Block Resistance of Low-VOC Acrylic Paints: Influences of Latex Design Parameters



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ne of the biggest challenges for low-VOC coatings is simultaneously attaining smooth film formation and acceptable block resistance and film hardness. Block resistance is a function of bulk and surface properties. This article investigates the influences of some latex design parameters on block resistance of acrylic paints. The effects of latex particle size, surfactant choice, and polymer T_{e} are discussed.

INTRODUCTION

Dry paint often comes in contact with itself, such as during the closing of windows and doors. Block resistance combats the tendency of paint films to stick together (or block). It is a key performance requirement for gloss and semi-gloss paints. A coating with good block resistance will retain its film integrity upon reopening of a window or door. Poor antiblocking properties cause the two contacting films to stick, resulting in tearing or peeling of the paints upon separation. The blocking behavior of a paint film depends on its hardness, the pressure, temperature, humidity, and the duration of surface contact.

With increasing regulatory pressure to reduce the amount of volatile organic compounds (VOC) in paints and coatings, softer polymers with low minimum film formation temperature (MFFT) are more frequently being utilized in waterborne architectural coatings. One of the challenges for low-VOC coatings is simultaneously attaining smooth film formation and acceptable block resistance and film hardness. Synthesizing structured latex with coreshell morphology is a common approach to enhancing block resistance of an emulsion binder.¹⁻³ The blending of two latexes, one with high MFFT and the other with low MFFT, has also proven to be a useful strategy to fulfill these contradictory requirements.⁴⁻⁸ Improved block resistance is attributed to increased bulk modulus and surface hardness of the blend system.⁴ For homogeneous particles, crosslinking can effectively increase film hardness and therefore block resistance.⁹⁻¹¹ Certain additives have also demonstrated antiblock characteristics in waterborne coatings systems.^{12, 13} Combinations of above techniques can be employed to improve antiblocking property of paints.^{14,15}

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This article examines the influences of some polymer design parameters on block resistance of a low-VOC acrylic paint. The effects of surfactant choice, latex particle size, gel content, and glass transition temperature (T_{σ}) of the acrylic polymer are discussed.

EXPERIMENTAL

Acrylic Latexes

The acrylic latexes used in this study were prepared by semi-continuous emulsion polymerization of an emulsified monomer mixture containing butyl acrylate, methyl methacrylate, methacrylic acid, and a wet adhesion monomer. Using the Fox equation, the T_g was varied from -10° C to 4° C by adjusting the ratio of butyl acrylate to methyl methacrylate. The latex particle size was controlled by the amount of a seed latex or initial surfactant for particle generation. The particle size ranged from 0.096 to 0.22 micron, determined by Nanotrac UPA150.

Two anionic surfactants were employed in emulsion polymerization at a level from 0.08 to 1.8 parts per hundred monomer (phm). The critical micelle concentrations (cmc) of surfactants A and B are 0.07 and 0.03 wt%, respectively. The surface tension at cmc is 29 and 33 dyne/cm, respectively.

Paint Formulations

A semigloss paint formulation with 26% pigment volume concentration (PVC) and 30% volume solids (VS) was used to evaluate block resistance of various acrylic latexes. *Table 1* shows the ingredients for the low-VOC acrylic paint (37 grams per liter).

Block Resistance Test

The block performance indicating face-to-face adhesion of two paint films pressed together was rated on the scale of 0 to 10 as defined by ASTM D 4946-89 (Table 2). The test paints were prepared on the Leneta 3B opacity charts using a 3-mil bird drawdown bar. The films were dried in the constant temperature and humidity (CTCH) environmental chamber for one day. For room temperature (RT) block, two square strips of 2.54 cm x 2.54 cm paint films were pressed together by a 454-gram weight. After 24 hr, the strips were separated and a numerical value was given according to the scale in *Table 2*. For the elevated temperature (ET) block test, the paint strips after one-day drying at CT/ CH were placed in a 120°F oven under 1000-gram weight for 30 min. The weight was transferred to the paint films via a one-inch diameter rubber stopper, generating approximately 2.2 psi on the film strips. The films were then allowed to cool for 30 minutes before

Table 1—Low-VOC Acrylic Paint Formulation

Ingredient	Pounds	Gallons
Grind		
Water	231.1	27.70
Cellosize™ HEC ER 4400	5.0	0.40
Propylene glycol	10.0	1.20
Colloid 226-35	7.0	0.70
КТРР	1.5	0.10
Triton [™] CF-10 Surfactant	2.5	0.30
Rhodaline 643	1.0	0.10
Ammonium hydroxide, 28%	1.0	0.10
TiPure R-706	225.0	6.80
Polygloss 90	25.0	1.20
Letdown		
Acrylic polymer, 50% TS	425.0	48.02
Water	97.0	11.63
RM 2020	10.0	1.14
Rhodoline 643	1.5	0.21
Ammonium hydroxide, 28%	2.0	0.26
Totals	1044.6	99.86
Weight solids, %	45.8	
Volume solids, %	30.3	
PVC, %	26.2	
VOC, g/L	37	

Table 2—ASTM Block Ratings

Block Resistance Numerical Ratings	Type of Separation	Performance
10	no tack	perfect
9	trace tack	excellent
8	very slight tack	very good
7	very slight to slight tack	good to very good
6	slight tack	good
5	m oderate tack	fair
4	very tacky; no seal	poor to fair
3	5–25% seal	poor
2	25–50% seal	poor
1	50–75% seal	very poor
0	75–100% seal	very poor

the ratings of film separation were given. The test was run in triplicate and the average value was reported.

RESULTS AND DISCUSSIONS

Surfactant Concentration

The concentration of surfactant A was varied from 0.8 to 1.8 phm. *Figure* 1 shows that the one-day room temperature block resistance of the paints increases with increasing surfactant concentration. At 0.8 phm surfactant concentration, the acrylic polymer with a low T_g (= -10 °C) received a poor block rating of 2. When surfactant concentration was increased to 1.8 phm, the polymer of identical composition yielded significantly better block resistance. The numeric value of 7 represents reasonably good block performance for a polymer with MFFT < 0 °C.

The data in *Figure* 1 suggests that surfactant enrichment at the air-film interface potentially contributed to the improved block resistance at higher surfactant concentrations. Exudation of surfactant to the film surface during latex film formation has been a topic of numerous publications.¹⁶⁻¹⁹ Surfactants move with the evaporating water toward the film surface as particle coalescence proceeds. Surfactant migration is also evident in the latex systems studied here. The atomic force micrography (AFM) image shows long, thin lamellar structure covering the latex film surface. X-ray photoelectron spectroscopy (XPS) of film surface and cross-section confirmed that surfactant concentration is higher on surface than in bulk, consistent with a previous publication.¹⁶

The surfactants that bloomed to the top of film surface function as a barrier layer that interferes with polymer interdiffusion across the interface. This effect is similar to the benefit of fluoroadditives reported in the literature.¹³ Adhesion between the two contacting

Figure 1—One-day room temperature block vs. surfactant concentration.



films is reduced and block resistance is improved. The elevated temperature block or hot block was poor. This is not surprising given the low T_g of the polymers. Soft binders deform readily at elevated temperature, resulting in increased contact area. High temperature and high pressure promotes polymer diffusion across the interface due to greater contact area and polymer chain mobility. Consequently, blocking is more severe at the elevated temperature.

Latex Particle Size

Particle size plays an important role in the latex film formation. Small particles form films with less void volume because of higher packing efficiency.²⁰ In a film formation study of poly(styrene-co-n-butyl acrylate) latex, Niu and Urban found that surfactant exudation to film surface is only detected in larger particle size latex.²¹ They concluded that a tighter film formed by smaller particles has less space for surfactant molecules to migrate, minimizing preferential location of surfactant on latex film surface. The beneficial effect of block improvement, therefore, may be diminished.

In this experiment, the total amount of surfactant used was kept constant at 1.8 phm. The latex particle size control was accomplished by adjusting the seed latex usage or initial surfactant concentration during latex preparation. Similar block resistance was obtained for the paints based on latexes of different particle size ranging from 0.096 to 0.22 micron (*Figure 2*). Particle size did not seem to affect the block resistance of the low-VOC acrylic paints. This is probably because surfactant migration during the film formation of a formulated paint differs somewhat from the process of neat latex particles. Previous studies have focused extensively on coalescence of pure latex systems and the factors affecting surfactant distribution during and after the film formation process. One can imagine that there may be



Figure 2—One-day room temperature block vs. latex particle size.

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Figure 3—One-day room temperature block vs. CTA concentration.

more passages for surfactant migration in a pigmented paint system than in the neat latex films. The polymers included in *Figure* 2 have the same T_g ; equal contribution of polymer bulk property to block resistance can be expected. Since block resistance has both bulk and surface components, the data thus suggests that good film formation facilitated by low MFFT (< 0°C) resulted in similar surface morphology after one day drying at room temperature, in spite of different particle sizes.

Gel Content and Molecular Weight

Polymer composition, gel content, and molecular weight have profound impact on end-use performance. Gel content is the insoluble fraction of the dried polymer in a solvent, typically tetrahydrofuran (THF). In addition to chemical crosslinking, chain transfer to polymer can also introduce high gel content. In emulsion polymerization of butyl acrylate, gel is produced by both intermolecular and intromolecular transfer to polymer.²²⁻²⁴

In the presence of a chain transfer agent (CTA), transfer of propagating radicals to the CTA dominates all other chain transfer processes. The degree of branching and, consequently, the amount of gel material is suppressed.²⁵ This is also true for the acrylic polymers in this study. The gel content of the acrylic polymer without CTA was approximately 65%. When CTA was present at 0.2 phm, the gel content was reduced to 1%, indicating the resulting polymer was substantially free of insoluble gel.

The amount of gel indicative of degree of branching has important implications for particle coalescence during film formation and polymer adhesion or interdiffusion in the block test. Using fluorescence resonance energy transfer (FRET) technique, Winnik et al. was able to prove that long-chain branching alters polymer



diffusion rates in the film formation of poly(butyl acrylate-co-methyl methacrylate) latex.²⁶ *Figure* 3 compares the room temperature block performance of the polymers prepared with and without CTA. The polymer with high gel content exhibits less blocking. Even though the polymer matrix with no branching may allow greater surfactant mobility, it also enhances film adhesion or polymer interdiffusion across the film interface. The net result is that the polymer with low gel content yielded lower block resistance, as shown in *Figure* 3.

Glass Transition Temperature of Polymer

The glass transition temperature of polymer is a characteristic property of the polymer. The T_g of the acrylic polymers was varied from -10 to 4 °C by changing the ratio of butyl acrylate to methyl methacrylate. This narrow range is chosen to ensure adequate film formation of the low-VOC paint formulations. *Figure* 4 presents the one-day room and elevated temperature block results. Increasing T_g did not effect significant change in the polymer's blocking behavior at room temperature. However, the hot block performance is improved considerably when the polymer T_g is increased to 4 °C. This result suggests that polymer T_g plays a more important role in block resistance at elevated temperature.

Increasing T_g by increasing MMA content in the latex has several effects. First, it improves polymer cohesive strength and decreases chain mobility, both of which should improve block resistance. At the same time, there is less free volume in the higher T_g polymer system. Surfactant migration is restricted, which lessens the contribution of surface-concentrated surfactant to block resistance. Secondly, increasing MMA reduces BA branching, which changes the diffusion rates of both polymer



Figure 5—Surfactant choice and block resistance.

and surfactant and their effects on block performance. Lastly, surfactant-polymer compatibility also depends on polymer composition. The interplays of all the abovementioned factors will lead to specific surface properties and morphological features. The block results thus reflect the balanced result of surface and bulk contributions.

Surfactant Type

Figure 5 displays the block results of the acrylic latexes stabilized with two different anionic surfactants. At the same polymer T_g and surfactant level, surfactant B provided improved antiblocking property and the differentiation is especially apparent for the hot block resistance. *Figure 5* demonstrates the impact of chemical composition of surfactants since the polymer bulk properties are similar (same T_g). The difference in block resistance emphasizes the influence of film surface properties. It has been shown that interfacial surface tension and surfactant-polymer compatibility dictates surfactant distribution in the latex films.²⁷⁻²⁹ The results in *Figure* 5 suggest that surfactants A and B likely have different migration profiles and/or orientation on the interface, producing different film surface characteristics.

CONCLUSIONS

The influences of some polymer design parameters on block resistance are examined. This article reveals that many factors can influence the block resistance of low-VOC acrylic paints. Since block resistance is a function of surface profile and bulk material properties, surfactant structure and concentration are important considerations in latex synthesis. Other latex design parameters such as increased T_g and gel content also have positive effects on block performance of acrylic polymers. The results presented in this article demonstrate that good block performance can be achieved with homogeneous acrylic latexes when the above parameters are optimized.

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