DIFFERENCES BETWEEN THE Ti PIGMENTS IN

INTRODUCTION

Titanium dioxide is the most important white pigment in waterborne architectural paints. Even though it is one of the most expensive raw materials in the formulation, subject to numerous price fluctuations and turbulence related to changes in the hazard classification, titanium dioxide is the most effective pigment for providing opacity to white and light shades.

In addition to opacity, the structure, surface treatment, and grade of titanium dioxide pigments are valued in architectural coatings, as described in ASTM D476.

Titanium dioxide in waterborne paints is used in architectural paints, on wood, and on metal and other substrates. Thanks to its very high opacity, it has replaced zinc oxide and barium sulphate in many applications.

However, to maximize the effectiveness of titanium dioxide pigment in a formulation, it must be incorporated into the paint in a specific manner. This involves the deagglomeration of the titanium dioxide particles; in its commercial form, titanium dioxide is a powder with aggregated and agglomerated particles.

In architectural paints, titanium dioxide is usually incorporated into wall and ceiling paints, along with other fillers, in the form of slurries and is combined with other raw materials. The slurries for waterborne paints for walls and ceilings are prepared by dispersing the primary particles at a high speed with a Cowles dissolver equipped with a serrated disc.

The appropriate selection of surfactants and grinding aids helps separate the primary particles so the degree of dispersion is sufficient to obtain paints with a semigloss or gloss above 60% at 60°. This is usually because latex paint formulations for walls are prepared by dispersing the primary particles with other fillers, such as calcium carbonate, nepheline syenite, and quartz, which act as an additional grinding medium for the titanium dioxide particles. This result occurs even when the paint production process consists of adding separate slurries from each type of filler in the let-down process and mixing them with a binder and thickeners in an increased viscosity of suspension.

Many types of titanium dioxide cannot be used in high-gloss waterborne paints without grinding the particles in a bead mill. In some cases, paint producers do not have bead mills in their machine park, so they produce high-gloss paints by using a Cowles dissolver. It is very important that the formulator of the recipe select the appropriate type of titanium dioxide for grinding in a Cowles dissolver, ensuring proper dispersibility and obtaining the highest possible gloss level. The selection should be based on data from research and case studies prepared in various devices to ensure grinding to a level that maximizes gloss in paints with low PVC. It is also very important to note the type of titanium dioxide used to produce the level of gloss that was achieved with the resulting coating, along with the related characteristics of hiding power, gloss retention, durability of the coating against solar radiation and weather conditions.

TIO_2 CLASSIFICATION

Typically, paint formulators use the recommendations of raw material manufacturers in selecting ingredients partly based on how they can be used

GRINDING PROCESS OF

GLOSSY ACRYLIC PAINTS

By Artur Palasz,
Spektrochem

in paint. It is similar in the case of titanium dioxide. Raw material manufacturers' recommendations are based on the titanium dioxide grades described in ASTM D476 and ISO 591-1.

Data from these standards can often be found in the technical materials of manufacturers of titanium dioxide pigments. These classifications include a list of different groups of anatase and rutile pigments, which are divided according to the TiO_2 content and other pigment parameters; in the case of ASTM D476, they are also divided in terms of use in paints with a diverse range of PVC and paint types in terms of gloss, durability of the coating, etc.

Table 1 shows the classification of titanium dioxide according to ASTM D476, while *Table 2* shows the classification according to ISO 591-1.

TABLE 1—Classification of titanium dioxide pigments according to ASTM D476

CLASSIFICATION TYPE	I	II	III	IV	V	VI	VII	VIII
Crystal type	Anatase	Rutile						
Chalking resistance, relative	Free chalking	Low-medium	Medium	High	High	Medium-high	Medium-high	Very high
Typical end use application	White exterior house paint and interior use	Low-medium % PVC	High % PVC	Exterior coatings requiring excellent durability	Exterior coatings requiring excellent durability with gloss	Interior and exterior medium-high % PVC	Interior and exterior low-high % PVC	Exterior colored coating and polymer requiring infrared reflectance with excellent durability
Titanium dioxide (TiO_2) content, min., %	94	92	80	80	90	90	92	92
Specific resistance, min., Ω · cm	5,000	5,000	3,000	3,000	3,000	5,000	5,000	3,000
Specific gravity	3.8 – 4.0	4.0 – 4.3	3.6 – 4.3	3.6 – 4.3	3.6 – 4.3	3.6 – 4.3	4.0 – 4.3	3.6 – 4.3
45-µm screen residue, max.	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1

The data in *Table 1* show which types of titanium dioxide pigments can be tested in each formulation type. When formulating high-gloss low-PVC paints, ASTM D476 type V is suitable for exterior paint application that require excellent durability with high gloss. When analyzing the data from *Table 2*, it is not possible to suggest which type of R-grade titanium dioxide pigment to use for the tests. Therefore, paint formulators do not usually take ISO 591-1 standards into consideration when selecting titanium dioxide pigments for testing in their formulations.

It should be emphasized, however, that the classification of titanium dioxide pigments, according to ASTM D476, and the assignment of high durability to the gloss coating, as for type V, are based on tests in solvent-based alkyd binder paints and exposure to natural atmospheric conditions at an angle of 45° south-facing Florida outdoor exposure testing.

However, these requirements are not clearly defined, and there are no indicated levels of acceptable variation in gloss or other parameters. The ASTM D476 standard only specifies the evaluation of the chalking of the coating after exposure, but there is no indication of the exposure time, and the test procedure is recommended to be performed against a reference paint with known chalking resistance agreed upon between the buyer and seller.

This causes some inaccuracies as the results cannot be translated into water-based paints. It also makes the Type V classification, which indicates high durability in glossy coatings, relate to chalking and not to gloss durability requirements.

For this reason, it is very important to provide appropriate case studies and recommendations based on dedicated laboratory tests in waterborne paint formulations (which supplement the ASTM D476 classification) and to educate formulators that class V does not mean durability in terms of gloss retention for waterborne paints.

TABLE 2—Classification of titanium dioxide pigments according to ISO 591-1

ESSENTIAL REQUIREMENTS					
Characteristic	**Type A (anatase)**		**Type R (rutile)**		
	A1	**A2**	**R1**	**R2**	**R3**
TiO_2 content, % (by mass), min.	98	92	97	90	80
Matter volatile at 105 °C at point of acceptance, % (by mass)	0.5	0.8	0.5	To be agreed between the interested parts	
Matter soluble in water, % (by mass) max.	0.6	0.5	0.6	0.5	0.7
Residue on sieve (45 µm), % (by mass) max.	0.1	0.1	0.1	0.1	0.1
Conditional requirements					
Color	Similar to that of the agreed reference pigment				
Scattering power	To be agreed between the interested parts				
Matter volatile at 105 °C after 24 h pre-conditioning at (23 ± 2) °C and (50 ± 5)% relative humidity, % (by mass) max.	0.5	0.8	0.5	1.5	2.5
pH of aqueous suspension	Similar to that of the agreed reference pigment				
Oil-absorption value					
Resistivity of aqueous extract	-	Similar to that of the agreed reference pigment	-	Similar to that of the agreed reference pigment	

DISPERSING AND GRINDING

When used in paint production, titanium dioxide is a ground powder that has undergone a surface treatment (organic, inorganic, or both). Primary titanium dioxide particles, usually about 0.2–0.5 µm in size, are joined together by edges and corners to form aggregates, which in turn combine to form agglomerates. Titanium dioxide is dispersed in this form during the production of paints, and the grinding processes are designed to break down both agglomerates and aggregates.

Aggregates are created during particle formation rather than particle grinding. The calcination process (in the sulphate process) affects the aggregation of primary particles, similar to the gas reaction phase in the chloride process where titanium tetrachloride reacts with oxygen.

The more particles are separated to form primary particles, the more specific surface the titanium dioxide particles will be able to use. This and the surface treatment of the particles will result in the most efficient use of the TiO_2 and the best possible efficacy of its properties. Particles that are not well ground will adversely affect not only the appearance of inclusions (particles) in the coating, but also a number of additional properties, ranging from opacity and gloss, and weather resistance. Therefore, a properly conducted grinding process is crucial.

The agglomerates formed in the liquid are called flocculates. They arise in improperly dispersed and grinded slurries, where they are the cause of color development disorders (rub-out), as well as the other problems described above.

The grinding process must be carried out correctly to not only break down agglomerates and aggregates, but also to prevent flocculation during storage of slurries or titanium dioxide paints, bearing in mind that the formulation usually also includes other pigments and fillers.

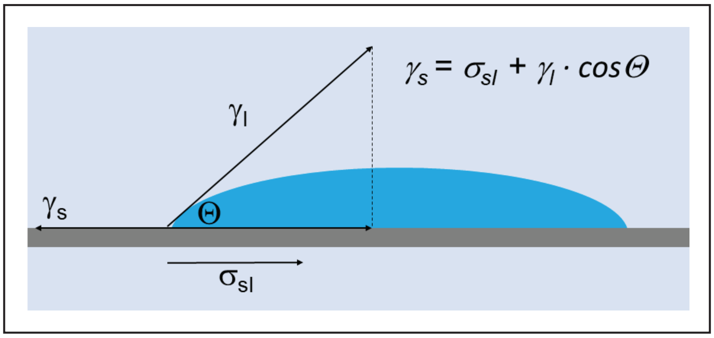
The term “dispersing” applies only to rupturing agglomerates connected to each other by adhesion forces, and the term “grinding” usually refers to the disintegration of particles joined into aggregates in which chemical bonds are broken as a result of the grinding process.

Upon dispersing, the particle separation process takes place practically simultaneously and is divided into three interpenetrating stages:

1. Wetting of the pigment surface by liquid ingredients of the mill base
2. Mechanical separation of agglomerates into smaller agglomerates and primary particles
3. Stabilization of primary particles against flocculation

If any of the above steps are disrupted or not handled correctly, the degree of dispersion and grinding will not be satisfactory.[1, 2]

FIGURE 1—A pictorial representation of Young equation



Surface treatment

Titanium dioxide, depending on the surface treatment, is one of the more dispersible pigments used for the production of paints. The surface treatment of the titanium dioxide is for this purpose is also very important for dispersal, especially surface treatments with organic materials. The organic surface treatment of titanium dioxide is carried out at 0.1–0.6% with TMP (1,1,1-Trimethylolpropane). Surface treatment can also be carried out with the dispersants used in the pigment and fillers in the production of paint. Surface treatment is usually carried out in the final stage of milling the titanium dioxide and happens in one or two stages.

Inorganic surface treatment affects the shift of the isoelectric point (IEP, pH_{IEP}, i.e., the pH value at which the zeta potential is 0), which in turn causes changes in the properties of titanium dioxide in terms of weathering resistance, gloss retention, and chalking resistance. For example, a surface treatment in the range of 0.5% to 4% silica increases gloss retention, chalking resistance, and reduces yellowing and graying. Increasing the level of silica surface treatment to 6–11% favors weathering resistance and scattering, especially in latex paints.

The alumina surface treatment also increases the weathering resistance, and the additional zirconium oxide treatment contributes to the integration of the surface treatment layers. Untreated titanium dioxide has a specific surface area of 4 m^2/g to 9 m^2/g, and after inorganic surface treatment, it increases to 7–45 m^2/g due to the spongy structure provided by the precipitated metal oxides.

The effect of surface treatment on titanium dioxide pigments and their properties in water-based paints has seldom been the focus of case studies. This necessitates extensive testing in various formulations, particularly for latex paints, where the surface treatment sometimes affects the coating's properties differently than the way it affects the properties of solvent-based coatings.[1, 2]

Wetting

When the agglomerates are placed in the mill-base liquid (e.g., in water), the liquid enters the agglomerates on each side. Capillary pressure causes penetration and tries to force liquid into all the gaps.

The relationship between free surface energy (γ_s), interfacial tension between solid (σ_{sl}) and liquid, and surface tension of liquid (γ_l) increases the contact angle (θ), which was first described by Thomas Young as the wetting behavior of the glass surface by mercury, water, and ethanol in the year 1805. The formula and diagram shown in *Figure 1* are the key to understanding the wetting relationship of solids by liquids, including titanium dioxide.

The liquid filling the spaces between the agglomerates must overcome the opposing pressure of the air between them. Therefore, the wetting process takes a certain amount of time and is crucial for the correct replacement of any air-filled spaces with liquid. The lapse of time for proper wetting can be replaced by mechanical breaking of agglomerates, for example, with high-speed impeller mills.

Otherwise, the deagglomeration would have to be done by wetting the pigment overnight (or even longer), which could cause re-agglomeration in the liquid and thus, flocculation. To avoid this, in the case of titanium dioxide, surface treatment and surfactants—the so-called wetting agents that do not allow flocculation—for faster wetting of the particles also accelerate the wetting process during the mechanical break-up of agglomerates.[3]

Mechanical deagglomeration

The mechanical deagglomeration of the titanium dioxide particles must ensure that the air is replaced by a liquid between the agglomerates, with the simultaneous supply of surfactants dissolved (in this case, in water), thus allowing for their further stabilization process.

Hence, mechanical grinding processes consist in setting the particles, including agglomerates, in motion by means of a dissolver disk or grinding elements in a bead mill. The flow during grinding should be Newtonian or slightly pseudoplastic, which is achieved by adding special grinding aids to the batch.

Mechanical deagglomeration then becomes the supply of energy which sets the particles in motion and their mutual collision and rubbing against each other (and with a Cowles dissolver) and additional rubbing between the beads and grinding elements in the bead mill. Due to the high mixing speed and the released energy as a result of the process is the temperature is controlled by the cooling jacket in the dissolver or mill tank. It is recommended that the temperature be kept at a level where the decomposition of the raw materials in the dispersed feed does not occur, where biocides are of particular importance, the effectiveness of which may fall off when the temperature rises above 40 °C (104 °F).

During the past 10 years, grinding machines have operated using homogenizers with a rotor-stator grinding element, which generate very high shear forces. These devices have become very popular and are widely used in the cosmetics industry for the production of emulsions; however, they are found in the paint industry more and more often.

Grinding is typically measured in the paint industry using a Hegman gauge, which is a polished block of stainless steel with a groove or grooves graduated from 0 to 4 mils (8 to 0 Hegman) or less. This block is used to assess the fineness of grind in accordance with ASTM D1210, a method in which a special knife is used to spread the grinded slurry or paint over the block so the agglomerates in the grooves can be accessed. The assessment can be made with the naked eye based on the light reflected in the path of the distributed slurry or with the use of automated grindometers, which enables a computer reading if equipped with a precise camera and software.

While the deagglomeration of very large agglomerates of titanium dioxide is possible to assess with a grindometer, grind sizes below ca. 12 µm (less than 0.5 mils) are difficult to assess with a Hegman gauge, especially by inexperienced laboratory technicians, and requires the use of grindometers with a much narrower scale (e.g., 0–15 µm).

Stabilization against flocculation

In a liquid medium, titanium dioxide particles flocculate due to London-van der Waals attractive forces. Stabilization of the pigment is necessary because of the usefulness of its suspension as a slurry for the preparation of latex paints and also in the paints themselves where stability is expected for at least few years in the liquid state.

The stabilization process is just as important, and you can even say that it is slightly more important, than the mechanical deagglomeration process. Stabilization against flocculation is achieved when each particle repels the other particles away, and the repulsive forces overcompensate for the attractive dispersion force.

The stabilization mechanism against flocculation can be divided into three stages:

1. Electrostatic stabilization
2. Entropic (steric) stabilization
3. Stabilization by adsorbed inorganic nanoparticles, carrying an electrostatic charge

Electrostatic stabilization takes place at the time of dissociation of surface groups, adsorption of large polyelectrolytes, and adsorption of low ions. Bulk migration takes place on the basis of, inter alia, the pH dependence of zeta potential and, so it is very important to use appropriate dispersing agents (dispersants).

Depending on the pH range, titanium dioxide may have a negative charge (e.g., in the range of pH 7 to 8.5), at which point it cannot be stabilized with anionic polyelectrolytes because they have the same charge. If the charge is positive, then the cationic polyelectrolytes are not working. Therefore, the selection of an effective stabilizing system for an environment with a specific pH is extremely important. Often the use of pH buffering additives is desirable to prevent the pH drift caused by other raw materials in the formulation.[1, 2, 3]

EXPERIMENTAL

Additional case studies of titanium dioxide pigments tested in waterborne paint formulations can supplement the existing technical materials. An experiment was conducted to test rutile-grade titanium dioxide pigments, which were classified by the manufacturer as type V in accordance with ASTM D476, in paint formulations with low PVC that were prepared with slurries grinded in three laboratory devices: bead mill, Cowles dissolver, and homogenizer.[4, 5, 6]

The aim of the experiment was to check to what extent the type of titanium dioxide used determines the gloss retention of the waterborne paint, how the grinding method affects coating parameters of the resulting coating, and which method of mechanical deagglomeration is the best at achieving the above parameters.

The focus was on the mechanical deagglomeration method, without analyzing the cases of particle stabilization with various auxiliaries. The slurries formulation presented in the paper was selected to ensure deflocculation stability and prevent particle reagglomeration.

Titanium dioxide for studies

Type V, rutile-grade titanium dioxide pigment, which has the characteristics of the parameters as presented in *Table 3* was selected for the case studies.

The titanium dioxide pigment selected for the tests was surface-treated in a moderate manner, which affected gloss retention and resistance to yellowing and graying. This level of surface treatment with an amorphous silica, alumina and organic surface treatment should increase the titanium dioxide particles' dispersibility.

Formulation and lab-scale paint preparation

The test paints were prepared from slurries obtained by grinding the ingredients in a Cowles dissolver (recipe is shown in *Table 5*). Dispersing into the Cowles dissolver was performed using a serrated disc according to ASTM D6619. Laboratory dissolver geometry: disk diameter D = 56 mm (vessel diameter 1.90 D). Dispersion was carried out at a circumferential speed of 4.2 m/s (ca. 826 fpm) in a container with a cooling jacket, and the temperature during dispersion was maintained below 28 °C (82 °F). Total time of dispersing in the Cowles dissolver: 15 minutes.

Then the prepared suspension was divided into three parts. The first was used to let-down and combine with the formulation ingredients as shown in *Table 5*. The remaining two portions of slurries were subjected to additional grinding. The first one at the bead mill and the second one at the homogenizer.

Grinding in the bead mill was carried out in accordance with the guidelines of ISO 8780-1 (general) and ISO 8780-4 (for bead milling) with 1.25 mm-diameter zirconium beads filling 40% by volume of the laboratory mill tank. Milling was carried out in a vessel with a cooling jacket at a speed of 6.0 m/s (ca. 1,180 fpm), which kept the temperature during grinding between 21–27 °C (70–81 °F). Milling was carried out for 20 minutes.

The third portion was grinded in an IKA® Ultra-Turrax® T18 homogenizer. Milling was performed for 4 minutes at a rotor speed of 18,600 rpm, and the batch temperature was kept less than 25 °C (77 °F). The short grinding time was dictated by the very high speed and the difficult-to-control temperature rise that happens over a long period, which results in significant evaporation of water during grinding.

The resulting titanium dioxide suspensions using different grind and dispersion methods were intended to be let down in the paint formulation according to the formulation shown in *Table 5*.

The characteristics of the constants are presented in *Table 6*.

TABLE 3—Titanium dioxide for the case studies

PROPERTY		DATA FROM TECHNICAL DATA SHEET
TiO_2 content		min. 93 wt %
Median particle size		0.36 μm
Oil absorption		13.9 g/100 g
Surface treatment	Amorphous silica	3.0 wt %
	Alumina	2.5 wt %
	Organic	Yes

TABLE 4—Formulation of titanium dioxide slurry

FUNCTION	RAW MATERIALS	LBS/GAL	WT %
Solvent/carrier	Tap water	4.361	22.73
Dispersant	Disperbyk®-199	0.215	1.12
Defoamer	BYK®-1640	0.096	0.50
In-can biocide	Acticide® LA 1209	0.038	0.20
White pigment	Titanium dioxide (Table 3)	14.336	74.73
HEUR thickener	BYK®-7420 ES	0.069	0.36
Mineral thickener	Acti-Gel® 208 (20 % in water)	0.068	0.35
Total		**19.2 lbs/gal**	**100 wt %**

TABLE 5—Formulation of acrylic gloss paint for case studies

FUNCTION	RAW MATERIALS	LBS/GAL	WT %
Slurry with pigment	Titanium dioxide slurry (Table 4)	3.585	33.28
Acrylic binder	Axilat™ 6492	5.540	51.43
In-can biocide	Acticide® LA 1209	0.021	0.20
Fungicide	Acticide® MKW 2U	0.129	1.20
Coalescing agent	K-Flex® 500P	0.222	2.06
Corrosion inhibitor	CHE®-COAT LNFA4	0.021	0.20
Mineral thickener	Acti-Gel® 208 (20% in water)	0.521	4.84
Solvent	Tap water	0.514	4.77
HEUR thickener	Viscolam® PS 202	0.019	0.17
Surfactant	BYK®-3455	0.068	0.63
HEUR thickener	Tafigel® PUR 80	0.133	1.20
Total		**10.8 lbs/gal**	**100 wt %**

TABLE 6—Formulation constants

CONSTANTS	CALCULATED VALUE
PVC	19.3%
CPVC	62.6%
Q (PVC / CPVC)	0.31
Weight per gallon	10.8 lbs / gal
(P+F) / B[a]	0.97
Volume solids	42%

[a] Ratio of Pigment plus Filler per Binder

Test results

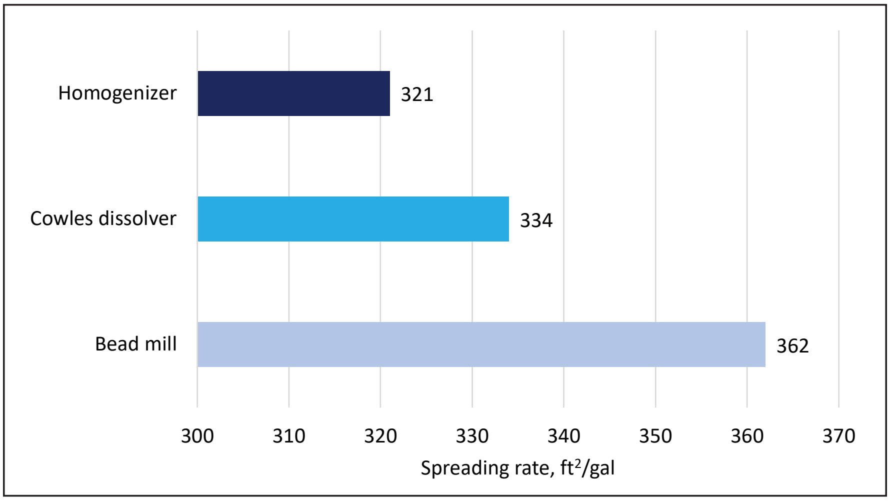
In the field of case studies, a number of parameters of coatings obtained from paints prepared with grinded titanium dioxide slurries were assessed in three different ways: bead mill, Cowles dissolver, and homogenizer. Dry hiding power, wet-to-dry hiding change (WDHC), gloss of coatings, and changes in gloss of coatings after accelerated artificial exposure in a UV chamber were assessed. The results are discussed in the following subsections.

Dry Hiding power

The hiding power test was carried out according to the ASTM D2805 method by calculating the spreading rate with a contrast ratio of 98%. The test was performed on Leneta 2A black-white charts and the measurements of the contrast ratio were taken with the Rhopoint Instruments Novo-shade Duo+ reflectometer with geometry 0/45.

The test results are shown in *Figure 2*.

FIGURE 2—Spreading rate at 98% contrast ratio



The paint prepared from slurries grinded in the bead mill has the highest spreading rate at 98% contrast ratio of 362 ft^2/gal (8.9 m^2/L). Compared to the paint prepared from slurries made by grinding using the Cowles dissolver, the bead mill paint had a spreading rate that was 28 ft^2/gal higher (0.7 m^2/L). When painting from a five-gallon container, the bead mill paint results in 140 ft^2 (13m^2) more painted surface area than the Cowles dissolver paint does, while maintaining hiding power.

On the other hand, compared to the paint with slurries grinded by the homogenizer, the paint with slurry with bead mill hiding power had a 41 ft^2/gal higher spreading rate (1 m^2/L), which, when painting with a five-gallon container, results in an additional 205 ft^2 (19 m^2) of painted surface area.

The dry hiding power results clearly show the differences in the impact of the grinding three devices used during the process.

TABLE 7—Wet-to-Dry Hiding Change, test results

PAINT PREPARED BY GRINDING TIO$_2$ SLURRY	SPREADING RATE TO OBTAIN 98% CONTRAST RATIO		Δh_s	WDHC, %
	Wet coating	Dry coating		
Bead mill	612 ft^2/ gal (15 m^2/ L)	414 ft^2/ gal (10.2 m^2/ L)	-8	-32
Cowles dissolver	612 ft^2/ gal (15 m^2/ L)	341 ft^2/ gal (8.4 m^2/ L)	-12	-44
Homogenizer	612 ft^2/ gal (15 m^2/ L)	341 ft^2/ gal (8.4 m^2/ L)	-12	-44

TABLE 8—Lightening power and color tint test results

COLOR DATA	COLOR CHANGES ASTM D2244			
	Cobalt blue pigment PB28 + 3.5 wt % colorant		Iron oxide red PR101 + 1.0 wt. % colorant	
	Cowles dissolver	Homogenizer	Cowles dissolver	Homogenizer
ΔL^*	-0.03	-0.07	0.18	-0.23
Δa^*	0.06	0.04	-0.14	0.13
Δb^*	-0.22	-0.02	-0.03	0.13
ΔE^*ab	0.23	0.09	0.23	0.29

Wet-to-Dry Hiding Change (WDHC)

The WDHC test was carried out in accordance with ASTM D5007 with a Leneta TG19 logicator allowing the application of paint strips at a defined spreading rate. Coatings were applied to black and white chevron-pattern cards and evaluated with a 98% contrast ratio reference coating, both wet and dry.

The difference in the wet-to-dry spreading rate coefficients defines WDHC as Δh_s (the difference in the hiding index of a paint between the wet and the dry state, expressed in logicator units, or LU.) and the percentage difference WDHC. The test results are shown in *Table 7*.

All paints show an identical wet-hiding index of 612 ft^2/gal, which means that wet paint strips at this spreading rate have a contrast ratio of 98%. After the paint strips have dried and the dry hiding index has been marked, there is a clear change in hiding power towards the weakening of the dry hiding index (hence, the negative signs in the WDHC column). This weakness is identical for the samples grinded in the Cowles dissolver and homogenizer and is 341 ft^2/gal (WDHC -44%). The paint sample prepared from the bead mill slurry grind has a spreading rate of 414 ft^2/gal (WDHC -32%), which ensures a dry film with a contrast ratio of 98%.

Lightening power

In order to evaluate the influence of the titanium dioxide grinding process on tinting, two sets of samples with colorants (pigment concentrates) were prepared. Colorants from the Colanyl® 500 series by Clariant® were used for lightening power: 3.5 wt % Oxide Blue COR 530 (cobalt oxide blue PB28) and 1.0 wt % Oxide Red B 530 (iron oxide red PR101).

Tinted paints were applied to BYK cards to evaluate the tristimulus coordinates after drying. $L^* a^* b^*$ measurements were made using a Konica Minolta® CM-2500d (d/8) spectrophotometer with an illuminate D65 and 10° observer (SCI—specular gloss included). Calculation of the change in color coordinates was made according to ASTM D2244 and the results are shown in *Table 8*.

The evaluation was performed using bead mill coatings as reference points (so the changes in color coordinates were measured in relation to them). Coatings tinted with cobalt oxide blue pigment concentrate show a noticeable difference in readings, with calculations of $\Delta E^*_{ab} = 0.23$ for the Cowles dissolver and 0.09 for the homogenizer.

It is true that the differences in the shade are so insignificant that they are not visible to the naked eye, while measurements taken with the spectrophotometer showed a clear difference, demonstrating the effect of the grinding method on lightening power. In the case of samples with iron oxide red, the ΔE^*_{ab} values are practically identical at 0.23 and 0.29 respectively, which also makes them invisible to the naked eye, but they show a drift compared to the tinted reference coating with the bead mill slurry.

Gloss

The gloss of the coatings was measured on BYK charts and on Q-Panel A-36 panels to which paints were applied using an applicator with a 7-mil gap. The gloss was measured with a Novo-gloss Trio glossmeter by Rhopoint Instruments in accordance with ASTM D523.

The intent was to obtain coatings with a gloss that would allow classification of the paints in MPI gloss level 6 (gloss), which means gloss at 60° above 70%, according to criteria MPI #114 and #119. Measurements were also made at 20° and at 85° to further evaluate and analyze the change in gloss after exposure to a UV chamber. The measurement results are shown in *Figure 3*.

Coatings at an angle of 60° meet the MPI criteria for gloss level 6 only for bead mill paints and homogenizer. The fulfillment of these requirements, however, is on the verge, slightly above the level of the required gloss. The coating obtained from the paint prepared with slurry with Cowles dissolver is close to the required level, but below 70%, which in this case disqualifies it as a coating that can be classified as gloss, but only semigloss (MPI gloss level 5, at 60° between 35% and 70%).

Of course, in this case, it can be said that we are talking about an average result for coatings prepared with a certain margin of error, however, for the purposes of this project, it was found that the coating does not meet the gloss level 6 criterion.

Figure 3 also shows the gloss values at 20°, i.e., at the angle which gives the greatest specular gloss impression. The results clearly show that the highest gloss at an angle of 20° came from the bead mill paint (about 17% higher than that of the Cowles dissolver and homogenizer paints). Sheen at 85° was only allowed to be interpreted in the context of changes after exposure to a UV chamber.

Artificial accelerated weathering exposure

The evaluation of the resistance of the coatings was carried out in the QUV chamber. Gloss was used as the indicator of any changes, because it is the most important criterion in this project for classifying which type of titanium dioxide, when used in a formulation, creates suitable waterborne gloss paint. The exposure was performed according to ASTM G154 cycle 6 in the run as in *Table 9*.

Cycle 6 has been deliberately selected for display, because it is one of the most stringent tests in terms of irradiance (1.55 W/m^2 at 340 nm) and the ultraviolet dose that the coating takes in order to observe whether the gloss retention will be satisfactory enough to be able to classify the used titanium dioxide as a Type V for high durability gloss waterborne coatings.

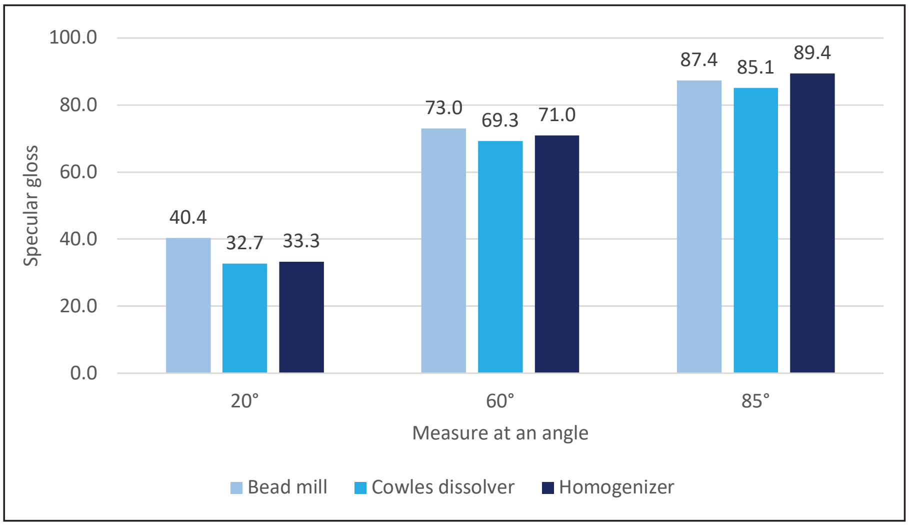
Exposure to radiation from UVB-313 lamps, which are used in tests of coatings with even higher durability requirements, was not carried out in the project; however, due to the presence of radiation in their spectrum outside the range from the sun, a higher dose of ultraviolet from the UVA-340 lamps was deliberately chosen.

Gloss assessments were made after 250 h and after 500 h with a gloss meter as noted above in accordance with

TABLE 9—The course of exposure of coatings in the UV chamber

EXPOSURE CYCLE	UV LAMPS AND IRRADIANCE @340 nm	TOTAL DURATION
8 h UV at 60 °C	UVA-340, 1.55 W/m^2	500 h
4 h condensation at 50 °C	Dark cycle	

FIGURE 3—Specular gloss differences



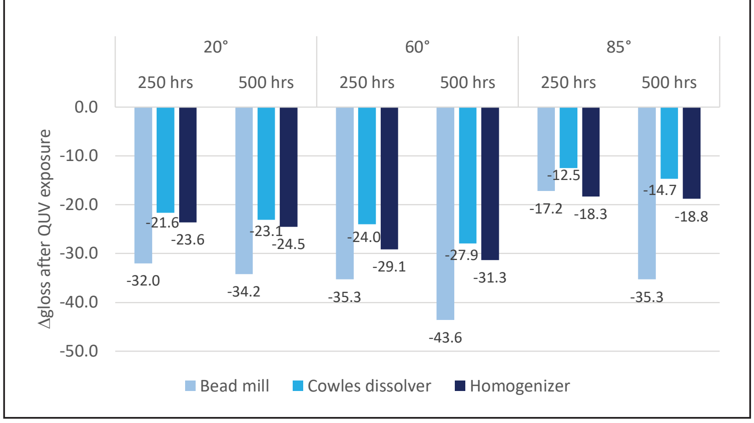


FIGURE 4—Change in gloss after exposure in the QUV chamber

ASTM D523. The gloss-change results as Δgloss are shown in *Figure 4*.

The gloss loss is extremely high for any coating. The highest gloss loss at 60° can be observed for the bead mill coating, both after 250 h (48% gloss reduction) and after 500 h (60% gloss reduction). The Cowles dissolver and homogenizer coatings also show a very large decrease, however, ranging from 35% to 41% after 250 h and ranging from 40% to 44% after 500 h.

Such a decrease in gloss means that the coatings that had the initial gloss classification at 60° in the level 6 range, after exposure, already have a gloss at 60° from about 38 to 42 after 250 h, which classifies them in the gloss level 5 category (semi-gloss). After 500 h, the bead mill coatings showed a gloss of 29.4, which means that the classification is downgraded to gloss level 3–4 (low sheen), where the criteria for a 60° angle describe a gloss in the range of 10–35. After 500 h, the Cowles dissolver and homogenizer still maintained a gloss of 40 at an angle of 60°.

The 20° gloss variation is also extremely large for all samples, ranging from 70% to 85%. On the other hand, at the 85° angle, the sheen of the coatings decreased by about 15–20% both after 250 h and after 500 h for the Cowles dissolver and homogenizer coatings, while by 40%, there was a deduction of sheen for bead mill coatings, which means that these coatings underwent the greatest decrease the sheen towards the flat.

CONCLUSIONS

The obtained results clearly show that the deagglomeration of particles takes place much more effectively in the bead mill than in the Cowles dissolver or homogenizer, which causes the breakdown of agglomerates and aggregates into primary particles much more efficiently, and due to the greater degree of particle separation of titanium dioxide ground in the bead mill, its hiding power is stronger.

It is surprising that in the homogenizer—in which the shear forces are even more energetic—no better dry hiding power was obtained and was even worse than in the Cowles dissolver. It is assumed that this may be due to high-shear forces and damage to the primary particles or the disintegration of the surface treatment on the titanium dioxide particles.

Regarding WDHC, a better result is shown for the sample prepared from slurry grinded in the bead mill. This is further evidence that the preparation of slurries at the bead mill allows for a better separation of primary particles from agglomerated forms, although titanium dioxide is not a favorite when it comes to prime pigments or extender pigments to improve wet-hiding power.

Lightening power showed differences in tinting strength but were so small they were only noticeable with a spectrophotometer. It should be remembered that such slight differences are the result of the use of only pigment and filler in the form of titanium dioxide, which is present in a large amount compared to the pigments in the form of pigment concentrates (colorants) used in the tests. It should be expected that these differences could be magnified in the case of paints with a lower content of titanium dioxide and other colorants.

The influence of the grinding process on the gloss is also noticeable. Waterborne paints based on acrylic polymer dispersion are less likely to obtain a high gloss compared to solvent-borne paints. Nevertheless, a gloss was obtained here, with the assumed PVC, meeting the MPI criteria in the range of level 6. This level was achieved only for samples that were subjected to high energy grinding, in this case, the bead mill and homogenizer.

The coatings exposure tests in the chamber showed unequivocally that the coatings showed a drastic decrease in gloss. Of course, it should be remembered that this is an exposure in a chamber that simulates only ultraviolet radiation, but it has been adopted as a criterion for assessing the durability of coatings and is recommended for testing coatings and other materials in terms of durability.

The very strong cycle of exposure to UV radiation has shown that the coatings do not show good gloss retention, despite a short exposure even after 250 hours. The greatest decrease in gloss was observed for the bead mill samples, which in other tests were characterized by the best results, equated with the highest degree of deagglomeration. This also contributed to the highest exposure of titanium dioxide surface treatment to UV radiation, which in turn proved by testing that there is a serious risk of the application of this grade of titanium dioxide in high durability gloss coatings and classification of the pigment as grade V according to ASTM D476; this is despite the fact that this pigment only has this classification in solventborne systems in terms of resistance to chalking.

This research work proved the necessity to conduct deliberate and extensive tests of titanium dioxide as pigments for coatings of water-based paints, especially those that are to be characterized by high durability of the coatings. This research proved that it is necessary to conduct deliberate and extensive tests of titanium dioxide used in pigments for coatings of water-based paints; this is especially important for coatings that will be deemed highly durable. These tests will help ensure customer satisfaction and save customers money on recoating costs.

References

1. Winkler, J. Titanium Dioxide. Vincentz, **2003**.
2. Winkler, J. Dispersing Pigments and Fillers. Vincentz, **2012**.
3. Heilen, W., et. al. Additives for Waterborne Coatings. Vincentz, **2009**.
4. Palasz, A. Methods of determining the classification of titanium dioxide in accordance with ASTM D476 and recommending its use in waterborne architectural paints. *Polymer Paint Color Journal, TiO_2 Buyer's Guide.* December **2021**.
5. Titanium dioxide comparisons in architectural paints, research work results made by Spektrochem R&D Lab (unpublished), **2021**.
6. Palasz, A. Influence of the surface treatment of titanium white on its properties in dispersion paints for wood and for exterior masonry. *Technical papers of 10th Spektrochem Seminar* (Poland), **2018**.

ARTUR PALASZ is R&D director at Spektrochem, Spektrochem, 15 Dabrowskiej Str., Tarnobrzeg 39-400, Poland. Email: *artur.palasz@spektrochem.pl*.