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How to Design and Analyze Mixture Designs that Include Process Factors and/or Categorical Variables

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Abstract
The latest versions of dedicated DOE software[1] exhibit more versatility than ever before to create optimal designs that handle any combination of mixture components, processing factors (such as time or temperature) and categorical variables (such as supplier and material type). These computer programs easily manipulate almost any number of responses in powerful optimization routines that reveal "sweet spots" - the operating windows that meet all specifications at minimal cost.

In this paper, we review the basic principles of mixture design. Then we apply state-of-the-art tools for optimal design to the formulation of a coating.

Laying the groundwork – a simple mixture problem

Let's begin with a simple mixture design that allows three components to vary from 0 to 100 percent. Other ingredients may be present in the final formulation, but by holding these at fixed proportions, the experimenter can set them aside. The resulting experimental region forms a simplex, a geometric figure with one more vertex than the number of dimensions. In two dimensions, a simplex is a triangle. In three dimensions, a simplex is a tetrahedron, and so on.

Figure 1 shows the experimental region, or "mixture space," for the three unconstrained components. The three corners, or vertices, of the resulting triangle (a simplex) represent the maximum allowed for a specific component. For example, at the top of the triangle component A reaches its upper limit of 100 %, with B and C at 0 %. At any point in the triangular region, the ingredients total to 100 %. This is called the "total constraint."

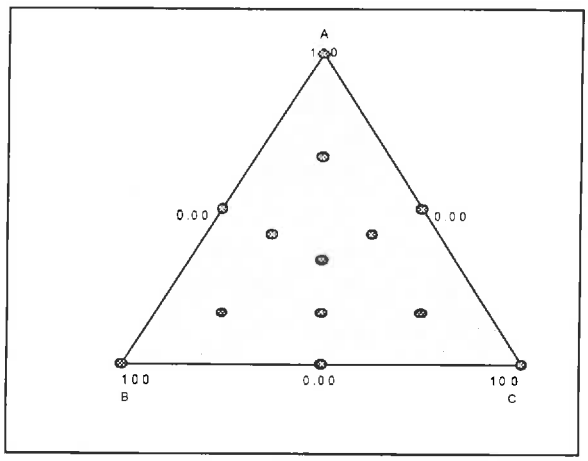

Fig. 1: A reasonable candidate set for a 3-component design

The points shown on Figure 1 represent a reasonable candidate set of points for a mixture design aimed at fitting a quadratic or special cubic polynomial model. It includes the pure mixtures of A, B and C shown at the vertices, plus the three binary blends (A-B, A-C and B-C), which are represented by the mid-points at the edges of the triangle. These points surround the three-part blend ($1/3^{rd}$ each of A, B, C) at the "centroid" of the triangle. The other six points in Figure 1, called "check blends", fill the remaining gaps in the mixture space. They form a small triangle within the bigger triangle. If time and materials run short, the check blends can be skipped.

A simplex will always result from designs where all components can vary from 0 to 100 percent. This geometry also occurs in special cases where components are constrained to equal ranges, such as those given for the following case study.

Adding categorical factors – A case study

Formulators of an automotive clear coat explored the impact of three components: monomer, crosslinker and resin on two key responses: hardness and solids. Based on knowledge of the chemistry, they restricted the component levels as shown in Table 1.

Component	Supplier(s)	Low	High
A. Monomer	M1 or M2	5 %	20 %
B. Crosslinker	C1, C2, C3	25 %	40 %
C. Resin	Fixed	55 %	70 %

Table 1: Mixture components for clear coat

Note the categorical choices for supplier of the monomer and crosslinker. To keep things simple, suppliers must not be mixed. For example, monomer M1 cannot be blended with M2. The same rule applies to the three possible crosslinker suppliers (C1, C2, C3). The formulators decided not to vary supplier of the resin.

The constraints shown in Table 1 form a simplex, so the pattern of points shown in Figure 1 could be used for the experimental design. However, in this case, each recipe must be re-applied as many as six times to cover all combinations of the two monomers and three crosslinkers. Multiplying these 6 categorical combinations times the 13 points for the proposed mixture design, produces a total of 78 blends, which far exceeds the limitations of time and material. As you will see, a smaller number of blends will provide enough information to get a decent fit of the data.

Optimal design tools pare down the number of required blends

The invention of computers made it feasible to apply matrix-based algorithms that select an ideal subset of experiments. The two most popular algorithmic methods are called "a-optimal" and "d-optimal." These are just a few of the so-called "alphabetic optimality criteria" developed by statisticians.[2] The general procedure for optimal design is:

1. Specify the order of polynomial: first, second, third or beyond, that you think will be needed to model the response.
2. Generate a "candidate set" with more than enough points to fit the specified model.

3. From the candidate set, select the minimum number of points needed to fit the model.

First-order polynomials will only model linear behavior. A second order polynomial, called a "quadratic," will reveal two-component interactions. More complex interactions can be modeled by third order polynomials. Design of experiments can be likened to design of bridges, where when in doubt, you build it stout. In other words, if you're not sure what to do, invest in a higher-order polynomial. The added blends needed to fit the bigger models may reap great benefits through discovery of unexpected interactions.

The actual selection procedure involves computer-intensive matrix calculations designed to produce model coefficients of maximum possible precision. Years ago, an experimenter who wanted to apply optimal design would have to describe the problem to a statistician, who then would go to a mainframe computer, and perhaps days later, come back with the experimental plan. Now, anyone equipped with a personal computer and the proper software can generate an optimal design. Let's see how this was done for the automotive coatings case.

The coatings formulators faced a difficult modeling task – combining mixture design with categorical factors. They decided to simplify matters by not trying to estimate interactions between the categorical suppliers. The resulting first order (categorical) model contains four terms: one to estimate the overall average effect, plus another term for the effect of changing from one monomer supplier to the other, plus two more terms for the effect of changing from one crosslinker to either of the two alternatives.

On the other hand for the mixture side of the problem the formulators expected some complex chemistry, the experimenters so they chose a third order mixture model called a "special cubic" (shown below):

$$\text{Predicted Response} = \beta_1 A + \beta_2 B + \beta_3 C + \beta_{12} AB + \beta_{13} AC + \beta_{23} BC + \beta_{123} ABC$$

The Greek letter beta represents the unknown coefficients in the model. The seven terms in the special cubic mixture model must be crossed with the four terms needed to estimate linear effects of the categorical factors. The end result is a 28-term combined model.

Given these design criteria, the software[1] generated a candidate set comprised of the 6 possible combinations of the two sets of suppliers for monomer and crosslinker, crossed with the 13 blends shown on Figure 1, for a total of 78 points. It then used d-optimal criteria to select the 28 points needed for the desired model. To add statistical power, the software replicated the five points with highest leverage, a statistical measure of relative influence. It also added 5 additional points to fill in some of the gaps and test for lack of fit. The resulting 33-point design, and associated response values for hardness and solids, can be seen in the Appendix. The blends are listed by an identification scheme that puts replicates in sequential order. However, the actual run order was randomized to insure against biases caused by lurking factors such as material degradation, machine wear and drifting ambient conditions. You must randomize the order of your experiments or risk invalidation of the entire design.

Response surface graphics tell the story

Using least-squares regression, the DOE software fitted the response data to the 28-term equation for the coatings system. Two statistically significant models were produced – one for each response. These models then became the basis for response surface graphics, which greatly simplify the interpretation of results. Figure 2 shows the predicted effect of the categorical factors on hardness.

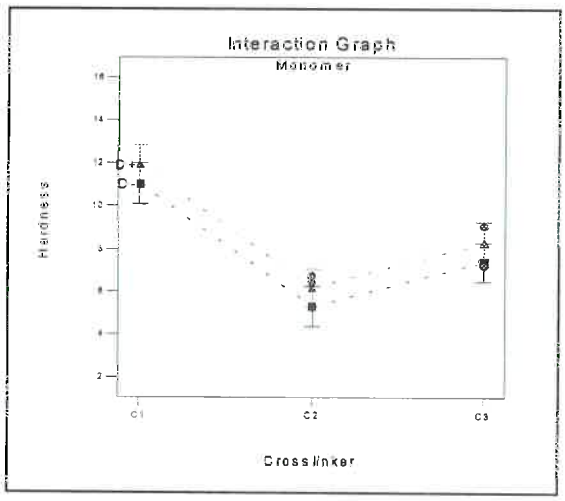

Figure 2: Effect of suppliers on hardness

The M2 monomer, labeled D+ with triangular symbols, comes out on top of M1 (labeled D-). The crosslinker supplier, shown on the x-axis, produced a much bigger effect on hardness. The customer required a level of 10 or higher for hardness. This can be achieved only by the C1 supplier of crosslinker.

Figure 3 shows the predicted hardness results as a function of the component levels for monomer M2, crosslinker C1 and the resin.

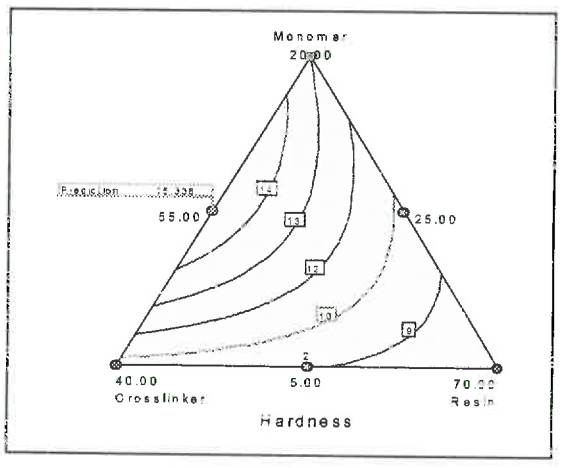

Figure 3: Hardness results at best combination of suppliers

The contour labeled 10 represents a critical boundary. To the right of this contour, hardness falls below specification. The most critical variable is amount of resin. As resin concentration approaches

the high level (70 %) at the lower right, the predicted hardness falls well below the target. The maximum hardness occurs somewhere along the opposite edge where resin amount is at its minimum level. The flag, which displays a predicted hardness value, stems from one of the actual points in the d-optimal design at concentration of monomer, crosslinker and resin of 12.5 %, 32.5 % and 55 %, respectively.

Figure 4 shows a similar plot for the second response, solids, which must exceed 50 %. The monomer and crosslinker remain fixed at M2 and C1, respectively, which were chosen to achieve maximum hardness.

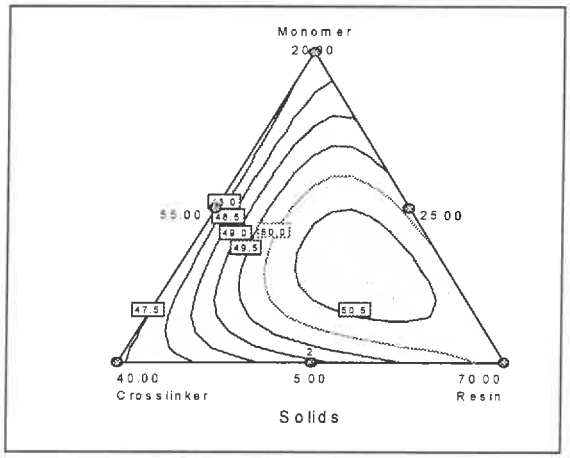

Figure 4: Contour plot for second response: solids

The area where solids exceed 50 % extends from the centroid down to the corner of maximum resin (70 %). This region did not exhibit outstanding hardness. Obviously a tradeoff must be made between maximizing hardness or maximizing solids. Ideally there will be an overlap of the in-specification areas on Figures 3 and 4.

Multiple response optimization finds the "sweet spot"

By shading out areas outside of specification, then overlaying the contour plots for the two responses, the software created the graph shown on Figure 5. It reveals a sweet spot for formulation of the automotive clear coat.

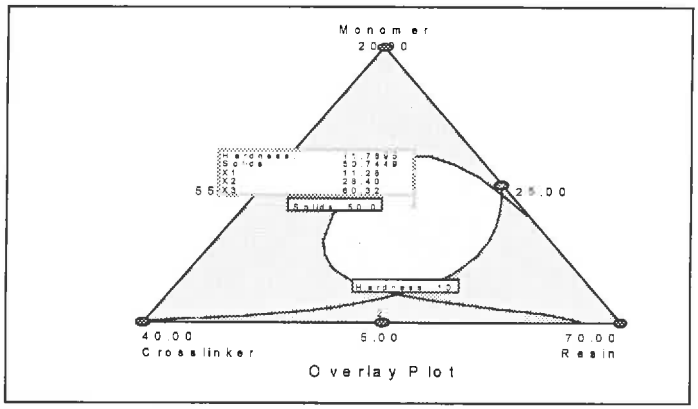

Figure 5: Graphical overlay plot for coatings

The flag is arbitrarily set near the middle of the operating window. It provides a reasonable choice for a good formulation: 11.28 % of M2 monomer, 28.40 % of C1 crosslinker, and the remainder (60.32%) as resin. The software offers more sophisticated numerical search algorithms that will find the most desirable mixture within the operating window. Cost can be taken into account before making the final decision. For example, in this case, if the M2 monomer is relatively expensive, an alternate solution can be found by switching to the M1 supplier.

Last, but not least, any recommended formulations must be verified via confirmation runs. Remember that the recommended optimum is only a prediction based on a very select (but optimal!) set of sample blends.

What's in it for you

The case study on the automotive clear coat shows how you can apply advanced tools of DOE to optimize your formulation. The optimal design approach, so handy in this case for dealing with categorical factors, more commonly finds application for formulations that don't fit a neat simplex space. It also handles the addition of process factors, for example in metallurgical applications.[3] Now you can mix your cake and bake it too! Yet another type of optimal design incorporates the amount of the formulation. For example, you can simultaneously vary component levels and the thickness of a coating. In all these cases specialized DOE software can provide optimal designs that explore critical variables in coatings systems. The ultimate benefit comes from discovery of operating windows that satisfy all customer specifications most economically. If you accomplish this, you and your company will gain a competitive advantage and generate big profits.

References

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2. Cornell, J. (1990) **Experiments with Mixtures**, 2nd edition, (John Wiley & Sons, Inc, New York,.NY).
3. Kraber, S & Whitcomb, P. (June, 2000) Innovative experiment design and optimization tool finds optimal settings for mixture and process variables, (presented to the Joint Research Conference, Seattle, WA).

Appendix: Design layout and response values for coatings case

Id	A: Monomer (%)	B: Cross-linker (%)	C: Resin (%)	D: Monomer (Supplier)	E: Cross-linker (Supplier)	Hardness (Knoop *)	Solids (%)
1	5.0	25.0	70.0	M2	C3	8.6	50.7
1	5.0	25.0	70.0	M2	C3	7.7	49.4
2	5.0	40.0	55.0	M1	C1	9.7	48.0
3	12.5	32.5	55.0	M1	C1	15.0	48.3

4	10.0	30.0	60.0	M2	C2	6.7	50.3
4	10.0	30.0	60.0	M2	C2	6.4	50.7
5	5.0	25.0	70.0	M1	C1	7.3	50.9
5	5.0	25.0	70.0	M1	C1	7.5	49.7
6	20.0	25.0	55.0	M2	C1	12.0	47.3
7	20.0	25.00	55.0	M1	C2	3.8	48.0
8	10.0	30.0	60.0	M1	C1	11.0	52.0
9	5.0	40.0	55.0	M2	C1	9.3	48.1
10	5.0	25.0	70.0	M2	C2	5.0	49.9
10	5.0	25.0	70.0	M2	C2	5.4	49.9
11	10.0	30.0	60.0	M1	C3	7.2	50.2
12	5.0	32.5	62.5	M2	C1	9.0	48.2
12	5.0	32.5	62.5	M2	C1	9.2	50.4
13	5.0	40.0	55.0	M1	C2	3.6	46.7
14	12.5	32.5	55.0	M2	C3	12.0	48.2
15	12.5	25.0	62.5	M1	C3	6.2	49.9
16	5.0	32.5	62.5	M1	C3	5.3	47.9
17	12.5	25.0	62.5	M2	C1	10.0	50.2
18	12.5	25.0	62.5	M2	C2	5.3	49.2
19	5.0	32.5	62.5	M2	C2	2.4	50.0
20	5.0	40.0	55.0	M2	C3	6.6	47.8
21	10.0	30.0	60.0	M2	C3	9.0	50.3
22	12.5	32.5	55.0	M1	C2	7.0	46.9
23	5.0	32.5	62.5	M1	C2	3.5	47.8
24	20.0	25.0	55.0	M1	C3	5.0	48.7
25	12.5	25.0	62.5	M1	C2	5.0	49.9
26	5.0	25.0	70.0	M2	C1	7.7	50.9
27	12.5	32.5	55.0	M1	C3	8.7	48.0
28	20.0	25.0	55.0	M2	C2	6.1	49.0
29	5.0	40.0	55.0	M2	C2	5.9	47.2
30	20.0	25.00	55.0	M1	C1	11.0	47.8
31	20.0	25.0	55.0	M2	C3	10.0	47.8
32	5.0	40.0	55.0	M1	C3	6.3	46.8
33	12.5	32.5	55.0	M2	C1	14.0	46.9

** A measure of microhardness obtained by dropping a diamond-shaped weight on on the coated surface. The reported measurement is a function of the depth versus width of the indentation.*