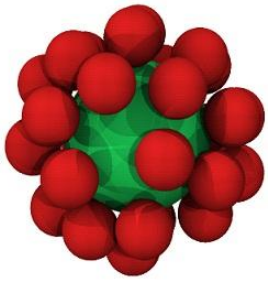
Nomination for the 2012 Presidential Green Chemistry Challenge Award

EVOQUE™ Pre-Composite Polymers

DECEMBER 31, 2011



Evoque™

Pre-Composite Polymer

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EVOQUE™ Pre-Composite polymers

Significant Milestones

- Laboratory testing demonstrates that EVOQUE™ Pre-Composite Polymer Technology facilitates quality paint making with 10% to 20% less titanium dioxide (TiO_2), a material which requires large quantities of energy and a complete digestion with harsh chemicals to produce from its ore. (2008)
- Exterior waterborne paints made with early versions of EVOQUE Pre-Composite Polymer Technology demonstrate equal or improved performance compared to conventional paints containing higher levels of TiO_2. (2008)
- Testing begins on selected commercial product offerings. (2010)
- Product officially launches. (March 2011)
- Broad product sampling is made available to architectural paint formulators. (September 2011)
- PricewaterhouseCoopers validates Life Cycle Assessment demonstrating reduced impact on air and water quality, primary energy consumption and greenhouse gas emissions stemming from paints made with EVOQUE Pre-Composite Polymer Technology. (September 2011)
- Commercial quantities of EVOQUE Pre-Composite Polymer Technology are produced. (September 2011**)**
- Paint makers in U.S., Europe and Latin America place orders for commercial quantities of EVOQUE Pre-Composite Polymer. (March - November 2011)

Category Eligibility

This entry is **Not Eligible** for awards in either the academic or small business categories.

Area of Focus

The primary focus is the use of greener reaction conditions. The novel processing of titanium dioxide (TiO_2) with EVOQUE Pre-Composite Polymer reduces the use of TiO_2, the world's most widely used white pigment and a highly energy-intensive component in paint-making that contributes a large share of potential impact on the environment in key areas such as air acidification and water eutrophication.

A secondary focus is the use of greener synthetic pathways. Novel reagents/catalysis were developed to facilitate the particular architecture needed to ensure the polymer pre-composites consistently interact with the surface of TiO_2 to achieve more uniform distribution of TiO_2 particles, more efficient light scattering and lower volumes of total TiO_2 used in white and pastel waterborne architectural paints.

Developmental Activities in the United States

EVOQUE Pre-Composite Polymer Technology was invented and developed in Spring House, Pennsylvania. This technology, and paint products employing this technology, is manufactured in factories on U.S. soil.

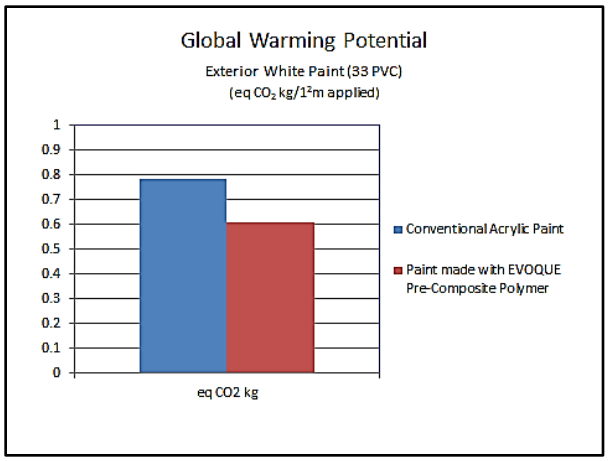
Abstract

EVOQUE Pre-Composite Polymer is a completely new class of material for paint making that reduces the need for TiO_2, the primary white pigment in paint and a very energy-intensive raw material that has a large impact on the eco-profile of house paint in key areas such as greenhouse gas emissions, water quality, air quality and resource consumption. From the 1950s through the 1970s, TiO_2 successfully replaced white lead, which was regulated out of paint to reduce toxicity and environmental impact. EVOQUE Pre-Composite Polymer Technology offers further improvement by facilitating quality paint making with 10% to 20% less TiO_2, a key raw material for paint that is derived from natural reserves of titanium ore and requires a complete digestion with an excess of chlorine or sulfuric acid and multiple purification steps.

As demonstrated by third-party validated Life Cycle Assessment (LCA), TiO_2 reductions facilitated by EVOQUE™ Pre-Composite Polymer Technology in exterior house paint reduces associated carbon footprint by 22.5%, water

consumption by 30%, NO_x and SO_x emissions by 24%, and the potential impact on water eutrophication (algae bloom) by 27%.[1] LCA also demonstrates a 30% reduction in potential chemical oxygen demand (COD) and a 35% reduction in non-methanic volatile compounds (NMVOC), two factors that impede water quality and air quality, respectively.[2]

Figure 1. Global warming potential from a conventional acrylic exterior house paint is compared to one that is made with EVOQUE™ Pre-Composite Technology



While a key advantage of EVOQUE Pre-Composite Polymer is TiO_2 efficiency and smaller environmental footprint, performance benefits resulting from improved film formation and reduced photodegradation (as a function of reduced TiO_2, which promotes photodegradation) are expected to improve exterior durability by 20%. This enhancement has been factored into LCA results for the exterior paint comparison in **Figure 1**.[3]

Cumulative Impact

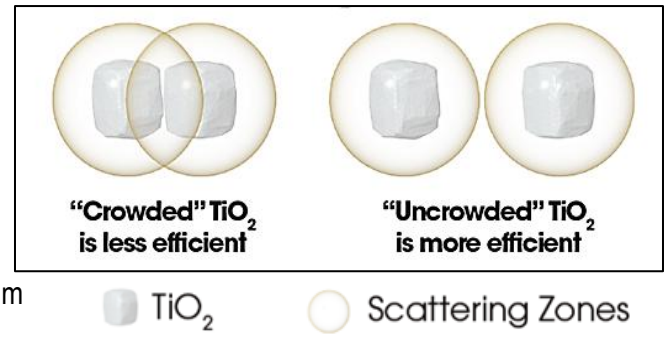
The highest levels of TiO_2 are found in white and pastel paints. These account for approximately 330 million gallons of house paint produced and sold in the U.S. annually.[4] Current versions of EVOQUE Pre-Composite Polymer Technology are compatible with white and pastel acrylics, which account for approximately 165 million gallons of U.S. paint produced annually. Based on TiO_2 removal alone, the adoption of EVOQUE Pre-Composite Polymer Technology in 50% of the paint in this segment has the potential to reduce associated greenhouse gas emissions generated by U.S. paint production by approximately 54,000 metric tons of carbon dioxide equivalent. When taking into consideration the enhanced paint performance and durability expected from paints made with of EVOQUE™ Pre-Composite Polymer Technology, the potential to reduce associated greenhouse gas emissions rises to 123,000 metric tons of carbon dioxide equivalent. This amount is comparable to the annual CO_2 emissions generated from the electricity used by approximately 15,000 homes, the gallons of gasoline used by approximately 14,000 cars, or the amount of carbon sequestered by approximately 26,000 acres of pine forest.[5]

Description of the Nominated Technology

Overview

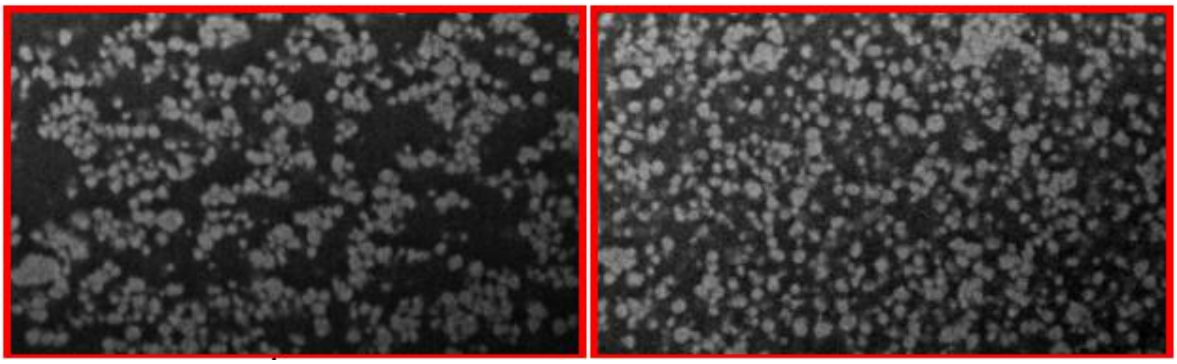
In a typical can of white or pastel house paint, the two major ingredients by volume and function are the binder and the TiO_2. The binder makes the paint adhere to the wall. The TiO_2 provides opacity by scattering visible light. This hides the wall surface and enhances paint color -- a feature known in the paint industry as "hiding." Paint formulators have a long-standing interest in stretching tight raw material supply and lowering formulation cost through more efficient use of TiO_2. However, uneven TiO_2 particle distribution in the paint film has been an ongoing obstacle. In theory, TiO_2 scatters visible light most efficiently when it is evenly distributed in the paint film.[6] This composition allows for full utilization of the light scattering zones that surround each TiO_2 particle, a concept illustrated in **Figure 2a**.

Figure 2a. **Figure 2b**.



In reality, TiO_2 distribution in the paint film is random, at best, because there is no driving force to order or separate the pigment particles from one another. This leads to areas of high and low TiO_2 particle concentration, as demonstrated in an actual paint film in the electron micrograph photo in **Figure 3a**[7]. When TiO_2 particles are crowded together, their light scattering zones overlap and reduce the net effect on hiding. (This concept is illustrated in Figure 2a.) For more information about TiO_2 scattering efficiency, go to www.dow.com/hiding.

Figure 3. Cryo-scanning electron micrograph of dried paint film shows TiO_2 distribution in normally dispersed paints (a) and when using EVOQUE Pre-Composite Polymer (b). White areas = TiO_2; black areas = binder.



3a. Regular TiO_2 **3b. Composite TiO_2**

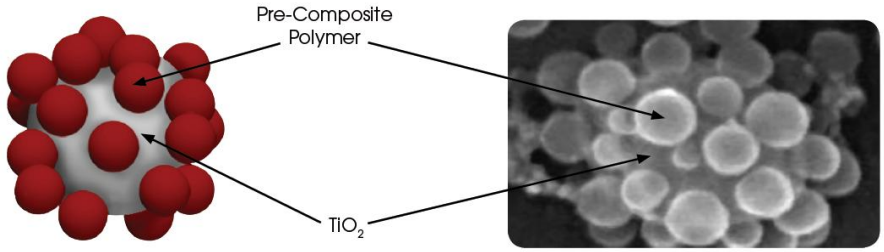
Pre-Composite Polymer Chemistry

EVOQUE™ Pre-Composite Polymer is a completely new class of material for paint that serves as both a binder and a hiding enhancer. The breakthrough technology improves TiO_2 particle distribution and reduces crowding, as demonstrated in an actual paint film in **Figure 3b**. This improvement in particle distribution leads to greater light scattering efficiency and the ability to make quality white and pastel architectural paints with 10-20% less TiO_2.[8]

How it works

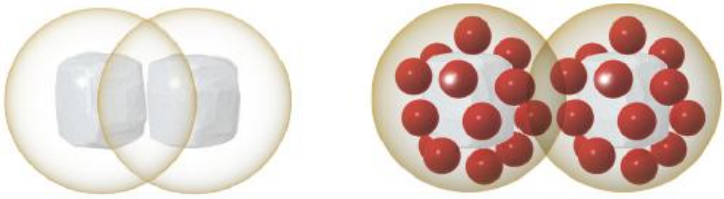
EVOQUE Pre-Composite Polymer Technology employs a film-forming polymer specifically designed to interact with the surface of TiO_2 particles. During paint making, the polymer surrounds and reacts with the surface of individual TiO_2 particles through a series of adsorptions. As more pre-composite polymer particles adsorb, the TiO_2 surface becomes increasingly saturated until there is no longer enough space between any of the adsorbed particles for another pre-composite particle to reach the TiO_2 surface. The result is a pigment-polymer composite, as demonstrated via computer simulation and electron micrograph in **Figure 4.**

Figure 4. Left: Computer simulation of pigment-polymer composite. Right: Electron micrograph of pigment-polymer composite.
Source: Dow Coating Materials



As the paint film dries and the pigment-polymer composites come together to form a film, individual TiO_2 particles are no longer capable of coming in close contact with one another because they are separated by the pre-composite polymers that surround them. This configuration encourages more even distribution of TiO_2 and reduces the area of light scattering overlap, as demonstrated by the drawing in **Figure 5.**

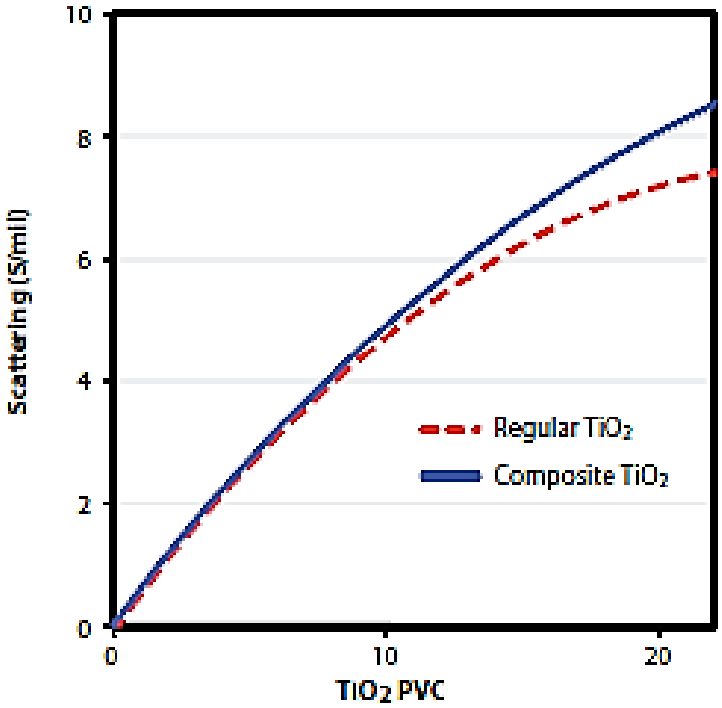
Figure 5. The zone of effective light scattering extends beyond the perimeter of each TiO_2 particle. When these zones overlap, light scattering (hiding) is less efficient. Source: Dow Coating Materials



TiO_2 in conventional paint. **TiO_2 in paint made with EVOQUE Pre-Composite Polymer.**

As demonstrated in **Figure 6,** EVOQUE Pre-Composite Polymer reduces scattering overlap and improves the efficiency curve of TiO_2 when light scattering is measured as a function of TiO_2 level in paint film (red line).[9]

Figure 6. Scattering overlap increases with increasing levels of TiO_2, creating a drop in light scattering efficiency when measured as a function of TiO_2 level in paint film (red line). EVOQUE Pre-Composite Polymer reduces overlap and improves the efficiency curve (red line).



A New Approach to TiO_2 Reduction

Other technologies impact TiO_2 distribution in paint and these are well established. Dispersants are universally used in the grind phase to prevent TiO_2 particles from sticking to one another or to the binder. Small particle size extenders are used in the letdown phase and primarily serve as fillers. In both cases, these technologies passively impact TiO_2 particle distribution and, like TiO_2 itself, their distribution in paint is random. EVOQUE Pre-Composite Polymer Technology is altogether different because it actively engages the binder with the TiO_2.

Pigment-binder interaction traditionally has been avoided in paint making because there has been no way to control the interaction to achieve the desired configuration of individual polymer-pigment particles with a single TiO_2 particle at the center. Uncontrolled interaction leads to agglomeration, macroscopic grit and, ultimately, solidification of the paint. The key to the success of EVOQUE Pre-Composite Polymer Technology was finding a way to control the interaction in order to achieve the desired TiO_2- centric structure surrounded by pre-composite polymer. This required finding the right balance of adsorption strength and adsorption speed. If the adsorption is too weak, the pre-composite polymer particles will not stay in place and there will be little impact on TiO_2 particle distribution. If the adsorption is too strong, the pre-composite particles already adsorbed to one TiO_2 particle will bridge to another TiO_2 particle, creating large clusters of unsaturated composites, as demonstrated in the drawing in **Figure 7**.[10]

Figure 7. When adsorption is too strong, areas of unsaturated TiO_2 will "bridge" to pre-composite polymer particles that are attached to other TiO_2 particles, resulting in uncontrolled agglomeration, grit and, ultimately, solidification of the liquid paint formulation.

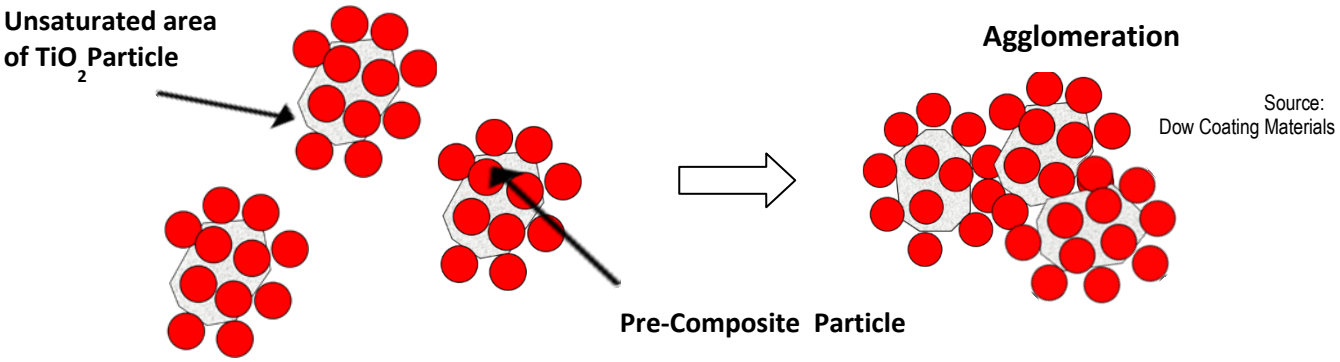
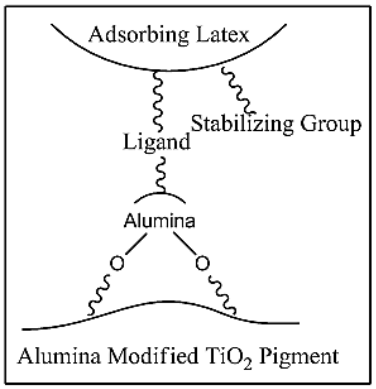


Figure 8. TiO_2-Pigment Interaction.



Source: J. Bohling/D. Bors, Dow Coating Materials.

Pigment-grade TiO_2 is made with an alumina-rich surface to facilitate dispersion, and certain affinity ligands are known to interact with alumina surfaces.[11] EVOQUE™ Pre-Composite Polymer Technology builds on these features, as shown in **Figure 8**, with modified ligand-binding and colloidal stabilizing chemistry. This drives a multitude of weak interactions through the ligand and alumina moieties. These interactions are dynamic, continuously attaching and detaching with enough cumulative strength to stabilize each pigment-polymer composite but not so strong that one pigment-polymer attaches to another pigment. The cumulative effect of these polymer-pigment interactions can be compared to the effect of the hook-and-loop links in Velcro. Each fabric hook and loop link may be weak on its own, but because of the large number of hook and loop links, the attachment is strong. In the case of the polymer-pigment composite, hundreds, and maybe thousands of interactions hold the composite together in a dynamic equilibrium.

To illustrate the potential for TiO_2 savings in a specific paint, a minimal sheen (eggshell) architectural paint was reformulated using EVOQUE Pre-Composite Polymer. The goal in this study was to match or exceed the hiding and gloss/sheen of the starting formulation while removing TiO_2 from the formulation. The main ingredients of the formulations and key appearance properties are given in **Figure 9**. With EVOQUE Pre-Composite Polymer, a 14 percent reduction in $Ti0_2$ use was made possible.[12]

Figure 9. A Quality Acrylic Minimal Sheen (Eggshell) Formulation made with EVOQUE Pre-Composite Polymer demonstrates excellent performance with 14% less TiO_2.

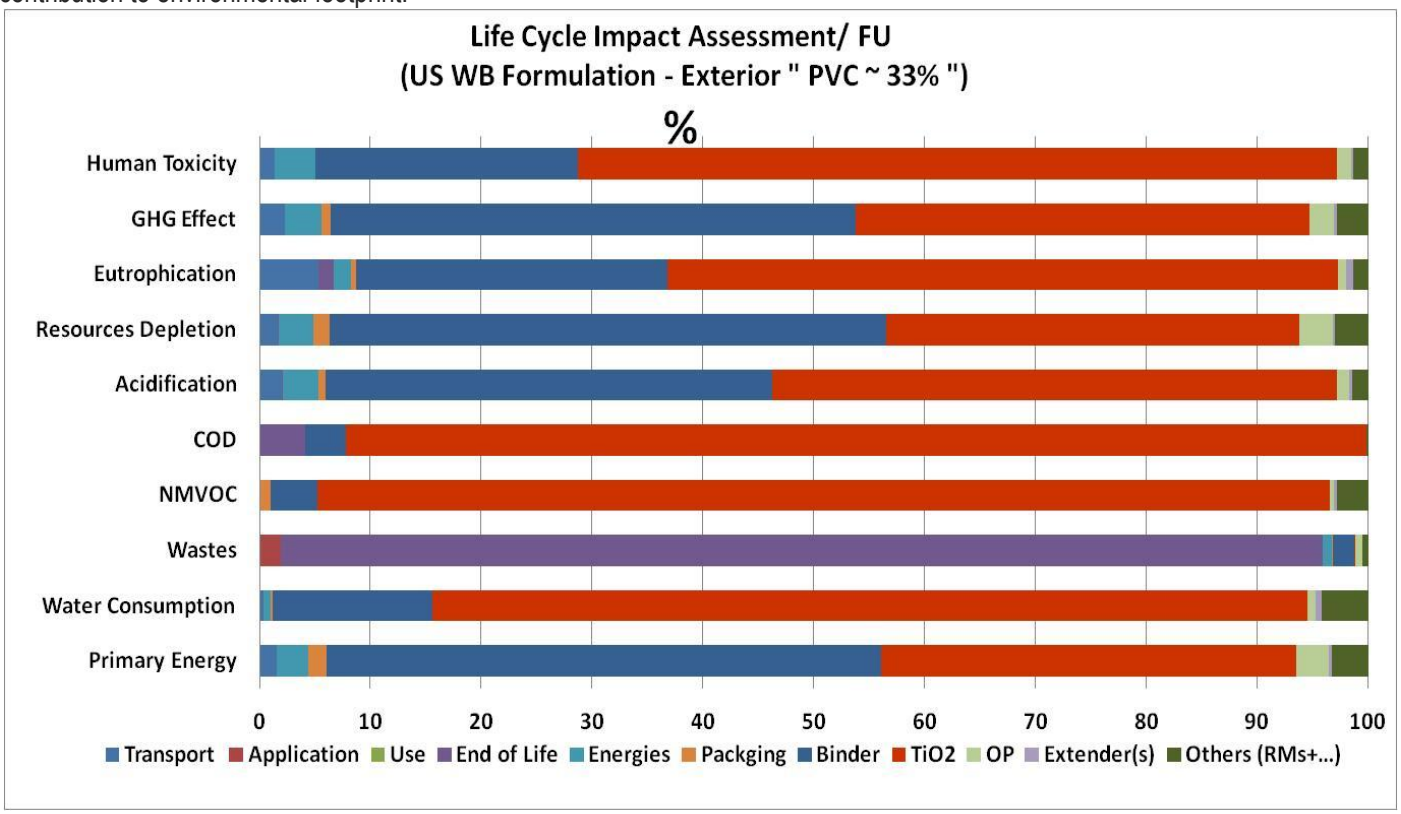
Raw Material (pounds/100 gallon)	Control TiO_2	EVOQUE™ Pre-Composite Polymer
TiO_2 Slurry (76.5%)	311	268
% TiO_2 Reduction	0%	14%
Calcium Carbonate	44	44
Nepheline Syenite	44	44
Diatomaceous Silica	2	2
ROPAQUE™ Ultra Opaque Polymer	0	15
RHOPLEX™ VSR-2015 Binder	423	174
EVOQUE Pre-Composite Polymer	0	279
Property	**Control TiO_2**	**EVOQUE™ Pre-Composite Polymer**
Contrast Ratio (wet)	0.966	0.971
S/mil (dry)	6.2	6.7
60° Gloss	20	20
85° Sheen	35	34

Environmental Benefits of Reducing TiO_2 in Paints

TiO_2 is the world's most widely used white pigment. In paints, it provides exceptional whiteness and brightness. TiO_2 is derived from titanium ore, which is contained in minerals such as rutile and ilmenite. Once mined, titanium ore is extracted from the mineral and undergoes intensive processing in which the material is digested, purified and precipitated to form 270nm particles, treated to coat the surface with alumina, and micronized. Global TiO_2 consumption in paints and coatings is estimated at 2.75 million metric tons.[13] Currently, TiO_2 supplies are limited, demand and prices are increasing, and concerns are growing over the energy-intensive mode of mining and processing titanium. Looking forward, a tight global TiO_2 market is expected until at least 2015.

Life Cycle Assessment (LCA) measures the potential environmental impact of a product from raw material sourcing through processing through consumer use and end of life. In many cases, the greatest environmental impact does not result from a product's manufacturing process, but from the sourcing and processing of its raw materials. This is the case with paint. An LCA conducted by Dow and validated by PricewaterhouseCoopers demonstrates that TiO_2 is responsible for a large – and sometimes the largest -- percentage of the environmental impact from production, use and disposal of waterborne white and pastel architectural paints, as shown in **Figure 10.**[14]

Figure 10. Life Cycle Impact Assessment for waterborne paints demonstrates that TiO_2 accounts for a large – or largest – contribution to environmental footprint.



LCA further demonstrates that TiO_2 reductions in paint facilitated by the use of EVOQUE Pre-Composite Polymer Technology reduce the potential environmental impact of waterborne white and pastel architectural paints in ten key indicators, as shown in **Figure 11.**[15]

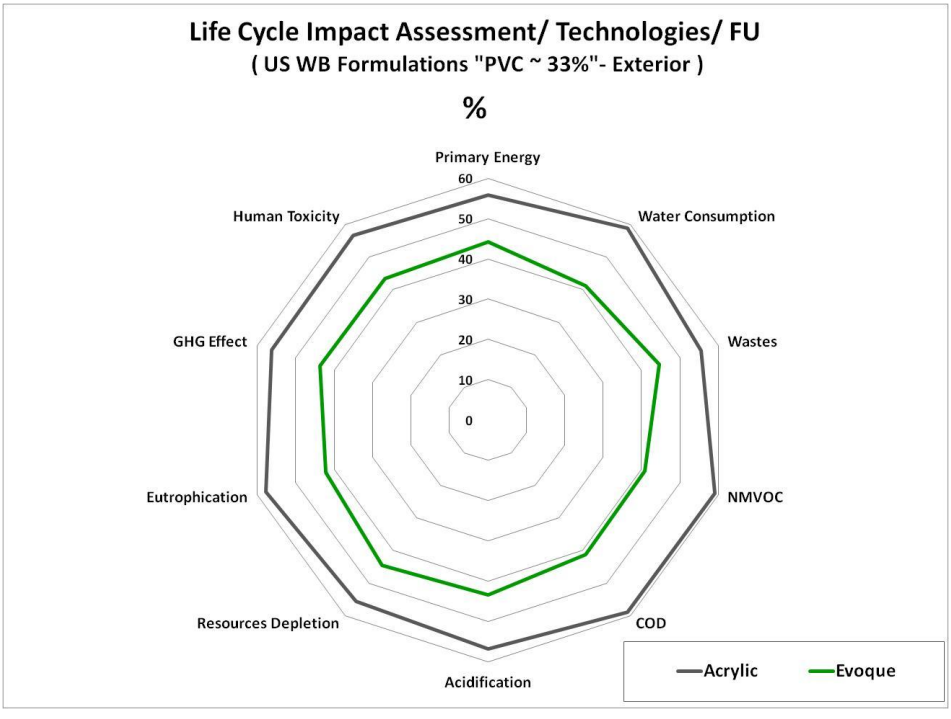


Figure 11. Exterior house paint made with EVOQUE™ Pre-Composite Polymer Technology reduces potential impact on environment in ten key indicators studied through Life Cycle Assessment.

Acceptance in the Paint and Coatings Industry

As reported in ICIS June 2011[16] and Bloomberg November 2011[17], world demand for TiO_2 exceeds current world supply of titanium ore and prices are at historic highs. In addition to reducing environmental footprint, EVOQUE Pre-Composite Polymer helps to reduce the cost of paint making and stretch a limited supply of titanium ore, which is a non-renewable resource. Commercial scale production of paints made with EVOQUE Pre-Composite Polymer demonstrates that no changes in paint-making equipment or process are required in order to take advantage of this technology. EVOQUE Pre-Composite Polymer Technology takes a standard ingredient in paint (the binder) and turns it into a multi-functional ingredient that not only provides adhesion, but also facilitates notable reductions in TiO_2 white pigment and thus improves key sustainability metrics associated with paint production. The technology achieves this without having to add an extra ingredient to paint. Furthermore, the technology is compatible with – and additive to – existing TiO_2 reduction technologies, including dispersants, small particle size extenders and opaque polymers. Dow developed opaque polymer in the 1970s. For 20 years following a TiO_2 shortage in the 1980s, the use of opaque polymer has grown at twice the rate of the paint market and today is a staple in quality paints. With even greater shortages – and historically high prices -- of TiO_2 at present, adoption of EVOQUE Pre-Composite polymer is expected to experience similar growth. Since its official launch in March 2011, EVOQUE Pre-Composite Polymer has already received customer orders in North America, Europe and Latin America. Even customers with a reliable supply of TiO_2 are looking for ways to decrease their dependence on the raw material.

Summary

A new innovation in the coatings industry offers the ability to improve the sustainability of paint making by reducing dependence on TiO_2, a raw material with a large impact on environmental footprint of white and pastel paints. This new class of material interacts with the unique alumina surface chemistry of TiO_2 to form a polymer-pigment composite which increases the light scattering efficiency of the pigment. This technology works in tandem with existing technologies such as opaque polymer, which have been reducing the dependence on TiO_2 for 30 years. Besides the economic, supply and sustainability advantages, EVOQUE Pre-Composite Polymer Technology helps make better films which are more resistant to stains and rust and require less thickener. EVOQUE Pre-Composite Polymers offer a powerful advantage by combining improvements in environmental footprint, performance and economics, making it a new innovation which provides cost-efficient improvements in key sustainability metrics as demonstrated by third-party validated life cycle assessment.

References

[1,2,3] "Comparative Life Cycle Assessment (LCA) of Water-borne paints for internal and external wall decoration and protection," Presentation to Peers for Project Review, Dr. H. Kheradmand, LCA and Sustainable Development Expert, Dow Coating Materials (DCM) EMEA, September 20, 2011.

[4] Bureau of Census Quarterly Data, www.paint.org/about-our-industry/item/309.html

[5] Greenhouse Gas Equivalencies Calculator, EPA, May 2011.

[6, 7, 8, 9] "Polymeric Hiding Technologies That Make TiO_2 Work Smarter," PCI Magazine, June 2011.

[10] TiO_2-Polymer Composite Formation in Latex Paint Making," European Coatings Journal, January 2012 (pending)

[11] Cotton, Frank Albert; Geoffrey Wilkinson, Carlos A. Murillo (1999). Advanced Inorganic Chemistry.

[12] "Polymeric Hiding Technologies That Make TiO_2 Work Smarter," PCI Magazine, June 2011.

[13] "Global Outlook for Paint & Coatings," TZ Chemicals International P/L, TZMI Congress, November 2010.

[14, 15] Comparative Life Cycle Assessment (LCA) of Water-borne paints for internal and external wall decoration and protection," Presentation to Peers for Project Review, Dr. H. Kheradmand, LCA and Sustainable Development Expert, Dow Coating Materials (DCM) EMEA, September 20, 2011.

[16] http://www.icis.com/Articles/2011/06/20/9470805/titanium-dioxide-buyers-feel-the-pain.html

[17] http://www.bloomberg.com/news/2011-11-22/dupont-faces-squeeze-as-titanium-ore-advances-most-since-97-commodities.html