Macromol. Symp. ***187****, 771–780 (2002)*

The Challenge of Achieving Traditional Exterior Durability Performance in Low VOC Architectural Coatings

*Matthew S Gebhard**

Rohm and Haas Spring House Technical Center, Spring House PA 19477 USA

Summary: Over the years the optimization of water-borne emulsion polymers has resulted in water-borne coatings with excellent exterior durability and significantly reduced solvent emissions versus solvent-borne coatings. In recent years, pressure to further reduce emissions has necessitated the use of softer polymer compositions which can negatively impact gloss and tint retention, and dirt pick up resistance. The use of heterogeneous polymer morphologies are addressing these short comings; however care must still be taken not to affect paint durability. The development of low solvent emission thickeners and mildewcides has allowed further reduction in paint emissions.

Keywords: Volatile Organic Compounds, Architectural Coatings, Exterior Durability

Introduction

Historically the advent of water-borne emulsion polymer technology in the mid to late 1900's led to the development of water-borne paints which offered substantial reductions in the amount of volatile organic compounds (VOCs) released when the paint was applied to a substrate. This advance offered some clear benefits to the end user such as low flammability, low solvent exposure, ease of clean up, and less impact on the surrounding environment. Throughout the later part of the 20th century advances in emulsion polymer design and performance led to the development of water-borne architectural paints with excellent exterior durability characteristics. In many cases the exterior durability performance of these water-based paints and coatings exceeded the performance seen from solvent-borne alkyd paints[1], especially in the area of gloss and tint retention, and crack resistance over wooden substrates. The currently accepted performance of these water-borne architectural paints has established a high level of expected exterior durability which must be considered when developing any new low VOC binder technology.

© WILEY-VCH Verlag GmbH, 69469 Weinheim, 2002 CCC 1022-1360/00/$ 17.50+.50/0

In recent years, legislation and public pressure to further reduce VOC emissions, has forced new constraints on polymer design which can negatively affect the exterior durability characteristics of emulsion polymer coatings. In particular, the need to form a high quality film with very limited or no volatile coalescing agents necessitates the use of softer polymer compositions. This is usually achieved by increasing the ratio of soft to hard monomers in the polymer backbone. Traditionally all acrylic polymers for architectural paints have T_g's* ranging from 11°C to 2°C depending on the desired balance of flexibility and hardness. These polymers typically require 5-10% coalescing solvent based on polymer solids. Eliminating the need for coalescing solvents requires lowering the T_g well below 0°C. This affects exterior durability characteristics, in particular gloss and tint retention, as well as dirt pick up resistance of the paints based on these binders. In some cases the impact can be quite significant. This ultimately reduces the service life of the coating, negating one of the benefits that many water-borne paints offer.

The use of more sophisticated polymer morphologies such as heterogeneous latex polymers[2] which contain at least two phases of differing T_g's is a classic way in which coalescent requirements of a binder are reduced without comprising surface hardness and block resistance. In fact, in many cases it is possible to develop latex binders which offer much reduced surface tack relative to an analogous homogeneous polymer. This technology has been used extensively in the development of water-borne polymers for interior clear wood finishes[3]. This technology has seen much more limited use in pigmented architectural binders, for two primary reasons:

1) The impact of a hard domain in a soft polymer can significantly reduce the binding capacity of the polymer, which is especially pronounced at high PVCs. This typically shows up as dramatically reduced abrasive scrub resistance
2) The exterior durability of paints made from these heterogeneous latex polymers is typically not very good, especially when the polymer has been designed to maximize hardness and block properties.

Low VOC Formulation Issues

In North America the push is to achieve architectural paints and coatings with as low as 50g/L

---

* The Tg's given are based Fox calculated Tg values not measured values

VOC[†]. In contrast, typical water-borne architectural paints sold in North America have been between 150g/L and 350g/L. One approach for addressing this gap is to reformulate with lower volatility or reduced VOC materials. In addition as paint formulations are prepared at low VOC's it is important to consider not only the contributions of coalescing solvents and glycols, but also the contributions from traditional paint additives such as film mildewcides, rheology modifiers, and surfactants. In particular mildewcides and rheology modifiers can bring in several grams per liter of VOC. In conventional VOC coatings these contributions were not significant, but at low VOC they can be the largest VOC source in the paint. It is worth while mentioning that the current VOC determination method as specified in EPA Method 24[4] does not specify a boiling point criteria for assessing whether a component is volatile, instead the method relies on a thermal desorption protocol[‡]. That being the case it has been our experience that many materials that might be assumed to be nonvolatile because of their high boiling points (>300°C) are actually surprisingly volatile in a coating.

In a typical paint formulation the contributions from the mildewcide and thickener can easily be 25g/l. When trying to hit 50g/l or lower as a VOC target these levels become problematic. Traditionally, mildewcides were provided in an organic solvent as a means of carrying these water-insoluble materials into the paint in an effective form. Simply adding 100% solid dry powders of the active ingredients to a paint causes many problems, and is often ineffective at providing mildew protection. For a typical mildewcide at 50% in an organic solvent the contribution of the organic carrier solvent is roughly 15g/L, or 33% of the allowable solvent. Recent developments in the design of water dispersed mildewcides (as represented by Rocima 342, Rocima 350 or the VOC free Rocima 371N) has reduced the VOC contribution from the mildewcide by 60-80%.

Many associative rheology modifiers also have significant levels of volatile organics such diethyleneglycol butyl ether, or propylene glycol. The solvents, which are present at 10-20% on total supplied weight, are required to reduce the as supplied viscosity to manageable levels. Another approach is to use surfactants to reduce the as supplied viscosity; however, this leads to many paint performance problems such as water-sensitivity, and surfactant staining. The

---

[†] The VOC of a coating is determined by a collection of tests known as EPA method 24, and is determined by subtracting the volume of water from the coating

[‡] 110°C for 30minutes in an ove.

development of alternative viscosity suppression technology in the early 1990's, opened the door for development of associative thickeners with extremely low VOC contributions. For example in a typical paint formulation there might be as much as 15g/l of VOC which comes from a traditional thickener which uses 20% organic solvent. As new low VOC binders are developed to address freeze-thaw and open-time issues, the trend is to be more hydrophilic and stabilized by alternative means requiring the use of more efficient associative thickeners having much higher as supplied viscosities. Thus the use of viscosity suppression technology will become increasingly more important.

As will be shown below the need for low VOC formulating capability means reducing the T_g of the base polymer. This leads to an overall reduction in tint retention of the paint. It also compromises block resistance. One intriguing way to gain back some tint retention and improve block is to use micro-voided polymers (Ropaque™ Ultra). These materials are essentially hard polymer additives which compensate for the reduction in the hardness of the base polymer. An intriguing aspect of the micro-voided polymers is they can deform under certain conditions and it has been observed that upon exterior exposure the voids can collapse causing a loss of some of their intrinsic hiding ability. This leads to an apparent increase in color strength from the colorant, thus counteracting the tint loss process. This approach has been shown to work quite well in pastel paints where there is 18-24Kg/100Liters of TiO_2. While it is true that the paints are getting darker as they age outside, the effect is quite even creating the illusion that the paint is not fading as fast. In paints with TiO_2 levels below 18Kg/100liters care must be taken to ensure that this general darkening is not large enough to cause an undesirable shift in color.

The contributions of TiO_2 choice to exterior durability have long been recognized as being very significant. Over the last several years TiO_2 suppliers have made great strides in improving the surface coatings on TiO_2 resulting in substantial improvements in gloss and tint retention. In a world of softer low VOC coatings this will become increasingly more important.

Despite many of the above formulation approaches which can either reduce paint VOC or improve exterior durability performance, the choice and design of the film forming binder is crucial to determining exterior durability performance. It is also clear that developing a low VOC binder technology based on lab properties can lead to products which have poor exterior performance. Unfortunately, there remains no substitute for evaluating exterior durability in real exterior exposures at many sites and in many formulations. This is a long process which requires several years and good planning.

Experimental Details

To address the effect of binder T_g and heterogeneous polymer morphology on exterior performance, butyl acrylate and methyl methacrylate homogeneous copolymers were prepared at varying T_g's using a conventional semi-continuous batch process, and are compared to two heterogeneous polymers which vary by T_g and the ratios of hard to soft phases. It is worth while mentioning that the process by which the polymer is made can significantly affect the film forming ability of the polymer, and thus plays a significant role in determining what polymer T_g is needed to get adequate film formation[§]. Paints at 22% PVC and 36 volume solids were prepared from these binders based on the formulation given in Table 1.

Table 1. Experimental Paint Formulation

Grind	**Kgs**
Tamol 731A	1.68
Tego Foamex 810	0.14
Surfynol CT-111	0.27
Ti-Pure R-706	31.68
Water	7.46
LetDown	
Water	2.40
Binder @ 50% solids	63.58
Texanol (Variable) (0-6% Based on Binder solids)	X
Surfynol CT-111	0.12
Mildewcide	0.96
Acrysol RM-2020 NPR	3.95
Acrysol RM-8W	0.56
Water	12.94

For the Blue tints 2.4Kgs Phthalo Blue per 100Liters of paint were used

The paints were then drawn down over aluminum panels and submitted to Q-Panel testing in south Florida[**]. The three properties followed were 60° gloss, L* which is a measure of dirt

---

[§] A discussion of these effects is beyond the scope of this paper

[**] Other sites were also chosen and the trends observed at S Fla were consistent with these other sites

pickup, and B* in a phthalo blue paint.

Experimental Results

Homogeneous Polymer Controls

Figure 1 shows the percent 60° gloss retention for a series of homogeneous BA/MMA polymers of varying T_g. As can clearly be seen the gloss retention decreases with decreasing polymer T_g. Typically the T_g of the polymer must be reduced to below 0°C to achieve adequate film formation in low VOC formulations, which results in substantially decreased gloss retention. Figure 2 is a similar plot looking at the change in b* for these paints. In this case, an increase in b* indicates that the blue pigment is losing its color strength, thus paints with larger changes in b* have poorer tint retention. As with the gloss retention there is a decrease in tint retention as the T_g of the polymer is lowered. Figure 3 also shows a similar story. As the polymer T_g is dropped, there is an increasing trend for the paint film to become darker with time (decrease in L*). This is indicative of the paints becoming dirty with exterior exposure. This data shows that simply lowering the T_g to get adequate coalescent free film formation is not an acceptable approach.

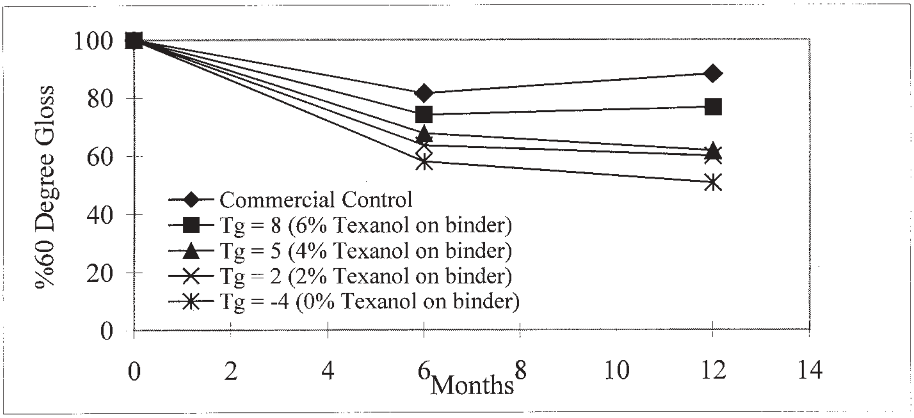

Figure 1. % 60 Degree Gloss for homogeneous latex polymers at various T_g's

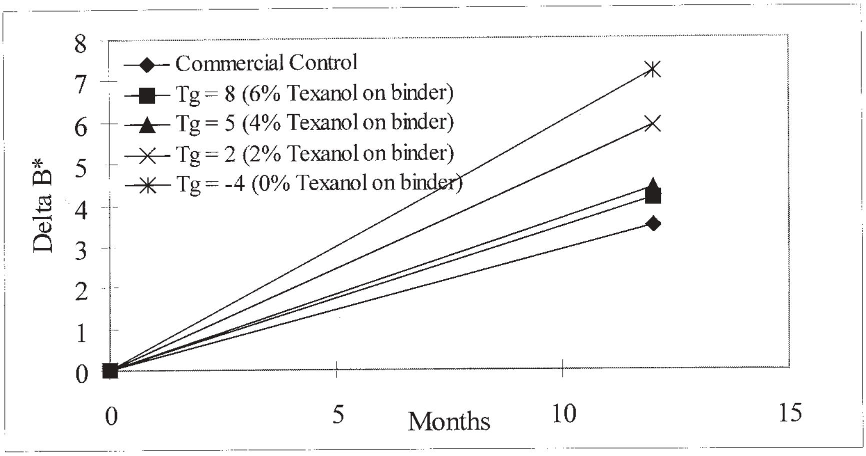

Figure 2. Delta b* for homogeneous latex polymers at various T_g's

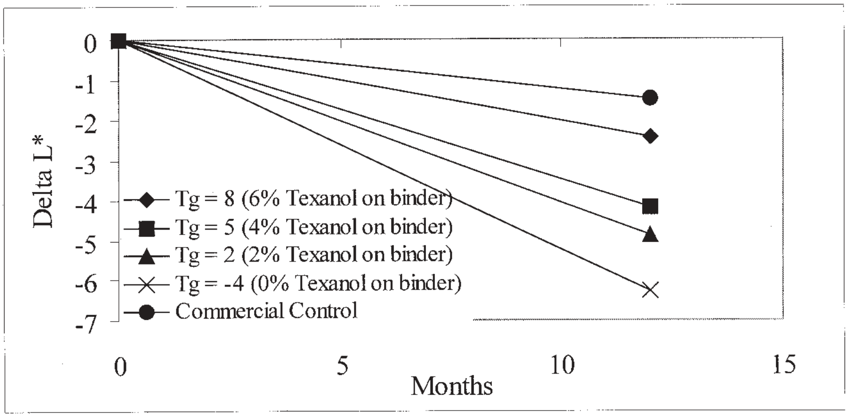

Figure 3. Delta L* for homogeneous latex polymers at various T_g's

Heterogeneous Polymers

Figure 4 shows the 60% gloss retention data for two homogenous polymer compositions (8°C and –6°C) and two heterogeneous polymer compositions. When making a heterogeneous polymer composition it often becomes necessary to further lower the T_g of the softer polymer phase in order accommodate the effect that the harder phase has on film formation. Hetero #1 represents an early attempt at using heterogeneous polymer morphology to eliminate the need for a coalescing solvent. Hetero #1 clearly has poor gloss retention. On the other hand hetero #2 shows very respectable gloss retention. These results drive home the need for assessing exterior durability for heterogonous polymer compositions. Figures 5 and 6 show the tint retention and L* (dirt pick up) data for the same polymer set in figure 4. Interestingly, in both cases the hetero polymers show very reasonable tint retention and dirt pick up resistance.

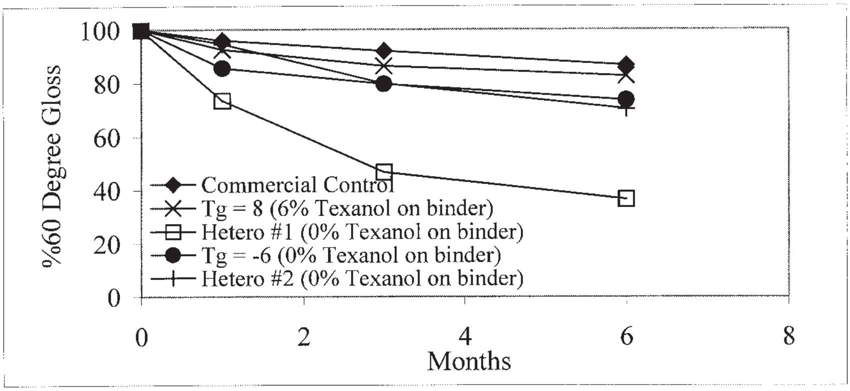

Figure 4. % 60 Degree Gloss for heterogeneous latex polymers

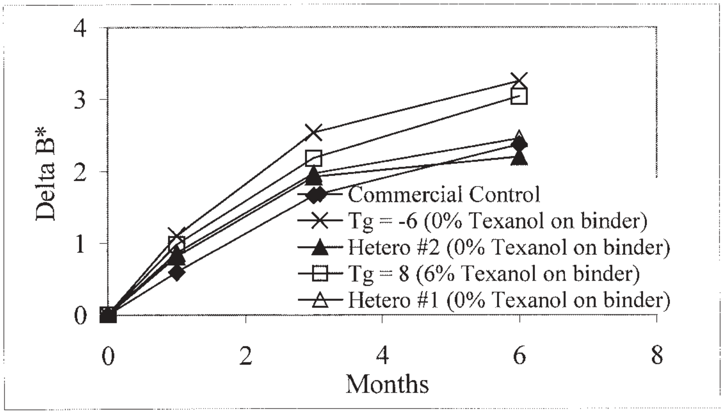

Figure 5. Delta b* for heterogeneous latex polymers

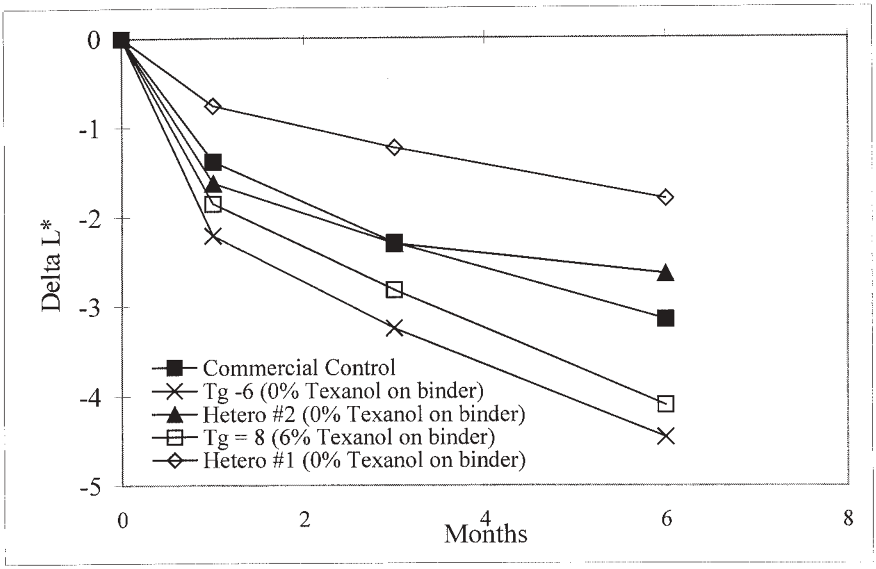

Figure 6. Delta L* for heterogeneous latex polymers

Discussion

The results presented here show that heterogeneous polymer morphologies can give substantial improvements in certain exterior durability properties; however care must be taken when designing these polymers. With appropriate design, heterogeneous polymer compositions can offer improvements in dirt pick up resistance and tint retention. Based on the dirt pick up resistance and tint retention data alone it would seem that it would be straight forward to design a multi-phase binder with exceptional exterior durability. On the other hand, if inappropriately designed a heterogeneous polymer can have very poor gloss retention, and in many cases can show very bad cracking over wooden substrates. We have found that the good results shown for hetero #2 tend to be the exception and not the rule. In fact it is quite challenging to design a heterogeneous polymer with acceptable gloss retention, and crack resistance. Aspects such as the morphology of the heterogeneous polymer particle play a significant role in the film forming capabilities of the binder and ultimately the need for coalescing solvents to achieve adequate film formation. Simply changing the T_g's of the phases is often inadequate to bring about the desired balance of exterior durability properties and general film properties. Moreover, if one is simply evaluating properties such as surface hardness, block resistance, and film forming capabilities it is highly likely that the binder will have terrible exterior durability. It is important to stress the need for assessing exterior durability when developing new binders based on heterogeneous polymer morphologies. However, with careful manipulation of the binder morphology and careful attention to optimization of film formation it is possible to design heterogeneous polymers with very respectable exterior durability.

References

1. "Organic Coatings Science and Technology" Z. Wicks, Eds, J. Wiley & Sons, New York, 1994.
2. a) J. E. Jonsson, H. Hassander, B. Tornell, *Macromolecules*, **1994**, *27*, 1932.
   b) J. E. Jonsson, H. Hassander, L.H. Jansson, B. Tornell, *Macromolecules*, **1991**, *24*, 126.
   c) C. L. Winzor, D.C. Sundberg, *Polymer*, **1992**, *33 no 18*, 3797
3. a) A.J.P Buckmann, G.C. Overbeek, T. Nabuurs, *Paint and Coatings Industry*, **August 2001**, 40.
4. "Manual on Determination of Volatile Organic Compound (VOC) Content in Paints, Inks, and Related Coating Products: Second Edition", Eds , J.J. Brezinski; ASTM, Philadelphia 1993.