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Protection of metal with a novel waterborne acrylic/urethane hybrid technology

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ABSTRACT

Coatings are often required to provide multiple properties that seem to be opposed to one another, or at least difficult to obtain at the same time. One key example for waterborne acrylic coatings is the desire for lower volatile organic compounds (VOC) without the loss of hardness properties. Coupling these seemingly conflicting properties with other high performance needs, such as excellent corrosion resistance and weatherability, can present a serious challenge for raw material suppliers and coatings manufacturers alike. A new waterborne technology that satisfies these many requirements will be introduced. This paper describes a unique acrylic/urethane hybrid technology which couples a hard acrylic dominant phase with a soft polyurethane minor phase, and the development of a new self-crosslinking hybrid polymer which combines the low VOC/fast hardness development balance with excellent corrosion resistance and weatherability in a single-component waterborne system. In the hybrid, the soft polyurethane phase acts as a conduit for the rapid diffusion and release of coalescent from the film, leading to improved hardness development relative to a hard acrylic alone. The soft polyurethane phase also contributes to good film formation at reduced VOC levels. The mechanism of the faster coalescent release will be discussed, along with application data showing improvements in block, print and dirt pickup resistance. The excellent corrosion resistance and durability are a consequence of the formation of polymer–pigment composite particles and a film formation process that offers improved pigment distribution in the dry film. Details of the mechanism will be discussed, along with performance properties of the new acrylic/urethane hybrid polymer in corrosion-resistant coatings for the protection of metal.

1. Introduction

Coating manufacturers and their raw material suppliers often have the difficult job of providing coating technologies that offer multiple performance properties which may seem to be at odds with each other and difficult to accomplish in a single coating. Attaining these contrasting properties can be even more complicated in a one-component thermoplastic waterborne coating such as an acrylic latex, where dense crosslinking is not available to build in properties such as chemical resistance or durability. For example, a typical method to increase gloss with an acrylic latex is to decrease polymer molecular weight, but doing so makes it difficult to obtain good solvent resistance or durability. The dichotomy between lower volatile organic compound (VOC) content and good hardness properties is another example which is actively being pursued in both the architectural and industrial coating markets, and is a particularly challenging target for waterborne acrylic latex polymers. Typical approaches to low VOC and good hardness properties involve preparing acrylic latex polymers with morphologies containing hard domains in a soft latex, such as core/shell particles with a hard core and soft shell, or blending hard and soft polymers. The hard phase can reinforce the soft phase and boost its hardness, while the soft phase promotes good film formation at low VOC. However, in practice this approach is often found lacking.

For many coating applications on metal substrates, having a low VOC coating with excellent hardness also needs to be coupled with other properties such as good corrosion resistance, adhesion, gloss and durability. This paper describes an ongoing technical effort to offer the coating industry a waterborne polymer technology that displays such a balance of properties. We report on efforts to combine two unique technologies that separately offer a piece of the puzzle, and describe the advantages and challenges that result. The first uses a novel blend of acrylic latex and polyurethane dispersion polymers, yielding a film structure that significantly improves the hardness development of a coating (via faster coalescent release) compared to a hard acrylic by itself. The second involves designing the acrylic portion of the acrylic/urethane blend so that it associates with the pigment particles in the coating, forming composite particles that can lead to improvements in gloss, hiding, corrosion and

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durability. Performance of polymers based on the combined technologies will be described, and compared to unmodified acrylic latex polymers and commercial waterborne offerings for metal coatings.

2. Experimental

A self-crosslinking acrylic/polyurethane polymer, PUA-1, based on a combination of the two technologies, was used in the evaluations. It is a blend of a hard self-crosslinking acrylic latex, AC-1, and a soft polyurethane dispersion, PUD-1. PUA-1 was prepared at 42.0% solids, pH 8.3 and a Brookfield viscosity (#3 spindle/30 rpm) of 50 cP. It has a minimum film formation temperature (MFFT) of 10 °C, and contains approximately 2.9% co-solvent on total, which gives it a VOC of 83 g/L as supplied. The acrylic latex AC-1 is based on the pigment association technology described below, and was used as a comparison to PUA-1 in many of the experiments. AC-1 is a hard acrylic latex with a glass transition temperature (T_g) of 35 °C. The polyurethane dispersion PUD-1 is an essential component to the coalescent release technology, also described further below. PUD-1 is a soft, aliphatic polyester polyurethane dispersion with T_g below 0 °C. AC-1 and PUD-1 are produced by standard synthetic procedures for acrylic latex and polyurethane dispersions (PUD), respectively. Because synthesis of PUD-1 is done in dipropylene glycol dimethyl ether (DMM) before it is dispersed in water, the blend PUA-1 does contain some VOC content, as already mentioned. DMM does act as a coalescent and aids in film formation for the blend PUA-1.

Several other acrylic polymers were used in the testing. Polymer AC-2 is a self-crosslinking acrylic copolymer used commercially in low VOC industrial maintenance coatings. It has a T_g of 18 °C, can be formulated below 100 g/L, and is also based on the pigment association technology described below. Polymers AC-3 and AC-4 have higher T_g values (35 °C), and are also commercial acrylic copolymers used in producing anti-corrosive coatings. AC-3 and AC-4 are typically formulated into coatings with VOC levels of approximately 200 g/L. Several commercial coatings (COM-1 through COM-4) designed for use in maintenance and protective coatings applications were obtained from their manufacturers, and used as supplied. All are gloss direct-to-metal (DTM) coatings, and their reported VOC levels are 0 g/L (COM-2), 100 g/L (COM-1) and less than 200 g/L (COM-3 and COM-4).

For hardness development, gloss and gloss retention, hiding, and chemical, block and print resistance tests, coatings were applied by drawdown bar to a treated aluminum panel (Q Panel Type AL-412 chromate pretreated aluminum, 10 cm × 30 cm) to yield approximately 40 μm dry film thickness. Panels were placed in a constant temperature and humidity room (25 °C and 50% RH) for the amount of time listed below for each test prior to testing.

(A) *Konig hardness* – Evaluated according to ASTM D4366 using a TQC SP0500 Pendulum Hardness Tester, and reported in seconds. Measurements were taken at various intervals over the course of 2 weeks. To measure an “ultimate” hardness, panels were then baked in a 60 °C oven for 1 or 4 days prior to testing.

(B) *Block resistance* – Panels were dried for either 1 or 7 days, and then two 4 cm wide strips were cut from the aluminum panel, and placed face-to-face forming a cross. A #8 rubber stopper was placed on the cross-section of the strips, and a 1 kg weight placed on top of the rubber stopper. Block resistance was rated under two conditions, (1) after 24 h at room temperature, and (2) after 30 min at 60 °C. The following 0–10 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.

(C) *Print resistance* – Panels were dried for either 1 or 7 days, and then a 4 cm × 4 cm square of cheesecloth was placed on the panel, a #8 rubber stopper was placed on top, and a 1 kg weight placed on top of the rubber stopper. Print resistance was rated after 24 h at room temperature on a 1–10 scale, with 1 being severe print, and 10 being no damage.

(D) *Gloss and gloss retention* – Coatings were dried for 2 weeks prior to testing. Film gloss was determined in accordance with ASTM-D523 using a Byk-Gardner micro-tri-gloss gloss meter. The effect of weathering on film gloss was determined artificially using a QUV accelerated weathering cabinet using UV-A bulbs (340 nm) and a cycle consisting of 8 h light and 4 h condensation. Gloss retention upon exterior exposure was measured at a site in eastern Pennsylvania.

(E) *Hiding* – Coatings were applied to Leneta 5C charts and dried for 2 weeks prior to testing. Dry hiding was estimated using ASTM D2805, by calculating the contrast ratio from *Y*-reflectance measurements using a 45°/0° reflectometer.

(F) *Corrosion resistance* – Corrosion resistance was evaluated by salt spray exposure (ASTM B117) on 10 cm × 30 cm clean cold rolled steel panels (Q-Lab Type R-412 dull matte steel). Coatings were applied by drawdown to give 50 μm dry film thickness per coat. Panels were scribed prior to exposure with a 5 cm vertical scribe centered at the bottom of the panel. Ratings for blistering, rusting and undercutting were made at various times during the exposure.

(G) *Microscopy* – Field emission scanning electron microscopy (FE-SEM) imaging studies were done using a JEOL 6700 FE-SEM. Samples for imaging were prepared by diluting titanium dioxide/latex blends and dispersing it onto silicon wafers, then coated with Au/Pd (∼10 nm).

(H) *Flexibility* – Flexibility was tested according to ASTM D522. Panels were dried for 7 days, and then 4 cm wide strips were cut from the aluminum panel. The strips were bent over mandrels of varying diameter, and the coating then inspected with a magnifying lens for any cracking. The diameter of the smallest mandrel for which there was no cracking is reported.

(I) *Impact resistance* – Impact resistance was tested according to ASTM D2794. Coatings were drawn down on iron-phosphate treated cold rolled steel panels, and then dried for 7 days prior to testing. The results are reported in units of inch-pounds, for the highest value where cracking of the film was not observed.

(J) *Chemical resistance* – Resistance to common chemicals was evaluated by applying spots of the chemical to the coated panel for 16 h, then cleaning the panel with clean water and a sponge, and drying prior to rating. Chemicals were applied to the surface by saturating a 2.3 cm filter paper and covering with a watchglass to prevent evaporation.

3. Results and discussion

3.1. Accelerating coalescent release

Once film formation has occurred, volatile coalescents and co-solvents employed in coating formulations are no longer needed in the film, and it is desirable for them to leave the dry coating film to enhance properties such as hardness. Some slow coalescents (e.g., 2,2,4-trimetyl-1,3-pentanediol monoisobutyrate) will remain in acrylic coating films for many weeks or longer. Acrylic/urethane blends based on the new technology provide a novel mechanism for the faster release of volatile materials, such as coalescents and co-solvents, from the drying film. The result is a dry film which offers faster hardness development and improvement in other film prop-