Shining New Light on Opaque Polymer

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An opaque polymer was developed in the 1970s to provide paint formulators with a light scattering pigment to supplement the use of titanium dioxide (TiO_2). The hollow-sphere structure of opaque polymer provides a controlled and consistent level of air void hiding in paint through the refractive index differential between the internal air void and the outer polymer shell. The encapsulated air voids provide hiding without the loss of resistance properties associated with other raw materials which provide hiding through increased film porosity. Extensive research and practical experience demonstrate that opaque polymer may be used to economically replace 10 to 20% of TiO_2 in white and pastel architectural paints. Recent and continued increases in TiO_2 price have raised the formulated cost of all paints. As a result, there is growing interest in using opaque polymer at higher levels of TiO_2 replacement in white and pastel acrylics. This interest extends to using opaque polymer in mid-tone tint bases, primers, and polyvinyl acetate (PVA) paints. Reformulation and performance studies coupled with a new proprietary reformulation tool demonstrate the expanded utility of opaque polymer in these formulation spaces. In addition, technology advances have led to the development of a next-generation opaque polymer that can be used in waterborne as well as solventborne alkyd architectural paints.*

**ROPAQUE™ Opaque Polymer.*

Photo courtesy of the Paint Quality Institute.

INTRODUCTION

Paint formulators have a long-standing interest in stretching tight raw material supply and lowering formulated cost through more efficient use of TiO_2. Dependent light scattering theory proposes that the scattering cross section of each TiO_2 particle is greater than the actual particle, a concept illustrated in *Figure* 1. When TiO_2 particles are crowded together, their light scattering zones overlap and reduce the net effect on hiding (*Figure* 2). Crowding occurs at high TiO_2 loadings or when large particle size extenders or binders are used in the paint formulation. Small particle size extenders and binders can reduce crowding and provide some improvement in the light scattering efficiency of TiO_2. Two technologies allow TiO_2 reduction using additional functionality beyond TiO_2 crowding reduction. Pre-composite polymer is a technology that produces more uniform TiO_2 particle distribution through the creation of a pigment–polymer composite. It maintains equal hide at lower levels of TiO_2. Opaque polymer is a synthetic white pigment that independently scatters light. When added to a paint film, it provides hiding and replaces a portion of the TiO_2.

HOW OPAQUE POLYMER SCATTERS LIGHT

Opaque polymer is a spherical pigment, with an outer shell comprised of hard, high T_g polymer, and a hollow core. Initially, the core is filled with water. Upon drying, water diffuses out of the core and is replaced with air (*Figure* 3). Due to its high T_g, the polymer shell remains intact and provides a permanently encapsulated air void.

The degree of light scattering that results from the refractive differential between the void and the shell is dictated by the size of the air void. The void size of opaque polymer must be carefully controlled to facilitate optimal scattering ability and consistency. The micrograph in *Figure* 4 shows the uniform particle size distribution and uniform void content for a sample opaque polymer. Not all commercial grades of opaque polymer are designed to these rigorous standards and, as a result, may not provide the same scattering performance or consistency.

At TiO_2 pricing scenarios predominant from the 1980s through early 2010, opaque polymer was commonly a cost-effective replacement for up to 20% of the TiO_2 in 100% acrylic white and pastel architectural paints. Today, TiO_2 pricing and its impact on formulated cost favor the use of opaque polymer at higher levels of TiO_2 replacement in these formulations, as well as in formulations with lower levels of TiO_2, such as mid-tones and primers. This effect can be seen in the idealized graphs in *Figures* 5 and 6.

PERFORMANCE AT HIGHER TiO_2 REPLACEMENT IN A FLAT FORMULATION

When TiO_2 was less than a dollar per pound, the maximum economic return was at 20% TiO_2 replacement with opaque polymer. Now that TiO_2 is near two dollars a pound, the maximum economic return is at 40% replacement, as shown in *Figure* 5. There is a wealth of data and practical experience to prove the performance properties of opaque polymer at 20%

Figure 1—Uncrowded TiO_2.

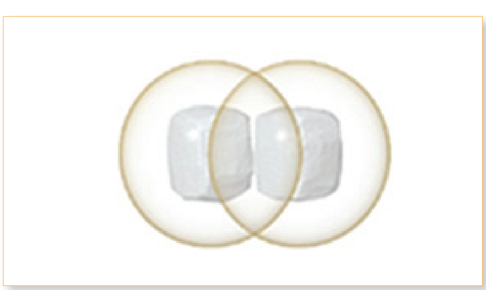


Figure 2—Crowded TiO_2.

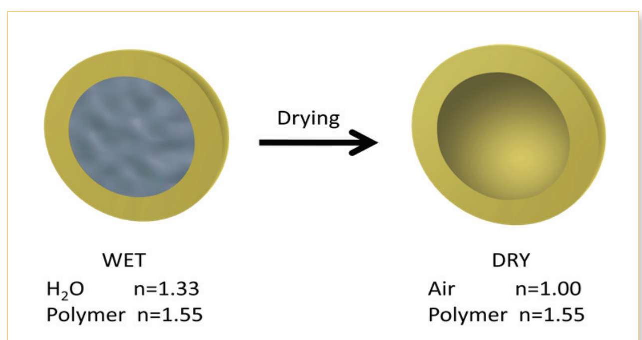


Figure 3—The difference in refractive index (n) between the air void and surrounding polymer gives opaque polymer the ability to scatter light.

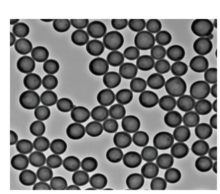


Figure 4—Transmission electron micrograph of the sample opaque polymer shows uniform void content.

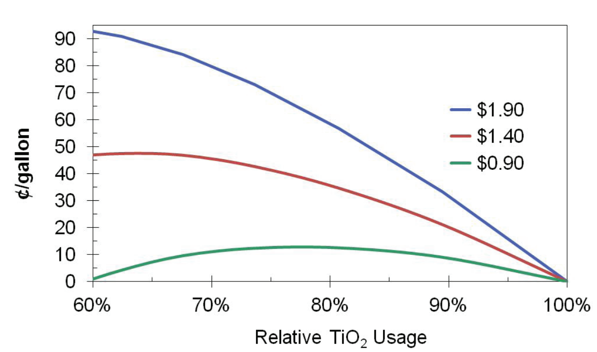


Figure 5—High-quality flat paint formulation starting with 200 lb TiO_2.

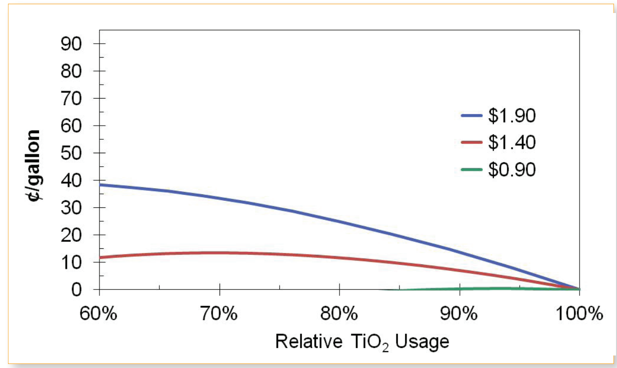


Figure 6—Economy flat paint formulation starting with 125 lb TiO_2.

replacement; however, less attention has been paid to higher levels of TiO_2 replacement. Studies were conducted to evaluate the performance properties and color matching of a high-quality flat paint formulation when reducing TiO_2, sometimes by as much as 50%. In one such study, a formulation with a starting level of 224 lb TiO_2 and 0, 10, 21, and 31% TiO_2 replacement with opaque polymer was evaluated. To match the dry hiding of the starting formulation, each level of TiO_2 reduction included an increased level of opaque polymer as determined using a proprietary reformulation tool. All four test formulations were tinted at 2 oz of colorant using 14 different colorants from the Colortrend 888 line.

When using opaque polymer at higher levels in flat paints, a slight increase in gloss may be observed. This experiment utilized different levels of diatomaceous silica in each reformulation to match the gloss of the starting formulation. Formulation details can be found in *Table* 1.

Gloss and hiding data are presented in *Table* 2. Gloss was measured using a standard gloss meter. Hiding was evaluated using contrast ratio and scattering (measurement based on Kubelka-Munk scattering theory) for white paint. For all levels of TiO_2 reduction, similar contrast ratio and scattering values were obtained. The tinted paints were also evaluated for Y-reflectance. Similar Y-reflectance values were obtained for each individual colorant indicating satisfactory color matches. Y-reflectance for the phthalo blue tints is included in the table as one example. For a visual analysis of the color matching for each of the 14 colors tested, the four paints with various levels of TiO_2 were drawn down on the same chart next to one another. *Figure* 7 shows samples from those drawdowns. In this photo, a one-inch strip of a drawdown has been cut and rotated 90° clockwise so that the top paint on each strip is the starting formulation and each paint lower on the color strip corresponds to a larger TiO_2 reduction. This experiment not only demonstrates how a formulation with no opaque polymer may be reformulated using less TiO_2 with similar dry hiding, tint strength, and gloss, but also shows how a formulation that already contains opaque polymer (Paint 2) may be reformulated to a larger TiO_2 reduction (Paint 3 or 4) to take advantage of the additional savings described in *Figure* 5.

Table 1—Quality Flat (49% PVC; 34.8% VS)

	Raw Material (lb/100 gal)					
	% TiO_2 Reduction	Ti-Pure R-706 Pigment	ROPAQUE™ Ultra Opaque Polymer	Nepheline Syenite	Diatomaceous Silica	RHOPLEX™ VSR-50 Binder (45.5% solids)
Paint 1	Control	224	0	224	0	368
Paint 2	10%	202	23	206	2	368
Paint 3	21%	176	51	171	14	368
Paint 4	31%	155	78	130	30	368

Table 2—Comparison of Gloss and Hiding at Three Levels of TiO_2 Reduction

	Gloss			Hiding Evaluation		
	20°	60°	85°	Contrast Ratio	Scattering	Y-Reflectance 2 oz Phthalo Blue
Paint 1	1.4	4.0	3.5	96.3	5.0	56.4
Paint 2	1.4	4.0	3.6	96.6	5.2	56.3
Paint 3	1.4	4.1	3.9	96.5	5.2	56.4
Paint 4	1.4	4.1	4.3	96.7	5.3	56.6

EXTERIOR DURABILITY AT HIGHER TiO_2 REPLACEMENT

To evaluate exterior film performance properties of paints formulated at higher levels of TiO_2 replacement with opaque polymer, an experiment was designed using multiple TiO_2 reductions for a high quality exterior flat tinted with 2 oz of phthalo blue. All paints were made at equal PVC and equal volume solids and applied over primed cedar. Boards were put on south vertical exposure in Spring House, PA in April 2008. After four years on exposure, all paints exhibited comparable exterior durability performance, including paints with higher levels of TiO_2 replacement with opaque polymer, as shown in *Figure* 8.

ECONOMY FLATS, PRIMERS, MID-TONES

As demonstrated in *Figure* 6, the rising price of TiO_2 makes replacement with opaque polymer economically favorable in low-load formulations, such as economy flats, primers, and mid-tones. Research data demonstrates equal dry hide and film performance properties when replacing low levels of TiO_2 with opaque polymer in 100% acrylics originally containing 200 lb of dry TiO_2 or more per 100 gal. However, less work has been conducted in formulations with lower levels of TiO_2, such as economy flats, mid-tones, and primers. To demonstrate the utility of opaque polymer use in a low TiO_2 containing formulation, a flat mid-tone PVA starting formulation was identified. *Table* 3 shows the starting formulation (Paint 1) as well as

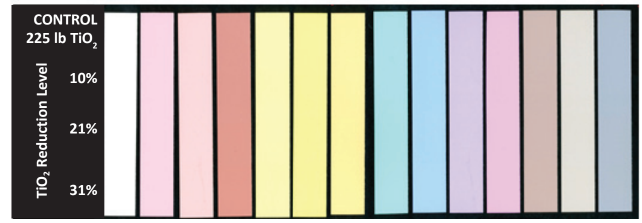
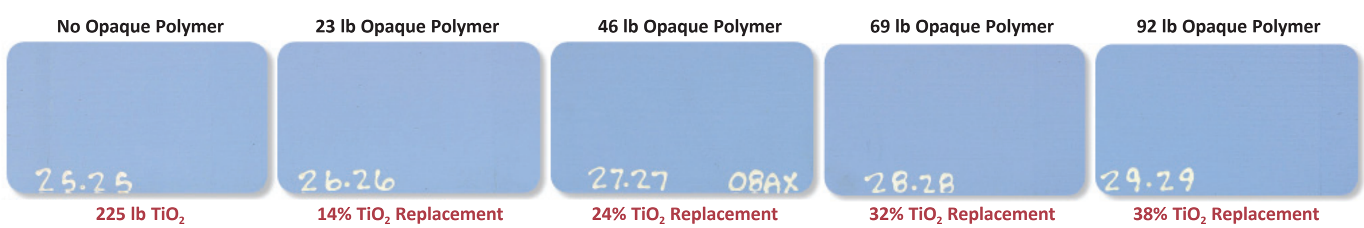


Figure 7—Color matching comparison at three levels of TiO_2 reduction.

a reformulation (Paint 2) with opaque polymer replacing 20% of the TiO_2 in the starting formulation.

Due to the different binder demand of the pigments in the reformulation, binder level was varied to keep fCPVC similar. Volume solids were held constant. Gloss and hiding data are presented in *Table* 4. Similar gloss was observed for the 20% reduction in TiO_2 as compared to the starting formulation. Similar hiding was also observed via three measurements: contrast ratio, scattering, and Y-reflectance for tinted paints. A comparison of abrasive scrub resistance (evaluated using a test method similar to ASTM Method D 2486-74A) demonstrated moderately reduced scrub with 20% TiO_2 replacement with opaque polymer.

Because of recent and marked increases in the potential savings associated with using less TiO_2, this experiment was expanded to explore the concept of decreasing fCPVC to improve performance. Paint 3 was formulated using the same level of TiO_2 and opaque



Series 08AX.Substrate: Primed Cedar; Direction: South Vertical; Paint: 49.5% PVC/35.0% VS; Exposure Date: April 2008. Individual images taken September 2011 using eXposure Vision™ System.

Figure 8—Comparison of a control and four opaque polymer levels and TiO_2 reductions after four years on exposure.

Table 3—Flat Mid-Tone 30%VS PVA

	Paint 1 (Starting Formulation)	Paint 2 (= fCPVC)	Paint 3 (Decreased fCPVC)
TAMOL™ 1254 dispersant	10	9	8
TiO_2, general grade	150	120	120
Calcined clay	83	76	61
Calcium carbonate, 5µm	100	91	73
Calcium carbonate, 10µm	100	91	73
ROVACE™ 9900 emulsion	212	203	245
ROPAQUE Ultra	0	42	42
PVC	60%	61%	53 %

Table 4—Effect of reformulation on gloss and hiding in flat mid-tone PVA.

	Paint 1	Paint 2	Paint 3
TiO_2 Reduction Level	Control	20%	20%
Gloss			
20°	1.3	1.3	1.3
60°	2.0	2.1	2.7
85°	1.3	1.4	2.1
Contrast Ratio	94.9	94.3	94.3
Scattering	4.9	4.7	4.6
Y-reflectance for Tinted paint			
4 oz Red Iron Oxide	27.1	26.8	27.0
4 oz Phthalo Blue	45.2	44.8	44.9
Abrasive scrub resistance	Control	70%	110%

polymer as Paint 2, but with additional binder and less extender. (Decreasing the fCPVC decreases the overall PVC of the paint.) Paint 3 was found to have similar hiding to the starting formulation as well as to Paint 2. Gloss was found to be slightly higher. Gloss could be adjusted through the use of flatting extender. The abrasive scrub resistance was found to increase beyond that of the control. These results show that decreasing fCPVC can be used to create paints with a different, and more favorable, cost performance balance.

PVA FORMULATION SPACE

Based on the results for the mid-tone flat PVA formulation described in the previous section, additional experiments were designed to explore the concept of decreasing fCPVC in other formulating spaces. A summary of these findings is presented in *Table* 5. Decreasing fCPVC was effective at improving scrub relative to an equal fCPVC reformulation in a mid-tone and an economy flat at low TiO_2 use levels. It was also demonstrated to be effective in a PVA flat formulation containing 240 lb of TiO_2.

Figure 9—Conventional opaque polymer (left) collapses due to interaction with the mineral spirits resulting in lower hiding. The newly developed opaque polymer (right) retains its ability to scatter light in the presence of mineral spirits. Drawdowns are a blend of ROPAQUE Opaque Polymer (30% in water) with alkyd resin (75% resin, 25% mineral spirits).

UTILITY IN SOLVENTBORNE ALKYDS

Dow's conventional opaque polymer was designed to have robust performance under ambient architectural coating drying conditions when formulated with typical raw materials such as coalescing agents. When this polymer is used with raw materials outside of this scope, however, its performance may not be as robust. This has limited the use of opaque polymer in solventborne alkyd formulations because these typically include mineral spirits as a raw material. When exposed to mineral spirits, traditional opaque polymers swell and experience particle collapse. As a consequence of void loss due to collapse, they lose the ability to scatter light and provide hiding. As a result, a novel opaque polymer technology* was developed to extend the utility of opaque polymer to solventborne architectural alkyds. *Figure* 9 shows a drawdown of two mixtures of a solventborne alkyd resin (supplied in mineral spirits) with opaque polymer. The mixture drawn down on the left is made of the traditional opaque polymer composition. On the right, the sample uses the new opaque polymer technology that offers resistance to mineral spirits. The conventional opaque

**ROPAQUE™ Dual Opaque Polymer.*

Table 5—Summary opaque polymer reformulation at a moderate TiO_2 reduction in PVA flat formulating spaces. Larger TiO_2 reductions may also be used with this strategy.

	Starting Formulation			**Reformulation A Equal fCPVC**			**Reformulation B Decreased fCPVC**		
	Lb TiO_2	PVC	Average Scrub Cycles	TiO_2 Reduction	**Cost Savings**	Scrub	TiO_2 Reduction	**Cost Savings**	Scrub
Mid-Tone	150	60	800	20%	++	550	20%	+	880
Economy	150	70	210	20%	++	190	15%	+	220
High Scrub	240	48	>2000	20%	+++	1600	10%	++	>2000

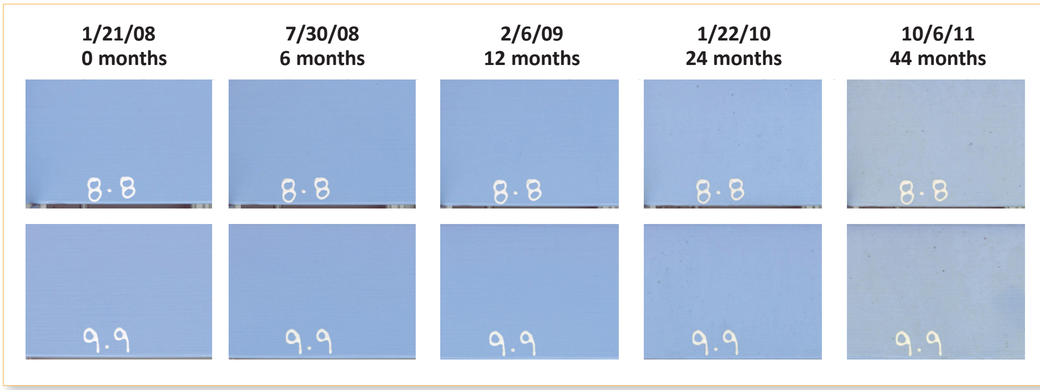


Figure 10—Exposure comparison of solventborne alkyd paint with and without the new opaque polymer.

polymer shows much weaker hiding due to its collapse from exposure to mineral spirits. As shown on the right, the newer opaque polymer retains its ability to scatter light in the presence of the mineral spirits.

The new opaque polymer can be used to partially replace TiO_2 in solventborne architectural alkyd formulations. In 2008, this technology was first put out on exposure. *Figure* 10 shows the exposure history of a solventborne alkyd paint with no opaque polymer (Paint 8.8: 0 lb ROPAQUE Dual; 208 lb TiO_2; 32.6% PVC/50.8% VS) and reformulated with the new opaque polymer technology (Paint 9.9: 72 lb ROPAQUE Dual; 170 lb TiO_2; 34.3% PVC/50.8% VS). Two coats of each paint were applied to a primed cedar board and exposed facing south vertical in Spring House, PA. After four years of exposure, similar durability is seen. The new opaque polymer is unique because it can be used in solventborne architectural alkyd formulations as shown, as well as in all of the traditional waterborne formulating spaces for the conventional opaque polymer.

REFORMULATING TOOL

A number of the test formulations cited in this article were generated using a proprietary tool developed by Dow Coating Materials to help formulators accelerate the reformulation process.* The tool can provide close to 200 formulation options and uses advanced algorithms to evaluate the potential cost savings and performance attributes of reformulating with opaque polymer, including dry hiding performance and tint strength. It can be used to quickly assess reformulation options in many formulating spaces, including high quality flat through semi-gloss, PVA flat through semi-gloss, economy interior flats, mid-tones and primers. It also has the ability to recommend reformulations with reduced fCPVC to aid in targeting a new cost/performance balance as discussed. While such a tool does not replace all of the testing involved during a reformulation, it is intended to significantly increase the speed at which a formulator can obtain the desired performance and economics. It also helps a formulator quickly assess the potential savings associated with opaque polymer across multiple product lines so work can be directed to the most profitable areas.

CONCLUSION

Until recently, opaque polymer was used mainly in white and pastel formulations. Current market conditions related to the rising cost of TiO_2 allow this product to deliver value at higher levels of TiO_2 replacement and in more formulating spaces. The newly developed opaque polymer is designed to perform in solventborne architectural alkyds as well as waterborne formulations. Reformulating with opaque polymer can be streamlined and made simple using a new tool recently made available. When looking at how the economics of hiding have changed, opaque polymer shines new light on more cost-efficient paint formulating. CT

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References

1. Fitzwater, S. and Hook, J.W., "Dependent Scattering Theory: A New Approach to Predicting Scattering in Paints," *J. Coat. Technol.*, 57, No. 721, 39-47 (1985).
2. Adamson, L.A. and Fasano, D.M., "Advancements in TiO_2 Composite Technology: How the World Has Changed in the Last Year," *PCI Magazine*, August 2012 (anticipated publication).
3. Hook, J., Moretti, J., and Bors, D., "Binder Pigment Composites Enhance Opacity of Emulsion Paints," *Eur. Coat. J.*, Issue 1 (2012).
4. Adamson, L.A. and Fasano, D.M., "Polymeric Hiding Technologies That Make TiO_2 Work Smarter," *PCI Magazine*, 22-28 (June 2011).
5. Williams, E.J. and Fasano, D.M., "Opaque Polymers," *Handbook of Coating Additives*, Vol. II, Calbo, L. (Ed.) 223-49, 1992.
6. Ross, W., "Theoretical Light-Scattering Power of TiO_2 and Microvoids," *Ind. Eng. Chem., Prod Res. Develop.*, 13 No. 1, 45-49 (1974).
7. Eckenrode, H. and Fasano, D., "Reduced TiO_2 Dependence in Both Water and Solvent-borne Architectural Coatings Using a Novel Opaque Polymer," Proc. 39th Annual Waterborne Symp., 588-603, February 2012.

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