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Characterizing and improving performance properties of thin solid films produced by weatherable water-borne colloidal suspensions on bronze substrates

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ABSTRACT

While the development and application for transparent protective coatings for metals continues and broadens, the use of these coatings on high-value outdoor bronze objects, such as statues and architectural elements, requires extensive testing before use. Recent efforts in coatings technology have produced high-performance water-borne latex dispersions containing polyacrylics and poly(vinylidene fluoride) (PVDF) targeting extended coating lifetimes and improved UV resistance. Our studies show that a two-layer polymer film with a solvent based primer (Paraloid^{TM} B-44) and a high performance water-borne topcoat (Kynar Aquatec^{TM} RC-10206) exhibits high impedance as measured by electrochemical impedance spectroscopy. Upon annealing, those films further increased in impedance, suggesting improved corrosion protection compared to unannealed films. When soaking in water, films that contained high loading levels of coalescing agent (Dipropylene glycol monomethyl ether, DPM) in the topcoat formulation resulted in a visible whitening of the basecoat and a decrease in coating resistance. Characterization of the whitened layer by FT-IR indicated the presence of coalescent in the basecoat, suggesting that coalescent migrated from the topcoat into the primer basecoat. Annealing studies were performed to reduce uptake and reverse or inhibit water whitening.

1. Introduction

In the field of conservation of material cultural heritage, the selection criteria for protective coatings for outdoor metalwork (bronze sculptures and architectural elements) are significantly different than the needs of typical consumers. Conservators select coatings based on protection against corrosion, durability, transparency, reversibility (i.e. how easily the coating may be removed), and ease of application onsite [1,2]. Cost of the coating is usually not considered (due to the high value of the object itself), as long as the coating satisfactorily meets the other selection criteria. Legislative restrictions have provided a motivation to reduce volatile organic component (VOC) levels in coatings and thereby limited the array of coating options for conservators as state and federal environmental regulations have positioned water-borne coatings to replace solvent based coatings in many applications.

However, replacing solvent based with water-borne coatings is not a trivial matter as the two coating types greatly differ in their ability to form protective films, even when the chemistry of the coatings is similar [3]. Water-borne coatings are also susceptible to blistering and water-whitening. In 1954, Wheeler et al. stated the need for a compromise in aqueous polymer dispersions between stability and performance, a tension which remains to this day [4]. The industrial push for widespread use of water-borne coatings, driven both by their decreased cost and reduced environmental impact, is generally at the expense of their protective barrier properties compared to traditional solvent based coatings [5]. Recently, new highly weatherable water-borne latex technology has become available, based on poly(vinylidene fluoride) (PVDF) hybrid dispersions. Potentially, compared to solvent based acrylic coatings, water-borne PVDF-based coatings may offer an environmentally friendlier alternative, with superior corrosion protection and durability under outdoor weathering. The specific aims of this study are to understand the performance characteristics on bronze substrates of a coating formulation based on one of these PVDF hybrid dispersions, as characterized by water sorption, water whitening, electrochemical impedance spectroscopy (EIS), and Fourier transform infrared spectroscopy (FTIR).

1.1. Background

Ideally, the polymer resins of organic coatings should be hydrophobic to prevent water sorption; however hydrophobic polymers are not normally stable as water-borne suspensions, and

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so require the addition of hydrophilic additives, or the modification of the polymer to include hydrophilic components, as a means of stabilizing these suspensions [6,7]. The ability of coatings to prevent corrosion also depends upon the chemistry and durability of the polymer, especially its ability to resist degradation due to UV light exposure [8–10]. Fluorinated polymer hybrid blends based on PVDF are among the most UV-resistant resin systems used today in commercial coatings for metals, with protective properties lasting in many cases for more than thirty years of outdoor exposure, as described by Wood et al. and others [8,10–12]. Since their debut in the 1960s, PVDF-containing coatings have primarily been supplied as non-aqueous dispersion or solution coatings, often at high VOC levels. Recent advances have produced water-borne (latex) hybrid dispersions with high PVDF resin content and the performance of these coatings continues to improve [13–15]. Commercial products of this type, such as KYNAR Aquatec® RC-10206, contain 70% or 50% PVDF on total resin weight, with the remainder of the resin being acrylics [8,12]. These proportions are similar to PVDF:acrylic ratios used typically in traditional solvent PVDF-containing coatings. Like solvent PVDF coatings, water-borne PVDF coatings of this type have been shown to offer superior barrier properties, after exposure to UV light, as compared to solvent based 100% acrylic coatings [12].

Because of their relatively inert chemistry (which confers resistance to oxidative degradation, and other components of coating durability), 100% PVDF coatings do not provide good adhesion to metals, compared to acrylic resins such as Paraloid® B-44, a methyl methacrylate/ethyl acrylate copolymer. We circumvent this adhesion problem by using an acrylic basecoat primer (for good adhesion) combined with a water-borne PVDF-based topcoat (for good weatherability).

However, we have identified a remaining challenge with some prototype systems of this type: the clear films are susceptible to whitening upon exposure to water. This whitening phenomenon is seen only for two-coat systems (solvent acrylic primer plus water-borne PVDF-based topcoat), not for either of the coating layers applied singly. Whitening is particularly problematic in outdoor applications for both aesthetic reasons, and for possible indications of poor short and long-term performance.

The causes of whitening in organic thin film coatings have been attributed in large part to the additives of the formulations and not to the polymer resins themselves [16]. The first to document the phenomenon of water whitening, Wheeler et al. implicated emulsifiers as the cause. They discussed possible interactions of the hydrophilic additive and the polymer network, leading to hydrophilic inclusions which swelled with water and caused increased light scattering [4]. Bindschaedler also noted whitening and ascribed the cause in cellulose acetate films to plasticizers and sodium dodecyl sulfate present for film formation [17]. Agarwal and Farris expanded the work on surfactants to a variety of acrylic-based latex blend films, and found that all formulations whitened upon immersion in water due to hydrated surfactant reservoirs that swell and scatter light, creating a “white and opaque film” [16]. Robeson and Hyder found increased water sorption correlating with the additive levels in emulsion polymer cast films [6]. Polymers of dissimilar chemistry were unable to diffuse and coalesce into one cohesive phase, which in turn created a percolation network at the interface where residual additives affected water transport through the films. Water uptake, and the visual whitening effect that may follow, is increased by the hydrophilic nature of water-borne coatings, and by sub-microscopic channels in the polymer film caused by the evaporation of slow cosolvents [18].

When describing surfactant effects, Keddie and Routh [19] detail a worst-case scenario that could create a hydrophilic pathway to the metal; they state that surfactant accumulation around particle boundaries creates hydrophilic pockets to trap water and speed water transport. The study by Agarwal and Farris also presented evidence that softer polymers were more prone to generate “islands” of surfactant molecules, when compared to rigid counterparts. Water diffusion into coatings produces a swollen layer above an unaffected pristine layer in the coating, where the characteristic length scale and total quantity of the absorbed water may affect electrochemical performance [18,20]. Based on these findings it is likely that for two-coat systems, there could be interactive effects on the system’s water sorption behavior, resulting from the use of different types of polymer in the basecoat and topcoat. For this purpose in situ electrochemical spectroscopy is ideally suited to differentiate active processes that change the barrier properties of the base and topcoat [21].

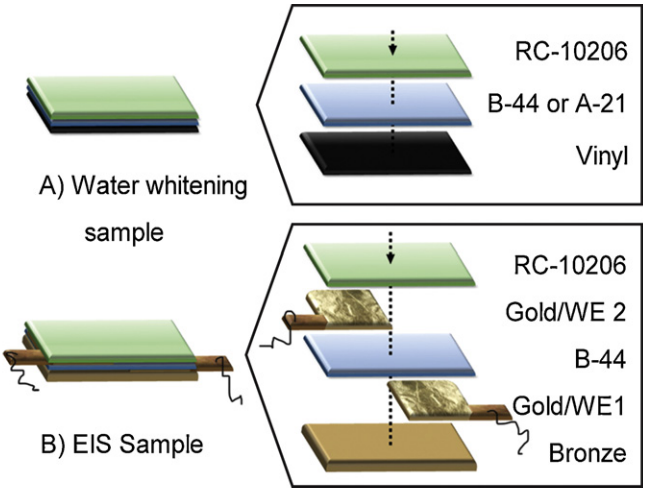

Fig. 1. Exploded view of coating layers on substrates. (A) Black vinyl scrub chart spray coated with a solvent based primer coat and Kynar Aquatec RC-10206 topcoat. (B) Bronze panel layered with gold foil and attached working electrode 1 (WE1), a primer of B-44, gold foil with attached working electrode 2 (WE2), and topcoat of RC-10206.

In our studies described below, solvent based acrylic primer coats (of various types) and latex Kynar Aquatec topcoat were applied to metal coupons of bronze. We hypothesize that the whitening, which can be localized by optical microscopy as occurring in the top part of the basecoat layer, is caused when the coalescent in the water-borne PVDF-containing topcoat migrates into the acrylic basecoat and is trapped there after the topcoat dries. This trapped solvent plasticizes the hydrophilic acrylic basecoat and increases its permeability to water. When the coated coupons are immersed in water, coalescent-rich pockets within the acrylic layer can preferentially take up water, and when these reach the appropriate size to scatter light they produce white or opaque coatings.

2. Experimental

To better understand the complete basecoat/topcoat system’s susceptibility to water whitenening, both individual layers were characterized by Electrochemical Impedance Spectroscopy (EIS), in an effort to probe whether there were defects leading to low impedance that could be related to water uptake and whitening. EIS measurements were performed using bronze coupons layered with various coatings and inter-layer electrodes, represented in Fig. 1. The electrochemical analysis of individual layers was performed before and after annealing, using several annealing methods. The annealing of organic coating systems has demonstrated an improvement in mechanical properties of the films [22]. While annealing in an oven is the ideal and most effective solution, alternative, more practical techniques for use in the field and