Predicting Properties of Architectural Coatings by Modeling Data Generated from a Designed Mixture Experiment

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Titanium dioxide (TiO_2) is a well-known pigment used in the coatings industry. It is also often one of the more expensive ingredients in the formula. Therefore, it should be of no surprise that a lot of materials are proposed by a variety of suppliers to reduce the amount of TiO_2, often claiming to have no influence on the properties of the paint. In this study, we seek a better understanding of the impact of a (partial) replacement of the TiO_2 with a selection of these alternative materials on the basic properties of the paint (e.g., hiding power, mechanical strength, color, etc.). Since many architectural coatings are formulated above the critical pigment volume concentration (CPVC), we focus in this study on this formulation area.

The traditional approach for evaluating the effect of a new ingredient in a paint formula is to add the ingredient to the formula, eventually compensating by (partially) leaving out another ingredient and then testing the new paint for a set of properties.[1] The formulator appears to build, with only a few experiments, a feel for the potential of this new ingredient. Although the trial-and-error approach can be very useful for initial screening, it can be very time-consuming to optimize paints because a lot of parameters have to be balanced and very often compromises have to be made. With this study, we will use an experimental mixture design approach for the formulation of paints.[2-4] In this approach, the boundaries for the composition paint are determined in advance (i.e., minimum and maximum values of all the ingredients). The levels of ingredients are changed in a systematic way, making sure that the whole formulation space is covered and with an additional requirement that the sum of all the ingredients adds up to 100%. Typically, a computer program is used in generating the customized "optimal" design, so that, with a minimal number of experimental points, the desired amount of information can be extracted from the data. Once the experimental runs are determined, paints are prepared and tested for the properties of interest. This leads to an extensive, experimentally generated dataset of paint compositions and properties of the respective paints. Through statistical regression analysis, mathematical relationships between properties and composition are determined. These mathematical relationships allow for the prediction of paint properties with an arbitrary composition in the formulation space studied.

EXPERIMENTAL

As a starting point for the formulation, we used a formula based on an ethylene vinyl acetate copolymer dispersion (EVA), in which we added several families of so-called functional fillers, each representing different technologies and mechanisms: zeolite, diatomaceous earth (DE), calcined clay (CC), and flash calcined clay (FCC). The maximum amounts of the functional fillers were calculated based on the recommendations provided by the respective suppliers.

	TiO_2	$CaCO_3$	Resin	Zeolite	DE	CC	FCC
Commercial grade	Ti-Pure® R-902+	Calcilit M4	Mowilith® LDM1871	Zeocross CG 180	CelTiX™	Polestar 200P	Opacilite™
Oil absorption[a]	24	18	N/A	60	100/220[b]	50	74
Particle size (d-50, μ)	0.3	4	N/A	1.2	1.7-11.0[c]	2	1.6
Refractive index	2.7	1.65	1.5	1.5	1.43	1.56	1.56
Min (mass %)	0	15	4.8	0	0	0	0
Max (mass %)	25	47.5	19.2	6	5	8	12
Proposed mechanism	High refractive index particle size	NA	NA	Improved spacing of TiO_2	Decrease CPVC air voids	Improved spacing	Sealed air voids

Table 1—Overview of the Relevant Characteristics of Materials Used in the Study. Minimum and Maximum Values for the Experimental Design Are Also Given

(a) Expressed as g oil/100 g solids, measured according to ASTM D281-95.
(b) Value depends on the source.
(c) Depending on the measurement technique: 1.7 is found by Sedigraph, 11.0 by laser diffraction. See product literature of Imerys.

	TiO_2	$CaCO_3$	Resin	Zeolite	DE	CC	FCC	Balance	PVC	CVPC	Rel. Cost
1	22.75	15.00	7.92	0.00	1.00	0.00	12.00	41.33	83	47	1.00
2	0.00	41.87	4.81	0.00	0.00	2.00	8.00	43.32	90	56	0.24
3	0.00	31.00	19.23	6.00	0.00	8.00	0.00	35.77	66	55	0.47
4	25.00	15.00	19.23	0.00	0.00	0.00	3.00	37.77	60	53	1.11
⋮	⋮	⋮	⋮	⋮	⋮	⋮	⋮	⋮	⋮	⋮	⋮
46	25.00	15.00	4.81	3.00	5.00	0.00	4.92	42.27	89	45	1.07
47	12.00	15.00	19.23	6.00	0.00	0.00	12.00	35.77	66	47	0.85

Table 2—Overview (Partial) of the Experimental Runs That Are Tested in the Lab, and Used to Feed the Model. (All amounts are in wt%)

	Dry Hiding Power (m^2/l)	Oiled Hiding Power (m^2/l)	Scrub Sensitivity (log μm)	Tinting Strength (L*)	Dirt Pickup (a.u.)	Oil Pickup (a.u.)	Gloss	b*	L*	BI
1	18.61	11.00	2.03	57.01	5.37	16.93	12.3	1.92	97.68	1.0
2	6.44	1.11	3.08	39.46	7.04	22.37	8.1	2.04	96.46	1.7
3	2.19	0.87	1.24	27.08	7.15	18.02	4.0	2.67	95.99	1.5
4	8.28	8.49	0.92	50.91	7.27	16.17	7.8	1.68	97.40	0.6
⋮	⋮	⋮	⋮	⋮	⋮	⋮	⋮	⋮	⋮	⋮
46	20.92	11.74	2.31	59.00	6.10	19.46	7.9	2.20	97.90	1.3
47	10.55	7.55	0.91	48.00	8.60	16.00	10.2	2.20	97.40	1.0

Table 3—Overview (Partial) of the Measured Properties of the Paint Modifications Shown in *Table* 2

To make sure that the boundaries for the amount of resin, calcium carbonate ($CaCO_3$), silicates, and TiO_2 reflected the values that are commonly used in the industry, we analyzed more than 150 commercial paints above CPVC from Turkey, Germany, France, and Russia, spread over different quality segments. Based on this study and discussions with cosuppliers, the type and the minimum and maximum levels of the different raw materials were determined. An overview of the materials used in the formulations can be found in *Table* 1.

Let X_1 through X_7 denote the weight proportion of each of the seven components shown in *Table* 1 (TiO_2 through FCC) present in the mixture, and let X_8 denote the balance (water) that makes these proportions add up to 100%. If the cost per unit weight of each component is b_1 through b_8, then the cost per unit volume of any mixture of these eight components is directly calculated by

$$cost = b_1X_1 + b_2X_2 + \cdots + b_8X_8.$$

However, for the physical properties of interest, we do not know these coefficients (b_1 through b_8) and we also cannot assume a linear blending model will be appropriate. Nonlinear blending terms (in the form of cross-products) should be included in these models, so each property Y would be modeled by

$$Y = b_1X_1 + \cdots + b_8X_8 + b_{12}X_1X_2 + b_{13}X_1X_3 + \cdots + b_{78}X_7X_8,$$

which is a model with 36 unknown coefficients (8 linear blending terms plus 28 nonlinear blending terms).

To allow for goodness of fit of the model to be assessed, we generated a customized "optimal" design of 40 different formulations to test, then added a (different) control sample, and finally replicated six of these 41 different formulations in the 47-run experimental design. Partial tables of the experimental design (*Xs*) and measured properties (*Ys*) are shown in *Table* 2 and *Table* 3, respectively.

The type of dispersant (a commonly used acrylic dispersant, DispexN40) was kept constant for the 47 formulations. However, the amount was corrected for the amount of dispersed pigment and extender and for their respective oil absorptions. Also, the amount of thickener was optimized in order to guarantee a good dispersion and an acceptable application of the paint (by an automated applicator). The applied paints were tested according to the test methods listed in *Table* 4. Since all of the paints are formulated above the CPVC, pores are present in the dry film and will contribute to the total hiding.

Table 4—Overview of the Test Methods and the Statistical Parameters Evaluating the Quality of the Statistical Model for the Different Tests

Tested Parameter	Test Method	R^2_{adj} (%)	R^2_{pred} (%)
Dry hiding power	Bruelhman and Ross,[5] Cremer,[6] and Crowther and Johnson[7]	99.59	99.06
Oiled hiding power	Bruelhman and Ross[5] and Cremer[6]	99.90	99.57
Scrub sensitivity	EN ISO11998	97.31	95.55
Tinting strength	Internal method[a]	99.78	95.66
Dirt pickup	Internal method[b]	92.94	85.88
Oil pickup	Internal method[c]	79.86	72.98
Gloss	EN ISO2813	94.11	70.86
b*	ASTM E1347	96.44	89.74
L*	ASTM E1347	97.40	93.94
Burnishing index (BI)	ASTM D6736	96.42	91.57

(a) Tinting strength was evaluated by mixing 13 g of carbon black Colortrend (888-9907B) in 70 ml of the white paint, followed by the measurement of the L* value of the applied paint.
(b) Dirt pickup is measured by scattering a mixture of silica gel, aluminum oxide powder, iron oxide, and lamp black powder on the applied paint. After removal of excess mixture, the L* was measured. The lower the value, the more the paint is sensitive to picking up dust particles.
(c) Oil pickup: similar to dirt pickup, but here carbon black is mixed in Vaseline and applied on a painted panel. The lower the L* value, the more the paint is sensitive to oil/fat stains or fingerprints.

Table 5—Overview of Different Paint Modifications and Some Calculated Parameters. (All amounts are in wt%)

Modifications	TiO_2	$CaCO_3$	Resin	Zeolite	DE	CC	FCC	Balance	PVC	CVPC	Rel. Cost
1	15	15	16	0	0	0	11	43	66	49	1.00
2	0	22	6	6	5	8	12	41	88	43	0.54
3	0	15	19.2	5.35	5	8	12	35.45	68	40	0.72
4	20	30	14	0	0	0	0	36	71	58	1.00
5	16	30	14	0	0	0	0	40	69	60	0.83
6	16	30	14	3	0	0	0	37	71	57	0.89
7	16	30	14	0	1.7	0	0	38.3	70	56	0.86
8	16	30	14	0	0	3.0	0	37	71	57	0.87
9	16	30	14	0	0	0	2.6	37.4	71	57	0.87

Table 6—Overview of the Predicted and Experimentally Determined Results for Each Paint Modification

Modifications	Dry Hiding Power (m^2/l)		Oiled Hiding Power (m^2/l)		TS[a] (a.u.)		Scrub (µm Removed)		Oil Pickup (a.u.)		Burnishing Index (a.u.)		b*	
	Pred.	Exp.	Pred.	Exp.	Pred.	Exp.	Pred.	Exp.	Pred.	Exp.	Pred.	Exp.	Pred.	Exp.
1	10.2	10.6	7.9	8.4	48.6	50.4	22	9	16	21	1.0	1.2	2.2	2.1
2	9.6	9.1	1.1	1.2	44.8	46.4	392	396	26	25	1.4	1.5	2.4	2.5
3	6.2	---	1.3	---	37.4	---	28	---	22	---	1.2	---	3.2	---
4	8.3	7.6	7.2	7.1	49.8	51.44	25	11	16	19	0.7	0.6	1.9	1.8
5	6.7	6.5	6.2	6.5	46.7	47.6	31	10	17	21	0.8	0.8	1.8	1.9
6	8.3	---	6.7	---	48.0	---	28	---	17	---	0.9	---	1.8	---
7	8.3	8.1	6.7	6.5	47.8	48.7	34	11	18	23	0.9	0.9	2.1	2.2
8	8.3	---	6.7	---	48.1	---	30	---	18	---	0.8	---	1.9	---
9	8.3	---	6.9	---	48.0	---	29	---	17	---	0.8	---	2.0	---

(a) Tinting strength.

By oiling the dried paint, these pores are filled with an oil with a refractive index of 1.6 (which is very close to the refractive index of the paint) and will no longer contribute to the total hiding power of the coating. Consequently, the oiled hiding power corrects for the hiding power generated by the pores in the film (dry flat hiding) and therefore is a good measure for the TiO_2 contribution in the total hiding power. A large difference between dry and oiled hiding power suggests a large contribution of pores that might have a negative impact on the overall mechanical strength of the film. This will translate in a greater scrub sensitivity (μm of paints removed). In this study, we worked via the logarithm of the scrub sensitivity, because this increased the accuracy of the predictions in the lower value range.

In addition to these experimental data, other properties (e.g., formulation cost, PVC, CPVC, etc.) of the modifications were calculated and modeled as well. Since these parameters are purely calcu-

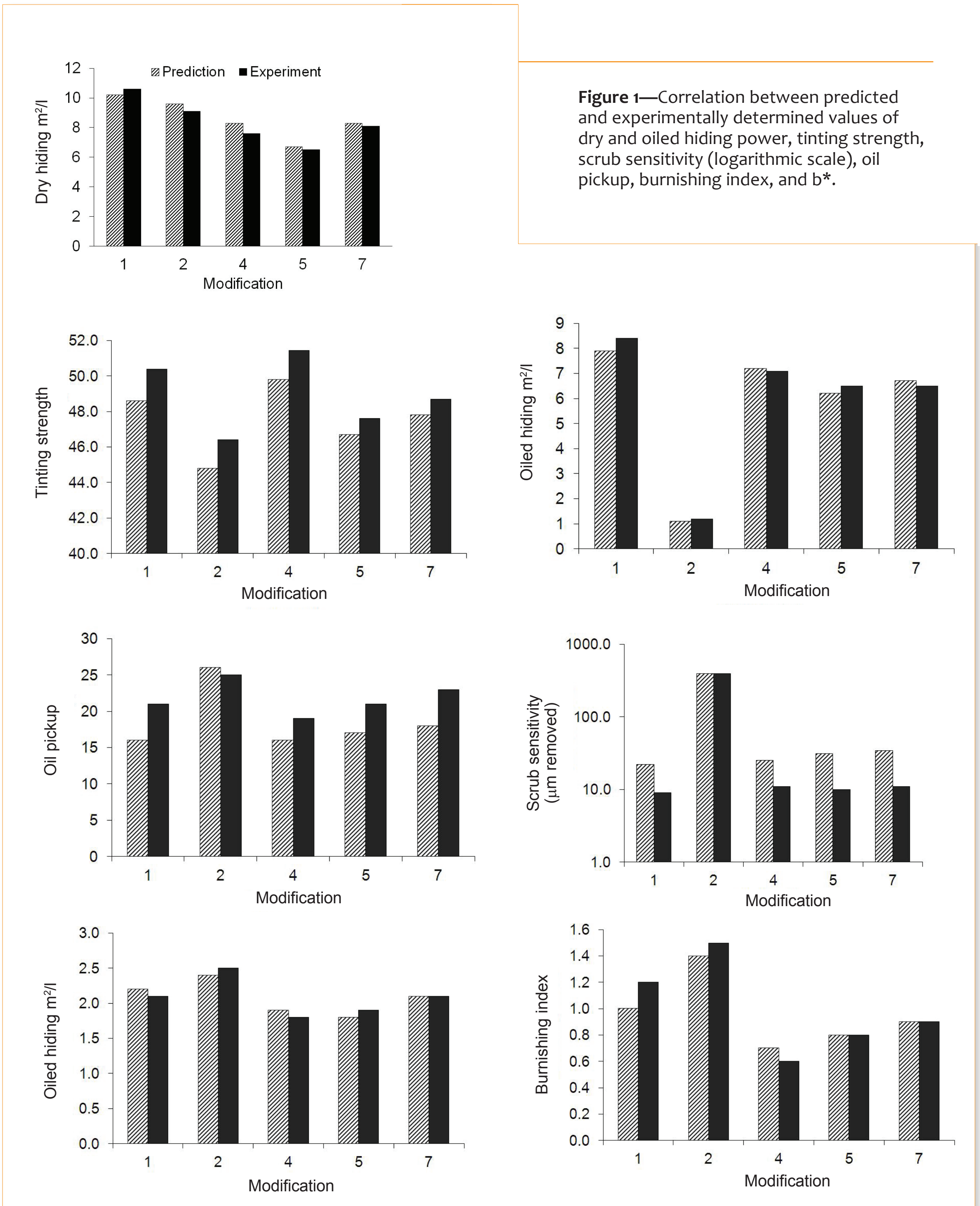

Figure 1—Correlation between predicted and experimentally determined values of dry and oiled hiding power, tinting strength, scrub sensitivity (logarithmic scale), oil pickup, burnishing index, and b*.

Table 7—Overview of Different Paint Modifications Used in the Optimization of a Commercial Paint. (All amounts are in wt%)

	Modifications	TiO_2	$CaCO_3$	Resin	CC	Zeolite	DE	FCC	Balance
Simulation	Ref	14	21	16	8	6	0	0	35
	Ref -10%	12.5	21	16	8	6	0	0	36.5
	Mod 1	12.5	21	16	8	6	0	1.5	35
	Mod 2	12.5	18	16	8	6	0	4.5	35
	Mod 3	12.5	19	16	8	6	0	3.5	35
	Mod 4	12.5	19	14	8	6	0	3.5	37
	Mod 5	12.5	19	16	8	6	3.5	0	35
	Mod 6	12.5	21	14	8	6	2	0	36.5
		TiO_2	$CaCO_3$	Resin	Talcum	PCC	DE	FCC	Balance
Experimental	Reference	14	27	16	7	7	0	0	29
	Ref -10%	12.5	27	16	7	7	0	0	30.5
	Mod 1	12.5	27	16	7	7	0	1.5	29
	Mod 2	12.5	21	16	7	7	0	4.5	32
	Mod 3	12.5	24	16	7	7	0	3.5	30
	Mod 4	12.5	24	14	7	7	0	3.5	32
	Mod 5	12.5	24	16	7	7	3.5	0	30
	Mod 6	12.5	27	14	7	7	2	0	30.5

lated values, fits are trivial (similar to what was previously discussed for cost) and they are not covered further here.

A forward selection mixture regression approach (using Minitab Version 16 software) revealed the mathematical relationships between the amounts of the different ingredients and the corresponding properties. These equations include all linear terms and the most influential nonlinear blending terms of the ingredients. The statistical summary parameters, shown in *Table* 4, demonstrate that the data cannot only be described accurately (high R^2_{adj}), but also that accurate predictions can be made (high R^2_{pred}). For some properties like oil pickup, dirt pickup, and burnishing index, lower R^2 are observed. This can be explained by the slightly larger experimental errors that are related with these tests. The lower R^2 for gloss (particularly R^2_{pred}) is somewhat unexpected, but can at least be attributed in part to the narrow range in gloss values seen in these flat paints. Since flatting agents can be used to adjust gloss rather easily and without significantly affecting other properties, the low R^2 values for gloss are of minor concern.

DISCUSSION

To illustrate the potential uses of this model, two scenarios were created. In the first scenario, the objective was to formulate a paint with a hiding power of 10 m^2/l and less than 20 μm loss of paint after 200 scrub cycles (scrub class 2[10]). Three modifications to the paint were conducted to obtain the desired result (modifications 1 to 3 in *Table* 5). As is shown in *Table* 6, the predicted values from the model indicate that, with the help of TiO_2, several combinations are possible (e.g., with modification 1, more combinations are possible, but only one is shown). Modification 2 demonstrates that without TiO_2, it is possible to get the required hiding power, but scrub sensitivity is far from acceptable (338 μm>>20 μm). Increasing the amount of resin (modification 3), to decrease the scrub sensitivity, results in a significant loss of hiding power. This demonstrates the impossibility of formulating a paint with good scrub resistance in combination with good hiding power in the absence of TiO_2.

In a second, less extreme, scenario, the effect of reducing the TiO_2 content from 20% was verified. Without compensation of extenders, this has a negative impact on the hiding power (modification 4 versus modification 5 in *Table* 5).[8,9] However, by adding the correct amount of extender, the model predicts that the dry hiding power can be increased to the same level as in the original paint formula (modifications 6 to 9), but at the cost of a decrease in performance for the other parameters, as shown in *Table* 6.

To get an independent verification of the values predicted by the model, modifications 1, 2, 4, 5, and 7 were prepared in the lab and the values were experimentally determined. *Figure* 1 and *Table* 6 indicate that the predicted values correlate very well for all of the verified paint properties.

In the previous sections, it was demonstrated that the model can quantitatively predict important

Modifications	Dry Hiding Power (m^2/l)		Oiled Hiding Power (m^2/l)		Scrub Sensitivity (μm Removed)		Rel. Scrub Sensitivity	
	Pred.	Exp.	Pred.	Exp.	Pred.	Exp.	Pred.	Exp.
Ref	10.5	11.4	7.6	8.3	24	6.5	1.00	1.00
Ref -10%	9.6	10.0	6.9	7.4	25	6.5	1.07	0.99
1	10.4	11.3	7.2	7.9	26	7.2	1.09	1.10
2	11.8	12.0	7.7	8.2	28	8.0	1.17	1.22
3	11.3	11.9	7.5	8.0	27	7.8	1.14	1.19
4	11.7	12.1	7.5	8.1	45	11.5	1.89	1.76
5	11.6	12.2	7.5	8.3	34	10.9	1.41	1.67
6	11.3	12.8	7.3	8.2	48	11.8	2.00	1.81

Table 8—Overview of the Predicted and Measured Properties of the Paint Modifications Mentioned in *Table* 7

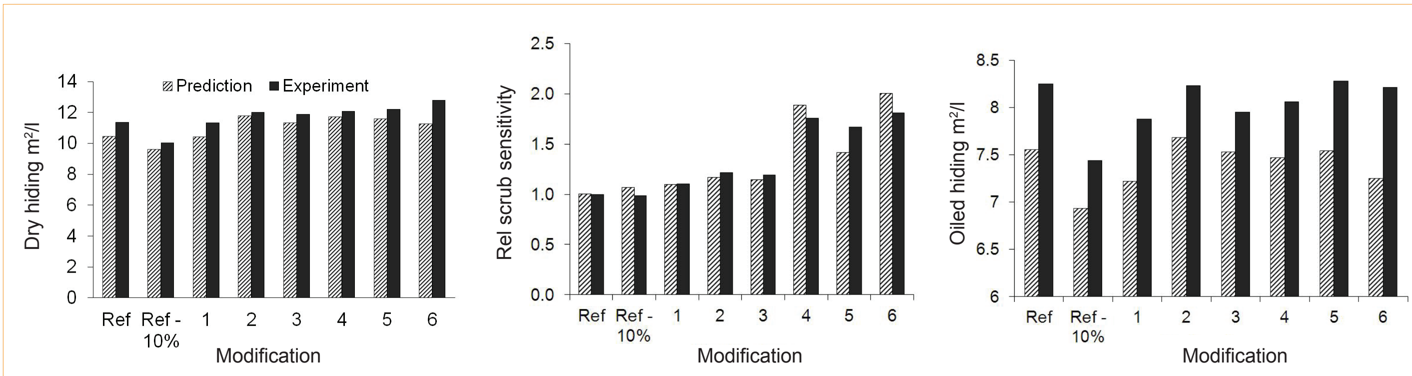

Figure 2—Comparison of predicted and measured dry and oiled hiding power and relative scrub sensitivity of the paint modifications mentioned in *Table* 8.

properties of paints in a relatively broad formulation space. However, given the number of different resins, extenders, etc. that are commercially available, a model has only limited value if it cannot predict trends in a variety of circumstances. Therefore, a robustness check was performed to determine how sensitive the model is to variations in input materials.

In collaboration with a customer, a commercial formula was selected that contained another type of resin (styrene acrylic instead of EVA), other types of extenders (e.g., presence of talcum), other types (diameters) of $CaCO_3$, other dispersants, thickeners, etc. Despite these differences, a paint with an amount of resin and TiO_2 equal to the commercial formula was defined in the model. The type and amount of extenders were chosen in such a way that PVC and CPVC of the simulated paint corresponded with the experimental formulations [e.g., the precipitated $CaCO_3$ (PCC) was replaced with the zeolite (both having small particle sizes)]. The composition of this paint is displayed in *Table* 7 as reference.

The amount of TiO_2 was reduced by 10% (Ref-10%) and functional fillers were added to compensate for the predicted loss of hiding power (modifications 1 to 6). For verification, the paints were made in the lab and the most relevant parameters (dry and oiled hiding power and scrub sensitivity) were experimentally verified. The results are shown in *Table* 8.

Given the significant differences between the raw materials used to build the model and the raw materials used in this example, it is no surprise that there is a systematic difference between predicted and experimentally determined values. *Figure* 2 shows that despite these significant differences, the trends in hiding power (both dry and oiled) that are predicted by the model are confirmed by the tests in the laboratory. As the scrub sensitivity is very much influenced by the type of the resin and the dispersants, significant differences are observed between the experimental and predicted values. However, if we normalize the values of the experimental and the predicted scrub sensitivity to the reference modification, it is clear that here also the trends are correctly predicted.

In other words, if one expresses the parameters relative to the values found for the reference paint, one can get a quantitative estimate of the improvements that are possible or the trade-offs that have to be made when changes are made in the formulation. This suggests that one can predict trends in a variety of paint formulations even outside the broad—but, given the variety of raw materials used in the paint industry, still limited—formulation space of the model.

CONCLUSION

Based on a mixture design approach, a model was generated that is able to quantitatively predict the change in essential quality parameters of a paint, like hiding power, scrub sensitivity, burnishing index, yellowness, etc. The predicted values were verified with independently prepared paints, confirming that there is a very good correlation between predicted and experimental values. It was demonstrated that it is possible to predict the trends correctly even when raw materials do not match exactly with the ones that were used to build the model. This robustness allows for the optimization of paint formulations in a very broad formulation space without extensive work in the laboratory. Once the most promising modifications are found, one can verify the predictions of this limited set of formulas experimentally, significantly reducing the time and work necessary to adapt/optimize formulations.

Through the use of this model, it is shown that in some cases it is possible to reduce the amount of TiO_2 with a limited impact on the overall paint quality, but in many cases significant trade-offs in overall paint quality are observed. These findings are confirmed by experimental data.

ACKNOWLEDGMENTS

The authors wish to thank DuPont for offering the possibility to work on this project. Thanks are also given to Chris Michiels and Sabine De Preter for their precise and accurate work in making up and testing the paints. The authors also acknowledge Sarah C. Richards for her assistance in preparing this manuscript.

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