Effective Utilization of Titanium Dioxide

Introduction

Coatings formulators and manufacturers are interested in producing and marketing low-cost, high-quality products to enhance profit. In many coatings, TiO_2 has an important effect on both quality and cost. So, it becomes worthwhile for a coating producer to answer the following questions with a high degree of certainty:

- Am I using TiO_2 at high efficiency to achieve opacity in my products?
- Am I using the best TiO_2 grade?
- Do I have the right amount of TiO_2 per gallon or am I using too much or too little for the quality I want to achieve?
- How can I use TiO_2 and toners to get the balance of brightness and opacity that I wish?

Often, answers to these questions have been qualitative with a low degree of certainty. Good answers are important and useful, especially when titanium dioxide is in tight supply worldwide and likely to remain so for some time.

To determine hiding power or opacity, coatings people generally use either visual or instrumental methods. In a visual comparison of two coatings, the observer will say that one coating has higher, lower, or perhaps equal opacity relative to the other. He/she may even guess how much. The story is much the same with contrast ratios, but observer bias is reduced.

For example, if Coating A has a contrast ratio of 0.920 and Coating B has a contrast ratio of 0.900, about all that can be said is Coating A has higher opacity than Coating B. We can say it is 0.020 higher, but it is not clear how to use this number to formulate Coating B to have equal hiding. Also, this is not helpful in deciding what to change in order to improve opacity.

Fortunately, quantitative answers to the questions above can be obtained with a reasonable amount of lab work using the equations of Kubelka and Munk. This approach is familiar to many workers in the field. We feel that using this technique is greatly facilitated by our user-friendly computer program. This paper will be devoted to explaining such a method and providing examples of how it can be used.

Background

In 1931, Kubelka and Munk published equations showing the relationship among contrast ratio, brightness, and the quantity of light-scattering material in pigmented film. The equations are quite complex and involve mathematical calculations that are tedious. Throughout the years, the equations have been modified[1] and even simplified to table or graphical forms.[2,3,4,5,6,7] The widespread use of computers by coatings manufacturers prompted us to develop an easy-to-use software program of Kubelka-Munk calculations for accuracy with speed and less tedium compared to other techniques.

The Kubelka-Munk general equation:

$$R = \frac{(Rg-R\infty)/R\infty - R\infty(Rg-1/R\infty)e^{SX(1R\infty-R\infty)}}{(Rg-R\infty)-(Rg/R\infty)e^{SX(1/R\infty-R\infty)}}$$

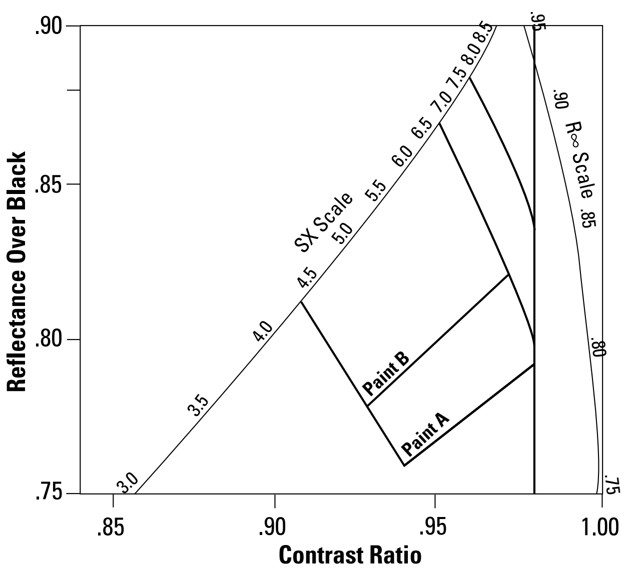
It expresses the reflectance, R, of film over a background of reflectance Rg as a function of the film's scattering power SX and R∞—the reflectance of a film so thick that further thickness increases do not change the reflectivity. This relationship can be used to determine a coating's scattering power, SX.

SX is a dimensionless product; S is the scattering coefficient, and X is the amount of scattering material. S is a constant characteristic of a particular coating and a direct measure of the effectiveness of TiO_2 in building opacity and brightness. The scattering power of SX of that coating can only be changed by varying X, the amount of light-scattering material. X can be expressed as film thickness in mil or gal/ft^2 (the units of S will be the reciprocal of X, for example, mil^{-1} or ft^2/gal).

X can also be expressed in terms of the amount of TiO_2 present in the coating, commonly g/m^2, that is, grams of TiO_2 over each square meter of coated surface. Again, the units of S will be the reciprocal of X, for example, m^2/g.*

A graphical form of the Kubelka-Munk equations is shown in **Figure 1**. It interrelates reflectance over black, R∞, contrast ratio, and SX. By experimentally determining contrast ratio and reflectance over black, **Figure 1** can be used to find both SX and R∞.

Figure 1. Kubelka-Munk Interrelationships



Scattering coefficients are affected by many factors in paint formulas. They provide quantitative measures useful in comparing paint formulas, different TiO_2 grades, and the effects of formulation changes.

The advantage of working with light-scattering coefficients, rather than contrast ratio alone, can be illustrated using the data in **Table 1** taken from the examples in **Figure 1**.

Both paints in this case have the same SX value of 4.3, indicating equal light-scattering power; Paint A does have more total hiding (higher contrast ratio) by virtue of more absorption (shown by lower R∞). Paint B toned down to 0.81 brightness would match Paint A. In this example, X, expressed as spreading rate, is the same for both paints.

Table 1
Example of Paint Comparison by Light-Scattering Power

Paint	Contrast Ratio	R∞	SX	Applied Spreading Rate, ft²/gal
A	0.94	0.81	4.3	800
B	0.93	0.85	4.3	800

Using the same data, we can calculate the spreading rate needed for each paint to achieve complete hiding.** As seen in **Figure 1**, Paint A requires an SX of 6.7 to reach complete hiding; graphically, this is seen at the point defined by contrast ratio of 0.98 and R∞ of 0.81. Because S is a constant, in order to increase SX, film thickness (X) must increase by a factor of 6.7/4.3 = 1.55. Because spreading rate is inversely proportional to X, the spreading rate for complete hiding is 800/1.55 = 510 ft^2/gal.

Similarly, Paint B requires an SX of 7.7 for complete hiding, meaning that film thickness X must increase by the factor 7.7/4.3 = 1.8 to achieve complete hiding. Its spreading rate at complete hiding by the dry film will be 800/1.8 = 445 ft^2/gal.

Our computer program, following the same concepts and using the same inputs, gives more accurate results than a chart or table because interpolation is not required.

Computer Program

A user-friendly computer program is available on a floppy disk to facilitate the calculations. This program will generate optical information, including scattering coefficients for TiO_2 and paint spreading rates at complete hiding, for the purpose of assessing performance of TiO_2 and coatings.

Inputs and outputs for the computer program are shown in **Table 2**.

The inputs are reflectances and other information that the paint chemist often measures. Practical coatings also depend on absorption of light as well as scattering to develop opacity. Light absorption by a coating can be quantitatively described by its absorption coefficient K. K/S is uniquely related to R∞, and when R∞ and S are known, K can be calculated. This is also done by our computer program.

An example of computer results is shown in **Table 3**. The thickness of the drawdown film of this commercial paint was 2.397 mil, calculated from measured drawdown weight and area and measured paint density. This film produced a contrast ratio of 0.971.

* Some workers may express X in microns, representing the thickness of TiO_2 in a cross section of the film; then S would have the units of micron.[1]

**In this discussion, we will arbitrarily define complete hiding as a contrast ratio of 0.98 developed by the dry film. Other definitions are possible.

Table 2
Spreading Rate Program Information

Inputs

- Measured White Substrate Reflectance
- Measured Reflectance over Black
- Measured Reflectance over White
- Measured Weight of Wet Paint on Drawdown
- Measured Drawdown Area
- Measured Density of Paint
- Known TiO_2 Concentration in Paint (Optional, required to obtain S in m^2/g)

Outputs

- SX
- Contrast Ratio
- X
- S, per mil of Coating
- S, m^2/g for TiO_2 in Coating
- Spreading Rate
  - Of Drawdown as Prepared for Above Measurements
  - At Goal Contrast Ratio
  - At Goal SX
- K/S
- K, per mil of Coating
- R∞ = R Inf
- Tabulation of Inputs for Future Reference

Table 3
Example of Computer Output

	Sample		Predicted at Complete Hiding
Substrate Reflectance	0.810		0.810
Thickness in mils	2.397		2.772
Reflectance over Black	0.805		0.813
Reflectance over White	0.829		0.830
Contrast Ratio	0.971		0.980
SX	6.344		7.336
S per mil	2.647		2.647
S m^2/g	0.309		0.309
	Spreading Rates		
Sample as is:	670 ft^2/gal	CR = 0.980:	579 ft^2/gal
	or		or
	16 m^2/L		14 m^2/L

Calculations based on the input data show that the drawdown had a contrast ratio of 0.971 and SX of 6.344, corresponding to a scattering coefficient for the paint film of 2.647 per mil or a scattering coefficient for the TiO_2 of 0.309 m^2/g.

From this information, the computer program can predict the SX needed for complete hiding and therefore the spreading rate at complete hiding. At a spreading rate of 579 ft^2/gal, this paint would produce a contrast ratio of 0.98.

These data would suggest that this paint is more than adequate for the usual objective of complete hiding at 450 ft^2/gal, and that savings in raw materials are possible by lowering TiO_2 content, total solids, or some combination of these.

Experimental Procedures

The output of a mathematical operation is no better than the input data, which depend on the design and execution of the experimental work. The experimental program should be planned to use as little effort as needed to get useful results. **Table 4** lists equipment we use for the experimental work. Many paint companies already have this equipment. A vacuum plate to hold paper charts gives more uniform films than a plate with no vacuum, and the automatic drawdown equipment is better yet, because the coating is drawn down at a uniform speed.

Table 4
Experimental Equipment and Procedures

Equipment

Drawdown Plate, Gardner	Calculator
Bird Applicators, Gardner	Charts, Leneta Form 14H
Top Weighing Balance, Mettler	Computer
Reflectometer	

Procedure

1. Measure green reflectance of white portion of contrast ratio chart and record.
2. Weigh contrast ratio chart and record.
3. Affix chart to vacuum plate and draw down coating using an appropriate applicator.
4. Weigh coated chart and record.
5. Repeat steps 1–4 three more times to make a total of four weighed drawdowns.
6. Allow coatings to dry overnight.
7. Read green reflectance over black and white areas and record each value.
8. Determine average reflectance over white and average reflectance over black.
9. Calculate coating weight on each chart and calculate average.
10. Repeat for each coating.
11. Using computer program, input: substrate reflectance, reflectance over black, reflectance over white, coating weight, drawdown area, density of wet paint, and (if known) TiO_2 concentration in paint.

The film thickness at which measurements are made is not as critical with the computer program as it is when charts and tables are used. Error due to interpolation are minimized or eliminated. **Table 5** shows the effect of various drawdown blade clearances on the calculated information. Note that S is constant, within experimental error, for thickness of 0.003–0.010 mil clearance drawdown. We recommend using a blade clearance of 0.005 mil to be in the mid-range.

The procedure of **Table 4** gives the basic information needed to determine SX, as well as S per mil of coating, S related to TiO_2 concentration, and X in g/m^2 of TiO_2. With this information, a number of comparisons and predictions can be made. Some of the possibilities are shown below.

Table 5
Effect of Drawdown Blade Clearance on Calculated Optical Properties of Two Paints

Clearance	Contrast Ratio	Spreading Rate at Complete Hiding, ft^2/gal	S, m^2/g	S^{-1}, mil	R∞
		Paint B			
0.0025	0.887	298	0.272	1.861	0.924
0.003	0.920	315	0.277	1.899	0.916
0.004	0.946	323	0.278	1.903	0.911
0.005	0.959	336	0.283	1.935	0.906
0.006	0.971	313	0.271	1.853	0.909
0.008	0.986	312	0.266	1.822	0.907
0.010	0.991	324	0.272	1.860	0.903
	Avg.	317			
		Paint G			
0.0025	0.916	457	0.282	1.932	0.814
0.003	0.945	459	0.285	1.952	0.814
0.004	0.966	459	0.282	1.931	0.813
0.005	0.977	453	0.279	1.911	0.813
0.006	0.989	451	0.278	1.901	0.812
0.008	0.996	433	0.265	1.815	0.812
0.010	0.999	460	0.282	1.929	0.811
	Avg.	453			

Practical Applications Comparison of Coatings

We tested two purchased commercial medium-quality flat emulsion paints for scattering power. We experimentally determined all of the inputs listed in **Table 2** except TiO_2 concentration, which was shown on the labels.

Paint B, although less expensive, shows better covering power, higher brightness, and better scattering, as shown in **Table 6**. It would appear to be a better value to painters.

Of importance to paint manufacturers, the scattering coefficients suggest that Producer A should work on getting improved efficiency from the TiO_2, by perhaps changing grades.

If the chemist noted the difference in brightness and removed toner from Paint A, he/she would observe a loss of hiding power. They should focus on improving the TiO_2 scattering coefficient.

Toning Effects

Toning of white paints is used as an inexpensive means for improving opacity through light absorption. To illustrate the efficiency of toning, two semigloss emulsion paints containing the same amount of TiO_2 were prepared: A (with no toner) and G (toned to a brightness of 0.811 with carbon black). Five other paints were made by blending A and G. Results from studies of these paints are shown in **Table 7**. The following observations can be made:

- The scattering coefficient S of the TiO_2 is about the same in each of the paints, as it should be.
- Untoned Paint A would have to be applied at 267 ft/gal to get complete hiding. This is too low to be practical.
- Paints F and G, toned to brightness of 0.825 and 0.811 respectively, have practical spreading rates at complete hiding.
- The absorption coefficient K is proportional to the concentration of carbon black, as it should be when no flocculation occurs.

Our computer program calculates R∞ from the inputs described in **Table 2**. It is clear from **Table 7** that, at high brightness, R∞ deviates from brightness measured on drawdowns of reasonable thickness. Untoned laboratory paints, like Paint A, sometimes

Table 6
Comparison of Two Commercial Emulsion Paints

Paint	Selling Price, \$/gal	TiO_2, lb/gal	Measured Brightness	Spreading Rate at Complete Hiding	TiO_2 Scattering Coefficient, m^2/g
A	14.98	2.1	0.87	470	0.236
B	13.95	2.1	0.88	530	0.273

Table 7
Effect of Toning on Coating Optics

Paint	Contrast Ratio	Measured Brightness	Calculated Spreading Rate, ft²/gal*	Calculated TiO_2, m²/g	Calc. R∞	Calc. K/S	K, mil⁻¹
A	0.887	0.923	267	0.279	0.978	0.000247	0.0004
B	0.887	0.896	298	0.272	0.924	0.00312	0.0058
C	0.899	0.899	354	0.281	0.889	0.00693	0.013
D	0.902	0.866	375	0.278	0.866	0.0104	0.020
E	0.912	0.839	417	0.286	0.844	0.0144	0.028
F	0.914	0.825	432	0.282	0.829	0.0176	0.034
G	0.916	0.811	457	0.282	0.814	0.0213	0.041
			Avg.	0.280			

Substrate reflectance, 0.800

Drawdown blade clearance: 0.0025 in for hiding power, 0.008 in for brightness measurements.

*At complete hiding, defined as contrast ratio = 0.98.

give data that appear in imaginary space of the Kubelka-Munk analysis, such space apparently corresponding to R∞ greater than 1.00.

The reason for this is that these films deviate from the ideal films considered by Kubelka and Munk. This phenomenon is well known and was discussed by Ross.[1] Our computer program will indicate such a circumstance by printing “R lnf = 1.000.”

Binder Effects

As might be expected, binders have a significant effect on TiO_2 performance and opacity of the dry paint film. **Table 8** shows results from a proprietary emulsion paint formula, prepared at equal volume solids and PVC, using two different binders—one an acrylic and one a vinyl-acrylic. The binders produce films that clearly are different in brightness, scattering power, spreading rate, and TiO_2 efficiency.

One can consider several mechanisms by which binders can affect dry film opacity; we made no effort to separate or prioritize these. These effects are significant and can be quantitatively studied using the procedures advocated here.

A formulator, seeing the results of **Table 8**, should next consider the value of the more expensive acrylic binder in relation to opacity. If the opacity of the vinyl-acrylic film is satisfactory, he/she could assess using the acrylic binder with less TiO_2.

Table 8
Optical Properties of Emulsion Paint Films: Binder Effects

	Acrylic	Vinyl-Acrylic
R∞	0.960	0.945
SX	6.66	5.74
S, per mil	2.30	1.99
S, m²/g	0.303	0.265
Spreading Rate at Complete Hiding, ft²/gal	398	298

Selecting a Grade of TiO_2

The approach suggested in this paper can be used to compare grades of TiO_2, based on relative optical performance and therefore cost-effectiveness. **Table 9** shows measurements on dry films made using two domestically produced chloride-route rutile grades of TiO_2 in a good-quality, acrylic emulsion, semigloss paint. Both paints had equal quantities of carbon black toner.

Table 9
Optical Properties of Emulsion Paint Films: Two Grades of TiO_2 with Equal Amounts of Toner

	TiO_2 Grade 1	TiO_2 Grade 2
R∞	0.880	0.866
SX	3.82	3.63
S, per mil	2.03	1.90
S, m²/g	0.296	0.278
Spreading Rate at Complete Hiding, ft²/gal	382	375

These data show that the two paints have about equal spreading rates, but that Grade 1 gives a higher brightness (0.880 vs. 0.886), owing to a higher scattering coefficient (0.296 vs. 0.278).

Two ways to take advantage of the higher scattering coefficient of Grade 1 are toning and reducing TiO_2 levels.

The paint made with Grade 1 can be toned to the brightness of Grade 2, with the benefit that the higher scattering at equal brightness would result in a higher spreading rate. The data verifying the merits of this approach are shown in **Table 10**. Scattering properties of the Grade 1 paint remain unchanged as expected, but the added toner reduces brightness, increases absorption, and significantly improves spreading rate.

Table 10
Optical Properties of Semigloss Paint: Two Grades of TiO_2 Toned to Equal Brightness

	TiO_2 Grade 1	TiO_2 Grade 2
R∞	0.863	0.866
SX	3.81	3.63
S, per mil	2.02	1.90
S, m^2/g	0.295	0.278
Spreading Rate at Complete Hiding, ft^2/gal	407	375

The other way to exploit the superior scattering of Grade 1 would be to match the effect of Grade 2 using a lower concentration of Grade 1 in the dry film. The results of **Table 9** suggest using 6% less of Grade 1 (0.278/0.296 = 0.94). This was experimentally confirmed as shown in **Table 11**. Volume solids was maintained constant, by adding barites in place of the TiO_2 reduction. The increase in scattering efficiency of TiO_2 Grade 1 is probably real, as explained by Fitzwater and Hook.[8]

Table 11
Optical Properties of Semigloss Paint: Two Grades of TiO_2 with Equal Amounts of Toner, But 6% Reduced Concentration of Grade 1

	TiO_2 Grade 1	TiO_2 Grade 2
R∞	0.864	0.866
SX	3.70	3.63
S, per mil	1.96	1.90
S, m^2/g	0.305	0.278
Spreading Rate at Complete Hiding, ft^2/gal	389	375

Commercial Paints

Table 12 shows results from a survey of interior off-the-shelf trade sales emulsion flat paints. In this table, "Dry SX" indicates the scattering power of the dry film, obtained as before. "Oiled S" is the scattering coefficient of TiO_2 calculated from measurements on films to which mineral oil had been applied to eliminate dry flat hiding or scattering from voids. An apparent S could be calculated for an *unoiled* film, but this would ascribe all scattering, from both TiO_2 and voids, to the TiO_2 and would therefore not be a suitable index of the TiO_2 performance; "SX, O/D" is the ratio of the SX of the oiled film to the SX of the dry or unoiled film. A value of 1 would indicate no porosity. A low value of "SX, O/D" indicates considerable porosity.

We have separated these paints into three groups that we feel describe the three types into which most emulsion flat paints can be classified. Type 1 are high-quality paints, typified by high TiO_2 PVC, large amounts of TiO_2 applied per unit area, and good film integrity (high "SX, O/D"). Type 2 are

Table 12
Survey of Commercial Interior Flat Paints

Dry SX	SX, O/D	TiO_2 PVC	Spreading Rate at Complete Hiding	Oiled S	Measured Brightness
Type 1 (High Quality)					
6.34	0.92	22	580	0.286	0.832
4.73	0.92	19	420	0.294	0.839
4.66	0.81	20	430	0.283	0.806
5.02	0.89	24	370	0.264	0.885
4.44	0.93	18	470	0.236	0.815
Type 2 (Medium Quality)					
7.23	0.72	19	630	0.320	0.839
5.67	0.70	12	420	0.358	0.875
4.98	0.72	17	330	0.291	0.894
5.13	0.67	16	410	0.349	0.856
4.62	0.57	12	410	0.264	0.815
5.54	0.60	14	520	0.328	0.841
6.62	0.58	18	470	0.236	0.872
Type 3 (Ceiling Quality)					
7.66	0.51	22	660	0.337	0.841
6.42	0.32	10	450	0.302	0.888
5.27	0.53	12	500	0.340	0.837
4.84	0.53	10	410	0.369	0.862
4.70	0.49	14	260	0.264	0.833

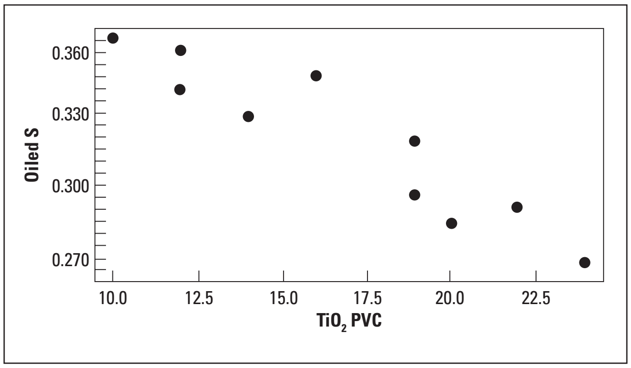
average-quality flat paints, representing an estimated 50% of the interior emulsion flat paint market. Type 3 are ceiling-quality paints with high porosity (low "SX, OD") and, owing to the large amount of dry flat hiding, no need for high TiO_2 content beyond what will provide the desired level of wet hide.

Paints of any type can give good initial opacity, indicated by "Dry SX." However, lower "SX, O/D" indicates less film physical integrity, which is why we refer to Type 3 as "ceiling quality."

To assess the efficiency of using TiO_2, we can look at "Oiled S." This ranges from 0.236–0.369. This is partially explained by the effect of particle crowding on scattering efficiency (see **Table 12**). If we compare, however, two Type 2 paints at 12% TiO_2 PVC, we see scattering coefficients of 0.264 and 0.358. The TiO_2 in the best paint is performing 36% better than the TiO_2 in the poorest paint. The poorer paint is getting high spreading rates by toning to a low brightness (0.815 vs. 0.875). We would say that the chemist for this producer should work on improving the TiO_2 efficiency; with improvement, he/she could make the same quality with less TiO_2 or get higher brightness from the same TiO_2 concentration.

Figure 2 shows Oiled S plotted against TiO_2 PVC for non-flocculated paints. The relationship shown represents the expected relationship between TiO_2 scattering power and crowding: scatter efficiency decreases as TiO_2 particles become more crowded. The magnitude of the changes and the linear relationship are compatible with theory.[8]

Figure 2. **TiO_2 Scattering Coefficients vs. TiO_2 PVC**



Summary

A method has been presented that enables a coating formulator to quantitatively determine the hiding efficiency of TiO_2 in different formulas and to compare hiding efficiency of different TiO_2 products.

The procedure can also be used to study the effect of toning on hiding power and brightness and to predict reasonably accurately what formulation changes are necessary to achieve given optical properties. The experimental work required is quite reasonable.

Many paint labs already have the equipment needed to use the method.

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