The Taming of the Shrew

Coatings Development

An Efficient Approach Using Design of Experiments

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Although the development of high-quality coatings is in fact tricky, there are situations where statistical Design of Experiments (also called DoE or Experimental Design) can be employed effectively. Design of Experiments allows, amongst other things, a quick identification of promising components in the initial raw material screening. This speeds up the development considerably. So why are there so few examples of successful applications of DoE in the area of coatings?
For one, high-quality coatings are complex mixtures. A thorough experimental exploration will therefore often require a large number of experiments. Another reason might be the lacking familiarity with the method. Even though the underlying concepts have been known for quite some time [1], many shy away from the seemingly difficult training:
Statistics - sounds scary…

Modern Times

With modern software tools however, most steps of a DoE project do not pose any difficulties at all.
In the expert system STAVEX [2], for example, it is only necessary to specify the desired response variables (i.e. quality characteristics) and the potential influence factors. The software then generates suitable designs. The user merely has to do the suggested experiments. After the results have been entered into the software, the tool performs all statistical analyses and presents the results in an easily understandable html report. Thus, the main challenge lies in correctly mapping the question to the software.

Raw Material Screening

A German manufacturer of high-quality coatings wanted to develop a water-borne one-pack single layer coating which can be applied to steel

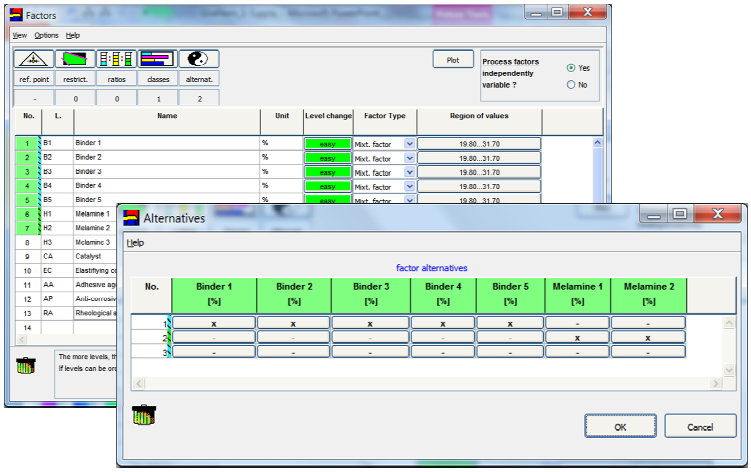

Figure 1: Easy specification of process and mixture factors (green), as well as of alternative factors, within the DoE expert system STAVEX.

surfaces directly (so-called direct to metal (DTM)). Although constituting a single-layer system, it nevertheless should provide sufficient protection.

In order to comply with the required drying and hardening conditions, as well as for achieving the desired UV resistance, an acrylate / melamine combination was selected. In a first screening, the most promising binders and hardeners, as well as the appropriate anti-corrosive pigments, were to be identified.
Based on information from the raw material suppliers, five binders and two melamine hardeners were selected, with the option to include a third melamine hardener if necessary.

It is also recommendable to identify the optimal anti-corrosive pigments on an empirical basis. Here nine candidates were chosen.
Additionally, the effects of the acid catalyst, the adhesive agent, an elastifying component, and the rheological additive were to be investigated.

Practical Implementation

It is however not the number of influence factors or alternative raw materials which poses a difficulty.
Any modern DoE software tool can optimize mixtures (here the binder / melamine hardener combination) as well as other potential influence factors together.

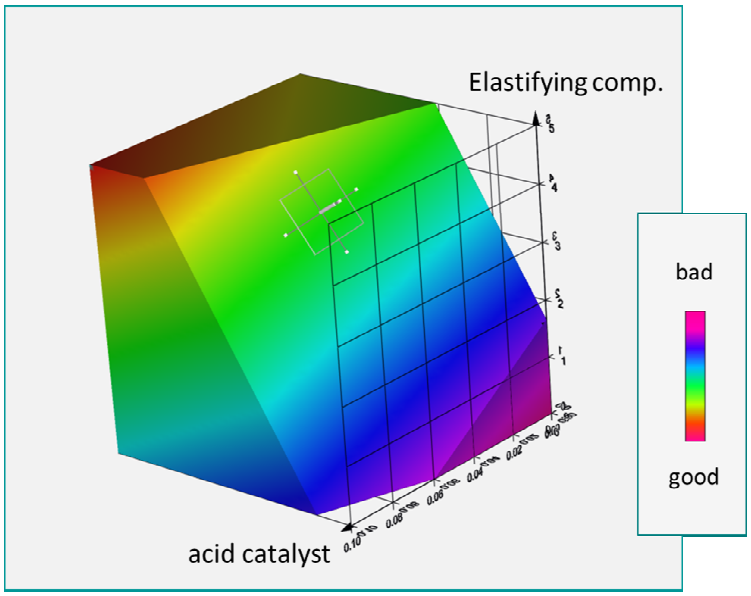

Figure 2: 4-D plot (STAVEX): x-axis: acid catalyst, y-axis (hidden): melamine hardener, z-axis: elastifying component.
The colour coding from red (min) to ultraviolet (max) shows the corrosion creep in the salt spray test. It is minimal at the highest concentrations of all parameters.

A distinctive feature of the expert system STAVEX is however the simplicity with which alternatives within the mixture can be specified: a special “alternative” button opens a window which allows entering these specifications with a mouse-click. *Figure 1* shows this for the five binders and the two melamine hardeners.
For the nine pigments a so-called qualitative factor is used, whose levels correspond to the different pigments. The remaining four influence factors are specified as “normal” quantitative factors.

Competence and Creativity

The question which requires some more thinking is how to deal with different solvent contents of the raw material alternatives.
In our case it was decided that the total binder content should be fixed at a constant level. Therefore, the upper and lower limits of the respective factor ranges were specified so that the sum of the binder and hardener components was always constant. Neither did the factor ranges of the other quantitative factors represent the actual amounts in the formulation. Since the amount of a raw material depends on its solvent content, calculating the actual ranges would have been a difficult task.
Instead, in order to simplify the procedure, the formulations given by the software were afterwards converted into the “real” formulation within Excel, with slight adjustments of the viscosity by adding distilled water when appropriate.

Specifying the Responses

In order to describe the quality of the coating, several parameters can be measured, such as corrosion and UV resistance, adhesive strength, visual assessment, as well as the gloss / gloss change. Most of these so-called response variables are quantitative and should either be minimized or maximized.
For other quality characteristics such as softening, blisters or yellowing after UV exposure, it is only of interest whether such problems do arise or not. Therefore, these parameters may be entered as qualitative responses (“yes” / ”no”).
In order to achieve a higher precision, however, it is worthwhile specifying them in a quantitative manner. For instance, the amount of yellowing may be rated on a scale ranging from 0 to 100.

Sequential DoE

When factors and response variables have been entered, the DoE software allows choosing a design. In STAVEX, no prior DoE knowledge is needed here, as the expert system automatically suggests suitable designs, depending on the number of potential influencing factors. Additionally, restrictions such as “not more than 15% of additives” can easily be taken into account. In case of contradicting specifications, the software-internal control will prompt the user for correction.
For the relatively rough initial screening only 20 experiments were needed, despite the rather large number of factors and alternatives.
Such a screening allows assessing first tendencies: Which components can probably be omitted, which should be kept at the maximum, whether a higher or lower concentration of the acid catalyst might be recommendable, etc.
In a second step, the remaining factors can be investigated more closely. This is in particular important for clarifying the interaction structure.
Finally, a detailed optimization of the final formulation is performed. This procedure, called “Sequential Design of Experiments”, guarantees maximum efficiency.

Quick Results

The most important response variable was the corrosion creep in the salt spray test. Analysing the measured data, it was found that a combination of the first binder, the second melamine hardener and the third anti-corrosive pigment shows the highest resistance. The first melamine hardener was classified as important in the analysis, however preferably at the lowest concentration possible. This is due to the fact that the model computed by the software suggests a connection between corrosion and a higher concentration of the first melamine hardener. Therefore, this component was eliminated from further investigations. Moreover, including the acid catalyst, the elastifying component and the rheological additive was beneficial. The other factors were judged as irrelevant.
The four dimensional plot from the software tool STAVEX in *figure 2* illustrates the system’s behaviour for a fixed concentration of the first binder with respect to the acid catalyst (x-axis), the third melamine hardener (y-axis, covered) as well as the elastifying component (z-axis), where all other factors are kept constant; the first melamine hardener at its minimum. Since the corrosion is desired to be as small as possible, the higher amounts of these components obviously tend to be more advantageous (red area).
The screening for pigments is equally simple. *Figure 3* shows a so-called multi-plot obtained from the expert system STAVEX. The plot displays the measured corrosion for the differ-

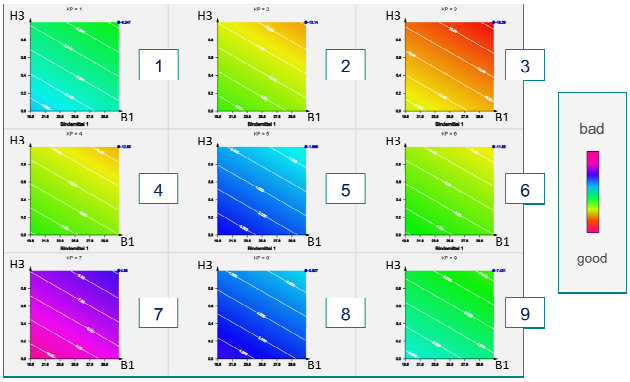

Figure 3: Comparison of the anti-corrosive pigments (STAVEX plot). x-axis: binder 1 (B1); y-axis: melamine hardener 3 (H3).
The colour coding from red (min) to ultraviolet (max) shows the corrosion creep in the salt spray test. It is minimal for pigment 3 (top right), in particular for high levels of binder 1 and melamine hardener 3.

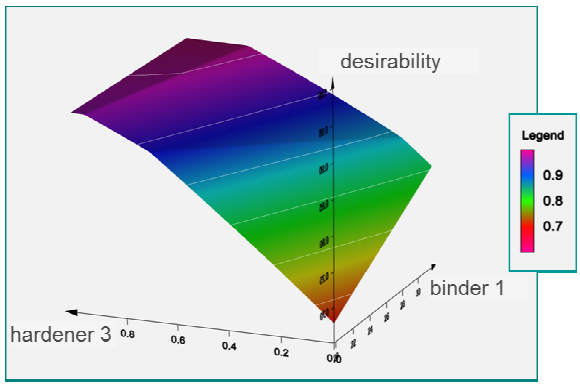

Figure 4: Response surface for the desirability (STAVEX plot). x-axis: binder 1, y-axis melamine hardener 3. The desirability (z-axis) shows how well various response variables might be combined. Thus it allows for an automatic compromise (here between corrosion creep, rust formation on the surface, and rust on the edges). A value of 1 (violet) means a perfect compliance to all specifica-

ent pigments versus the first binder and the third melamine hardener – again with all other factors being kept constant and the quantity of the first melamine hardener at the minimum.
Based upon this plot, the pigments can easily be classified into different categories. The smallest (i.e. best) values are obtained using pigment 3 (red colour), followed by pigments 2 and 4, then pigments 1, 6 and 9. Pigments 5, 8, and especially 7 perform substantially worse.
Analogous plots for the other relevant response variables show that pigment 3 yields good results in every case. Also pigments 2 and 4 are satisfactory, whereas pigment 7 performs worst in each case. Other pigments, such as 9 and 1, yield different results for various response variables. These findings allowed a further optimization of the formulation subsequently.

Multiple Response Variables

If multiple response variables are to be optimized simultaneously, the so-called "desirability function" is a good option. It allows finding automatically a compromise between different quality criteria. *Figure 4* visualizes the desirability for the intended combination of minimum corrosion creep, minimum surface rust grade and minimum rust on the edges in the salt spray test (versus the amounts of binder 1 and melamine hardener 3, keeping all other factors constant).
As soon as one of the response variables is out of specification, the desirability equals 0. On the other hand, an ideal compromise, where all response variables attain their desired optimum, is indicated by a desirability of 1. It is evident that this is the case for the larger amounts of both components. If needed, the desirability even can be weighted. One could for instance specify that the visual assessment and the gloss should carry less weight compared to the observed corrosion creep in the salt spray test, e.g. by choosing exponents of 0.5.
This implies that very unsatisfying results for these criteria still lead to bad "marks" for the coating system; but that small deviations are not considered as relevant.

Limitations

Although statistical design of experiments (DoE) often facilitates work due to its systematic approach, there are some limitations, in particular in complex situations. The expert of the coating manufacturer stresses that, in his opinion, DoE is best suited for an initial raw material screening and for the final formulation optimization at the end of the development cycle.
Often, coating formulations consist of a multitude of components, exhibiting many, sometimes unpredictable, interactions.
A systematic analysis of all interactions would therefore lead to a large number of experiments. Moreover, a detailed modelling might also require considering quadratic or even cubic effects, which increases the number of experiments even further. With exception of high-throughput methods, such a vast number of experiments cannot be performed in practice.
Therefore, the usual procedure in the modelling stage is to repeatedly exchange single components, where interactions with the other ingredients must be taken into account. This step significantly depends on the researcher's knowledge and experience, since a pure trial-and-error procedure would obviously fail to be efficient. Formalizing this knowledge, so that the situation is correctly represented within the software and therefore the effort is reduced to a feasible number of experiments, would require an enormous effort. When fine-tuning the formulation, however, DoE again facilitates work substantially.

Information Gain

A systematic approach using DoE requires some effort. The information gain, however, is worth the trouble. Not only a formulation is found which satisfies the specified requirements, but it also is proven that this formulation is optimal within the investigated factor range.
Moreover, the interplay between the various components is much better understood. Ideally even new ideas about the underlying mechanisms have been created. Knowing which components can safely be disregarded is extremely helpful as well.

Results on a glance

- **Statistical Design of experiments (DoE) is an efficient approach for performing the necessary experiments.**
- **With a user-friendly software tool, the training period is short. In this article, the DoE tool STAVEX was presented (www.aicos.com).**
- **For coatings, being able to specify mixtures with alternatives flexibly and easily is an important issue.**
- **In only 20 experiments, the screening delivered results for 5 binders, 3 melamine hardeners, 9 anti-corrosive pigments, and 4 process factors.**

Finally, optimality can be defined flexibly: Should only the classical resistance parameters such as corrosion creep or rust formation (which are best optimized simultaneously by means of a so-called desirability function) be taken into account, or should the gloss level be weighted more strongly than usual? By assigning cost rates to the factors it is also possible to determine the formulation which satisfies the specified requirements at minimum cost.

Conclusion

In order to efficiently apply DoE, a software tool which allows a flexible mapping of the research question is indispensable. In order to be accepted by the involved staff, software must be user-friendly and easy to apply. Then the tool can be used without the need of much previous training, and a successful project gives instant gratification. *Figure 5* provides an overview of the software requirements. For coatings, an important point is that mixtures with alternative components can be treated easily, which is the case for the expert system STAVEX.

Acknowledgements

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Dr. Stefanie Feiler, VP Consulting Services at AICOS Technologies, studied mathematics and chemistry, obtaining her PhD in statistics from the university of Heidelberg, Germany. She works for AICOS Technologies since 2005. There she provides services in data analysis and coached a multitude of DoE projects.

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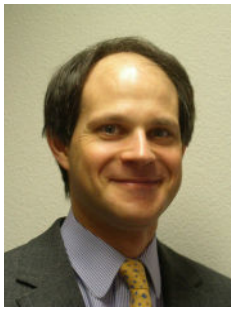

Interview with the author, Dr. Stefanie Feiler

By Kristen Wrede, Farbe und Lack

For whom is the application of Experimental Design (DoE) suited?

DoE is the method of choice as soon as experiments have to be performed. It is a structured approach. In contrast to the traditional procedure, where only one factor at a time is modified, the entire factor space is covered, and interactions can be taken into account. Moreover, the method is completely independent of the area of application, because the relationship between the factors and the response variable is investigated in a purely mathematical way.

Therefore, DoE is equally suitable for developing a coating formulation, increasing API yield or for the process optimization on a large plant – for pigment manufacturing, in pharmaceutical areas, for plastics…

Why are coatings considered as difficult?

A coatings formulation consists of various components, for which there are again multiple alternatives: For instance the different anti-corrosive pigments mentioned in the article. This means that the development of a coating is extremely complex. Without additional knowledge and a well-planned experimental stage, the number of experiments rises quickly. The subsequent process optimization is again easy, however.

Which are the limitations of Experimental Design (DoE)?

There are (almost) none. For some complex applications, there are specialized designs, and in the area of engineering (aerospace), DoE and computational simulations are often employed in combination.

But, frankly speaking, you probably won't get far in developing a coatings formulation without a certain professional competence – additional knowledge on interactions and a feeling for promising components.

Nevertheless, this best should be incorporated into the DoE. Otherwise, your "favourite" components might mislead you in the end.

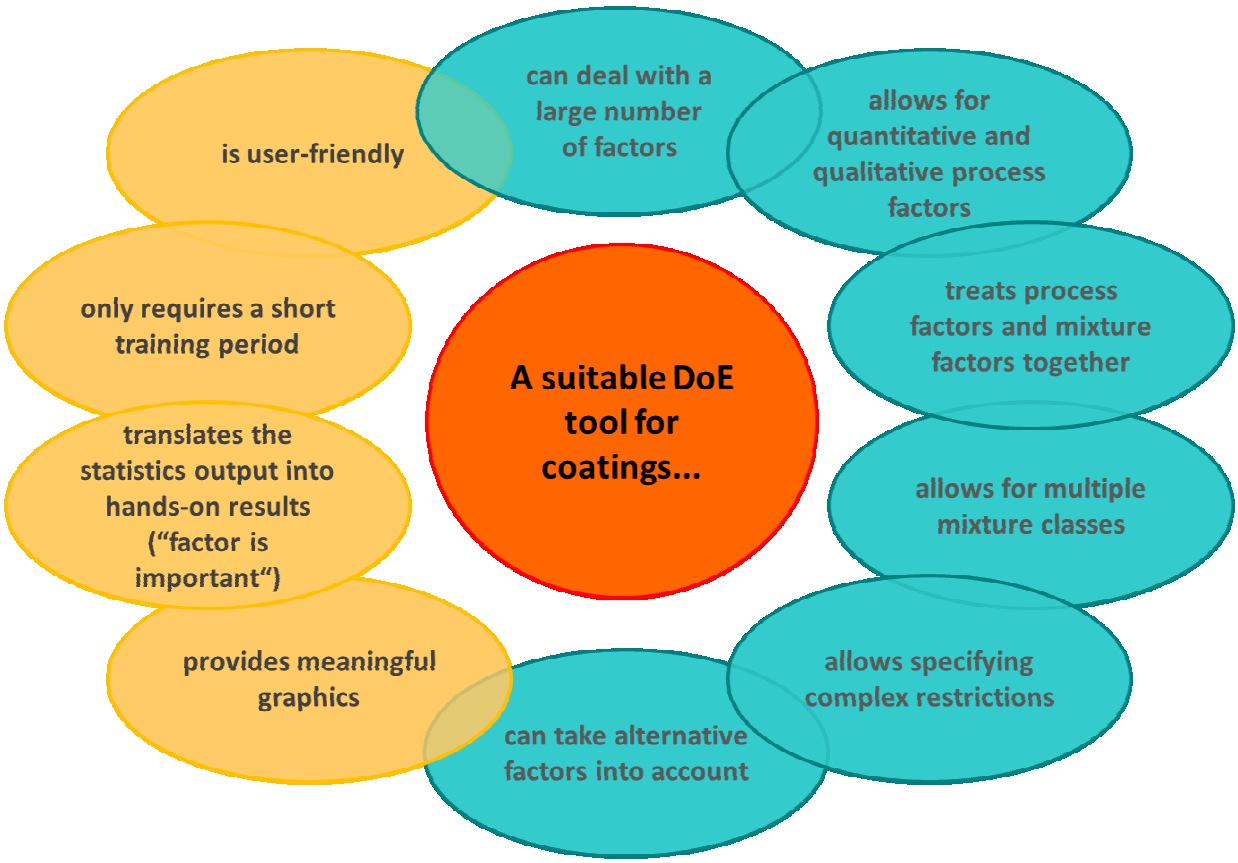

Figure 5: Requirements for a DoE software tool in the coatings area.