



Understanding and Improvement of TiO_2 Efficiency in Waterborne Paints Through Latex Design

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This article explores the influence of functional acid monomers incorporated into polymer latex dispersions for their ability to effectively disperse TiO_2 pigment particles in flat paint applications. The functional acid monomer type (i.e., vinylphosphonic acid, acrylic acid, methacrylic acid, and itaconic acid), the partitioning of acid monomer in the polymer or aqueous phase during the emulsion polymerization and the role of the latex polymer particle size were investigated. The model latex dispersions were then formulated into their corresponding paints. Through the use of Cryogenic Scanning Electron Microscopy (Cryo-SEM), it is possible to qualitatively observe the TiO_2 efficiency of the paints in the wet state.

Furthermore, these results can be correlated with measurable performance properties (i.e., abrasion resistance/tint strength) of the same paints in the dry state. Finally, the sole interaction of these tailored latices with TiO_2 itself is investigated through Cryo-SEM to gain a comparative insight into how these particles orient themselves with one another dependent on the functional acid monomer employed.

INTRODUCTION

As environmental regulations for formulating architectural coatings become ever more stringent, the role of the polymeric latex in bringing out the utmost in performance properties has never been greater. In particular, the South Coast Air Quality Management District (SCAQMD) legislation, which is to be fully implemented in July 2008, offers new challenges and opportunities to architectural coatings manufacturers in providing latex dispersion products which are VOC compliant at 50 g/l. As a result, such properties as freeze/thaw resistance, scrub resistance, and substrate adhesion, which in the past were mainly imparted by the high levels of VOC components in the

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paint formulation, are now optimized through developing technologies that are centered around the nature of the latex design. At the same time, there is an increasing demand to develop the latex to be more compatible with the other raw materials in the paint formulation. As costs rise for paint manufacturers, the need to minimize the amount of costly raw materials gains a growing importance. Figure 1 shows a rough raw material cost breakdown for a gallon of paint in high-gloss, semi-gloss, and flat sheens.

It is plainly evident in Figure 1 that TiO_2 inorganic pigment contributes greatly toward the total cost, especially in instances of the lower sheens. Not surprisingly, it has been a continuing goal of the paint industry to achieve a higher level of TiO_2 efficiency, resulting in less TiO_2 consumption. This article explores the role of latex design toward optimizing the property of TiO_2 efficiency in flat sheen paints and shows the consequences of TiO_2 efficiency toward the physical performance improvements of the dried paint film. Specifically, the role of functional acid monomers is examined to further elucidate their interaction with TiO_2 particles.

TiO_2 is the primary white pigment used in paints due to its high refractive index ($n_D \approx 2.6$), scattering efficiency, ideal particle size ($\phi \approx 250$ nm), and particle spacing behavior.¹ However, TiO_2 particles tend to be difficult to randomly disperse due to van der Waals colloidal attractive forces. Consequently, clusters of TiO_2 particles are formed which detrimentally influence the characteristics of the paint film in its dried state. These clusters severely reduce the scattering efficiency of the paint film and increase the roughness or the number of defects of the paint film surface. TiO_2 particles that are well dispersed and separated from each other have been useful in preparing respective coatings with improved hiding power and tint strength. In addition, the dispersibility of TiO_2 particles throughout the paint ensures that the paint itself becomes a fully integrated composite material which has improved scrub and abrasion resistance.

TiO_2 is typically sold as a dried powder and milling is often required prior to formulating the pigment into the paint; however, agglomeration, flocculation, and settling of the particles can still occur. TiO_2 pigments are also available in a concentrated slurry form using polyelectrolyte dispersants and surfactants. These auxiliary components usually contain anionically charged polycarboxylate or polyphosphate moieties which directly interact with the positively charged TiO_2 particle surface and disrupt interparticle aggregation. Although these moieties are effective in breaking up TiO_2 agglomeration, they still do not provide the optimum performance in pigment efficiency. By designing the latex dispersions with anionically charged functional

acid groups, which can interact directly with the pigment particle, an additional steric barrier can be created that can further prevent pigment agglomeration.

This article is continuing, in part, the previous work that we conducted concerning the use of Cryogenic Scanning Electron Microscopy (Cryo-SEM) to elucidate the behavior of the model latices themselves and their respective paints in the wet state. This qualitative analytical method has in the past given key insight into better understanding and improving freeze/thaw behavior of latex dispersions and the assessment of the TiO_2 efficiency in paints.²⁻⁵ In this article we evaluate the TiO_2 efficiency of several latex prototypes where both the type of the functional acid monomer is varied along with its degree of partitioning throughout the polymer particle and aqueous phases of the polymer latex dispersion. Through Cryo-SEM, we are able to survey the sole interaction of TiO_2 particles with latex particles in their appropriate mixtures and in the formulated paints.

EXPERIMENTAL

Latex Synthesis

The acrylic polymer latices were synthesized by a seeded semi-continuous emulsion polymerization process under monomer-starved conditions. The seeded process affords easy control of particle size while the slower-than-polymerization feed rates for the monomers avoid composition drift in the copolymers formed throughout the polymerization process. Two surfactants, a sulfated fatty alcohol ethoxylate and

Figure 1—Raw material cost assessment of different paint sheens.

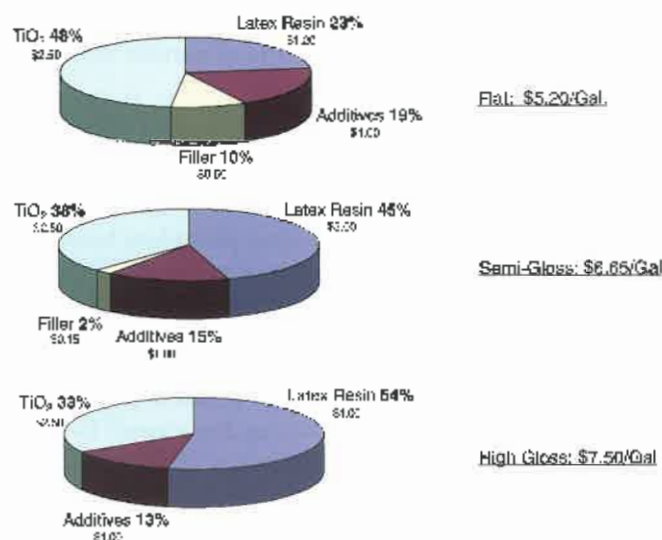
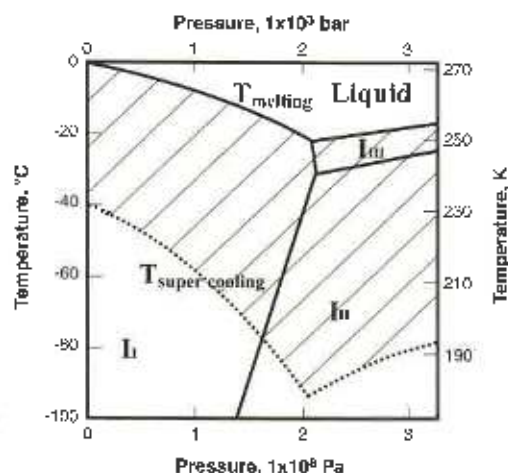


Figure 2—Phase diagram for the super cooling of water at atmospheric pressure and at 2100 atm.



sodium dodecyl sulfate (SDS), were used. Two pairs of monomers were used in making up the backbones of the model copolymer latexes: methyl methacrylate (MMA) and n-butyl acrylate (n-BA). Functional acid monomers, such as acrylic acid (AA), methacrylic acid (MAA), itaconic acid (IA), and vinylphosphonic acid (VPA), were incorporated for enhancing latex stability and paint compatibility (especially with the target component in this study: TiO_2 pigment particles). These functional acid monomers were neutralized to various degrees in the pre-emulsion prior to it being fed into the emulsion polymerization vessel. In addition to the functional acid monomers, a variety of other proprietary functional monomers (~4–6%) were used in the emulsion polymerization to further promote latex stability and wet adhesion. The latexes were neutralized with ammonia to 8–9 pH at the end of the synthesis. The particle sizes were determined using photon correlation spectroscopy. Particle sizes of the prototypes range between 216–246 nm unless noted otherwise when evaluating the role of particle size on TiO_2 efficiency.

High Pressure Freezing, Fracture, Surface Treatment, and Cryogenic SEM

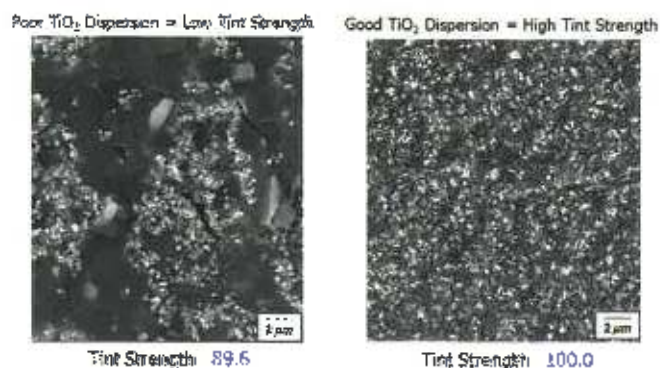
The detailed sample preparation procedure has been described elsewhere.^{6a,b} A droplet of paint or TiO_2 /latex mixture was sandwiched between two brass discs, each with a cylinder-shaped indentation. The assemblage was quickly frozen in a Bal-Tec HPM 010 high pressure freezing machine at 2100 bar. High pressure freezing is critically important for minimizing disturbance by large ice crystals to the original morphology of an aqueous sample. It works as follows: high pressure lowers the temperature range of supercooled water from 233–273

K at atmospheric pressure to 183–251 K at 2100 bar so that freezing water has a better chance to reach the glass transition temperature and be vitrified (zone I_{II}) before ice crystals grow (zone I_I). (This phenomenon is nicely described in Figure 2.) The frozen sandwich was then fractured in liquid nitrogen. One side of the fractured sample was mounted on a cryo-transfer stage and was sublimed for 18 min to improve the topographical contrast. The fracture surface was then sputter-coated at -130°C with platinum to a nominal thickness of 4 nm to avoid the charging artifact. The metal-coated fracture surface sat on the cold stage and was examined in the in-lens Hitachi S900 field emission SEM. Both secondary electron (SE) and backscattered electron (BSE) images were recorded. The former provides better topographical contrast while the latter is more preferred for maximum contrast between organic and inorganic phases. All electron micrographs shown in this article are BSE images, which show the contrast of the white TiO_2 pigment particles with respect to the latex particles or other paint ingredients seen in the micrograph.

Tint Strength

The tint strength was evaluated by an internal test method in accordance with ASTM method D 2745 where the respective paints were tinted with identical amounts of (phthalo blue) tint paste and mixed thoroughly. In this method where we are measuring the tinting strength of the white pigment, the higher tint strength values are comparative to lighter and superior TiO_2 efficient paints. Note: tint strength of the white pigment is a comparative method and not an absolute one to quantify the reflectance measurements with regard to the degree of the TiO_2 dispersion in the dried paint film. Therefore an internal control sample must be included and subsequent measurements are comparatively based on that control. The commercial control and standard for this study is the binder that resulted in the paint with a good tint strength value of 100 in Figure 3. The resulting tinted paint was drawn

Figure 3—Direct observation of wet paints by Cryo-SEM.



down with a 7 mil blade or a 3 mil bird bar onto a Leneta chart Form WB or BYK Gardner AG-5342. The paint film was allowed to dry overnight. After drying, a color difference was run between the control and the test paint using the SP62 X-Rite Spectro-photometer, which measures the lightness of the dried paint films. A lighter film will have better TiO_2 utilization; a darker film will have worse TiO_2 utilization.

Scrub Resistance

The scrub resistance was evaluated in accordance with ASTM standard test method D 2486. This test method mainly applies to testing dry film integrity and abrasion resistance. The test paint was drawn down side by side with a suitable control on a Leneta scrub test panel using 7 mil side of the Dow film caster. The samples were allowed to dry/cure for six to eight days or as specified. The samples were then oriented over the shim on the glass plate in the Gardco scrub machine so that the coating direction is perpendicular to the direction of the brushes. Next, 7 mL of scrub media (Leneta SC-2) was applied evenly into the brushes, which are then attached onto the moveable arm. Before starting the test, it was ensured that the samples were centered and the brushes would travel over all shims during its full cycle. Immediately after starting the scrub machine, 5 mL of water was placed on the scrub test sample along the path of each brush. Approximately at every multiple of 400 cycles, the process was stopped and another 7 mL of scrub medium to the scrub brush and another 5 mL water to the scrub path was added. The sample was scrubbed to failure and cycle number was recorded. Because of the high degree of variance with this particular measurement, the samples were run in duplicate and the average scrub number is reported.

RESULTS AND DISCUSSION

As mentioned in the introduction, this article explores the influence of functional acid monomers incorporated into polymer latex dispersions for their ability to effectively disperse TiO_2 in flat paint applications. We decided to examine both commercial and experimental latices to first gain an assessment of the performance of TiO_2 efficiency of the paints. In this regard, we were able to obtain an excellent qualitative differentiation through Cryo-SEM images of the paint in its wet state as well as mixtures (in the same proportions as in the paint formulation) of the latex and TiO_2 slurry in its wet state. Initial studies targeted commercial binders in order to get an accurate assessment of the pigment efficiency of products already in the marketplace. For example, Figure 3 shows the Cryo-SEM images of the

wet formulated paints based on two commercially available latex products. In both micrographs one is able to clearly see the correlation of TiO_2 dispersibility and tint strength value. The SEM micrograph on the left shows TiO_2 particles heavily aggregated together, whereas with the micrograph on the right, the TiO_2 is more homogeneously distributed in a random-fashion throughout the paint film. The clustering of TiO_2 particles severely decreases the scattering efficiency of the pigment and leads to lower tint strength values ($\sim 10\%$ less).

All latices, experimental or commercial, were formulated in the same flat paint formulation, which has an amount of volatile organic compounds (VOC) at 50 g/l, a pigment volume composition (PVC) of 45%, and the solids volume of the paint is at 39.0%. The flat paint formulation used in this study is shown in Table 1.

Four classes of experimental latices were used in the formulation and evaluated through the following test/methods to show the influence of the functional acid monomer with regard to TiO_2 efficiency:

1. Comparative Cryo-SEM imaging of the paint in its wet state
2. Comparative tint strength measurements of dried paint film

Table 1—Flat Paint Formulation Used in TiO_2 Efficiency Study

Latex Solids %	60
Latex MFFT ($^{\circ}\text{C}$)	4
Water	150
Ethylene glycol	5.1
Natrosol 250 MHBR	3.1
DuPont 11-Pure R-746	255
AMP 95	1.53
Dreplus L-475	2.86
Mix for 5 min at medium speed	
Igepal CIA 639	2.45
Tamol 731	8.16
Pruxel BD-20	3.06
Omyacarb 3	50
Omyacarb 10	103
Minex 4	100
Grind at high speed for 20 min	
Texann	7.35
Polyphase CST	5.1
Premix next 3 items and add	
Water	100
Natrosol 330 +	2.45
Dreplus L-475	3.57
Total paste	802.73
Latex (amount normalized to 60% solids)	316
Water	45
Total	1163.7

Figure 4—Influence of acid type on pigment dispersibility/paint film durability.

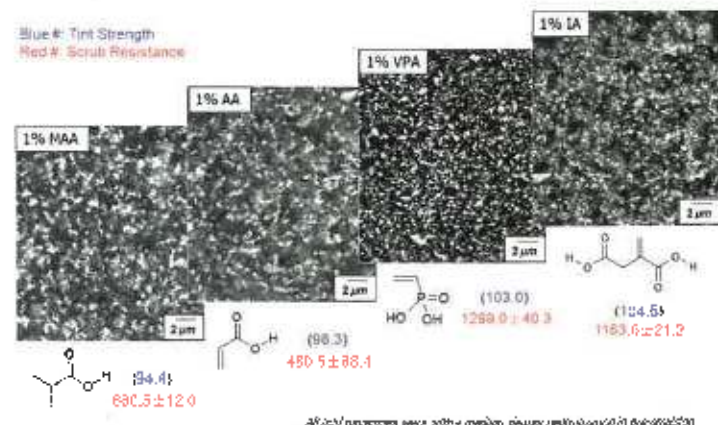
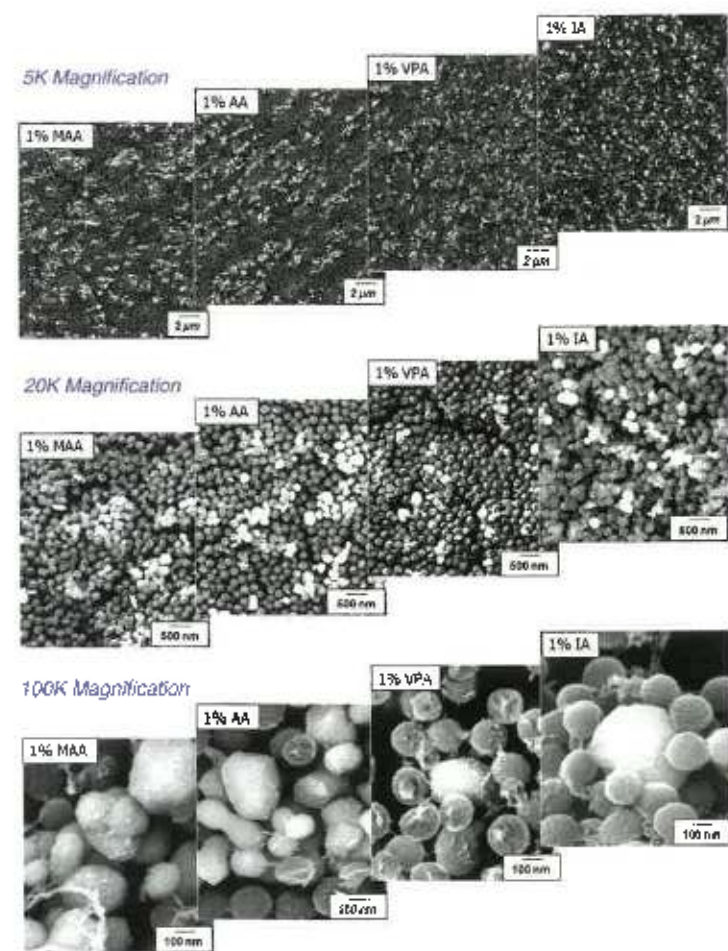


Figure 5—Influence of acid type on TiO_2 pigment dispersibility (latex/ TiO_2 blends).



All samples were submitted for 24 hrs of abrasion test at 1000000

3. Scrub/abrasion resistance: measurements of dried paint film

Although measuring hiding power is another way of determining TiO_2 efficiency, it is very difficult to differentiate between samples since the paints are formulated to give a very high degree of reflectance ($\sim 95\%$) at the required film thickness for the test method. In this regard it is easy for the differences of the values to lie within the degree of error for the measurement. Due to this high degree of variability and lack of reproducibility, we decided to focus primarily on the tint strength measurements of the white pigment over those of hiding power.

The first series of experimental lattices explore the type of functional acid monomer used during the emulsion polymerization; all other recipe ingredients/parameters in this particular series are identical (including degree of acid neutralization in pre-emulsion). The functional acid monomers employed in this series are AA, MAA, VPA, and IA. VPA was evaluated in this series, in addition to the functional acid monomers that contain carboxylate groups, due to recent work which promotes its use and the use of other monomers that contain dibasic phosphate groups for the improvement of TiO_2 efficiency.⁷⁻¹⁰ Figure 4 shows the influence of acid type on the performance properties that reflect on TiO_2 efficiency. The micrographs represent the formulated flat paints in their wet state.

Figure 4 shows that lattices where VPA or IA is incorporated give superior pigment efficiency when compared to AA or MAA functional acid monomers. This can be seen by the degree of clustering of the TiO_2 particles in the Cryo-SEM micrographs. Lattices that have AA or MAA produce paints that have high degrees of clustering, whereas those that contain VPA or IA give paints with lower degrees of clustering. Both the tint strength and scrub resistance data of the dried paint films correlate nicely to the qualitative SEM images. To further evaluate the interaction between the latex and TiO_2 particles, raw blends of the latex dispersion and TiO_2 slurry were mixed together and

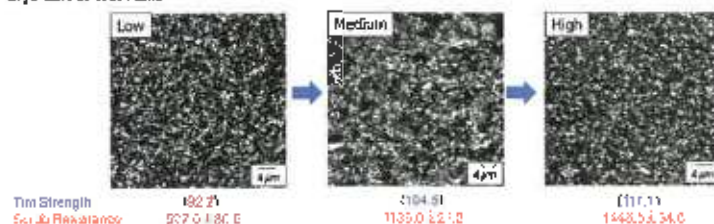
the samples of the mixtures were frozen and analyzed through Cryo-SEM. Figure 5 shows these micrographs for the same series of latices at 5K, 20K, and 100K magnification, respectively. One can clearly distinguish the latex's ability to disperse the pigment throughout the paints when observing the different SEM magnifications of the TiO₂ slurry/latex blends.

In addition to evaluating acid type for its ability to influence TiO₂ efficiency, it was also of interest to investigate the degree of neutralization of the functional acid monomers before they were incorporated during the emulsion polymerization. In this regard, the pre-emulsion was neutralized to various degrees which influence how the functional acid monomers are partitioned and distributed during the emulsion polymerization throughout the latex particles (particle interior/particle surface) and in the serum of the dispersion. At higher degrees of neutralization the acid groups will be driven more to the aqueous phase as seen in previous publications.¹¹⁻¹³ Just as importantly, however, the influence of the degree of neutralization strongly relies on the type of acid monomer used. From our series of latices we chose two binder prototypes with high TiO₂ efficiency (dispersions containing either 1% IA or VPA) and varied the degree of neutralization of these monomers before they were fed into the emulsion polymerization. Figure 6 shows the influence of the degree of neutralization for IA and Figure 7 shows the same for VPA.

With the use of itaconic acid, as the degree of neutralization increases, the TiO₂ efficiency of the binder also increases. This trend is evident in the dramatic increase of scrub resistance and tint strength data along with qualitative comparative assessment of the different TiO₂/Latex blends with the Cryo-SEM. At low degrees of neutralization, clustering of the TiO₂ particles takes place. With higher degrees of acid neutralization the TiO₂ is more evenly distributed across the micrograph. This nicely demonstrates the sole interaction between pigment and latex without any interference from

Figure 6—Influence of degree of itaconic acid neutralization on TiO₂ efficiency.

Cryo-SEM of Wet Paint



Cryo-SEM of TiO₂/Latex Mixture

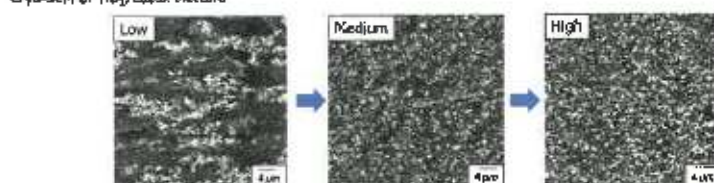
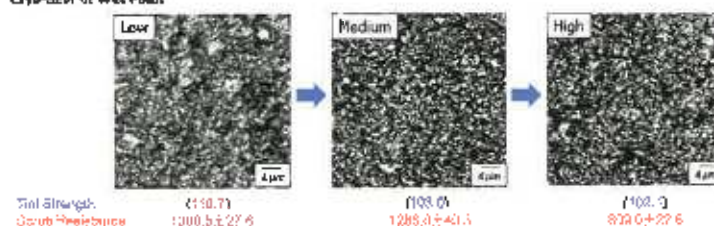


Figure 7—Influence of degree of vinylphosphonic acid neutralization on TiO₂ efficiency.

Cryo-SEM of Wet Paint



Cryo-SEM of TiO₂/Latex Mixture

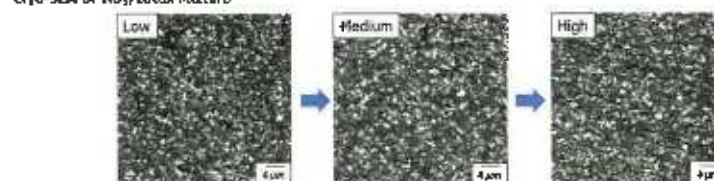
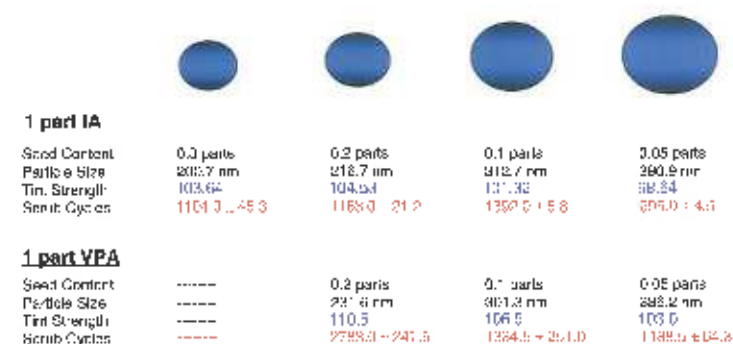


Figure 8—Effect of particle size on latices which contain one part of IA or VPA.



*All acid monomers were with a medium degree neutralization in pre-emulsion.

the other ingredients in the paint formulation. Interestingly, in the Cryo-SEM evaluation of the wet paint containing the same latices with different degrees of neutralization, it is difficult to differentiate between the micrographs despite the contrast in the tint strength numbers of the same paints in their dried state. We also looked at SEM micrographs of the dried paints and we were unable to differentiate between high and low levels of neutralization in the latex, despite its evident effect on the tint strength and scrub resistance results. Further investigations at BASF will center on observing how the TiO_2 particles are distributed in the different strata of the coating's thickness.

When vinylphosphonic acid (VPA) is employed, as seen in Figure 6, we see the opposite effect as the degree of acid neutralization increases. Lower degrees of VPA neutralization in the pre-emulsion yield latices with higher degrees of TiO_2 efficiency. This is opposite to the trend that we see in using itaconic acid. At low pH values (<2), VPA is thought to be readily incorporated onto the polymer particle surface and effectively interacts with TiO_2 particles.¹⁰ While both VPA ($\text{pK}_{a1} = 2.6$; $\text{pK}_{a2} = 7.3$) and IA ($\text{pK}_{a1} = 3.8$; $\text{pK}_{a2} = 5.4$) are very water soluble at high degrees of neutralization in the pre-emulsion, they behave very differently during the emulsion polymerization. VPA is believed to either form water-soluble oligomers or remain as unreacted monomer in the aqueous phase. These species apparently do not have the ability to disperse TiO_2 effectively. This is seen in the Cryo SEM of the latex/ TiO_2 blends for VPA, where it appears that the TiO_2 particles tend to aggregate at higher levels of acid neutralization. This observation is further confirmed by lower tint strength and scrub resistance values. In contrast, itaconic acid does not oligomerize with itself but instead is believed to copolymerize readily with other monomers (i.e., n-butyl acrylate and methyl methacrylate) to form oligomers which are believed to eventually localize themselves onto the polymer particle surface. Current work is ongoing to further prove and elucidate the behavior of latices containing these functional acid monomers.

Finally, the effect of latex particle size was examined for its influence over TiO_2 efficiency. We looked primarily at the tint strength measurements of the dried paint films to quantify this phenomenon. Figure 8 shows the effect of particle size on tint strength for latices which contain one part of IA or VPA, respectively. In addition to the tint strength, these figures also show how particle size influences scrub resistance. As polymer particle size increases within a series (designated by the type of functional acid monomer used), the scrub resistance decreases. Note that TiO_2 efficiency has a major influence between series over the property of scrub resist-

ance only when particle sizes are identical or close to identical. As seen in all the examples, when particle sizes of the latex vary in large degrees, there are differences in effectiveness of film formation that have the greatest influence over scrub resistance. Also, for latices with higher particle sizes, the likelihood of defects in creases and greatly influences the integrity of the consequent dried latex or paint film.

SUMMARY

In this study we were able to define the main contributing factors in latex design which have a positive influence over TiO_2 efficiency. Both functional acid monomer type and degree of acid neutralization in pre-emulsion before the emulsion polymerization greatly influence the ability of the latex and TiO_2 particles to interact with each other, which consequently prevents TiO_2 particle aggregation. The chemical nature of the phosphonic acid moiety in VPA and the structural orientation of the two carboxyl groups in IA make both monomers suitable for scattering TiO_2 particles very effectively. However, functional acid monomers with one carboxylic acid group do not appear to disperse the TiO_2 pigments effectively, as seen with latices that contain the AA or MAA functional acid monomer. In the example using IA, the increase of its degree of neutralization in the pre-emulsion before polymerization takes place greatly influences the TiO_2 efficiency of the latex. The trend observed in this instance is that the higher the degree of neutralization, the better the TiO_2 efficiency. The reverse is seen when VPA is used as the functional acid monomer: a lower degree of acid neutralization prior to polymerization yields latices with improved TiO_2 efficiency. Finally, the effect of latex particle size was examined and the general trend shows that as particle size is decreased, the TiO_2 efficiency of the latex increases. This is also the general trend observed in the decrease of the scrub resistance property of the paint film as latex particle size increases.

ACKNOWLEDGMENT

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