Solid Ink Formulation Optimization Using Design of Experiment (DOE) Methodologies

Michael B. Meinhardt
Xerox Corporation
Wilsonville, Oregon

Abstract

A novel solid ink system enables significant enhancements to jetting frequency, automatic document feed (ADF) performance, and enhanced "feel" while maintaining the excellent durability of legacy solid ink technologies. Development of this solid ink system required the balance of numerous performance properties against a host of system requirements. Design of Experiment (DOE) methodologies were used extensively to define the interrelationships between materials and their contributions to the various performance factors. Mechanical properties of the inks were defined by dynamic mechanical analysis (DMA). These mechanical properties were characterized as a function of component proportions and the ink components were classified according to their mechanical contributions to the system. Critical performance factors such as durability and ADF were linked to these properties throughout the developmental process. Finally, tradeoffs of performance features were defined and tolerances for component variation were established to ensure robust design performance.

Introduction

Solid ink printing represents a significant portion of the networked office color printing market utilizing the unique combination of PZT-driven jetting, phase change inks and an offset printing process. This technology provides excellent image quality due to the high holdout and excellent color reproducibility derived from solvent based dyes delivered via the solid ink carrier. These strengths simultaneously present significant technological challenges for implementation. The requirement of low viscosity (enabling high frequency jetting) conflicts strongly with the desire for polymer-like properties to impart durability and facile handling in document handling systems. The former is associated with low molecular weight materials, while the latter is associated with high molecular weight materials such as those found in xerographic toners.

Recent introduction of the Xerox Phaser® 860 and its ink system represents a significant departure from previous solid ink technologies. This novel ink system significantly improves document handling capability, reduces a "waxy feel" characteristic of previous solid ink carrier formulations and enables a substantially greater jetting frequency by means of decreasing the ink viscosity. These technical achievements have been accomplished by significantly hardening the ink formulation while simultaneously maintaining and improving the durability.

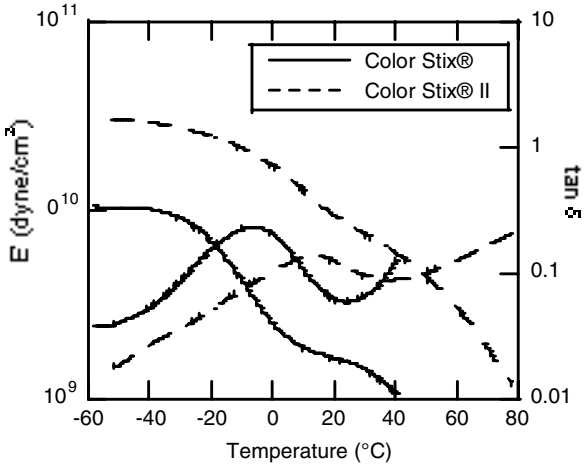

Figure 1. Dynamic Mechanical Analysis Profiles of Color Stix® and Color Stix® II Solid Inks

The dynamic mechanical analysis (DMA) profile shown in Figure 1 compares a legacy solid ink formulation to the novel ink formulation. Examination of the plots of elastic modulus as a function of temperature indicates that the storage modulus (E') of the novel ink formulation is significantly higher that previous solid inks. This translates to a harder and more resilient ink formulation; characteristics that greatly improve performance in document handling systems. An additional feature is the loss of definition in the rubbery plateau in the region from 0 to 40°C. The glass transition temperature, T_g, determined by the maximum in tan δ, is also approximately 20°C higher in the novel solid ink.

To obtain these physical characteristics and to maintain the requirements related to efficient jetting performance an entirely new set of ink carrier materials was required. A number of patents describing suitable materials for phase change inks have been published. However, the problem of

developing these materials into a fully functioning system subject to a host of pre-existing design constraints was a substantial one.

While previous published work has described the application of DMA to solid ink formulations,[1,2] this paper details how design of experiment methodologies were used to direct the formulation efforts and to quantitatively characterize the formulation space and finally optimize specific performance attributes.

Screening DOE

Initial ink definition required a broad screening method across a wide range of formulation and performance space. Four of the materials selected for development were loosely classified as viscosity modifiers (components A and B) or resins (components C and D). A fifth material, component E, was held to a constant level throughout the screening process.

A graphical technique was developed wherein the ratio of the viscosity modifiers to one another was plotted against the corresponding ratio of the resins. Treating each set of components as a constant, the ratio of viscosity modifiers to resins was adjusted pair-wise while maintaining a stringent viscosity constraint. Inks were prepared and characterized by several responses. Automatic document handling performance (ADF), jettability, and durability were mapped against the formulation ratios.

Examination of the response map clearly indicated that a high proportion of component A, a polyethylene wax, was desirable for optimal ADF performance. A second viscosity modifier, component B was requisite for jettability and material compatibility, albeit in low overall proportion. Durability was driven by the relative ratios of the resins. Whereas the high levels of component A proved enabling for ADF performance, a significant negative durability bias was simultaneously observed.

The net result of this screening method was to identify a workable region of formulation space based on the proportionality of the several components. In addition, the conflicting demands of two performance responses, ADF performance and durability, were made apparent and were noted for further optimization experiments.

Formulation DOE

Once a desirable region of the formulation space was identified, a more directed DOE in formulation was undertaken. This experiment served several purposes. First, a semi-mechanical model of the influences of the several components and their respective influences on the ink formulation was developed. Next, quantitative relationships between the formulation and the responses were established. These relationships served as "rules of thumb" for modifycation of ink behavior, as tools for manufacturing adjustment or for demonstrating mechanical robustness of the ink. Finally, the experiment permitted the development of an understanding of any trade-off between different responses.

The mechanics of performing these experiments are ably described in the works of Diamond[3] and Box, Hunter and Hunter.[4] As a practical matter, each component was varied by 20 percent around the nominal formulation determined in the screening experiment.

For most solid ink systems a linear response model as shown in Equation 1, is sufficient to model the ink performance.[2]

$$R=c_0+c_1x_1+c_2x_2+c_3x_3+c_4x_4+c_5x_5 \quad (1)$$

In this expression, a response, R, is seen to be the sum of the fraction of each component multiplied by its response coefficient and a central constant, c_0. For small changes in formulation around this central formulation Equation 1 reduces to (2) which can be derived from the fundamental theorem of multivariable calculus.

$$\Delta R=c_1\Delta x_1+ c_2\Delta x_2+ c_3\Delta x_3+ c_4\Delta x_4+ c_5\Delta x_5 \quad (2)$$

Since solid inks are known to exhibit polymer-like properties, a series of rheological responses were chosen as experimental responses. Specifically, the viscosity, η, the glass transition temperature, T_g, and the elastic modulus at various temperatures, $E'(T)$, were considered of primary importance. Additionally, the integral of log(tan δ) over a selected temperature range, where tan δ is the ratio of the loss and storage moduli, was monitored as a measure of toughness.

Response Matrix

The results of an eight trial designed experiment in five variables permitted a Resolution III analysis of the data. This resolution is adequate for a linear system devoid of substantial interactions of components.

Table I. Formulation DOE Response Coefficients

	Ink Component				
Response	**A**	**B**	**C**	**D**	**E**
η	-0.07	-0.09	0.19	0.08	0.01†
T_g	0.06†	-0.05†	-0.20	0.71	-0.92
$\int \log \tan\delta \, dT$	0.04	-0.14	-0.10	0.33	-0.17
$E'(25°C)$	0.10	0.03†	-0.23	0.03†	-0.11†
$E'(48°C)$	0.05	0.01†	-0.10	-0.02†	-0.05

The table above presents a series of response coefficients resulting from this designed experiment. The average response, c_0, has been withheld to emphasize the utility of the coefficients in estimating changes to the response of an ink formulation. The units of the coefficients should be read as the unit response change per one percent change component. Thus, a one percent change in the

proportion of component A yields a viscosity change of 0.07 units. The dagger symbols within the table indicate that within the range of the formulation DOE, the determination of the coefficient is statistically insignificant.

Characterization of Components

Analysis of the table above provided a means of identifying the mechanical contributions of each of the components. Viscosity modifiers A and B both served to decrease the viscosity of the ink formulation while resins C and D raised the viscosity. Resin C demonstrated the largest overall effect per unit formulation change.

A second example focuses on the glass transition temperature, T_g. Component C, a resin, exhibited a comparatively small effect on the glass transition temperature. The viscosity modifiers A and B were robust with respect to the T_g. Component E significantly decreased T_g, acting as a plasticizer. Finally, component D, a second resin, served to raise the glass transition temperature. The balance of the resin D to component E proved critical to controlling the durability of the printed inks.

The viscosity modifier A, a polyethylene wax, was the largest contributor to the storage modulus of the ink. In fact, a high proportion of this component was required for the most efficient document handling performance. However, the storage modulus in practice was quite robust with respect to formulation changes.

Formulation Sub-Optimization DOE

DOE methods were also used to optimize competing performance criteria at the printer system level. Specifically, fold durability was a function not only of the ink formulation but also the transfix architecture and parameters. At one point in the product development cycle a designed experiment to improve durability performance was undertaken. The experiment varied each component by 10% around its nominal value subject to the viscosity constraint. A good relationship between fold durability and E'(48°C) was empirically determined. In Figure 2 a graph of this relationship is shown. Smaller values of the durability response were preferred

The figure plots a durability metric over several media types as a function of formulation. The general robustness of the ink formulations was demonstrated by the cluster of six of the eight formulations in modulus and fold durability in the range of E' from 0.5 to 0.6 x 10^9 dyne/cm^2. Two formulations stood out as having significantly improved fold durability. The formulation with the lowest modulus and smallest durability response was chosen for the final product form.

Summary and Conclusions

Designed experiment techniques have been demonstrated in several ways to be an extremely efficient means of defining, characterizing, and enhancing the performance of phase change inks within a system of complex constraints. Coupled with mechanical models of physical behavior using techniques such as dynamic mechanical analysis, the formulator can envision and quantify the behavior of a solid ink formulation against the host of responses required to develop a robust printing system.

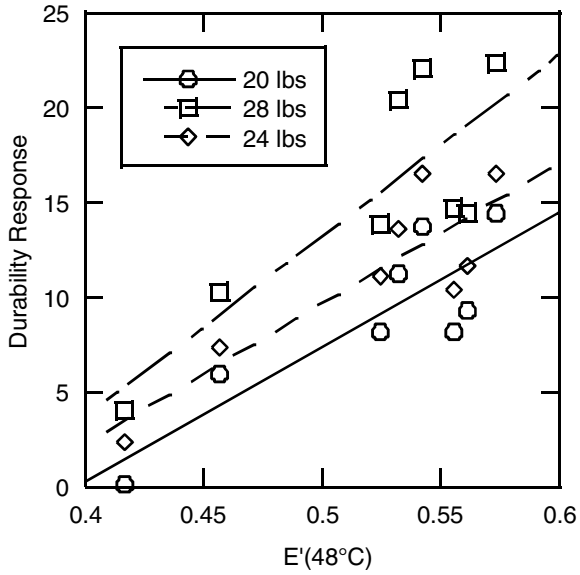

Figure 2. Durability Response versus Storage Modulus(48°C) for Various Media Weights

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Biography

Michael Meinhardt received his B.S. degree in Chemistry from The College of William and Mary in Virginia in 1985 and a Ph.D. in Organic Chemistry from the University of Wisconsin-Madison in 1992. As a post-doctoral researcher at Sandia National Laboratories he developed dyes for nonlinear optical applications. In 1994 he joined Tektronix, Inc. where he has continuously developed solid ink technologies. Dr. Meinhardt continues this work for Xerox Corporation since its acquisition of Tektronix Color Printing and Imaging division in January of 2000. He is a member of IS&T and the American Chemical Society.