

Effect of TiO₂ Pigment on Gloss Retention:

A Two-Component Approach

by Michael P. Diebold DuPont Company* he gloss retention of a coating depends in part on the grade of ${\rm TiO}_2$ used. Traditionally, the ${\rm TiO}_2$ contribution to gloss retention has been attributed to the fact that ${\rm TiO}_2$ is a photocatalyst, and that gloss retention differences between different grades of pigment are due to different levels of ${\rm TiO}_2$ photocatalytic activity. However, there is poor correlation between photoactivity and gloss retention performance. In addition, there is commonly very poor correlation between exterior exposure rankings of ${\rm TiO}_2$ pigments and accelerated exposure rankings in the same coating. In this article, we describe a second property of ${\rm TiO}_2$ —beyond photoactivity—that explains these observations and allows us to better predict both exterior and accelerated gloss retention results.

INTRODUCTION

Consumers place many demands on the coatings they use, whether they apply the coatings themselves directly (e.g., DIY) or purchase them already applied (e.g., automotive finishes). Of initial concern are the appearance characteristics of the paint film: color, gloss, distinctness of image, etc. In the longer term, consumers expect exterior coatings to maintain their protective properties and remain visually appealing, even after extended exposure to the elements. This expectation is often manifest as a warrantee that consumers demand from the coatings producer. These demands are, in turn, often passed on to the raw materials suppliers.

Degradation and failure of a paint film can take on many guises. These two terms can refer to changes over time of appearance properties, as referred to above, of mechanical properties, such as adhesion, peeling, and cracking, or of chemical properties such as corrosion protection of the substrate. A wide variety of formulating parameters affect these different aspects of coating durability, including choice of raw material (resin, pigments, and addi-

Presented at FutureCoat! 2008, sponsored by FSCT, October 15–16, 2008, in Chicago, IL. *Chestnut Run Plaza 709/246, Wilmington, DE 19880. michael.p.diebold@usa.dupont.com.

tives), method of application, and in-service conditions such as high temperature or UV light intensity. In this article, we focus on the effect of a single ingredient—TiO₂ grade—on a single failure mode: loss of gloss.

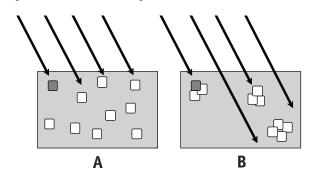
TiO, pigments are used to give opacity to paints, but are also important because of their effect on appearance changes over time during exposure. These appearance changes are color change (fade, yellowing, or other discoloration) and gloss loss over time. TiO2 pigments affect both of these appearance changes in complex and contradictory ways. 1-4 First, because TiO2 is a strong UV light absorber, it protects underlying resin molecules from the harmful effects of UV radiation.* Direct absorption of UV light by resin molecules can lead to the disruption of carbon-carbon, carbon-hydrogen, or carbon-oxygen bonds, depending on the UV wavelength and resin chemistry. This process is termed "direct degradation" because the UV light photons directly interact with the resin. By removing the harmful UV rays from sunlight, TiO, pigments enhance the longevity of paint films.

However, in addition to this beneficial role, ${\rm TiO}_2$ pigments can also be harmful to binder durability. This is because ${\rm TiO}_2$ is a photocatalyst and, when exposed to UV light, generates hydroxyl and superoxide radicals that can attack the organic resin molecules. This process, referred to as "photocatalytic degradation," leads to degradation pathways that in many ways mimic those seen for direct degradation.

The choice of TiO₂ pigment grade can directly affect the total rate of resin degradation in three ways. First, some grades are intentionally modified so as to decrease the rate of photocatalytic degradation. This is most often done by applying a thin shell of silica or alumina onto the pigment surface.^{5,6} This interrupts one of the many reactions that must occur in series for radicals to form. More specifically, it physically separates the oxygen and water molecules from the activated TiO₂ surfaces, preventing these molecules from reacting with the TiO₂ to form hydroxyl or superoxide radicals. General purpose TiO₂ grades have relatively slow rates of radical formation while superdurable TiO₂ grades have a greatly reduced activity.

Secondly, TiO_2 pigments are not pure TiO_2 . Instead, they are surface treated by the TiO_2 manufacturer not only to decrease photocatalytic activity, as noted above, but also to enhance other pigmentary properties such as dispersibility, gloss potential, compatibility with other paint components, etc.⁷ These treatments, which typically constitute 5–10% of the pigment mass, dilute the TiO_2 content of the pigment. For grades that are heavily treated, there is less TiO_2 per pound of pigment and

Figure 1—Effect of TiO₂ dispersion on the balance of direct and photocatalytic degradation pathways. Arrows denote the paths of UV light photons; squares denote TiO₂ pigment particles. (A) Good TiO₂ dispersion; (B) poor TiO₂ dispersion.



therefore less UV light screening and lower rates of photocatalytic degradation rates of the resin.

Finally, the choice of TiO₂ grade can affect the total rate of degradation because some grades of TiO₂ disperse more completely than others. This affects the rate of resin degradation because it changes the balance between the numbers of photons capable of causing direct binder degradation versus the number capable of causing photocatalytic degradation.^{8,9}

This effect is shown pictorially in *Figure* 1, where we compare the balance of rates for the two degradation pathways in a well dispersed paint film (Figure 1A) and a poorly dispersed paint film (Figure 1B). Focusing attention on the shaded TiO, particles in Figure 1, we see that in a well dispersed system the TiO₂ particles primarily shield the underlying resin from UV light, whereas in the poorly dispersed system the TiO, particles primarily shield other TiO₂ particles. In the situation where a photon of UV light is more likely to initiate an undesirable reaction when it is absorbed by the resin (rather than a TiO₂ particle), good dispersion leads to improved durability. In the opposite situation, where absorption of a UV photon by a pigment particle is more likely to lead to degradation, poor dispersion actually improves durability. 10,11 As a practical observation, with today's high durability pigments, this latter situation will apply only rarely, if at all.9

Pigment photocatalytic activity can be measured in a number of ways; perhaps the most meaningful of which is a chalk/fade technique. 12 In this measurement, the TiO_2 pigments of interest are incorporated into paint and the paint applied to a panel. The panels are then exposed under artificial or natural conditions. As the paint degrades, pigment particles begin to emerge from the film surface, eventually leading to a surface that is

 $^{^*\}mathrm{TiO}_2$ is such a strong absorber of UV light that a single 0.25 micron pigment particle removes essentially all of the UV component in impinging sunlight.

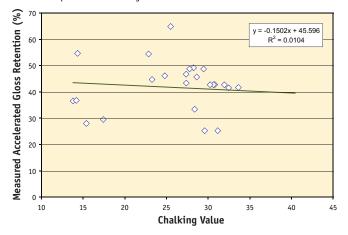
entirely covered in a white ${\rm TiO}_2$ powder. This occurs when the binder above the ${\rm TiO}_2$ in the unexposed paint degrades to the point where the near-surface pigment particles become uncovered. Because of the superficial similarity of the released ${\rm TiO}_2$ to gypsum, the exposed powder is referred to as "chalk."

TiO₂ pigment manufacturers prefer using chalking as a means of characterizing the durabilities of different grades of TiO₂. The reason for this is consistency: as described above, total resin loss is the sum of the loss due to direct degradation and the loss due to photocatalytic degradation. When comparing different TiO₂ grades to one another in a particular paint system, the rate of direct degradation will be essentially independent of TiO₂ grade, since the same resin is used in all paints. Therefore, any differences in chalk rates can be unambiguously attributed to differences in photocatalytic activity. For this reason we always get the same relative order of pigment performance in all paint systems under all exposure conditions.

That said, coatings manufacturers tend not to use chalking values to characterize the durability of their coatings because chalking is usually not as important to the paint consumer as gloss retention. This is not meant to imply that paint consumers would be indifferent to the appearance of chalk—indeed, chalking is quite unacceptable. However, chalking occurs relatively late in the degradation process, long after the gloss drops to unacceptable levels. So, for the paint consumer, the paint has already failed before chalking is seen.

As a first approximation, one would expect chalk performance and gloss retention to closely relate to one another. After all, both should worsen as resin degrades. However, in practice such a relationship can be slight or even nonexistent. ¹³ This is demonstrated in *Figure 2*, where we compare gloss retention (measured as percent

Figure 2—Gloss retention as a function of TiO₂ photocatalytic activity, as measured by the chalk/fade test.¹² Higher chalking values denote improved durability.



34

gloss retained after exposure in a weather-ometer) to pigment chalking performance for 25 different pigment samples in a medium oil alkyd paint system. As is apparent from both a cursory inspection of the plot and the low R² value, there is no relationship between these two measures of durability in this case (indeed, the best-fit line has the opposite slope from what is expected).

Because of the long times required to measure out-door durability, coatings manufacturers and their suppliers routinely turn to accelerated testing as a predictor of end-use weatherability. In this regard, accelerated tests can be used in two ways: first, as a developmental tool to test new coatings formulations; and secondly, as a screening tool to characterize the effect of different raw materials on paint durability. In this article, we are concerned with this second application, specifically with the characterization of the effect of TiO₂ grade on paint film weatherability.

While accelerated testing has the benefit of speed, it is often a poor predictor of actual end-use gloss retention. 14 Even when used in a relative way to rank the order of durabilities in a series of paints, the accelerated results quite often poorly correlate with exterior exposure results. This can occur for a number of reasons, the most common of which include the uncontrolled nature of outdoor exposure conditions, and the fact that different reactions may be occurring under the temperature and UV intensity and wavelength extremes present in the accelerated weathering chambers. For example, some accelerated tests use UV-B radiation to speed up the paint degradation and gloss reduction. However, UV light of these wavelengths is completely absent from terrestrial sunlight, meaning that the degradation reactions occurring in the weather chamber are not the same as those occurring in natural exposures.

We report here our efforts to improve the ability to predict gloss retention, whether measured by natural or artificial exposure, based on properties of the paint and TiO₂ pigment that can be measured easily and quickly.

EXPERIMENTAL

A series of seven grades of commercial TiO₂, differing in durability from moderately durable to superdurable, were incorporated into five different coatings. The coatings chosen are all employed in high durability applications. Four different testing protocols, including both natural and accelerated exposure conditions, were used to characterize the gloss retention durability of the paint films, although not all methods were used for each coating type. *Table* 1 gives a summary of the 10 combinations of paint type and exposure conditions employed in our work.

Gloss retention was characterized either by time required to lose 50% of the initial gloss or % gloss re-

May 2009 JCT CoatingsTech

| Table 1—Coating Types and Exposure Conditions | | | | | |
|---|---------|-----|---------|---------|--|
| | Xe Lamp | QUV | EMMAQUA | Florida | |
| Medium oil alkyd | Х | | | | |
| Colored coil | X | | | X | |
| White coil | X | | | | |
| Aliphatic coil | Х | Х | X | X | |
| Automotive topcoat | | | X | Х | |
| | | | | | |

tained after a set period of time. In addition, chalk/fade values for the seven pigments, measured as described by Madson and Daiger, 12 were separately determined for the seven pigments in the medium oil alkyd paint.

Discussion: The Nature of Gloss and Gloss Retention

Gloss is a measure of surface smoothness at the optical scale. ^{15,16} For visible light, this scale is about 0.25 microns—that is, surface features that are significantly smaller than 0.25 microns will not scatter light and thus will not negatively impact gloss. ^{3,17} Features larger than this do interact with the light, causing it to scatter in all directions. This decreases the amount of light reflecting from the surface at the mirror angle, thereby decreasing gloss.

It is noteworthy that TiO, pigments are intentionally made as 0.25 micron particles, as this is exactly the right size to most efficiently scatter visible light. Surface features created by TiO₂ particles therefore will be of the right magnitude to scatter visible light (and thereby create poor gloss). 18 Since the surface tension of the drying paint pulls the surface flat, this effect is somewhat moderated in practice, and features caused by individual particles near the film surface are normally too small to scatter light. However, for undispersed flocculates or agglomerates, the surface tension is not strong enough to pull the pigment grouping down, and this results in features that are large enough to scatter light. 13 Grade-tograde differences in the gloss potential of different TiO, pigments are attributable to differences in the degree of flocculation or agglomeration of the pigment particles. In fact, the relationship between agglomerate size and gloss is so strong that particle size distribution (PSD) is routinely used to predict gloss for different grades or batches of TiO₂.

If gloss is a measure of surface smoothness, then gloss retention is a measure of the resistance of a film surface to topographical changes during exposure. In general, the surface roughens on exposure for two reasons. First, using a purely statistical argument, degradation should occur randomly—not evenly—on the coatings surface. Through chance, some areas of the surface will suffer numerous degradation events while others will remain untouched. ^{19,20} This causes the formation of valleys (where many degradation events occurred)

and hills (where none occurred). The roughness of the surface, quantified as the root-mean-squared of deviations from the average surface height, is expected to follow a normal (Gaussian) distribution since the tenets of the Central Limit Theorem are satisfied in this situation.^{4,21,22} This effect, which occurs at the topmost section of the paint film, should be seen in any paint system, independent of the presence of pigment or other particles within the paint film.

Croll has further shown that, for unpigmented clearcoats, the rate of gloss loss over time should follow an exponential decay.^{23,24} This means that the initial rate of gloss loss is greater for very high gloss systems compared to lower gloss systems. While we agree that this is true for clearcoats, our experience has shown that for TiO₂ pigmented paint films, the opposite trend is seen. That is, higher initial gloss gives a lower rate of gloss loss (better gloss retention), whether measured on an absolute or relative basis. This indicates that an additional mechanism for gloss loss occurs in pigmented systems.²⁵

To best understand this alternative mechanism for gloss loss, we refer to the early literature on the subject. Initially, an erosion mechanism was used to interpret paint film degradation. ^{26,27} According to this mechanism, all resin loss would occur at the paint surface—that is, at the air/film interface. Gloss loss would initially occur because of the random nature of the degradation events (c.f., Croll's mechanism for unpigmented coatings) and would initially occur at a relatively low rate. However, once the resin overlying the topmost layer of TiO₂ particles was degraded, pigment particles would become exposed and gloss loss would occur at a higher rate. This change in gloss loss rate would be coincident with the beginning of chalking, and such a relationship is seen in many gloss retention measurements.

An explicit assumption in this model is the existence of a clear layer of resin at the surface of the paint film.⁴ We would expect that all TiO₂ particles are covered by at least a monolayer of resin, the thickness of which would exclude particles from the very topmost section of the paint film (in latex paints, this monolayer would be the diameter of a latex particle). However, the clear layer theory went beyond this, instead postulating that TiO₂ pigment particles were excluded from a significantly thicker section at the film surface. This relatively thick clear layer was crucial to the erosion theory because experiments measuring weight loss as a function of exposure showed that a significant amount of resin loss before chalking was first seen. For example, while a reasonable estimate as to the thickness of the monolayer of resin encapsulating a TiO₂ particle would be 0.1 micron, the amount of resin lost prior to the initiation of chalking was the equivalent of several microns.^{3,18}

www.coatingstech.org May 2009 35

Figure 3—Film contraction and surface roughening in an unpigmented resin following an internal degradation event. (A) Destructive absorption of UV photon; (B) void left after degradation products are released from the film; (C) subsequent relaxation of resin into the void, leading to a depression feature on the film surface.

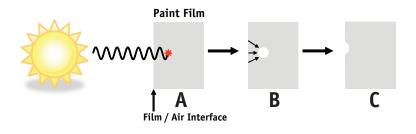
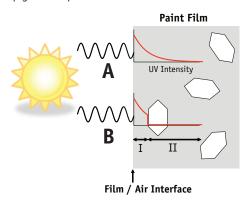


Figure 4—Side-on view of UV light penetration into a pigmented paint film.



Although a clear layer would explain the experimental observations of gloss loss and chalking, the magnitude of the clear layer seemed inconsistent with microscopic analyses²⁸⁻³⁰ and with common experience. This inconsistency led Colling to postulate an alternative theory: the contraction model.^{3,18} According to this model, degradation occurs not only at the surface of the paint film, but also at significant depths within the film. UV light penetration would be expected, based on the Beer-Lambert law, to decrease logarithmically with depth. Since the UV light absorption coefficient is small for many durable resins, this would lead to deep UV penetration into the film, with degradation events occurring throughout the coating.³¹

The initial result for those degradation events that occur in the bulk of the paint film would be a concentration of degraded resin at the point of degradation. These degradation products are chemically different from the original resin molecules in two important ways. First, they have lower molecular weights because some degradation occurs via the rupture of carbon-carbon bonds in the polymer. Second, they have an increased concentration of oxygen functional groups (alcohols, ketones, and carboxylic acids) because the oxygen atoms in the photogenerated hydroxyl and superoxide radicals attach to the degradation products. Both of these differences make the degradation products more volatile and more water soluble than the original resin molecules. Thus, the resin degradation products are removed from the paint film either through volatilization^{32,33} or washing.¹⁴

Removal of the degradation products initially produces a void within the paint film. However, because the resin in most paints is somewhat pliable, this void is filled via contraction of the paint film, with the formation of a depression on the film surface. The mechanism for this surface roughening is shown in *Figure 3*. In *Figure 3A*, UV light penetrates the film and is absorbed with a disruption of resin chemical bonds. The degradation products leave the paint film, either as volatiles, or

36

during washing or rainfall. This leaves a void within the film (*Figure* 3B). The resin polymer is pliable enough to contract around this void, ultimately filling it by pulling the surface of the film down. This leaves a surface feature that is large enough to scatter visible light and that, therefore, leads to a loss in gloss (*Figure* 3C). Note that this surface roughening can happen in either the presence or absence of TiO₂ pigment particles.

In *Figure* 4, we consider what happens when TiO₂ pigment is present in the paint film. In this figure the intensity of UV light as a function of penetration depth is plotted for two regions in the paint film. As light enters the film from the left, it is adsorbed by the resin following the Beer-Lambert law (i.e., the intensity declines logarithmically).²⁰ A fraction of the absorbed UV light energy disrupts chemical bonds in the resin, leading to the loss of organic at the point of UV light absorption (that is, leading to direct degradation). As noted above, this temporarily causes a void to appear in the paint film. However, the resin is pliable enough to contract into the void, filling it from above and leading to a decrease in film surface height above the point of absorption.¹⁸

In *Figure* 4A, there are no near-surface pigment particles and UV light penetration is deep. Direct degradation, while somewhat concentrated at the film surface, ^{3,19,21} occurs throughout a large section of the paint film. Resin that degrades anywhere along this path will cause a void in the film, which will be filled by collapse of the overlying resin, resulting in the film surface contracting at this point.

By contrast, in *Figure* 4B, a near-surface ${\rm TiO}_2$ particle absorbs the UV light, terminating the penetration of the UV light into the paint film. Less direct degradation occurs in this case since the pathlength of the light is shorter. If there is no photocatalytic degradation (or very low levels of photocatalytic degradation), this will result in a bump in the resin above the ${\rm TiO}_2$ particle, since less resin is degrading and contracting. If the amount of photocatalytic degradation from the ${\rm TiO}_2$ particle matches

May 2009 JCT CoatingsTech

the amount of direct degradation that is "missing" due to termination of the UV light, then the surface will remain smooth since the film contracts the same amount at points A and B. If the amount of photocatalytic degradation is quite high compared to the direct degradation rate, then a low point will form in the film surface directly above the TiO₂ particle.²² This is because more *total* degradation will occur.

One consequence of this mechanism is the importance of matching the durability of the ${\rm TiO}_2$ particles (photocatalytic degradation rate) with the durability of the resin (direct degradation rate). 1,4,9,18,34 For a paint system with an even balance of direct and photocatalytic degradation rates, decreasing the rate of one reaction pathway, without a concomitant decrease of rate for the other reaction pathway, will, paradoxically, decrease gloss retention even though the total rate of resin degradation has been reduced. This explains the counterintuitive findings that, for some paint systems and exposure conditions, increasing the durability of the ${\rm TiO}_2$ actually increases the rate of gloss loss. 35

This also explains why the order of accelerated gloss retention performance of a series of TiO2 pigments is often quite different from the order of the same pigments in the same paint when exposed to natural conditions. Eagerton and King³⁶ showed that increasing UV photon intensity, as is done in accelerated weathering experiments, increases the rates of both direct and photocatalytic degradation reactions. However, the relationship between light intensity and degradation rates is different for the two kinds of degradations. For direct degradation, there is a linear relationship between degradation rate and UV light intensity. However, TiO2 photocatalytic degradation rates increase as the square root of light intensity. Thus, increasing the UV light intensity to accelerate degradation, as is done in accelerated gloss retention tests, changes the balance between direct and photocatalytic degradation rates. This, in turn, changes the relationship between the amounts of resin lost and gloss loss.

For example, if the two rates are approximately equal under natural exposure conditions, then the direct degradation rate would dominate under high UV light intensity in accelerated gloss retention test. Thus, under natural conditions the gloss retention will be good while

under accelerated conditions the gloss retention of the same paint will be poor.

As a first order approximation, one would expect the rate of gloss loss to be directly proportional to the rate of resin degradation. After all, each degradation event should, on average, increase surface roughness and therefore lower gloss. However, this expectation has been shown to be incorrect—as evidenced in *Figure 2*. There is clearly more to gloss retention rates than can be explained by simple degradation. We suggest that one missing factor (although not the only one) is what we term the sensitivity of the paint film to resin loss. For the same amount of resin loss, different coatings can show different degrees of gloss loss.^{3,9,37} One coating may be relatively insensitive to resin loss and retain a high gloss while another coating may be very sensitive and show a large decrease in gloss.

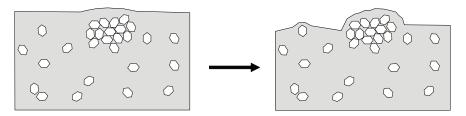
What would make the gloss of one coating more sensitive to resin loss than another? One explanation lies in the different degrees of TiO₂ pigment dispersion that can be found in paint systems. As noted earlier, pigment agglomerates can decrease the initial gloss of a paint film. This occurs when the agglomerates are near the surface; the surface tension of the drying paint is not great enough to pull the agglomerates away from the surface.¹³ When the resin degrades and the surface contracts, what was initially a small surface feature becomes a very large surface feature (*Figure* 5).²⁰ This implies that the gloss of a film with poor TiO₂ dispersion is much more sensitive to resin loss than a film with well dispersed particles. This has, in fact, been reported by many researchers.^{1,3,4,9,17,18,35,38}

If this explanation is correct, then we would expect to see a positive correlation between the initial gloss of a paint film and its gloss retention value. This is exactly what is seen in some instances. An example of this is the relationship between gloss retention and initial gloss for the paints shown in *Figure 2*. In *Figure 6*, we plot the same accelerated gloss retention values, but in this case we plot them against initial gloss rather than chalking performance. As can be seen, the correlation between the two is quite high. The gloss retention of this paint, under these exposure conditions, is clearly very sensitive to the loss of resin. When the paint is better dispersed, or the

exposure conditions are different, we would expect the paint gloss to be less sensitive to resin loss.

Thus, we see that there are two important film properties with regard to gloss retention—the overall resin degradation rate and the sensitivity of the film to resin loss. The grade of TiO₂ used in the coating will affect both of these properties, since the resin degrada-

Figure 5—Evolution of a small surface imperfection into a large surface imperfection.



www.coatingstech.org May 2009 37

Figure 6—Relationship between initial gloss and gloss retention for the paints shown in *Figure* 2.

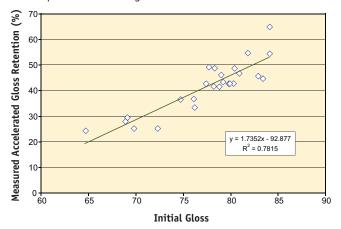
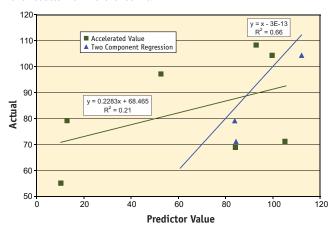


Figure 7—Comparison of one- and two-component analyses of the results from reference 14.



tion rate depends on ${\rm TiO}_2$ photocatalytic activity and its screening ability, and the ${\rm TiO}_2$ grade also determines the degree of flocculation present in the wet and dry film (and, therefore, the paint gloss). Our approach to this understanding is to quantify the importance of both mechanisms on the gloss retention values for different grades of ${\rm TiO}_2$, different paint chemistries, and different exposure conditions.

We begin with the overall resin degradation rate. The direct degradation rate will be determined by the resin chemistry. The photocatalytic degradation rate will depend on the grade of ${\rm TiO}_2$ used, and the ordering of the relative rates of a number of different ${\rm TiO}_2$ grades should be the same from one resin system to another. Therefore, we can use chalk/fade values as a measure for photocatalytic degradation rates. ^{39,40} Note that once we determine the relative rates in one paint system, this information will apply to other paint systems.

A useful measure of the sensitivity of paint is somewhat less obvious. Many researchers have reported that poor pigment dispersion is the cause of high sensitivity of gloss loss to resin loss (vide supra), but measuring the degree of dispersion in a dried paint film is difficult and costly since an electron microscope is required to image the particles.⁴¹ We propose that a simpler alternative is to use initial gloss as a proxy for pigment dispersion. As seen in *Figure 6*, this approach can be successful, at least in the case where the TiO₂ photocatalytic activity is of relatively minor importance.

With the means of measuring these two components of pigment grade effect on gloss retention identified, the next task is to determine the relative importance of them. This can be done by exposing a series of paints, made with different TiO₂ grades, under the exposure conditions of interest. A two-component regression can be made, correlating gloss retention to initial gloss and chalk value. The resulting equation can be used in the

future to predict gloss retention for new pigment grades for which relative chalking values are known. Each combination of resin chemistry and exposure type will have its own set of equations, but once the equations are determined one time, this information can be used to predict the gloss retention of other grades.

To test this approach, we analyzed the gloss retention data of seven TiO₂ grades in five different paint systems. In each case we correlated gloss retention to pigment chalk/fade value, initial gloss, and the two-component regression analysis. Results show this new technique is, in some cases, a powerful predictor of actual gloss retention values (*Table 2*). With that said, there are still effects that we have not yet identified, as evidenced by, for example, Florida exposure of the automotive topcoat formula.

This process of improving our ability to predict the gloss retention has the potential to be more widely useful than just for characterizing TiO₂ pigment performance in gloss retention experiments. For example, Gebhard et al. recently published the results of their study to predict the exterior gloss retention of seven paints based on different emulsion polymers. 14 They found that accelerated gloss retention results were very poor predictors of exterior exposure results ($R^2 = 0.22$). This experiment was different from ours since Gebhard kept the TiO₂ pigment grade the same and varied the resin. However, the two-component analysis can still apply. In this analysis, we use the initial gloss to estimate sensitivity of the paints to resin loss and the accelerated gloss retention results to estimate the total degradation rate.* A two-component regression analysis using this data results in an improvement in R², giving a value of 0.66 (see Figure 7).

^{*} Note that this approximation assumes that the response between gloss loss and resin loss is constant for the seven different resins.

Table 2—Correlation Coefficients (R²) between Three Predictors and the Measured Gloss Retention. The predictors evaluated are: chalking rate, initial gloss, and two-component regression

| | Deg. Rate (Chalking) | Sensitivity (Gloss) | Two Component |
|------------------------------|-------------------------|------------------------|------------------|
| Medium oil alkyd – Xenon | 0.02 | 0.79 | 0.80 |
| Colored coil – Florida | 0.05 | 0.02 | 0.06 |
| Colored coil – Xenon | 0.05 | 0.51 | 0.52 |
| White coil – Xenon | 0.40 | 0.04 | 0.58 |
| Aliphatic coil – Florida | 0.11 | 0.17 | 0.62 |
| Aliphatic coil – Xenon | 0.01 | 0.49 | 0.59 |
| Aliphatic coil – QUV | 0.44 | 0.70 | 0.77 |
| Aliphatic coil – EMMAQUA | 0.00 | 0.57 | 0.79 |
| Automotive topcoat – Florida | 0.00 | 0.00 | 0.00 |
| Automotive topcoat – EMMAQUA | 0.49 | 0.00 | 0.74 |

CONCLUSIONS

Accurate predictions of ${\rm TiO}_2$ grade performance in terms of gloss retention can be made based on a simple model that takes into consideration the effect of ${\rm TiO}_2$ grade on the overall resin degradation rate and on the gloss sensitivity of a particular paint film to loss of resin. Chalk/fade data is used to quantify the effect of ${\rm TiO}_2$ grade on total resin degradation rate, and initial gloss of the paint is used as a proxy for gloss sensitivity. Using this simple model as the basis for regression analysis, we see an improvement in predictability (measured as ${\rm R}^2$) over using either chalk/fade value or initial gloss alone. This technique shows promise for certain combinations of paint chemistry and exposure conditions. However, not all combinations can successfully be modeled with this two-component approach.

References

- (1) Balfour, J.G., "Titanium Dioxide Pigments," Surfactant + Sci. Ser., 69 (1994).
- (2) Sperry, P.R. and mercurio, A., "Exterior Durability of TiO₂ Pigmented Acrylic Resins," Amer. Chem. Soc.–Div. Org. Coat. Plast. Chem. Ont., 30, 1, 400 (1970).
- (3) Colling, J.H. and Wilkinson, T.W., "Implication of the Paint Film Contraction Theory," J. Oil Colour Chemists' Assn., 58, 377 (1975).
- (4) Simpson, L.A., Melville, I., and Moulton, D.V., "Influence of Pigmentation the Morphology of White Paints," *Polym. Paint Colour J.*, 177, 4186, 139 (1987).
- (5) Diebold, M.P., "The Causes and Prevention of Titanium Dioxide Induced Photodegradation of Paints, Part 1," Surf. Coat. Int., 6, 250 (1995).
- (6) Diebold, M.P., "The Causes and Prevention of Titanium Dioxide Induced Photodegradation of Paints, Part 2," Surf. Coat. Int., 7, 294 (1995).
- (7) Braun, J. H., Baidins, A., and Marganski, R. E., "TiO₂ Pigment Technology: A Review," Prog. Org. Coat., 20, 105 (1992).
- (8) Cutrone, L., Moulton, D.V., and Simpson, L.A., "Studies on the Effect of Titanium Dioxide on Durability," *Pigment Resin Technol.*, 16 (January 1989).
- (9) Simpson, L., "Influence of Titanium Dioxide Pigment on Durability of Paint Films," *Polym. Paint Colour*, 176, 4184, 408 (1986).
- (10) Schmelzer, J., "Accuracy of the Weathering of Paints Containing Titanium Dioxide Pigments — A Critical Retrospective on 20 Years of Weathering," Surf. Coat. Int., 6, 270–276 (2007).

- (11) Cutrone, L., Moulton, D.V., and Simpson, L.A., "Studies on the Effect of Titanium Dioxide on Durability," *Pigment Resin Technol.*, 8 (December 1988).
- (12) Daiger, W.H. and Madson, W.H., "Chalk-Fade Evaluation of Pigmented Finishes by Use of Instrumentation and Computer Analysis", J. Paint. Technol., 39, 399 (1967).
- (13) Braun, J.H. and Cobranchi, D.P., "Durability and Gloss," J. Coat. Technol., 67, No. 851, 55 (1995).
- (14) Gebhard, M.S., Clark, M.B. Jr., Willey, K.F., Antrim, R.F., Acholla, F.V., Newman, J.B., Weidemaier, K., "Assessment of Various Analytical Techniques on Naturally Weathered Paints as a Predictor of Long-Term Gloss Retention for Waterborne Acrylic Architectural Paints," J. Coat. Technol. Res., 3, No. 1, 15 (2006).
- (15) Braun, J.H., "Gloss of Paint Films and the Mechanism of Pigment Involvement," J. Coat. Technol., 63, No. 799, 93 (1994).
- (16) Braun, J.H. and Fields, D.P., "Gloss of Paint Films II. Effect of Pigment Size," J. Coat. Technol., 66, No. 828, 93 (1994).
- (17) Gross, P. and Schmelzer, J., "Impact of the Dispersion Quality of TiO₂ Pigments in Coatings on Their Optical Properties and Weathering Resistance," Macromolecular Symp., 641 (2002).
- (18) Colling, J.H. and Dunderdale, J., "The Durability of Paint Films Containing Titanium Dioxide—Contraction, Erosion, and Clear Layer Theories," Prog. Org. Coat., 9, 47-84 (1981).
- (19) Wood, K.A. and de Robien, S., "A Quantitative Model for Weathering-Induced Mass Loss in Thermoplastic Paints," In Press.
- (20) Hunt, F.Y., Galler, M.A., and Martin, J.W., "Microstructure of Weathered Paint and its Relation to Gloss Loss: Computer Simulation and Modeling." J. Coat. Technol., 70, No. 880, 45-54 (1998).
- (21) Hinderliter, B. and Croll, S, "Monte Carlo Approach to Estimating the Photodegradation of Polymer Coatings," J. Coat. Technol. Res., 2, No. 6, 483 (2005).
- (22) Faucheu, J., Wood, K.A., Sung, L-P., and Martin, J.W., "Relating Gloss Loss to Topographical Features of a PVDF Coating," J. Coat. Technol. Res., 3, No. 1, 29 (2006).
- (23) Croll, S.G. and Skaja, A.D., "Quantitative Spectroscopy to Determine the Effects of Photodegradation on a Model Polyerster-Urethane Coating," J. Coat. Technol., 75, No. 946, 85 (2003).
- (24) Hinderliter, B.R. and Croll, S.G., "Simulations of Nanoscale and Macroscopic Property Changes on Coatings with Weathering," J. Coat. Technol. Res., 3, No. 3, 203 (2006).
- (25) Wood, K.A., Hedhli, L., and Willcox, P.J., "Patterns of Erosion from Acrylic and Fluoropolymer Coatings in Accelerated and Natural Weathering Tests," J. Coat. Technol., 74, No. 924, 43 (2002).
- (26) Ritter, H.S., "Durability of Paint Films from Erosion Rate Studies," J. Paint Technol., 43, 552, 74 (1971).
- (27) Stieg, F.B., "Weathering and Titanium Dioxide," J. Paint Technol., 43, 555, 82 (1971).
- (28) Tunstall, D.F., J. Oil Colour Chemists' Assn., 50, 989 (1967).
- (29) Jettmar, W., FATIPEC Congress, III-497 (1966).
- (30) Saris, H.J.A., FATIPEC Congress, III-490 (1966).
- (31) Gu, X, Michaels, C.A., Drzal, P.L., Jasmin, J., Martin, D., Nguyen, T., Martin, J.W., "Probing Photodegradation Beneath the Surface: A Depth Profiling Study of UV-Degraded Polymeric Coatings with Microchemical Imaging and Nanoindentation," J Coat. Technol. Res., 4, No. 4, 389 (2007).
- (32) Allen, N.S., Regan, C.J., McIntyre, W.A.E., and Johnson, B., "Aspects of the Thermal, Photodegradation, and Photostabalization of Water-Borne Fluorinated-Acrylic Coating Systems," Polym. Degrad. Stab., 58, 149 (1997).
- (33) Chiantore, O., Trossarelli, L., and Lazzari, M., "Photooxidative Degradation of Acrylic and Methacrylic Polymers," Polymer, 41, 1657 (2000).
- (34) Balfour, J.G., "Back to Basics: Durability and Titanium Dioxide Pigments," J. Oil Colour Chemists' Assn., 12, 478 (1990).
- (35) Diebold, M.P., "Unconventional Effects of TiO₂ on Paint Durability," Proc. 5th Nurnberg Congress, 371.
- (36) Eagerton, T.A. and King, C.J., "The Influence of Light Intensity of Photoactivity of TiO₂ Pigmented Systems," J. Oil Colour Chemists', 62, 386 (1979).
- (37) Dunderdale, J., Craker, W.E., and Colling, J.H., XIIth FATIPEC Congress, 69 (1974).
- (38) Aik, D.T.T., "Durability and TiO₂ Pigments," PaintIndia Annual 1995, 84–93 (1995).
- (39) Kaempf, G., Papenroth, W., and Holm, R., Farbe Lack, 78, 606 (1972).
- (40) Kaempf, G., Papenroth, W., and Holm, R., Farbe Lack, 79, 9 (1973).
- (41) Diebold, M.P. and Staley, R.H., "Quantitative Determination of Particle Dispersion in a Paint Film," Paint Coat. Ind., 38 (October 1, 2005).