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High-Throughput Paint Optimization by Use of a Pigment Dispersing Polymer

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Introduction.

During the last two decades the pharmaceutical industry has been constantly using of automated and parallel workflows to increase their productivity in the R&D process. The use of automated high-throughput screening methodologies to develop new structures using fast identification systems has resulted in an important reduction of time-to-market and an increase in cost savings[1].
Recently, researchers in the field of polymeric coatings and polymeric formulations started using these tools. It is well known that a rainbow of formulation and process parameters affect the performance of coatings formulations. From these parameters one can mention the formulation composition (structure and composition of the polymeric binder(s), leveling agents, cross-linkers, thickeners, defoamers, pigments, photoinitiators, etc…), the application of the coating (blading, brush, spraying, etc…), and the processing conditions (drying, aging, curing, etc…). All these parameters need to be varied in order to develop a correlation between them and product performance, therefore combinatorial methods seem to be a powerful tool for the optimization of these systems[2]. Nevertheless, there is quite a large amount of variables and choices in every formulation for a specific coating application which make the number of possible combinations between formulation and process parameters an overwhelming puzzle. To overcome this problem, the design of experiments (DoE) is decisive to extend the coverage and understanding of variable correlations in parameter space. Moreover, DoE software employed must act as statistical station to process the extensive amount of data created by the designed (and quite necessary) high-throughput workflows (HTWs). Over the last 10 years also Nuplex started building up experience with both high throughput experimentation as well as design of experiments. Especially the combination of these two tools has proved to be beneficial.
Recently Nuplex has developed a carboxyl functional acrylic block copolymer (DBC-1) which has shown excellent performance (when used both as binder and pigment dispersing agent) for enhancing among others the stain resistance of wood white top coats. However, there was a need for understanding the role and the interaction of this DBC-1 in a formulated paint, in order to maximize its performance and optimize paint properties in the most comprehensive and efficient manner.
The following work presents the DoE proposed and the experimentation that was carried out throughout 2 different HTWs: the first one designed at Nuplex R&D laboratories and the second one designed at Van Loon Chemical Innovations (VLCI). Both HTWs were run in parallel and the statistical analysis of their responses as well, the main target being the evaluation of the robustness of both the DBC-1 and the HTW's of both locations.

Background of the polymer dispersing agent (DBC-1).

The main pigment used in coatings is titanium dioxide (TiO_2) because of his brightness and very high refractive index, being the rutile type preferred over anatase because of superior outdoor durability. In waterborne (WB) coatings the TiO_2 is incorporated preferably to the polymeric binder by means of the previous preparation of a pigment paste, to ensure a better dispersion of TiO_2 and hence better performance. Anionic surfactants are the major type used to disperse and improve wetting of TiO_2, enhancing hiding power and leveling. Pigment floating and settling may be prevented by using a combination of non-ionic and anionic surfactants. The interchange of the air/pigment interface by a pigment/liquid interface can be recognized as the pigment wetting process, which can be accomplished by dispersing the pigment in the liquid (mostly aqueous phase) by mechanical means, preferably high-speed mixing. The role of the surfactant here will be by means of electrostatic repulsion of steric hindrance, to prevent agglomeration and settling during storage, while promoting good compatibility with the polymeric binder phase. The dispersing agents used in waterborne coatings are polymers that have groups such as carboxylate, phosphate or tertiary amine groups that might be serve as anchors to the pigment surface. Usually, the polymer backbone is based on polyesters, polyethers, acrylics or polyurethanes. The anchoring groups can be designed to be randomly over the polymer backbone or in a more segmented manner where the anchoring groups form a first block and the second block consist of a polymer that is soluble in the continuous phase. The pigment dispersing agents usually contain a relatively high level of hydrophilic groups which might be deleterious for water and chemical resistance. Therefore there is a need for improved pigment dispersants.

Nuplex has developed a resin (DBC-1) with a dual purpose being: pigment stabilizer as well as film forming binder[3]. DBC-1 is a carboxy functionalized block-copolymer can work as binder – being highly compatible with the main dispersion binder – as well as stabilizing TiO_2 particles in the pigment paste (see Figure 1: the DBC-1 adheres as particles to the TiO_2 and can subsequently coalesce with the main binder during film formation). Moreover, the use of this resin has shown to enhance stain resistance and color acceptance in wood coatings, as described in Figure 2a and 2b, respectively. The classic solid-to-solid stabilization mechanism[4] seems to avoid pigment being reached by stain molecules such as caffeine and/or resveratrol. Figure 2a shows that when DBC-1 is used as both binder and pigment dispersant or in combination with other commercial binders (GF: gradient morphology / PS: polymer stabilized) the white top coat presented less stain damage as compared to traditional dispersants (TDS). On the other hand, this solid-to-solid stabilization could enhance the compatibility with tints acting as a bridge between them and TiO_2 while offering the right rheology to avoid the deposition or floating of inorganic material (namely TiO_2 and tints) causing color tone differences when shear is applied (as presented by rub-out test in Figure 2b). Nevertheless, the interaction between DBC-1 and the components from the pigment paste and afterwards the let down's components is still unknown. This issue creates some complexity when trying to develop a formulation for a WB coating that fulfills certain specifications with regards to the performance in the evaluated application. Therefore a DoE combined with a HTE workflow which allows covering a larger parameter space, is necessary to get a better understanding of the role of DBC-1 in a formulated pigmented coating.

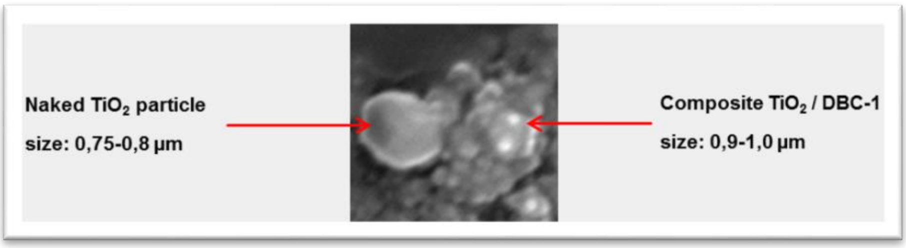
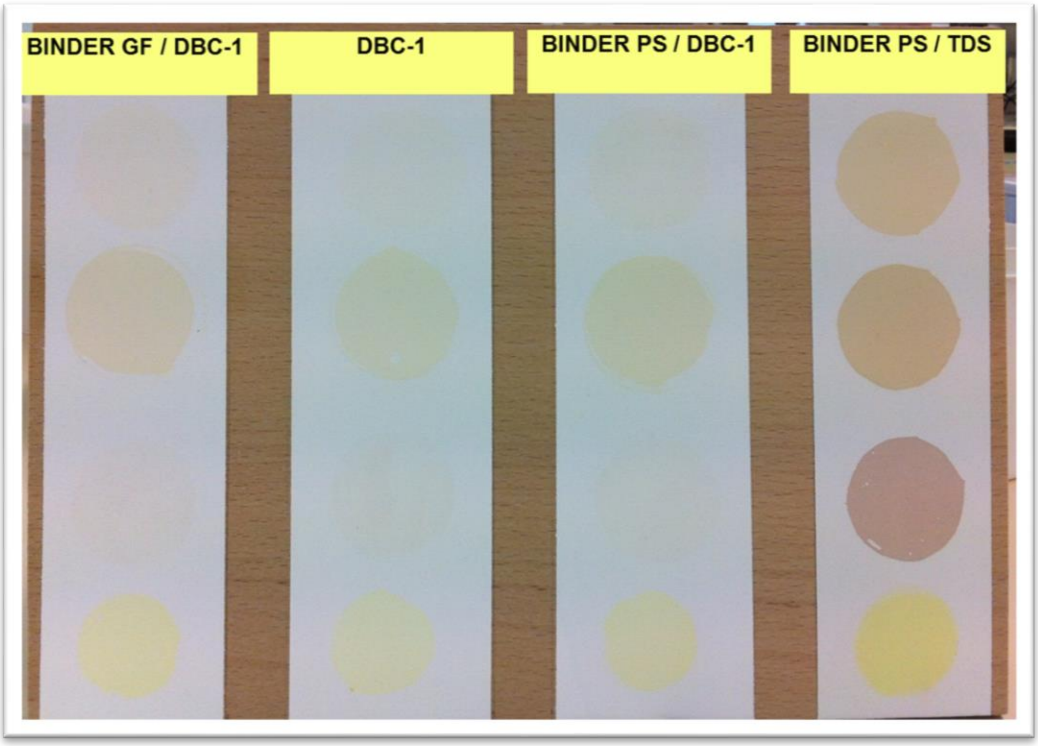
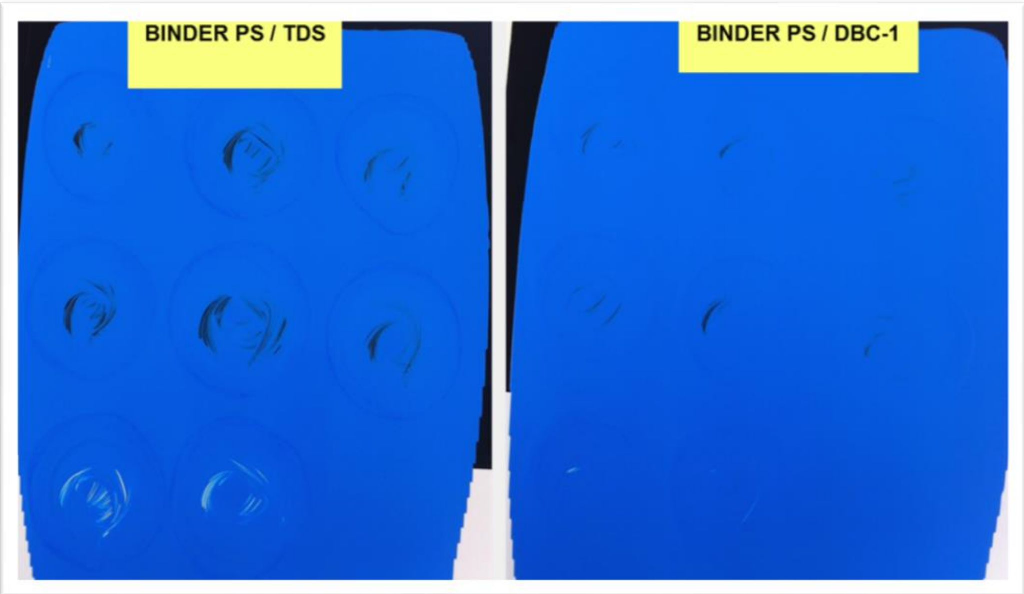


Figure 1. SEM picture of DBC-1 in a TiO_2 pigment paste.



(a)



(b)

Figure 2. Performance of DBC-1 in a pigmented waterborne wood coating. a) Stain resistance test (from up-down: Coffee 1 h, Coffee 16 h, Wine 16h and Mustard 8h; b) Color acceptance / rub-out test.

DoE and HTE workkflows

The DoE in this work was carried out with the aid of the software Design Expert® version 9.0. The type of design used was Surface Response since it offers the possibility of mixing numerical and categorical factors with high accuracy[5,6]. This set up allows us to predict paint formulations in the space of the variables, that have the preferred performance of parameters provided, the parameters have a "fit" in the model. Table 1 presents the 36 experiments proposed which includes 4 repetitions. In this study the components of the pigment paste were varied while the composition of the letdown was kept fixed. For these series of experiments the binder used was a commercial GF. In order to evaluate the effect of the use of a traditional dispersant in combination with DBC-1; two different dispersants were used: Disp Agent 1 and Disp Agent 2. The type of pigment used was included as a key variable having differences in the surface modification: PigAl2O3-Zr-I (Alumina and Zirconium treated type I), PigAl2O3-Zr-SiO2 (Alumina, Zirconium and Silica treated), PigAl2O3-SiO2 (Alumina and Silica treated) and PigAl2O3-Zr-II (Alumina and Zirconium treated type II). Butyl glycol and Butyl diglycol were evaluated as different type of cosolvents.

The following challenge for this work and the core of the experimentation was to design a HTE workflow that allows a non-time-consuming and efficient interconnected process to prepare the coatings and evaluate them; this in combination with a consistent and systematic statistical analysis of the responses. The main goal being to define statistical models to describe the interactions between the DBC-1 and the different components in the formulation and their effect on the coating performance. Furthermore Nuplex preferred to validate the outcome of their own DoE work with "external" DoE work of Van Loon Chemical Innovations VLCI. To do so, two different HTE workflows were designed: 1) Nuplex workflow (See Figure 3) and 2) VLCI work flow (See Figure 4). The workflow's are different in set up since this is inherent to the HTE equipment present in both labs.

Experiment Number	Ratio Binder:DBC-1	Extra Dispersing Agent (Traditional)	Pigment Type	Cosolvent Type
1	80.00	Disp Agent 2	PigAl2O3-Zr-I	Butyl diglycol
2	80.00	Disp Agent 2	PigAl2O3-Zr-SiO2	Butyl glycol
3	80.00	Disp Agent 1	PigAl2O3-Zr-SiO2	Butyl diglycol
4	80.00	None = Water	PigAl2O3-Zr-II	Butyl diglycol
5	90.00	Disp Agent 1	PigAl2O3-Zr-SiO2	Butyl diglycol
6	87.00	Disp Agent 2	PigAl2O3-Zr-I	Butyl glycol
7	88.50	Disp Agent 2	PigAl2O3-SiO2	Butyl diglycol
8	84.00	None = Water	PigAl2O3-Zr-I	Butyl diglycol
9	90.00	Disp Agent 2	PigAl2O3-Zr-II	Butyl diglycol
10	82.24	None = Water	PigAl2O3-Zr-II	Butyl glycol
11	89.50	None = Water	PigAl2O3-Zr-SiO2	Butyl glycol
12	83.00	Disp Agent 2	PigAl2O3-Zr-SiO2	Butyl diglycol
13	86.00	Disp Agent 1	PigAl2O3-SiO2	Butyl diglycol
14	80.00	None = Water	PigAl2O3-Zr-SiO2	Butyl diglycol
15	90.00	Disp Agent 1	PigAl2O3-Zr-I	Butyl diglycol
16	80.00	Disp Agent 2	PigAl2O3-Zr-II	Butyl glycol
17	89.10	Disp Agent 2	PigAl2O3-SiO2	Butyl glycol
18	90.00	None = Water	PigAl2O3-SiO2	Butyl glycol
19	86.50	Disp Agent 1	PigAl2O3-SiO2	Butyl glycol
20	83.00	None = Water	PigAl2O3-SiO2	Butyl diglycol
21	83.00	Disp Agent 2	PigAl2O3-Zr-SiO2	Butyl diglycol
22	90.00	Disp Agent 1	PigAl2O3-Zr-SiO2	Butyl diglycol
23	80.00	Disp Agent 1	PigAl2O3-Zr-II	Butyl glycol
24	90.00	Disp Agent 2	PigAl2O3-Zr-II	Butyl glycol
25	80.00	Disp Agent 1	PigAl2O3-Zr-SiO2	Butyl glycol
26	90.00	None = Water	PigAl2O3-Zr-II	Butyl diglycol
27	80.00	Disp Agent 1	PigAl2O3-Zr-I	Butyl glycol
28	90.00	Disp Agent 1	PigAl2O3-Zr-I	Butyl glycol
29	90.00	None = Water	PigAl2O3-Zr-I	Butyl glycol
30	80.00	Disp Agent 2	PigAl2O3-SiO2	Butyl glycol
31	87.00	Disp Agent 2	PigAl2O3-Zr-I	Butyl glycol
32	86.50	Disp Agent 1	PigAl2O3-Zr-II	Butyl diglycol
33	80.50	Disp Agent 1	PigAl2O3-SiO2	Butyl diglycol
34	89.50	None = Water	PigAl2O3-Zr-SiO2	Butyl glycol
35	86.02	Disp Agent 1	PigAl2O3-Zr-SiO2	Butyl glycol
36	82.24	None = Water	PigAl2O3-Zr-II	Butyl glycol

Factor	**Name**	**Type**	**Minimum**	**Maximum**	**Mean**	**Std. Dev.**
A	Binder/DBC-1	Numeric	80	90	85.1	4.17
B	Extra disp agent	Categoric	None = Water	Disp Agent 1 & 2	**Levels:**	3
C	Type TiO2 (4 types)	Categoric	PigAl2O3-Zr-I	PigAl2O3-Zr-II	**Levels:**	4
D	Coalescents	Categoric	Butyl glycol	Butyl diglycol	**Levels:**	2

Table 1. Experiments proposed by DoE.

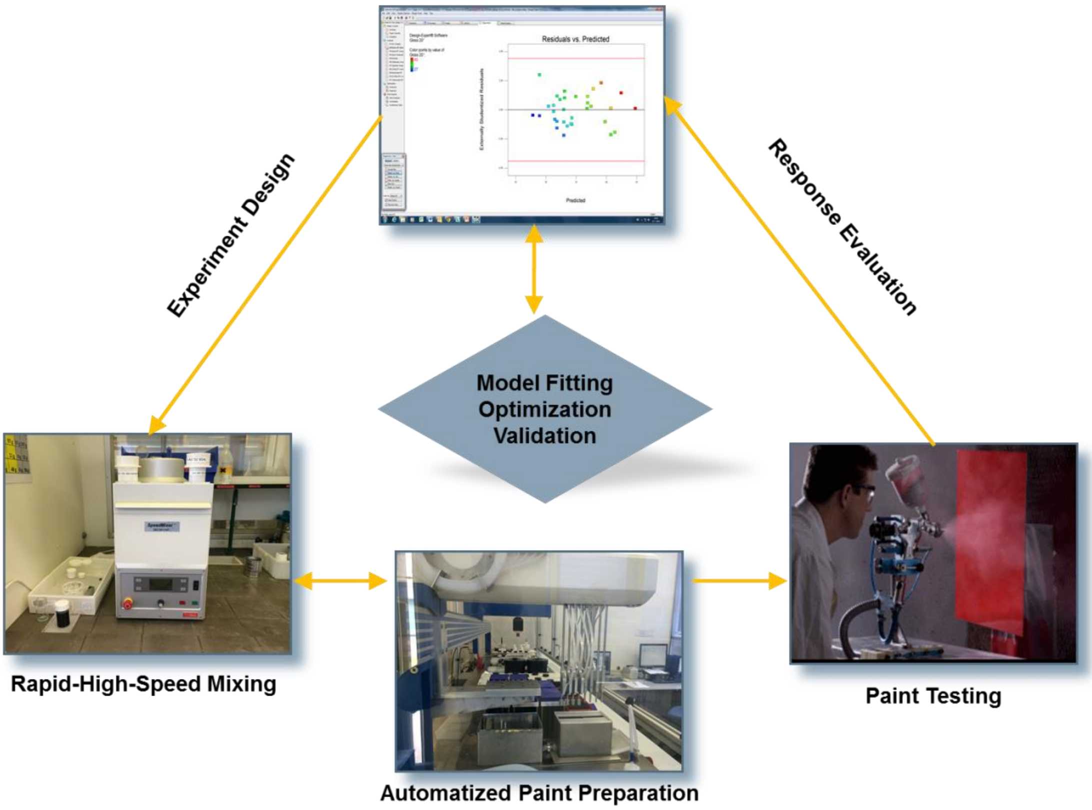


Figure 3. Nuplex HTE workflow.

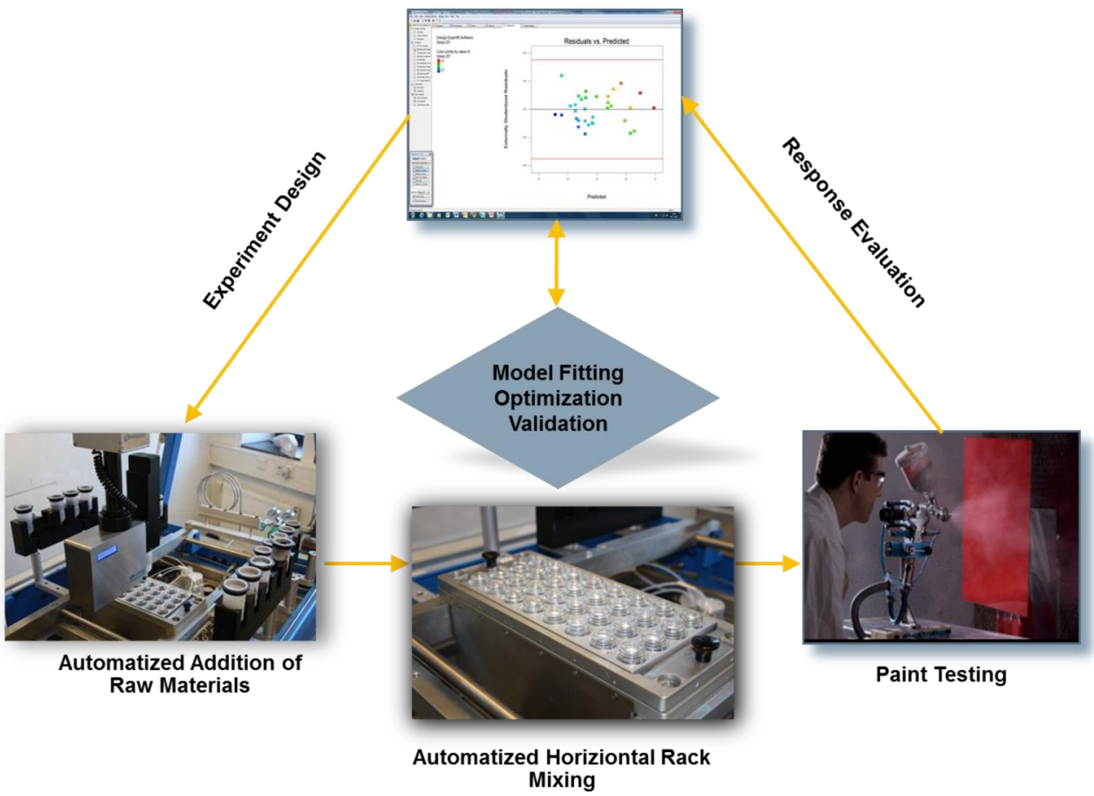


Figure 4. VLCI HTE workflow.

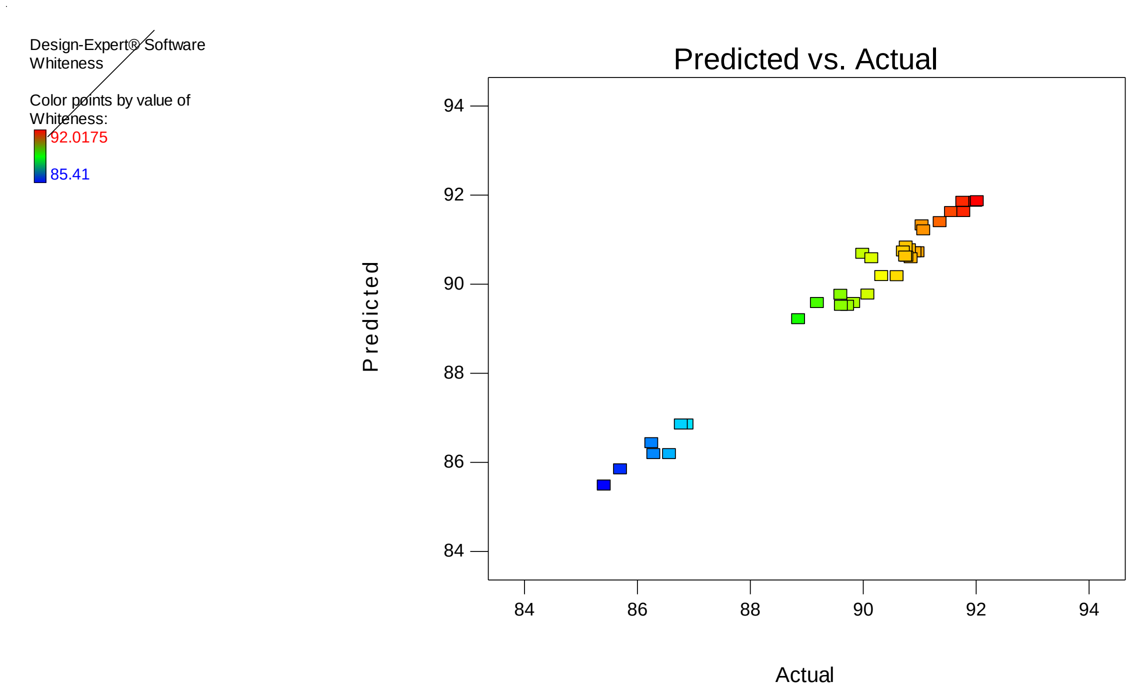
From the different workflows it can be rapidly noticed that the main difference lays on the preparation of the pigment paste and subsequent mix with letdown components. It is worth pointing out that that the DoE, Response Evaluation and Model Fitting were done for both cases under the same conditions, this is the same software Design Expert® version 9.0. Similar situation applied for the Paint Testing where similar methods and conditions were used to test the prototypes obtained from DoE.
In the Rapid-High-Speed Mixing process for Nuplex workflow, the Dual Asymmetric Centrifugal Laboratory Mixer was employed to make the pigment paste, followed by automatized letdown preparation and mixing to obtain the full paint in the Paint Robot. For the case of VLCI workflow the pigment paste and letdown preparation and mixing to obtain prototypes were done in the units GDU-P and GDU-HV from the HT system Formax®, respectively. In this case of VLCI HT workflow, all ingredients were thus added and processed automatically. The time needed to prepare all the 36 prototypes for the case of Nuplex was 24 h and for VLCI was 11 h.
The coatings were manually tested for Gloss (20º and 60º), Haze, Whiteness, Opacity, Hand Cream and Coffee stain resistance (when film dried at RT and 50 ºC). Both workflows employed similar methods to assess the performance of the paints produced. Afterwards, all the responses were evaluated and fitted (whenever possible) into a statistical model, with the intention of describing the influence of the formulation variables on the performance variables and robustness of DoE.
As mentioned above the statistical analysis was carried out with the aid of the software Design Expert®. The core of the evaluation was performed with basis on the collection of statistical models used to analyze the differences between group means and their associated procedures well known as ANOVA[7] (Analysis of Variances).

Response Evaluation: Model Fitting, Optimization and Validation.

As mentioned before, the responses (results from paint test evaluation) for both HTE-workflows were studied and checked for the possibility of fitting into a statistical model. Table 2 presents a summary of the fitting performance and the match between models results/trend for the different responses.
The first column of Table 2 reveals the feasibility of fitting a certain response into the statistical different statistical models employed, in this most of the response fitted well, while no possible fitting was found for the Hand Cream resistance. This means that both Nuplex and VLCI workflows resulted in “fits” for 7 out of the 8 parameters and the non fitting parameter was in both investigations the same: hand cream resistance. Both Coffee and Hand Cream resistance are known as spot test and are evaluated by naked eye being 5 the best result where no damage is found in the film surface; while 1 represents the opposite. In the case of Hand Cream resistance only 4 and 5 were found for the different experiments which made very difficult assessing a model to describe the effect of the other formulation variables. Figure 5 presents a comparison between a well fitted response (Whiteness) versus a response (Hand Cream resistance) that was not possible to fit.

	NUPLEX	MATCH	VLCI
Good-fitting performance	Gloss 20º	Trend OK-Partial	Gloss 20º
	Gloss 60º	NOK	Gloss 60º
	Haze	NOK	Haze
	Whiteness	Trend OK-Partial	Whiteness
	Opacity	Trend OK-Partial	Opacity
	Coffee RT	Trend OK	Coffee RT
	Coffee 50 ºC	OK	Coffee 50 ºC
Non-fitting performance	Hand Cream	N/A	Hand Cream

Table 2. Response's model fitting performance and match for Nuplex and VLCI HTE-workflows.



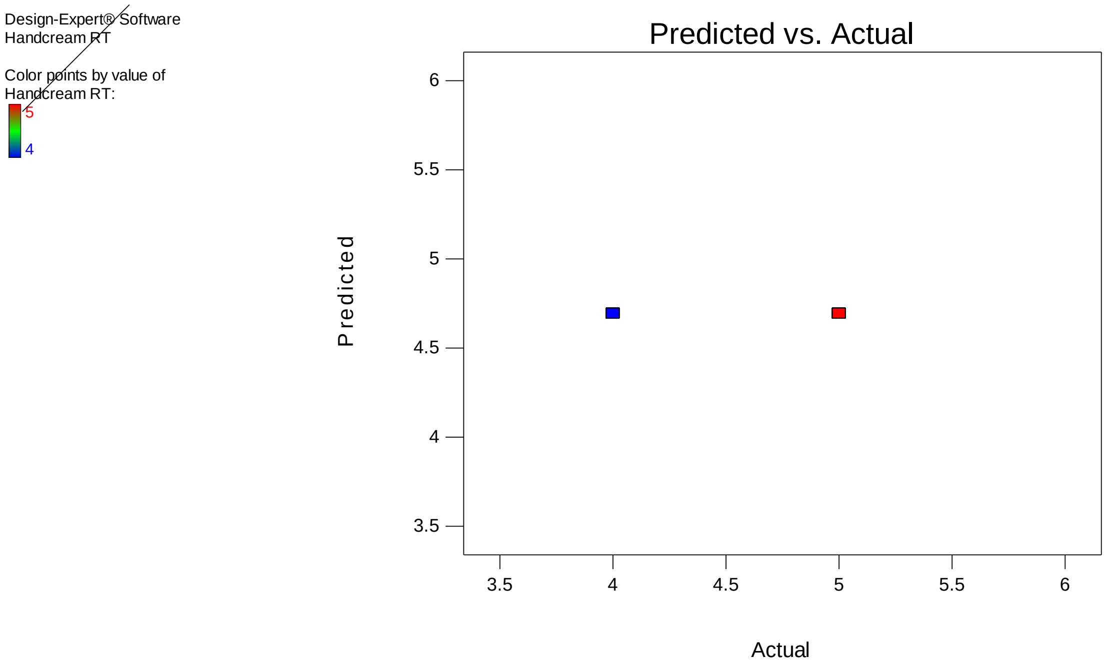


Figure 5. Model response's fitting performance for Whiteness and Hand Cream resistance.

The third column of Table 2 accounts for the match extent between the results obtained for the fitted responses from the 2 different workflows. It can be noticed that for the case of Gloss 60º and Haze there was no match between the two response's models, the results obtained rather deviated from each other and the effect of the other formulation variables on these responses showed different trends. This might be attributed to the differences between the pigment paste preparation procedures where the TiO_2 could go throughout different dispersion levels (better or worse spacing between pigment aggregates). However, the models for Gloss 20° presented good match for their trends (effect of the other formulation variables on this response), only the PigAl2O3-Zr-SiO2 results deviated from each other. The Opacity and the Whiteness are responses that are directly affected by the level of TiO_2 dispersion as well, nevertheless; their model trends presented similar behavior. For example higher levels of DBC-1 (lower Binder:DBC-1 ratio) increased the Whitness and the Oppacity, while using none or an Extra Dispersing Agent had no effect on these variables. The deviation in their trends came from some differences associated to the responses with similar TiO_2 types. For the case of Whiteness, the Nuplex model showed that PigAl2O3-Zr-II gave the best results while for VLCI model PigAl2O3-SiO2 was the best. The Nuplex model revealed that PigAl2O3-Zr-I offered the best Opacity, in contrary the pigment PigAl2O3-Zr-SiO2 was for the VCLI model optimum. Following the reasoning of these results, then finding the root for the deviation found in response models for Gloss 60º and Haze, becomes a difficult task. Here one might found then their differences in the human error associated with the film application and preparation, this is not conclusive though.
The response's models for Coffee Resistance showed a good match in both cases when films were dried at RT and 50 ºC. In that sense a closer analysis on the model performance will be developed. Equation (1) and (2) are the final model equations in terms of coded factors for Coffee Resistance 50ºC for Nuplex and VLCI workflows, respectively.

*Coffee 50ºC = 2.71-0.15*A+0.43*B$_1$-0.21*B$_2$-0.02*C$_1$-0.30*C$_2$-0.28*C$_3$* **(1, Nuplex)**

*Coffee 50ºC = 2.69-0.15*A+0.20*B$_1$-0.12*B$_2$+0.46*C$_1$-0.68*C$_2$-0.57*C$_3$* **(2, VLCI)**

In the above mentioned equations the Binder: DBC-1 ratio, the type of Extra Dispersing Agent and the type of TiO_2 are represented by A, B and C, respectively. These equations can be used to make predictions about the response for given levels of each factor, where the high levels of the factors are coded as +1 and the low levels of the factors are coded as -1. Moreover, the coded equation defines the relative impact of the factors by comparing the factor coefficients. These equations can lead to a large amount of combinations and might be difficult to analyze individually. In that sense using the equations in terms of actual factors offer a clearer understanding when comparing models. A better example of this comment can be seen in Figure 6 where the evolution of the Coffee Resistance 50ºC as function of the Binder: DBC-1 under different formulation conditions is described using the equations in terms of actual factors. Figure 6 shows good agreement between the 2 models as they follow a similar trend and results are comparable. On the other hand when all the equations are combined it is possible then to have an extended view of the effect of all the variables on the use of DBC-1, this is shown in Figure 7. Here indeed it is possible to confirm that: i) Higher amount of DBC-1 enhances Coffee Resistance, ii) The Type of TiO_2 has a strong influence on the response being PigAl2O3-Zr-II the best and PigAl2O3-Zr-SiO2 the worst, iii) The use of an Extra Dispersing Agent and different Type of Cosolvent had minor to no effect on the response.
Finally it is worth pointing out that despite the lack of fitting and match for Hand Cream resistance, Gloss 60º and Haze, the DoE in combination with both HTE workflows showed excellent robustness as only 3 responses out of 8 failed.

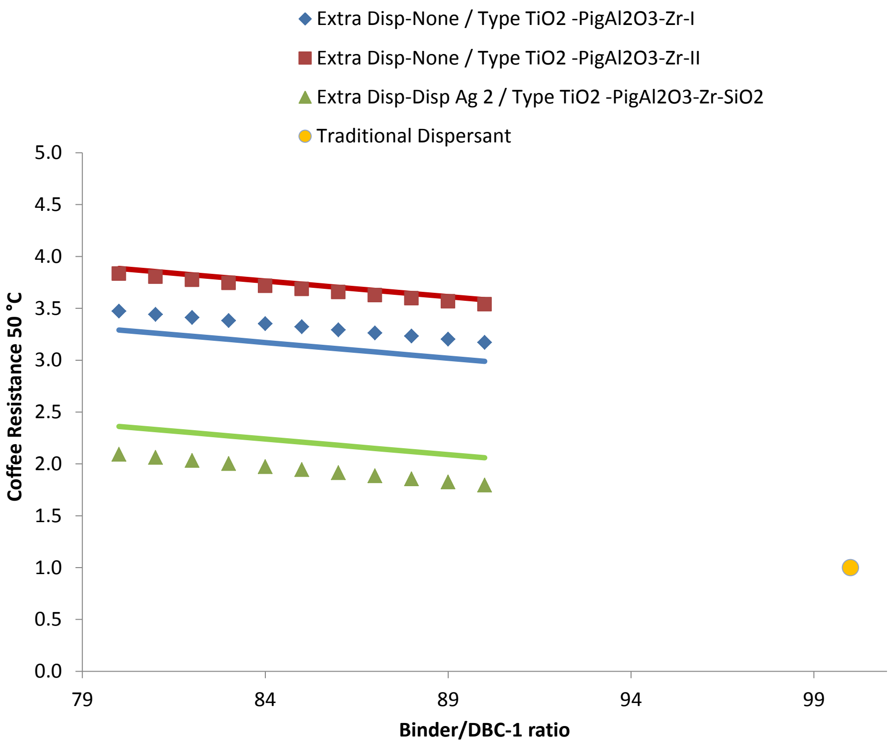


Figure 6. Effect of Binder:DBC-1 ratio on the Coffee Resistance 50°C (Continuous line: Nuplex Model; Discontinuous line: VLCI Model) .

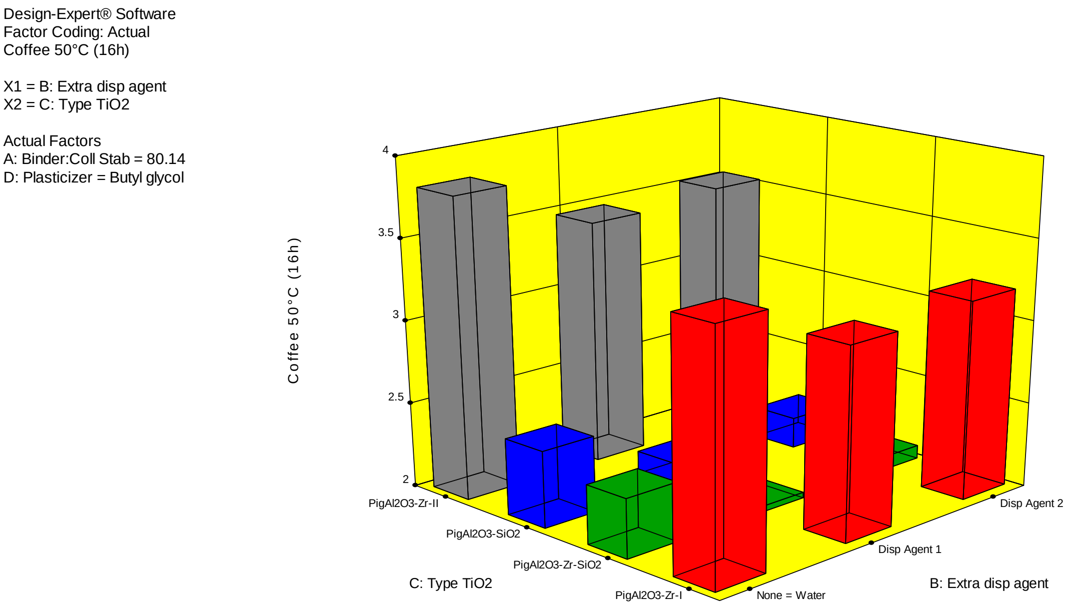


Figure 7. Effect of the different formulation variables on the Coffee Resistance 50°C (Binder:DBC-1 was fixed to 80.1 and both Cosolvent types had similar effect).

One of the main motivations of using these HTE tools in combination with statistical analysis is to optimize these complex systems to desired targets. In that sense, 2 formulations (1 and 4) targeting a Coffee Resistance 50°C of 4 while maintaining a good appearance were designed. On the other hand, 2 formulations (2 and 3) with a poorer performance were included for the sake of comparison. These 4 formulations were prepared using the Nuplex HTE-workflow and by traditional methods. The 8 paints were tested in parallel and their performance compared as showed in Table 3.The results obtained by preparing the paints using traditional methods were quite close to those obtained by HTE techniques; this validated the model used to obtain optimized formulations. Finally, it should be pointed out that model aimed target excellent as formulations 1 and 4 (for both preparation methods) gave results of Coffee Resistances around 3.5-4.

Formulation	Appearance			Pigment Performance		Chemical Resistance			
	Gloss 20°	Gloss 60º	Haze	Whiteness (%)	Opacity (%)	Coffee RT	Hand Cream RT	Coffee 50°C	Hand Cream 50°C
1-HTE	43.0	76.0	84.0	85.4	96.5	3.5	4	3.5	4
Model-1 (+)		69.0	154.0	91.4	98.0	4		4	
1-TRAD	43.0	71.0	84	84.1	96.7	3.5	4	3.5	4
2-HTE	29.0	67.0	155.0	91.1	97.3	3.5	4	3.5	4
Model-2 (-)		63.3	155.0	90.1	97.6	3		3	
2-TRAD	30.0	69.0	116	91.2	96.8	2	4	2	4
3-HTE	27.0	65.0	127.0	90.1	97.0	2	5	3	5
Model-3 (-)		70.0	145.0	91.1	97.8	2		2	
3-TRAD	25.0	65.0	89	89.7	96.6	2	4	2	4
4-HTE	36.0	72.0	140.0	91.8	97.5	4	5	4	5
Model-4 (+)		71.6	166.3	91.2	98.1	4		4	
4-TRAD	39.0	71.0	107	91.2	98.1	4	4	4	4
DEVIATION									
1	0.000	-0.070	0.000	-0.015	0.002	0.000	0.000	0.000	0.000
2	0.033	0.029	-0.336	0.001	-0.005	-0.750	0.000	0.000	-0.750
3	-0.080	0.000	-0.427	-0.004	-0.004	0.000	-0.250	0.000	-0.500
4	0.077	-0.014	-0.308	-0.006	0.006	0.000	-0.250	0.000	0.000

Table 3. Results and model validation from the Nuplex model, for Coffee Resistance optimized (1 and 4) and poorer performance formulations (2 and 3).

Conclusions.

The use of HTE-solutions in combination with a solid statistical analysis resulted in an excellent tool.

- It affords understanding in the behavior and the interaction of a complex polymer colloid such as DBC-1 in a pigmented paint.
- If offers the potential and fine tune the performance of DBC-1 in terms of Coffee Resistance, Whiteness and Opacity.
- Basically the workflows performed at Nuplex and VLCI led to the same results: described robustness as the statistical analysis of the DoE resulted in response (paint tests) models that were similar in trends and results.
- The models generated by DoE can be used to predict certain performances when using predicted paint formulations. The positive validation to real "live" larger scale preparation shows the real strength of performing HTE and DoE.These features were obtained without an excessive amount of experiments and in a quite shorter experimentation period as compared to conventional bench work.

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