Use of Experimental Design Techniques to Build a Formulation Model for Phase Change Ink Jet Inks

Don Titterington and Ron Burr
Color Printing and Imaging Division, Tektronix, Inc., Wilsonville, Oregon

Abstract

Results from a classic multivariable matrix experimental design were mathematically reduced to a linear mathematical model of the physical properties of a phase change ink jet ink formulation. Properties of the ink in both the solid and liquid phases are important for the application, and are included in the model.

Introduction

For the last several years many of the engineers and scientists in our group have been working on a new printer architecture that is an evolution of the phase change ink jet technology first used used in the Tektronix Phaser® III and Phaser® 300 color printers. This design was recently introduced as the Tektronix Phaser® 340. The 340 uses a transfer process where the ink is first jetted onto a receiving drum, then transferred to the final media. There are several advantages of this approach, one being that this provides a very simple paper path. Another is that architectures using this approach are inherently faster than previous products. The last big advantage is that a combination of heat and pressure can be used during this transfer process to smash and spread the pixels of ink to a much greater extent than is possible in the Phaser 300. This enhances the durability of the image, lowers the cost per copy for the user since less ink is required per pixel, and allows the printing of transparencies that project well without any post processing.

The phase change inks designed for this process must meet many different requirements. In addition to the requirements for high quality color, thermal and light stability, lack of toxicity, etc. the four colors of ink must meet the same tight specification for viscosity at the jet operating temperature. There are five ingredients in the ink vehicle (or clear base), four of which have a direct effect on the viscosity of the formulation. The dyes also affect the viscosity, but the effect varies from dye to dye. In order to adjust for the effect of the dyes and normalize the four colors, the ratios of the base ingredients are varied from ink to ink.

A new factor that the transfer process adds is the need for understanding and control of the mechanical properties of the ink as a solid. The ductility of the ink and it's absolute stiffness are important both on the finished print and at the elevated temperature where the ink is being smashed and spread during transfer. These mechanical properties are also a function of the ratio of the different base ingredients and dyes. Changes made in the base ingredients in order to normalize the viscosity can dramatically affect the mechanical properties if not done correctly. It is also very important to know how equipment and mixing tolerances in the manufacture of the ink can affect these properties.

Experimental Design and Results

The study described here was done in order to quantify the effect of each of four of the ink ingredients on viscosity and on certain mechanical properties, these being the glass transition temperature of the formulation, the toughness, and the Young's Modulus at certain temperatures. Viscosity information was obtained on a Bohlin CS-50 rheometer and the properties of the ink as a solid were measured on a Rheometrics RSA II dynamic mechanical analyzer. A classic eight-trial, three-variable, full-factorial matrix was used, but with an interesting twist. Instead of using the direct amounts of each of the ingredients, which would have required four variables and a sixteen-trial matrix, we used ratios of the amounts of three of the ingredients to the amount of the fourth as the three matrix variables. In addition to reducing the number of trials, this makes the resulting mathematical model very easy to use since it is independent of the absolute quantity of any of the materials or the units in which they were originally measured. The effect of any one ingredient can easily be backed out of the results by incorporating the model into a spread sheet and entering a few test cases on the ingredient of interest.

The eight trials and the results from analyses of the matrix for one of the test responses is shown below. "S-

---

Originally published in *Proc. of IS&T's Eleventh International Congress on Advances in Non-Impact Printing Technologies,* October 29-November 3, 1995, Hilton Head, South Carolina.

Variable	High (+)	Low(–)
A	TA/S-180 = .459	TA/S-180 = .340
B	KE-311/S-180 = .577	KE-311/S-180 = .428
C	278/S-180 = .203	278/S-180 = .149

Storage Modulus @ 25°C (Dyne/Cm^2 × 10^9)

TRIAL	A	B	AB	C	AC	BC	ABC	**RESPONSE**
1(1)	-	-	-	-	-	-	-	2.54
2(a)	+	-	-	-	-	+	+	2.54
3(b)	-	+	-	-	+	-	+	2.27
4(ab)	+	+	+	-	-	-	-	2.59
5(c)	-	-	+	+	-	-	+	2.31
6(ac)	+	-	-	+	+	-	-	2.24
7(bc)	-	+	-	+	-	+	-	1.68
8(abc)	+	+	+	+	+	+	+	2.13
EFFECT	.17	-.24	.21	-.40	.01	-.13	0	

180” is the trade name for the wax used in the formulation. “TA” is our acronym for the oligomeric polyamide that imparts clarity and toughness to the formulation, “KE-311” is the trade name for the tackifier, which imparts flexibility and clarity to the formulation, and “278” is our shorthand for the plasticizer used in the formulation. The ratios listed below were chosen to represent the outer boundaries of what we wished the model to cover, and are much wider than the variations that we use for normal formulations.

Construction and Use of the Model

The mathematical model that utilizes the results above was constructed using the following premises:

1) The effects of each variable were linear and additive. This was tested by comparing results from the finished model against data obtained from several replications of actual ink formulations that are near the center point of the ex-perimental design. This assumption was found to be true.
2) The effect of each variable and interaction on the experimental responses are quantified by the calculations done on the matrix and listed in the row labeled “EFFECTS” above. Assuming the responses are linear the term for each main effect in the regression equation that describes the response is:

$$\Delta Y_A/\Delta X_A(a - a_{ave}) \tag{1}$$

where “ΔY_A” is the effect coefficient for variable A, “ΔX_A” is the range of variable A studied, i.e. ($A_{high} - A_{low}$), “a” is the level of the variable to be plugged into the model and “a_{ave}” is the median of the variable range studied, i.e. ($A_{high} + A_{low}$)/2.

The term for the interaction of variables A and B is

$$(\Delta Y_{AB}/\Delta X_A{\cdot}\Delta X_B)\ (a - a_{ave})\ (b - b_{ave}) \tag{2}$$

where the definitions are the same as above. The first factor in each term can be reduced to a constant and, assuming the effects of the variables are additive, the full equations reduced to:

Main Effects:

$$\Delta R_{MAIN} = K_A(a - a_{ave}) + K_B(b - b_{ave}) + K_C(c - c_{ave}) \tag{3}$$

Interactions:

$$\begin{aligned}\Delta R_{INT} = {} & K_{AB}(a - a_{ave})\ (b - b_{ave}) + K_{AC}(a - a_{ave})\ (c - c_{ave}) + \\ & K_{BC}(b - b_{ave})\ (c - c_{ave}) + \\ & K_{ABC}(a - a_{ave})\ (b - b_{ave})\ (c - c_{ave})\end{aligned} \tag{4}$$

The final calculated response is:

$$R = R_{AVE} + \Delta R_{MAIN} + \Delta R_{INT} \tag{5}$$

In our case there was only one place where there were significant interactions (the Young’s Modulus data) and the values for R_{INT} were very small everywhere but there, and can typically be ignored. These equations were first assembled and used in Mathcad® and eventually incorporated into a simple-to-use format in Excel®.

As mentioned earlier, the model was tested with some known formulations, some of which were near the center points of the design. The results of some of these tests are tabulated below.

	Calculated	**Measured**
Test Formula #1		
Viscosity	12.1	12.2
T_G	6.7	7.1
Toughness	28	26
Modulus @25°	2.0 × 10^9	1.9 × 10^9
Test Formula #2		
Viscosity	11.3	.3
T_G	6.6	7.2
Toughness	26	28
Modulus @25°	2.2 × 10^9	2.1 × 10^9
Test Formula #3		
Viscosity	12.8	12.9
T_G	6.5	7.1
Toughness	30	28
Modulus @25°	2.0 × 10^9	2.2 × 10^9

The utility of the model can be illustrated by the following calculations dealing with manufacturing tolerances for the ink:

Example—If the weighing tolerances on all raw materials are +/- 3%, what is the worst variation expected for viscosity and $T_{G,}$ and can a viscosity spec of +/- 0.4 cPs be maintained? Plugging this variation into the model for a test formulation gives the following predictions:

Mean viscosity = 12.14 ($T_G = 6.7$)

Viscosity worst case high = 12.61 ($T_G = 8.0$)

Viscosity worst case low = 11.80 ($T_G = 5.5$)

Therefore the spec cannot quite be maintained with those tolerances if the worst case mixing error occurs.

Summary

This study illustrates a practical example of converting the “effect factors” from a standard “Hadamard” matrix experiment into a simple, easily used mathematical model. This model has been of use to us both as a formulation guide and in predicting changes in ink properties due to known or proposed manufacturing tolerances.