Design of Experiment to Achieve Optimum Properties of UV Pigmented Inks

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Abstract

In a UV Curable ink, one of the most important and most expensive components of a formulation is the photoinitiator. The photoinitiator can determine how fast the reaction will take place, to what level is the material cured and the impact on other properties (i.e. cost, scratch resistance, chemical resistance, etc.). How is it possible to achieve the desired effects at the lowest cost? With computer and software advances, an optimized blend of photoinitiators can be obtained utilizing Design of Experiment.

Introduction

Today, many Research and Development labs have approached the best way to run experiments very differently. One method used, is to start experimenting with a hunch on the values needed. The starting values can be due to previous experiments or historical values. This approach would be comparable to finding a one-caret diamond lost in the Sahara Desert with only a vague recollection of where you lost it. The factors to find the diamond are varied and arbitrarily set. If you find it, then you are done, but if the diamond is still missing, what factors are you going to change to find the diamond? What direction are you going to travel? Would it be easier to find it in the dark with a flashlight? What equipment might you need? Using this method, you have no further information on how to find that diamond than when you had started. [1]

The next approach commonly taken is the one-variable-at-a-time. With this technique, one factor is varied from a set point while the other factors are held constant. The response is measured and a conclusion is made with respect to the set point. The biggest drawback from this technique are the interactions of factors, are not taken into account. For example, what factors affect the blowing up of a balloon to get the largest diameter? Factors such as the size, rubber thickness, amount of air and temperature may all play a roll in obtaining the largest size of the balloon. If we look at each of the factors, we might see that, as the size of the balloon increases, the maximum diameter obtainable increases. As the thickness of rubber increases, the larger the maximum diameter of the balloon will be. As you put more air into the balloon, the bigger the diameter. Temperature will also play a roll in the size of the balloon. As the temperature increases, the air expands resulting in an increase in the size of the balloon. If the interactions are not taken into account, the largest balloon diameter would be to use the largest balloon, the thickest rubber, the greatest amount of air and the hottest temperature. It could be seen that if these factors were all set at the greatest value, the balloon would not have a diameter at all. If the initial testing was conducted at room temperature and the largest amount of air was determined to be five cubic meters of air, however, if the room temperature was raised to 150°F, the balloon would burst. So the interaction of all of the factors will play a role in obtaining the largest balloon. [1]

Finally, the process by which the interactions of factors are examined to help solve a problem by running the fewest number of experiments is called, Design of Experiment (DOE). Not only will an optimized set of factors be obtained, but knowledge of the entire process will be modeled. [1]

Experimental

When developing new energy curable inks (UV) one of the biggest costs to the formulation is the photoinitiator. It would be very beneficial to optimize the photoinitiator mixture to help reduce the cost but still obtain the needed properties of the final printed material. This application would be considered a mixture DOE. A mixture DOE is a special consideration where the ratio of the ingredients, rather then the total amount, will impact the properties of the final ink. With the use of the computer, more than three components can be examined and complex models can be obtained for the optimum mixture. If more than five components are examined, a screening design is recommended. For example, if there are seven different materials which are needed to be looked at, there would be over 30 separate experiments which would be run using a linear with interaction model. For a full screening (partial cubic) model, the same seven materials would need over 90 different experiments to be completed for the design.

To visualize the interactions of each of the components, a triangular plot is used (Figure 1). In this case, if values are set for two of the components, the third value is automatically set. Materials which do not reside on the plot are called off-axis and can also have a value associated with them. If this is the case, the axis of the plot will be reduced by the proportion of the off-axis value.

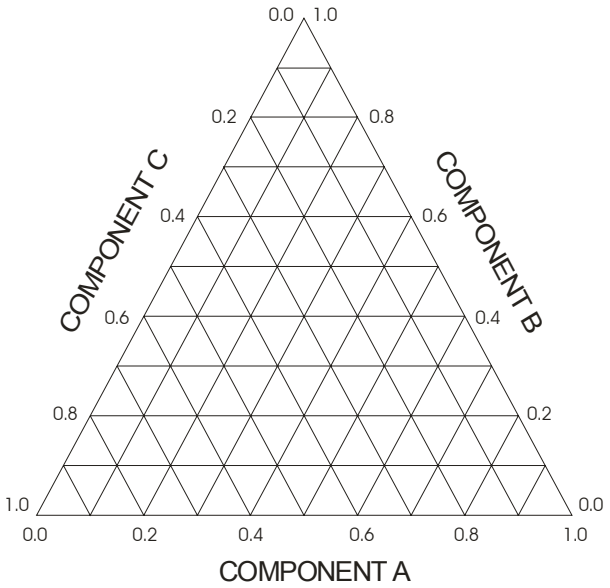

Figure 1
Triangular Plot

For this experiment, we will use 7 different photoinitiator materials. (See Table 1)

Table 1

Name	Abbreviation	CAS #	List Price (USD/lb)[*]
2- and 4- isopropylthioxanthone	ITX	5495-84-1 & 83846-86-0	$20
2,4-diethylthioxanthone	DETX	82799-44-8	$30
Benzil Dimethyl Ketal	BDK	24650-42-8	$10
1-hydroxycyclohexyl acetophenone	HCPK	947-19-3	$12
2-methyl-1-[4-(methylthio)phenyl]-2-morpholino propan-1-one	MMMP	71868-10-5	$30
Benzophenone	BP	119-61-9	$4
4-Benzoyl-4'methyldiphenylsulphide	BMS	83846-85-9	$30

* Values are approximate list price obtained 2003 from multiple sources.

Since there are greater than 5 different components, we should perform a screening design to reduce the number of trials which will be performed. To do this, the software program is used and an interaction design is produced. (For this example there are 33 unique trials and 5 replicates for a total of 38 trials) For each of the components, interaction between two other components is measured. The candidate trials are the 3 vertices, 3 edges and the center. (See Figure 2)[2]

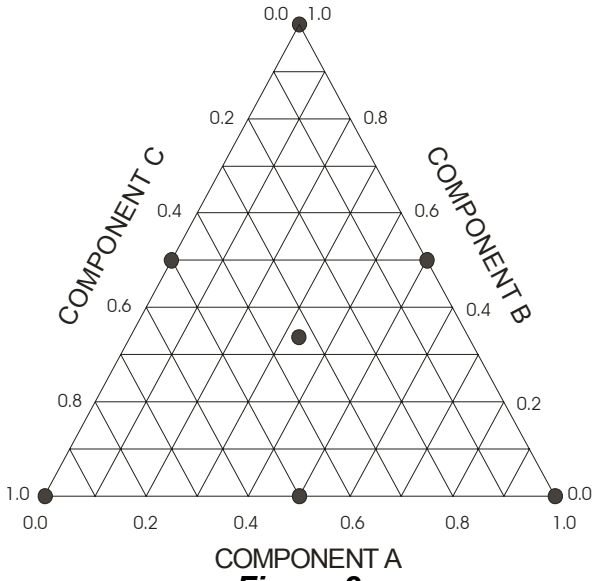

Figure 2
Interaction Design

The candidate mixtures were dissolved 50/50 in a low viscosity multifunctional acrylate monomer and allowed to sit for 24 hours. (If needed, slight heat was applied to fully dissolve the photoinitiators in the monomer) The mixtures were then checked for signs of re-crystallization or gelation. Two different inks were made up using multifunctional monomers, epoxy acrylates, urethane acrylates, polyester acrylates, amine synergist and either PB15:3

(PCN Blue) or PY13 (Yellow AAMX). Each of the compounds to be tested were incorporated into the test ink at a level of 10% photoinitiator and measurements were then taken on the following properties: Ink Cure Analyzer™ (ICA), ink transfer, crystallization, ink grind, cost, and MEK rub density loss.

Using a Prufbau Printability Tester, many prints were made for testing purposes. Each print was prepared on a non-porous substrate (PET) printed at 0.5 m/sec with a pressure of 700 N. The printed samples were then cured under a 300 Watt/linear in. medium pressure mercury bulb at a speed of 300 fpm for 3 passes through the curing unit.

Ink transfer was determined by printing a known volume of ink using a Prufbau Printability Tester. The speed of printing was 0.5 m/sec with a pressure of 700 N applied to the print. The printed samples were then cured under a 300 Watt/in. medium pressure mercury bulb at a speed of 300 fpm for 3 passes through the curing unit.

One print for each candidate was tested using the Ink Cure Analyzer™ (ICA). The ICA utilizes a radioactive tracer element to help determine cure of the ink film. Printed samples with equal densities were used to ensure that the thickness of the ink was approximately the same. [3]

Another print for each compound was used for testing the solvent resistance. MEK (methyl ethyl ketone) rubs were performed on, similar density, printed samples which represents the cure and the ability of the ink to resist solvent. An MEK soaked cloth was applied over the surface of the print and a 100 g weight was applied. The cloth was then moved back and forth for ten times and then removed. At that point density was read using an X-Rite 528 Spectrodensitometer along the area in which the MEK was applied and an average of five readings was taken.

The grind of the ink was measured using the NPIRI 1-mil grind gauge according to ASTM Method D1316-93. [4]

Cost was determined utilizing list prices from various photoinitiator suppliers.

All measured responses were then placed into the design of experiment software and analyzed. It is imperative to check the statistic values such as P values (determines significance), Cross Validation RMS values (predicting power of model), and R squared values (determines variability in the model) to make certain that the model is valid for the experiment. [5] The design of experiment software allows the ability for each individual response to be analyzed and optimized for that feature. Most design of experiment programs contain a function in which a combination of properties can be looked at and a weight is given to each of the factors. For our example, it was seen that the optimized materials to use was a combination of BP, HCPK and MMMP for the yellow ink and BP, BMS and MMMP for the blue ink. (A weight of 1.0 was given to cost, 0.7 was given to cure and 0.7 was given to crystallization) Due to the absorption of the different pigments, different photoinitiators are needed to give the optimum results. See Figure 3 for yellow ink optimization and Figure 4 for blue ink optimization.

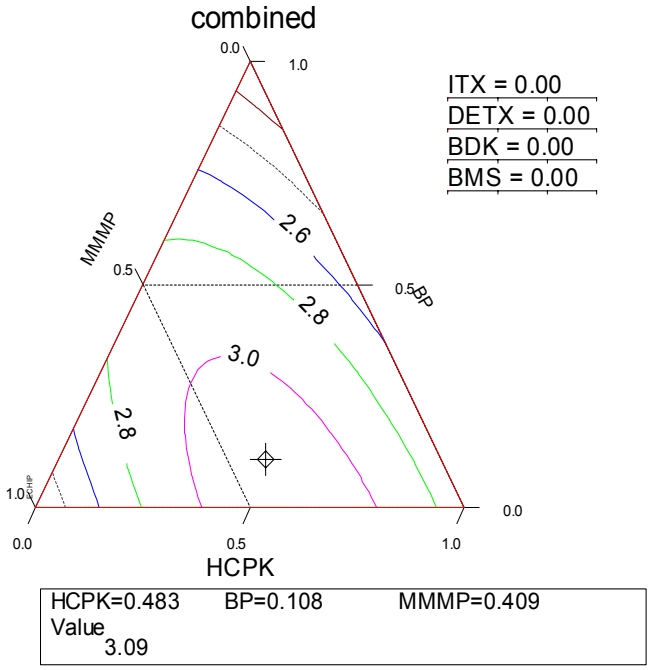

Figure 3
Yellow Ink Optimization

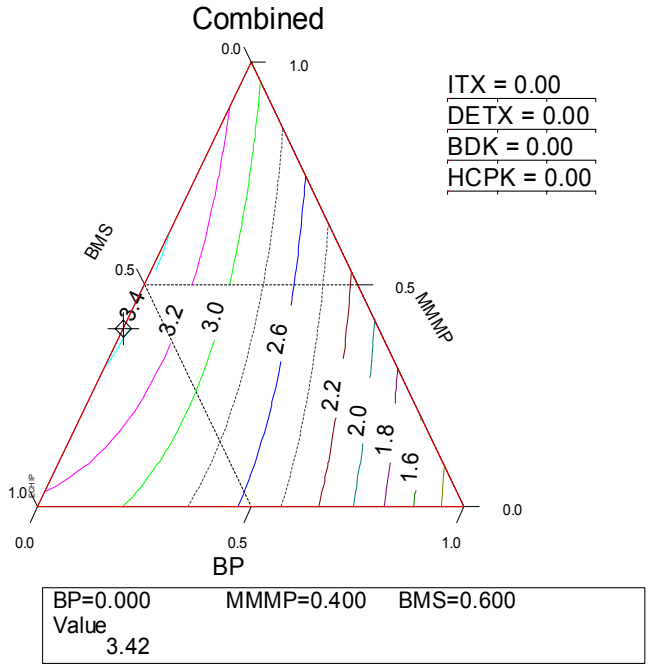

Figure 4
Blue Ink Optimization

Now that the candidates are narrowed down to only three per color, we can now expand the experiment to fully characterize the process and look at more combinations. By utilizing a partial cubic model, many more points are looked at to help in determining the true model of the system. See Figure 5 (A total of 15 unique trails and 5 replicates) [2]

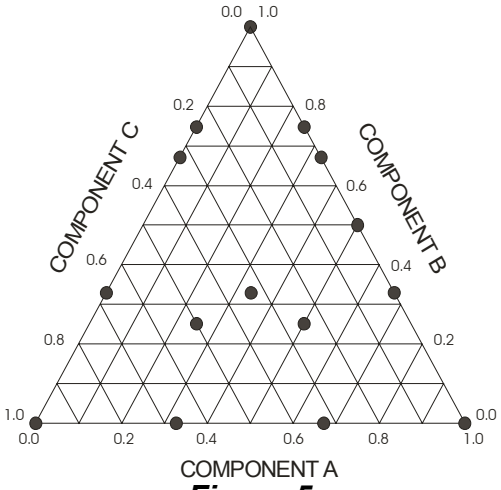

Figure 5
Partial Cubic Model

The same methods as mentioned earlier were used for sample preparation and testing and the following optimizations were obtained. (Weights of 1.0 were given to cost, ICA, solvent resistance, and crystallization) See Figure 6 for yellow ink optimization and Figure 7 for blue ink optimization.

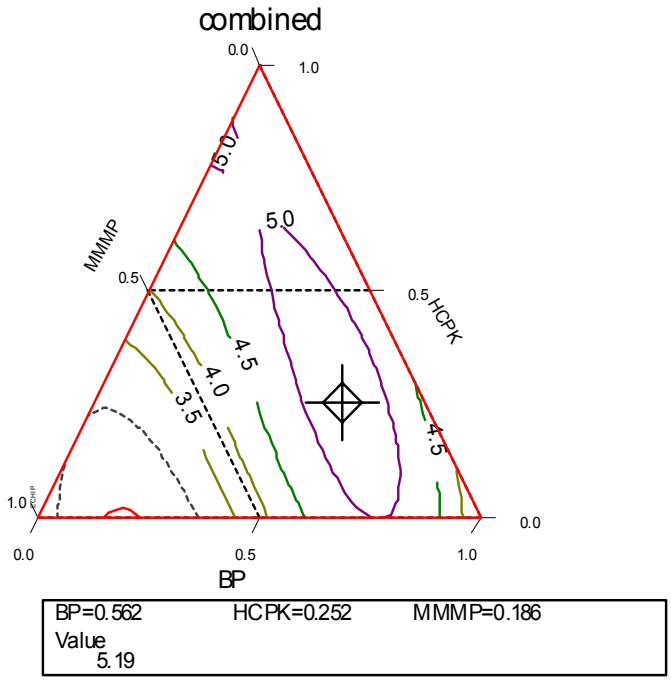

Figure 6
Yellow Ink Optimization

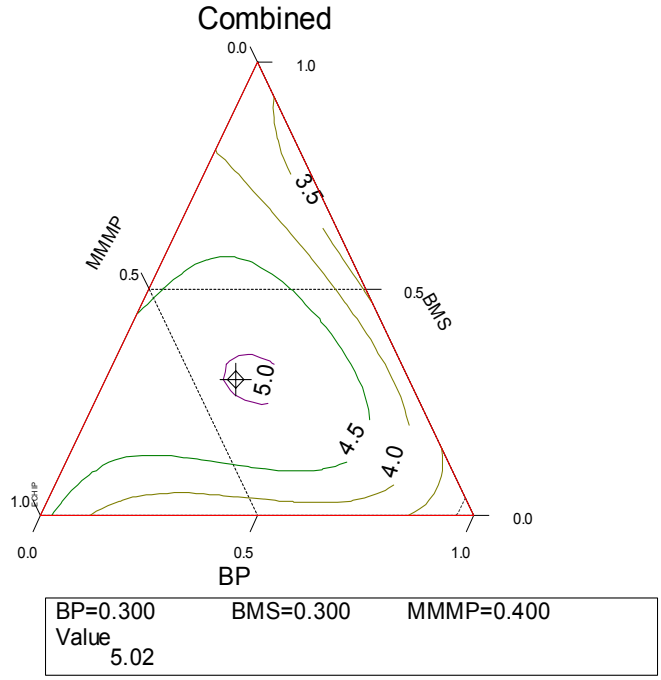

Figure 7
Blue Ink Optimization

Results and Conclusions

After the optimization is completed, the model built by the software can be used as a prediction tool. Different combinations of materials can be placed into the software and values are given which should represent the responses obtainable. By looking at the predicted values and performing checks points, the model can also be verified. The model built for the photoinitiator compound used in the yellow ink showed that the optimized photoinitiator compound should be 56% Benzophenone, 25% 1-hydroxycyclohexyl acetophenone, and 19% 2-methyl-1-[4-(methylthio)phenyl]-2-morpholino propan-1-one. This combination gives no re-crystalization, very good ICA cure, good ink transfer, good solvent resistance and at a cost of approx. $10.90 USD/lb. The reliability of the model was checked and found to be a very good predictor for ICA cure, cost, and re-crystallization. There is however a lack of ability to predict the ink transfer and the solvent resistance for this model. This is most likely due to errors associated with the measurement of these values.

The model built for the photoinitiator compound for the blue ink showed that the optimum combination should be 30% Benzophenone, 30% 4-Benzoyl-4'methyldiphenylsulphide, and 40% 2-methyl-1-[4-(methylthio)phenyl]-2-morpholino propan-1-one. This combination gives no re-crystallization, very good ICA cure, good ink transfer, very good solvent resistance and a cost of $22.20 USD/lb. The model was checked and was found to be a good predictor for ICA cure, cost, and solvent resistance. There is a lack of the model to predict the ink transfer and the re-crystallization of the compounds used in the ink. Once again this is most likely due to

errors within the measurement of the density and the repeatability of the compound to stay in solution.

Other factors could be measured in order to help in identifying the optimum photoinitiator composition, including cure rate, odor, amount, etc. Most of the work is already completed and all that would be needed is to measure those properties. The factors (i.e. ink transfer) which were not predictable by the model can also be looked at. This could help in determining if any modifications in the measurement systems are needed. Values for the modified measurements can be entered and re-analyzed to modify the model as needed to hopefully obtain reliable predictions for all of the responses.

Now that the model is built, many combinations can be looked at even before going to the bench. It is a lasting model for this system and can now be used as a very powerful tool for the formulator. But caution must be taken, if the vehicle system has changed, this might affect the ability for the model to accurately predict the responses.

Design of experiment is a very powerful tool when used correctly and gives the formulator the ability to optimize many responses at one time. We can now find that lost diamond in the Sahara or have the biggest balloon on the block if we use this tool and look at interaction of the components and the responses obtained from them.

References

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