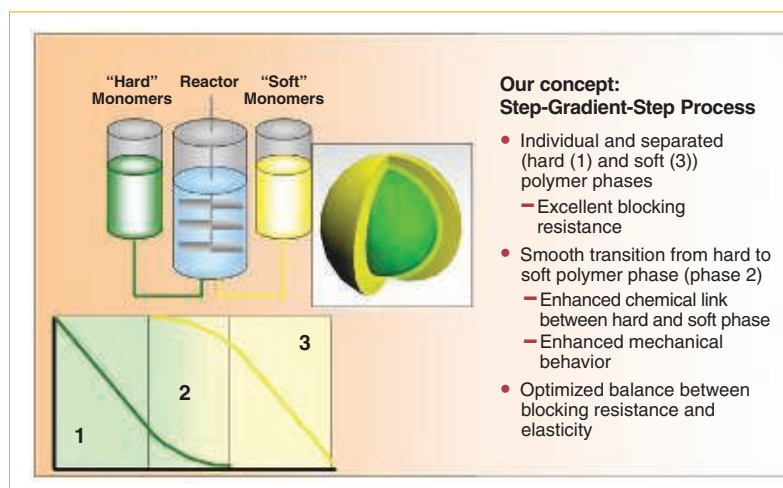


Figure 4—Step-gradient-step process.

described here, with known variables such as monomer composition, initiator type, temperature profiles, agitation, flow rates, pressure, surfactant composition, and many other factors playing a role. Once understood, these factors—when controlled—can create some novel polymers with unique properties.

FORMULATING GUIDELINES WITH MULTI-PHASE DISPERSIONS

Formulating coatings with multi-phase dispersions is really no different than formulating with their single phase counterparts, but care should be used with regard to several areas, such as freeze/thaw, coalescing solvent choice, and pigment volume concentration (PVC) limits.

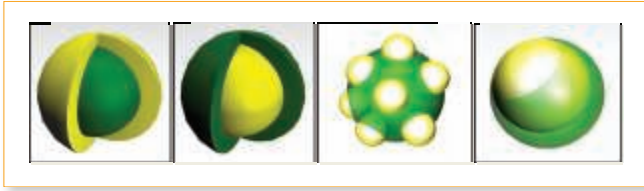


Figure 5—Possible particle morphologies.

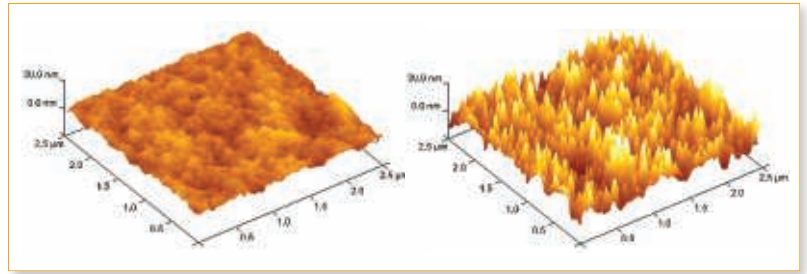


Figure 6—AFM 3-D images of a single phase (left) and multi-phase acrylic³

We have observed that freeze/thaw performance in low-VOC formulations of multi-phase dispersion can be a challenge. Hydrophilic coalescing solvents such as Butyl Carbitol™, Butyl Cellosolve™, and DPM glycol ether tend to help, but time and again it has been shown in our work that the “thawing” may take an overnight period or even a day rather than the specified seven hours indicated in ASTM D2243-95. This may be acceptable to customers, provided the paints do indeed “thaw” and other properties have not changed. As with any emulsion, coalescing solvent selection is critical for early development of properties such as block resistance and effective reduction of MFFT. At times, with “soft core” particles, the hydrophobic type solvents tend to diffuse into these domains creating “tacky” portions that cannot be overcome even with the harder domains present. For pigmented coatings, it is apparent that the hard phase of the dispersion can act almost like an extender pigment especially in low-VOC coatings. This can therefore reduce the critical pigment volume concentration (CPVC) to levels around 25% in some cases. Studies should be completed to determine the CPVC point for a coating, as this affects properties such as corrosion resistance, stain resistance, flexibility, etc.

BENCHMARKING STUDIES OF SINGLE PHASE VERSUS MULTI-PHASE EMULSIONS IN COATINGS APPLICATIONS

Multi-phase acrylic coatings can be applied to various substrates including wood, concrete, and metal with significant benefits. Research in our laboratory over the last few years has focused on creating multi-purpose, multi-phase dispersions that can function as either primers or topcoats to protect against elements in the environment such as moisture. To perfectly design a very high performance product for very different substrates, several considerations have to be addressed to develop products with optimum performance. Specifically, focus has been given to the following parameters:

- Maximum water resistance
 - Optimization of monomer system
- Optimal film formation
 - Focus given to MFFT, particle size, and distribution
- Adhesion
 - Functional monomers and additives

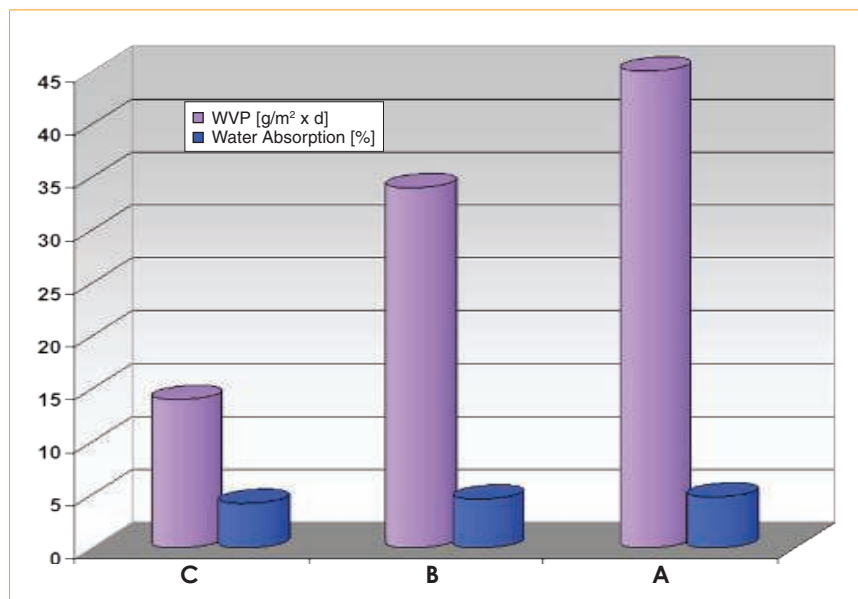


Figure 7—Water absorption and permeability results.

- Reduction in electrochemical processes on metal surfaces
 - Optimization of the hydrophilic load of the emulsion
 - Optimization of latex stabilization
- High blocking resistance
 - Design of particle morphology
- High chemical resistance
 - Incorporation of self-crosslinking chemistry

Several multi-phase emulsions have been prepared with consideration of the aforementioned parameters. Some properties of these emulsions in a white pigmented formulation (18 PVC, 50 g/L VOC) are compiled in Table 1.

To meet low VOC requirements, low MFFT were targeted. The surface hardness varied as a function of the hard/soft phase composition, but all emulsions showed excellent gloss potential with good blocking resistance. The water absorption and water vapor permeability were measured as well and results are summarized in Figure 7. All emulsions performed similarly for water uptake, but the performance of emulsion C was far superior for water vapor permeability. Such barrier properties could have a significant impact on the durability and lifetime of a substrate. Further evaluations were conducted with this emulsion on multiple substrates to investigate its coatings performance.

Efflorescence Resistance

Porous substrates such as concrete and brick pavers can absorb moisture leading to efflorescence on the surface. The following illustrates how efflorescence occurs. The capillaries in the substrate act as wicks, which pull dissolved salts in the soil and substrate to the surface. When the coating dries, the salts are left as a white deposit. Considering the low water vapor permeability of Sample C, sealer formulations were prepared and applied to a cement board to investigate whether efflorescence could be reduced by minimizing moisture uptake into the substrate. Formulations were compared to unsealed sections of the board as well as to a commercial concrete sealer on the market. A stucco mixture at a pH = 11 was applied to cement board and allowed to dry for 16 hr. It was then primed with the sealer and allowed to dry for 8 hr. A red vinyl acrylic topcoat was applied and allowed to dry for 16 hr. The board was then placed in a humidity

Table 1—Summary of Emulsion Properties

Multi-phase Emulsion	A	B	C ^e
MFFT (°C) ^a	17	0	16
Konig hardness (s) ^b	65	45	30
Gloss (20°/60°) ^c	60/82	57/84	56/79
Blocking resistance ^d	9.5	10	7

(a) According to ASTM D2354.

(b) Measured with a BYK-Gardner Pendulum Hardness Tester (model 5854).

(c) Measured with a BYK-Gardner TRI-Gloss Meter.

(d) According to ASTM D 4946-89.

(e) 100 g/L VOC.

chamber for 72 hr at 50 °C. Figure 8 displays the exposed board from the humidity chamber. It is clear when the board is unsealed the soluble salts freely migrate to the surface and, upon evaporation of the water, salts remain. The commercial sealer reduced this migration to some extent, but the sealer based on Sample C produced the best results with very little surface deposition.

Wood Primer Applications

It is well known that certain wood types contain exceptionally high levels of tannic acid. These tannins are soluble in water and, when water-based primers are applied to wood substrates, the tannins migrate to the surface. At the surface, tannins mix with the air and oxidation occurs causing the surface to discolor and produce yellow or brown stains. Typically, an oil-based primer can be applied that will prevent tannin bleeding into the topcoat. Some latex based primers are effective as well. To further investigate the coatings performance of multi-phase emulsions, the tannin blocking/locking properties were evaluated on cedar substrates (Figure 9). Multi-phase emulsion samples A, B, and C were selected for this investigation, along with a commercial exterior topcoat. The cedar panel was primed with each sample by brush application and allowed to dry overnight at ambient temperature. The commercial topcoat was then applied and dried for seven days. The coated panels were placed in a Cleveland Condensation Chamber overnight and inspected for discoloration the following morning. Color measurements were taken using a Color-guide Sphere in the primed layer (referred to as blocking) and the topcoat

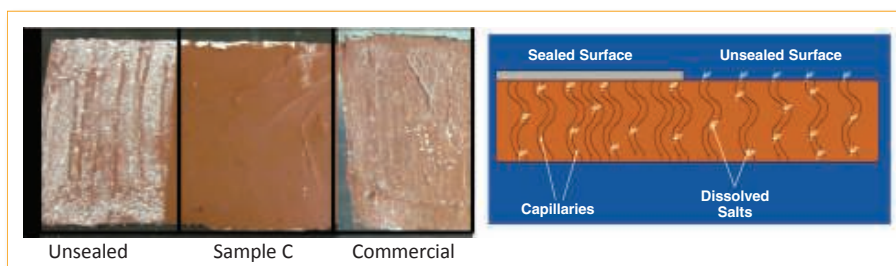


Figure 8—Efflorescence results for Sample C vs commercial product.

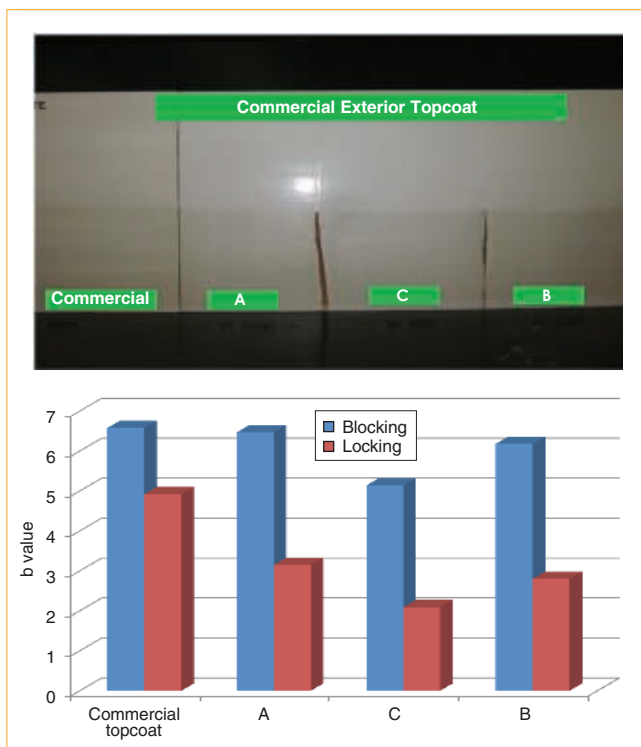


Figure 9—Tannin resistance for multi-phase emulsions.

layer (referred to as locking). It is clearly seen that tannin migration occurs to a large extent through the primer layer. Varying degrees of yellowness were measured with the highest value resulting when the topcoat was not applied over a primer. However, the migration to the topcoat occurred to a much a lesser extent when the multi-phase emulsions were applied. Specifically, the appearance of the section where Sample C was applied produced the best results with very little yellowing. It is not clear whether the tannins are bound chemically in this primer, but the optimized ionic load of this emulsion, ultra hydrophobic nature, and morphology control produces a high barrier film with unique properties.

Direct-to-Metal Applications

Many of the water-based products on the market for direct-to-metal (DTM) are single phase polymer dispersions. Thus, a benchmarking study was conducted comparing several types (single phase and multi-phase) of commercial emulsions in a DTM application. Evaluations were conducted in 100 g/L VOC white formulation at 18% PVC and 35% volume solids (Table 2). Typical tests included blocking and corrosion resistance, gloss retention in QUV and exterior exposure, impact resistance, and adhesion to various metal substrates.

Table 2—Dispersion Characteristics/ Descriptions for 18 PVC White

Name	A2	B2	C	D	Com Paint A	Com Paint B
Type	Single phase	Single phase	Multi-phase	Multi-phase	Zero VOC waterbased	Alkyd or oil-based high gloss
MFFT	30	33	16	15	Na	Na
Self-crosslinking	None	None	Type 1	Type 2	Unknown	Oxygen

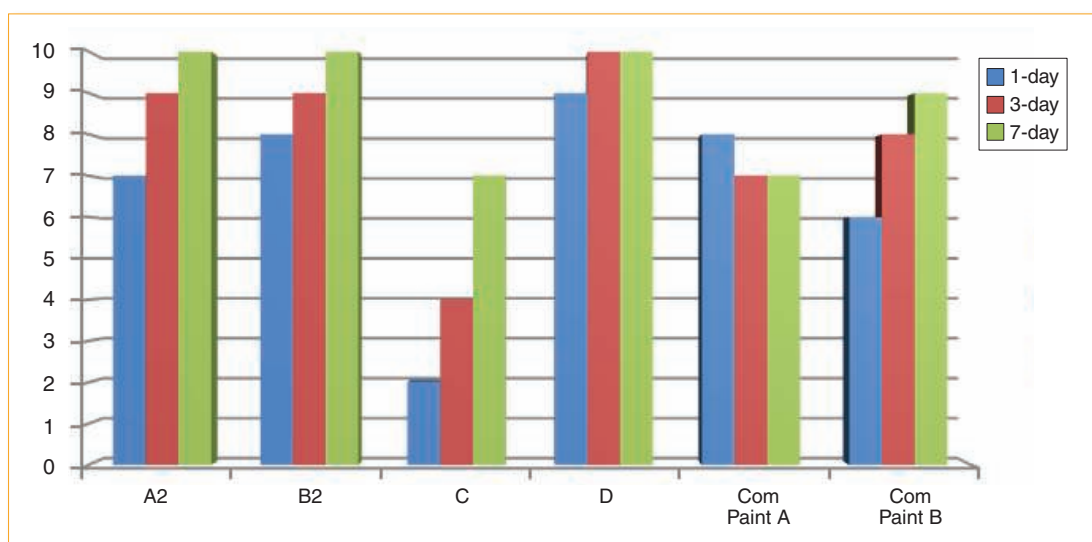


Figure 10—Room temperature block resistance vs. time.

Block Resistance

As expected, the harder single phase dispersions (A2 and B2) performed exceptionally well, along with the commercial paint B (Figure 10). Results of C and D reflect the differences which can be exhibited in multi-phase dispersions that have essentially the same MFFT, but different particle morphologies. In further work with dispersion C, the block resistance was slightly improved to a rating of “8” when changes were made in the coalescing aid from slower solvents such as DPnB and Texanol to faster ones such as ethylene glycol monobutyl ether (EB). However, the original formula has been used throughout the completion of this study.

Corrosion Resistance

Paints were sprayed out with a typical cup gun set to give the best application over precleaned, untreated cold-rolled steel panels. The dry film thicknesses were controlled with measures between 1.7 mils and 2.0 mils obtained. They were allowed to dry for seven days prior to exposure in a typical corrosion chamber programmed to run the ASTM B117 standard (Figure 11). The visual results are stark, but it should be noted that white paints had no anti-corrosive additives or pigments in the baseline formulation. Dispersion C was the only exceptional result. The solvent-based commercial paint B also was excellent.

Gloss Retention

Another quality for gloss DTM coatings is gloss retention. In a limited evaluation of dispersion A2, C, and the commercial paints, samples were prepared in the same fashion as the corrosion testing. They were allowed to dry for seven days prior to exposure in an accelerated fashion with UVA 340 nm and on a test fence with a south 45° exposure angle located in Greensboro, NC. Using a tri-gloss meter, each film was evaluated for the 60° gloss initially and then after every 500 hr in QUV and every six months on the test fence. Reported in Figure 12 is the gloss retention after 2000 hr QUV, and Figure 13 reflects exposure data for the past 16 months.

Dispersion C exhibited excellent retention in both evaluations, and the worst performer was the commercial paint B.

Impact Resistance/Flexibility

Impact resistance is a key property of coatings for metal door frames, pipe coatings, and other light industrial maintenance applications. Coatings were applied with a 6-mil bird-type applicator to thin cold-rolled steel substrates. After drying for 24 hr, a direct impact test was accomplished following the ASTM D 6905-03 standard (Table 3). Each indentation site was examined for cracking /tearing and given the maximum inch-pounds force measure that corresponded to no damage observed.

It is evident that the higher MFFT of the single phase dispersions A and B were significantly less

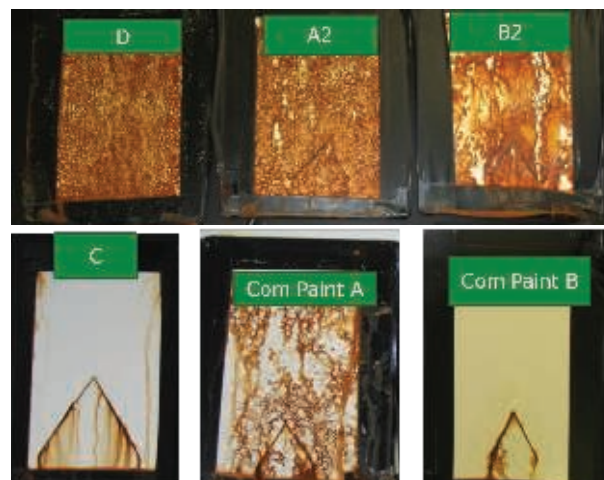


Figure 11—One week salt spray visual results.

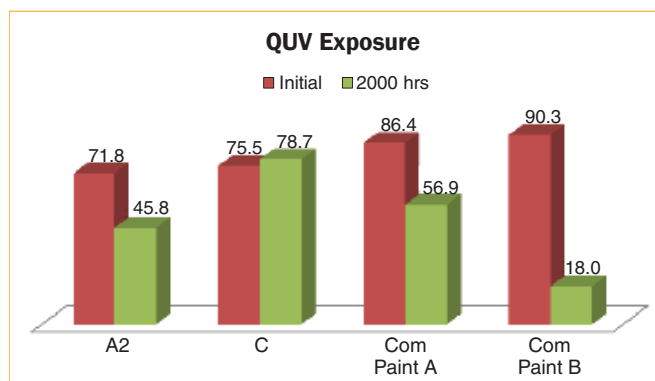


Figure 12—Gloss retention after 2000 hr QUV.

flexible than the multi-phase C and D emulsions. It is theorized that the soft phase of these contributes to the added flexibility.

Tape Pull Adhesion Method B (Crosshatch Version)

The last property evaluated was tape pull adhesion following ASTM D 3359-09. Paints were applied by 6-mil bird applicator bar to galvanized metal, cold-rolled steel, and aluminum. Films were allowed to dry at standard room temperature conditions for 24 hr and were then evaluated for cross-hatch tape pull adhesion. A rating of 5 is best with no adhesion failure, and 0 is worst with greater than 65% of cross-hatched area removed. Both dry and wet adhesion tests were performed. For wet adhesion, a soaked paper towel square was placed over the cross-hatched area for one hour, then wiped dry and allowed to sit for 15 minutes, after which the tape pull was accomplished.

At this time we are unable to rationalize why dispersion B and commercial paint A did not stick well to galvanized metal, but the remaining coatings showed excellent performance (rating = 5), with the exception of dispersion D which failed wet adhesion to aluminum.

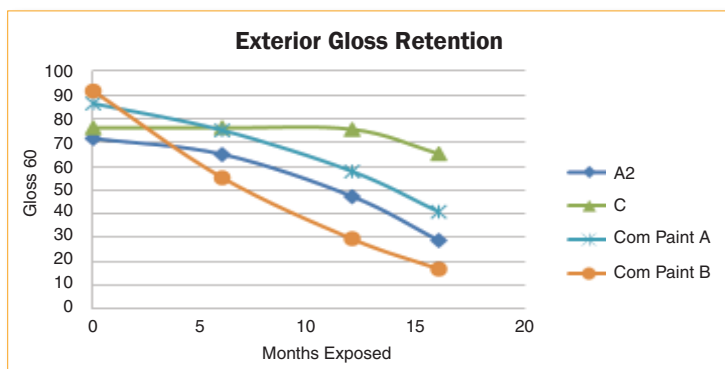


Figure 13—Gloss retention after 16 months' exposure.

Table 3—Direct Impact Inch-Pounds Force

A2	B2	C	D	Com Paint A	Com Paint B
60	20	160	160	140	100

CONCLUSION

Multiphase emulsions have the potential for high blocking resistance, outstanding gloss retention, low dirt pick-up, and excellent water resistance. A new multi-purpose multiphase emulsion (Sample C) has been developed with good corrosion resistance, excellent efflorescence resistance,

and tannin locking properties. This technology enables low VOC without sacrificing performance for not only direct-to-metal but also concrete and wood coatings. Further work will continue to optimize formulas for this product to enhance its performance.

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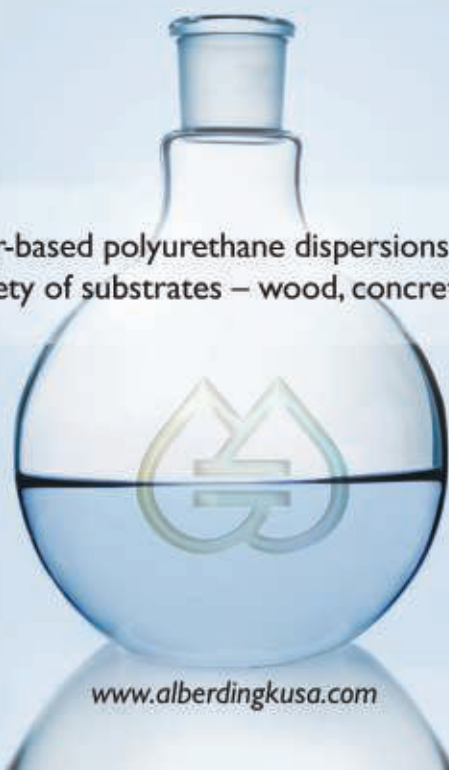
AUTHORS

Ivan Tyre and Dr. Terri Carson, Alberdingk Boley, 600B High Point Rd., Greensboro, NC 27407; TCarson@alberdingkusa.com.



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