Titanium dioxide—the most opaque of all white pigments—is a crucial component of most modern coatings. Coatings formulations continually evolve to meet increasingly challenging performance, regulatory, and economic demands, and as they do it is critical that the TiO₂ pigments evolve as well. The technical challenges for pigment manufacturers include understanding, anticipating, and satisfying both the current and the emerging technical needs of the coatings industry. This article describes some of these needs and how they are being met by the TiO₂ pigment industry.

INTRODUCTION

“The Spirit of Innovation.” This phrase, the theme of ICE 2003, succinctly describes the technical driving force of the coatings industry. This is one of mankind’s most mature industries, with origins dating back tens of thousands of years to the time of Cro-Magnon cave painters. Yet even with its ancient origins and expansive history, the coatings industry today is far from static. Indeed, the one constant in this industry seems to be change. Pressure for change comes from the industry’s three stakeholders—the community, shareholders, and customers—and continually drives the industry to develop new technologies. New formulations that have less negative impact on the environment and offer greater performance for its users, yet at the same time garner a greater return to company owners, are continually being developed and commercialized.

Raw materials suppliers must move fast to meet the existing and emerging needs of the coatings industry. We must anticipate not only the new requirements of our customers, but also the development work of co-suppliers,
since the new properties or chemistries developed for one type of ingredient must be compatible with (and preferably additive to) those developed for other ingredients.

This is particularly true for manufacturers of titanium dioxide pigments. A necessary ingredient in most coatings, the properties of this one material can affect—for better or worse—numerous performance properties of both the liquid paint and the dried paint film. The combination of high prevalence and strong impact on coatings performance, coupled with the rapid changes occurring in the coatings industry, place TiO₂ pigment manufacturers under a special obligation to continually develop new grades—grades that will assist coatings manufacturers to satisfy the often conflicting demands of their shareholders, their customers, and the community. In this article we discuss some technical challenges to the TiO₂ pigment industry as we, too, balance the needs of our customers with the demands of our shareholders and the community.

**DISCUSSION**

**Overview of TiO₂ Pigments**

Most workers involved in the coatings industry equate TiO₂ to opacity. Indeed, it is unmatched opacity that makes TiO₂ ubiquitous in the coatings industry. Figure 1 compares the hiding abilities of pigmentary TiO₂ to a number of other colorless materials. It is clear that rutile phase TiO₂ (the only phase used in coatings) is unsurpassed in opacity. This opacity is derived from three sources: First, opacity is dependent on particle size, and the TiO₂ pigment industry has perfected ways of producing nearly uniform particles of the optimal size. Second, high opacity depends on an even distribution of particles at the micro-scale, and the surface characteristics of TiO₂ pigments facilitate good dispersion in the finished paint film. Finally, opacity is highly dependent on index of refraction, and the index of refraction of rutile TiO₂ is extremely high. Combined, the properties of TiO₂ pigments insure that it has unsurpassed hiding power compared to all other known colorless solids.

While it is true that TiO₂ is used in the coatings industry for its high opacity, TiO₂ manufacturers tend to view their product from a different perspective. For them, TiO₂ is more than just a great opacifier; it is the largest volume specialty chemical made today. This perhaps arguable statement can be justified as follows: First, that TiO₂ is a large volume chemical cannot be doubted. Figure 2 shows that the 2002 global consumption of TiO₂ pigments exceeded four million tonnes, with sales exceeding the $7 billion mark. Our estimates show this volume continuing to grow at an average annual rate of about 2.5% for the foreseeable future.

It is more difficult to address the assertion that TiO₂ is a “specialty” chemical for the simple reason that there is no widely agreed upon definition for this term. However, there are several characteristics that most people would agree are critical to the classification as “specialty chemical.” Undoubtedly one of the most important is that a specialty chemical is one that is manufactured in high purity. This is certainly the case for TiO₂ pigments. As an example, consider the iron content of pigmentary TiO₂. TiO₂ ores typically contain roughly 40% iron while the iron levels in finished pigment average about 20 ppm—a reduction of 99.995%! Similarly, low levels are seen for other contaminants.

A second important characteristic of specialty chemicals is that they are manufactured to exacting specifications. Again this is true of titanium dioxide pigments. As one example, consider particle size control. As mentioned above, optimal particle size is essential to TiO₂ pigments because opacity is dependent on particle size. Pigmentary TiO₂ is manufactured with an average particle size of roughly one quarter micron (the wavelength of light in TiO₂) and with a very narrow particle size distribution (typical standard deviations are about 0.05 microns). This can be contrasted with many of the other particulate ingredients typically found in paints (mainly extenders), which are orders of magnitude larger and span a much wider range of particle sizes within a given grade.

(c) This does not mean, however, that titanium dioxide pigments are pure TiO₂. Other materials—typically hydrous alumina, silica, and/or organic agents—are added to all coatings grade titanium dioxide pigments to improve a variety of properties. These are not impurities as they are intentionally added to the pigment.

(d) The average particle size varies from one grade to another. While the variations are slight on an absolute scale (the range for averages goes from 0.25-0.30 microns), they lead to noticeable differences in the undertone of the pigment. Small particle sizes give pigment with a bluish cast while larger average particle sizes give pigment with a more neutral undertone.
The final defining characteristic of specialty chemicals that we will consider here is that specialty chemicals are normally customized for specific applications. Titanium dioxide is used in a wide variety of pigmen-
tary applications, with an even wider variety of critical-
to-quality requirements that must be satisfied. These
include such varied coatings applications as emulsion-
and solvent-based architectural coatings, e-coats, gel
coats, powder coatings, high PVC coatings, thin-film
applications, general industrials, etc., as well as a vari-
ety of applications in the plastics and paper industries.
It would be unreasonable to expect a single grade of
TiO₂ pigment to meet this spectrum of needs, and, in
fact, pigment manufacturers offer dozens of grades to
satisfy these different applications.

Overall, very demanding expectations are placed on
TiO₂ pigments, and rightly so. The myriad effects this pigment has on coatings properties necessitates
such demands, and, for the most part, the TiO₂ industry is able to
meet these expectations. However, as is also true for most coatings
manufacturers, TiO₂ producers find
themselves in a position where they must innovate or fall behind.

**Driving Forces Behind Innovation**

The TiO₂ industry, like the coat-
ings industry and, indeed, most
other manufacturing industries, is
driven to innovate by its share-
holders or investors, by the com-

2002 Total : 4.09 MM tonnes

![Map of TiO₂ demand by region](image-url)
years detailing programs to do this. The technical challenge for the industry is to devise process improvements that both remove cost and maintain—or even improve!—product performance.

The most exciting technical challenges, and the topic of the remainder of this paper, are those posed by our customers. As detailed above, the coatings industry is one of constant technical change, and it is incumbent on pigment manufacturers to update their product portfolio to match the ever-changing needs of this industry.

Over the past decade the most prevalent need was to produce universal products that could be used in a wide variety of high volume coatings. These grades have provided logistics benefits and manufacturing simplifications that, in turn, have contributed meaningfully to the profitability of the coatings industry.

Universal grades are certainly used and valued by coatings producers. However, the “one size fits all” approach does not work in every instance. By virtue of their universal nature, these pigments are not optimal for many highly specialized, highly demanding coatings applications. These tend to be premium applications, such as ultra-high durability coatings, where the coatings customer is willing to pay for improved performance. Special grades of pigment have been, and will continue to be, developed to enable paint manufacturers to make the best performing coating possible. Below we will consider three areas that are under active development.

**Improved Paint Weatherability**

Paint degradation is a major concern for many paint consumers. Durable, exposed articles, such as cars, buildings, bridges, etc., are both expensive to purchase (or construct) and expensive to repaint. Consumers demand that the coatings on these objects resist changes in appearance, yet such demands are counter to fundamental thermodynamics. Organic binders, like most organic materials, are fundamentally unstable towards oxygen. Carbon dioxide and water, the products of the reactions between oxygen and organics, are both extremely stable compounds and represent deep thermodynamic wells for the carbon and hydrogen atoms present in paint binders. While these reactions occur slowly at ambient temperatures, their rates can be significantly increased in the presence of UV light, which is energetic enough to initiate such reactions via the rupture of chemical bonds within the binder molecules.

While the thermodynamics of degradation is mostly beyond the control of paint manufacturers, the kinetics of degradation is not. Coatings makers strive to retard degradation rates and maximize service life using a number of different strategies. For example, they add UV light absorbers or hindered amine light stabilizers (HALS) to slow the generation and propagation of the radicals responsible for degradation. Additionally, coatings manufacturers use resins from which the weakest links, thermodynamically speaking, have been removed. For example, perfluoro resins are void of C–H bonds. Siliconized resins improve paint film durability by using a similar strategy.

These approaches work well, but can be expensive. It is important that the coatings producer who is using these tactics also ensures that other paint ingredients have been optimized for durability, particularly those known to affect durability. Titanium dioxide pigment is one ingredient for which grade selection has a strong influence on paint film durability. In general, TiO₂ can affect paint durability by two conflicting mechanisms.

First, TiO₂ is an oxidation photocatalyst. UV light that strikes TiO₂ is invariably absorbed by the particles. Much of the UV light energy is dissipated as heat, a relatively benign way of disposing of this energy. However, a small—and yet significant—fraction of UV light energy is converted to chemical energy in the form of
The width of this curve is determined both by the width of the primary particle size curve and by the degree to which these primary particles are found in aggregates.
try. Much work has been done over the past few decades to improve control of particle size while at the same time increasing production rates to match increases in worldwide demand. The focus of this work has been on control of both average primary particle size and on the width of the particle size distribution curve.

However, particle size management entails more than insuring that the majority of particles are of the proper size. Attention must also be directed towards the far edges of the particle size curve. In particular, the amount of material present as very large particles (or as agglomerates)\(^1\) may be so little as to have no significant impact on properties such as opacity or gloss, but still adversely affect other properties. In some applications, even ppm levels of these grossly oversized particles can have strong detrimental effects on performance. This is particularly true in abrasion sensitive applications—such as inks—or very thin film applications (where the film thickness is comparable to the diameter of these very large particles). In these instances it is especially important to minimize or entirely eliminate these grossly oversized particles.

The technical challenge of eliminating these large particles is significant. These particles form by different mechanisms than the particles that make up the vast bulk of TiO\(_2\) pigments. Identifying these mechanisms, and determining means to prevent the formation of these particles, will result in grades with improved performance in inks and thin film applications.

At the other end of the size scale, very small particles can also be detrimental to coatings performance. In traditional TiO\(_2\) pigments, such particles can increase the photocatalytic activity of the pigment as well as alter the rheological characteristics of the liquid paints made with them. Small particles such as fumed silica are, in fact, sometimes added to paints to increase viscosity. In addition, these particles scatter light poorly and so can decrease the opacity of the pigment, although this is seldom a problem in commercial TiO\(_2\) pigments.

While these small, nano-sized particles are undesirable in pigmen\(\text{\-}\)tary TiO\(_2\), they can be quite useful in some coatings applications as a product in their own right. For example, these particles are excellent UV light absorbers and, as such, compete with organic UV light absorbers and light stabilizers in superdurable coatings applications. Unlike the organic materials, though, nano-TiO\(_2\) is not consumed or degraded on weathering.

As is the case for pigmentary TiO\(_2\), manufacture of nano-TiO\(_2\) requires careful particle size control. Oversized particles are not only less efficient than nano-particles, they also confer partial opacity in situations where transparency is preferred (e. g., automotive clearcoats). As was true with the grossly oversized particles found in pigmentary TiO\(_2\), concentrations of larger particles in nano-TiO\(_2\) on the order of parts per million can significantly degrade the value of nano-TiO\(_2\) products. Control of large particle formation is an area of active technical investigation, with a potentially valuable payoff for the coatings manufacturer.

**Improved Opacity**

By far the most highly valued property of TiO\(_2\) pigment is its opacity. While unsurpassed by any other white pigment, increasing opacity even beyond current levels would be welcome by most coatings manufacturers. This would not only result in the potential for cost savings (equal hiding with less pigment), it would also considerably increase formulation flexibility. As the maxim goes, one can only get a gallon’s worth of material into a gallon of paint. By removing some TiO\(_2\), the coatings formulator would be able to add any of a number of other ingredients to his or her advantage.

One determinant of opacity is particle size, as described above, but there are many other factors that play important roles as well. For optimal opacity, the particles in the final paint film must be completely dispersed. This means that they must first be completely dispersed in the liquid paint, and then remain dispersed as the paint dries.

---

\(^1\) Agglomerates are responsible for essentially all of the material with sizes greater than one-half micron.
shows that tightening the particle size distribution (decreasing GSD) improves opacity. Extrapolating the experimental data to the optimal, mono-sized situation gives an opacity that is about 15% greater than that seen for commercial pigments. Consistent with this, calculations done on a Cray supercomputer have confirmed an upper limit of slightly less than 15% improvement.3

However, this value is somewhat misleading because it assumes that there is a single optimal particle size for TiO2 pigment. In fact, the optimal particle size is dependent on the wavelength of light to be scattered, and visible light spans a significant range wavelengths (the shortest wavelength of visible light is less than half the longest wavelength). Thus pigment particles must also span a range of sizes, so that different particles efficiently scatter the different wavelengths of visible light. This factor alone quite significantly decreases the expected improvement in opacity from tighter particle size control.

Decreasing the width of the particle size distribution curve could also lead to undesired optical effects. Preferential scattering of one wavelength of light over another, which would be expected for a very tight particle size distribution, could lead to color effects similar to those seen for a film of oil on water.

**BETTER DISPERSION—GENERAL:** The other strategy for improving TiO2 opacity—ensuring maximum separation of particles in the finished paint film—is more likely to bear fruit, at least for some coatings. Here the problem to be overcome is that close proximity of TiO2 particles decreases their light scattering efficiency. Close proximity occurs for a number of reasons—particles were never properly dispersed in the first place, or they were attracted to one another during paint storage or drying, or they simply happened to be close to one another when the film dried. The effect on opacity is the same regardless of the reason—close proximity hurts opacity.

There are two distinct strategies for insuring good particle dispersion in the drying paint: electrostatic repulsion and steric repulsion. For the latter, pigment particles are coated with a bulky material. Steric repulsion results from physical contact of the bulky coatings on different particles, which prevents the embedded TiO2 particles from close approach. Paint formulators typically associate steric repulsion with certain types of dispersant molecules, but very small oxide particles can provide the same result. TiO2 grades have been specifically developed with heavy oxide coatings (mixtures of alumina, silica, and aluminosilicates), and these grades are very effective in situations where steric repulsion is used to get opacity (see Figure 8a for an electron micrograph of such a grade).
Electrostatic repulsion results when particle surfaces are highly charged. This is normally achieved by anchoring an easily charged polymer (e.g., a dispersant molecule) to the pigment surface. The effectiveness of this technique in preventing close particle-particle contacts is determined by two factors: the identity of the dispersant molecule, and the density and quality of appropriate anchoring sites on the TiO$_2$ surface. Pure TiO$_2$ has very poor anchoring sites, and as such pure TiO$_2$ is nearly impossible to disperse and stabilize. However, all grades of TiO$_2$ used in the paint industry are coated with nano-particles of a material that has a high surface concentration of extremely effective anchoring sites (see Figure 8b for an electron micrograph showing a TiO$_2$ particle covered in nanoparticles). Different TiO$_2$ grades differ in the quantity and identity of these nanoparticles.

The question as to which dispersion strategy is most effective depends on the PVC of the paint in question. For relatively low PVC coatings, ideally dispersed pigment particles will be relatively far apart. In this situation, through-space interactions are the most effective means of keeping the particles well separated, and so the pigments in these paints are best stabilized by electrostatic repulsion. For high PVC coatings (near CPVC and above), particle-particle contacts are unavoidable. In this case steric repulsion is the most effective means of optimizing pigment dispersion in the final paint film.

**Better Dispersion—Flat Grades:** How well do currently available TiO$_2$ pigments perform at dispersion stability? For flat grades, the simple answer is very well. The oxide coatings on these particles are thick yet extremely porous, allowing for maximum particle separation with a minimum dilution of the TiO$_2$ content of the pigment. Over the years, many coatings manufacturers, driven by the cost savings potential of consolidating raw materials, have tried to replace these grades with a combination of a universal TiO$_2$ pigment and small particle size extenders. However, for a number of reasons, success has been limited.

The primary reason can be seen by comparing Figures 8a and 8b. It is difficult to imagine how a physical combination of pigment particles and extenders could match the intimate arrangement found in the flat TiO$_2$ grades. It is invariable that at least some—and often much—of the extend does not end up where it is needed—on the TiO$_2$ surface. Other problems with this approach include the cost of small particle size extenders and their tendency to unduly thicken paints (cf. the use of small amounts of fumed silica as a rheology modifier in some paints).

**Better Dispersion—Lower PVC Grades:** The situation is a little different for TiO$_2$ grades used in lower PVC paints (where electrostatic repulsion is the means of maintaining good dispersion). An electron microscopy survey of dried, low PVC paint films spanning several segments of the coatings market has shown a range of success at obtaining good dispersion in the finished paint film. As shown in Figure 9a, some dried paints clearly suffer from pigment flocculation. But even with a random distribution of particles (Figure 9b), there are a significant number of close particle-particle contacts. The ideal situation is when the particles strongly repel one another, forcing an even distribution of particles, as is the case in Figure 9c.

The films shown in Figure 9 are representative of commercially available paints. We conclude that the optical efficiency of the TiO$_2$ in some paints can be improved on, while in other paints it cannot. Specifically, improvement is possible only in paints that are currently sub-optimal in performance; we expect no improvement in paints that already contain well dispersed pigment particles.

Is there value for TiO$_2$ improvements, since it is already possible to formulate a paint with near optimal dispersion (and therefore very efficient use of TiO$_2$)? The answer is yes. Although an improved grade will not...
change in the maximum possible opacity, it can give a
general improvement in opacity performance by mak-
ing it easier to achieve this maximum. In addition, even
in paint systems where the pigment is already well dis-
tributed (e.g., Figure 9c), an improved pigment should
be welcomed by the paint maker because an improved
pigment would be easier to disperse. This would lead to
lower energy costs, and could allow production simpli-
fication (elimination of some grind operations, or at
least a decrease in grind times and energies) and in-
creased grind throughput (grinds could be done not
only more quickly, but also at higher percent solids).
Decreases in dispersant requirements are also possi-
ble, and this would be valued not only for decreased
ingredient costs, but also for increased formulation
flexibility.

The combined benefits of a pigment that is more
completely dispersed at lower dispersant levels and re-
duced energy requirements make this an active area of
research. Current emphasis is on modifying or even re-
placing the nano-particle coatings on the pigment to
improve the ability to anchor dispersant molecules.

CONCLUSIONS

Innovation is key to the long-term viability of the
coatings industry. The ability of coatings manufacturers
to change their products, processes and technologies
has been—and will continue to be—indispensable to
the health of this business. The demands placed on it
by shareholders, customers, and the community are sig-
nificant, and through innovation the industry will con-
tinue to meet and, at times, exceed these demands.

The same is true of the TiO₂ industry. Shareholders,
customers and the community all challenge this indus-
try, and these challenges will be met by different
means. Community challenges will be met by decreas-
ing the environmental footprint of the industry; share-
holder challenges by removing cost from the process. In
many ways the challenges that require the most innova-
tion are those posed by our customers. Pigment pro-
ducers must act responsively, not only to meet these
challenges, but to anticipate them, so that the desired
products are available when needed.

REFERENCES

(1) Colling, J.H. and Wilkinson, T.W., J. Oil & Colour Chemists’ Assn.,
87, 377 (1975).
(2) Fields, D.P., Buchacek, R.J., and Dickinson, J.G., J. Oil & Colour
(3) Thiele, E.S. and French, R.H., J. Am. Ceramic Soc., 81, 3, 469