
Rheological, Thermo-Mechanical and Viscoelastic Requirements of a Phase Change Ink for an Offset Ink Jet Printing Process

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Abstract

This paper will detail the development of a phase change ink for an offset ink jet printing process. The offset printing process is based upon a full array printhead delivering the molten ink on demand to a heated intermediate surface. The ink is then transfixed, fused and transferred, to the final media. The final printed ink must exhibit sufficient flexibility and durability, such that it does not crack or flake off when being folded or creased.

The ink was formulated to have specific fluidic properties to meet jetting requirements. Compression testing was performed on an MTS SINTECH 2/D to tailor the ink with the desired compressive and yield stress properties. In addition, Dynamic Mechanical Analyses (DMA) were carried out to determine the dynamic moduli, glass transition temperature (T_g) and $\tan \delta$ of the ink. The optimized ink represents a formulation customized for high temperature jetting and offset printing process.

Introduction

The Phaser® 340 printer, code name “ROGUE” during development, posed several additional technical challenges, due to the offset ink jet printing process, to the Tektronix phase change ink.¹ The phase change ink jet technology using a full array head jetting at 11 KHz required that all four of the process color inks to have uniform fluidic properties at jetting conditions. In addition, these inks must also have matched temperature dependence for jetting to account for any thermal profile across the head from normal production process variation.

Once jetted onto the drum, the inks will be fused at a slightly elevated temperature under high pressure onto

the paper and transferred off the drum in a peeling mode. During the hot fusing process, the inks are compressed above the yield stress. It is of paramount importance that the inks must not crumble or crack during the fusing process to ensure sufficient mechanical property for the concurrent transfer step.

Typical offset processes in lithography or electrophotography report transfer efficiencies near 80%.² This means that a cleaning station will be required and the printing speed (PPM) will suffer on continuous printing. We overcome the 80% transfer efficiency by changing the loci of failure during the transfer step. First, we optimized the ink physical properties to maintain its cohesive strength during the fusing and peeling steps. In addition, we coated the drum with a thin layer of silicone oil to lower the surface energy of the drum and serve as a sacrificial layer to ensure adhesive failure during the transfer step.

After being transfixed onto the media, the ink must possess the desired hardness needed to prevent blocking when being stacked together. Additionally, it must be tough, abrasion resistant and durable during the normal handling of the prints. To be a practical solution for office color printing, the ink must be flexible enough not to crack when the prints are folded or creased.

Experimental

The viscosities of these inks were measured on a Ferranti-Shirley cone and plate viscometer. The jetting data were obtained from a single-jet strobe stand. The compressive yield data were measured on an MTS SINTECH 2/D mechanical tester manufactured by MTS Sintech, Inc., using small cylindrical samples. The dimensions of a typical sample are about 19.0 ± 1.0 mm \times 19.0 ± 1.0 mm. Isothermal yield stress was measured as a function of temperature and strain rate. The material was deformed up to about 40%. The viscoelastic properties were measured on the Rheometrics Solid Analyzer (RSA II) using a dual cantilever beam geometry. The dimensions of the sample were

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about $2.0 \pm 1.0 \text{ mm} \times 6.5 \pm 0.5 \text{ mm} \times 54.0 \pm 1.0 \text{ mm}$. A time/cure sweep was carried out under a desired force oscillation or testing frequency of about 1 Hz and an auto strain range of about 1.0×10^{-5} to about 1%. The temperature range examined was about -60°C to about 90°C .

Results and Discussion

The viscous behavior of most liquids change dramatically with temperature.³ For Newtonian liquids and for polymeric fluids at temperatures far above their glass transition temperature or melting point, the viscosity follows the Andrade or Arrhenius equation to a good approximation:

$$\eta = K e^{E/RT} \quad (1)$$

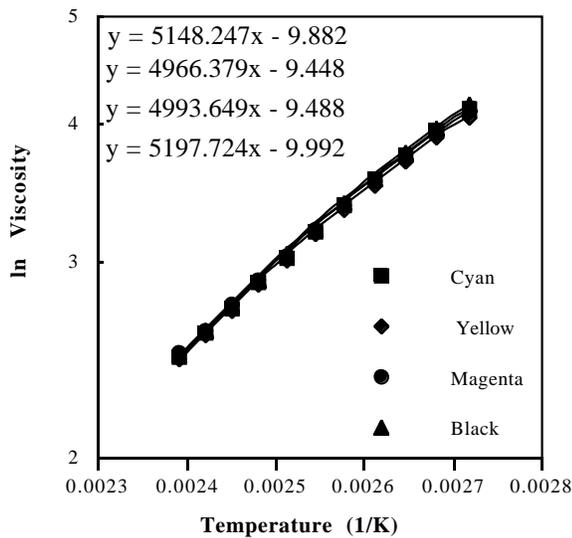


Figure 1. Arrhenius plot (\ln viscosity versus $1/T$ (K)) for Phaser 340 printer inks

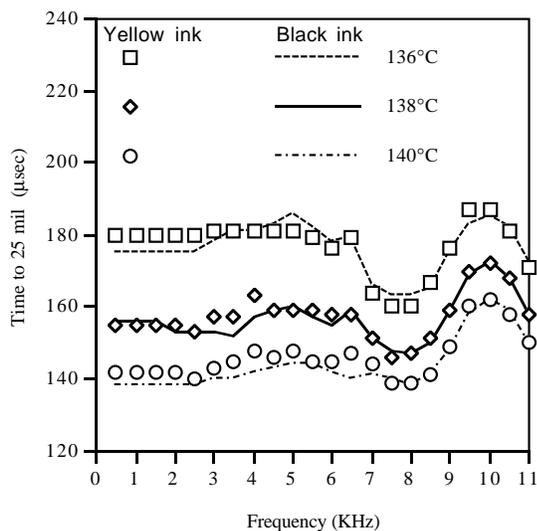


Figure 2. Jetting data as a function of frequency of two primary colors at various jetting temperature

At a given shear stress, K is a constant, characteristic of the polymer and its molecular weight, E is the activation energy for the flowing process, R is the gas constant, and T is the temperature in degrees Kelvin. The activation energy for polymeric fluids is in the range of 5 to 50 kcal/mole. Poly(dimethylsiloxane) has the lowest activation energy known, 4kcal/mole, due to the great flexibility of the oxygen-silicone linkages. The phase change ink used with the Phaser 340 printer is comprised mainly of waxy low molecular weight hydrocarbons, none of which are polymeric.^{4,5} Figure 1 shows a plot of \ln viscosity versus $1/T$ (K) for the four primary color inks. From equation 1, the average activation energy (E) for viscous flow of the inks is calculated to be about 10.1 kcal/mole. This value is in the range of values reported for high density polyethylene, 7.0 kcal/mole, and low density polyethylene, 11.7 kcal/mole.⁶ For high temperature jetting performance, the temperature dependence of each color ink must match exactly to enable precise dot placements and production of secondary colors. Figure 2 shows the jetting data as a function of frequency of two primary colors, black and yellow, at three different jetting temperatures. The jetting characteristics of all primary colors were normalized to the black ink.

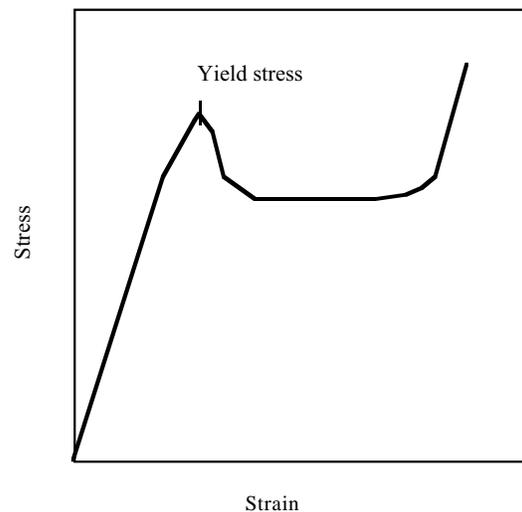


Figure 3. Typical stress strain curve of an ink coupon in compression

Figure 3 shows a typical stress strain curve for an ink coupon in compression. The yield stress, σ_y , is taken at the peak in the curve. Above the σ_y , the ink continues to flow without any additional applied stress. Figure 4 gives the plot of yield stress as a function of temperature. The isothermal yield stress curve shows two characteristic slopes with distinct changes in physical deformation. At lower temperature, the ink coupons yielded in a ductile manner giving barrel shape coupons. As the temperature increases in the range of about 30 to 50°C , the ink still yielded in a ductile manner, but there were appearances of shear bands criss-crossing at about a 45° angle. This seems to be the transition to a weak, crumbly behavior observed at higher temperature. Figure 5 is a plot of the yield stress versus temperature of

one of the key ingredients in the formulation, the viscosity modifier, superimposed over the previous yield stress curve. It is important to note that the yield stress value of the viscosity modifier follows the slope of the weak, cheesy yielding behavior observed in the ink. The deformed samples of the viscosity modifier show crumbly behavior over the entire temperature range.

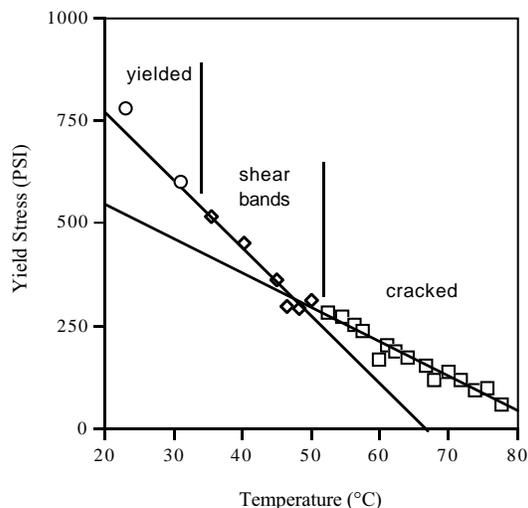


Figure 4. Yield stress as a function of temperature

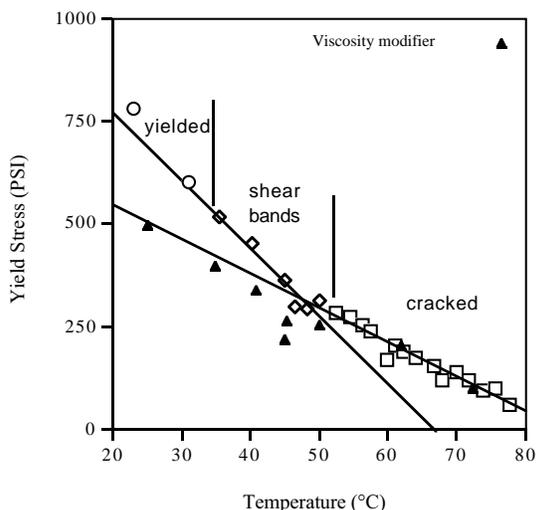


Figure 5. Overlay of yield stress data of the viscosity modifier

Under compression, inks deformed above the yield point will continue to flow without any additional applied stress. This must be due to the fact the yield stress has exceeded the activation energy for solid flow. It is of academic interest to see if the yielding of our ink follows the simplified Andrade-Eyring's model for solid flow:

$$\sigma_y = K e^{E/RT}. \quad (2)$$

Figure 6 shows a plot of $\ln \sigma_y$ as a function of $1/T$ (K). The activation energy for the solid flow during yielding is calculated to be about 9.3 kcal/mol, which is in

good agreement with the activation energy of the ink in liquid flow.

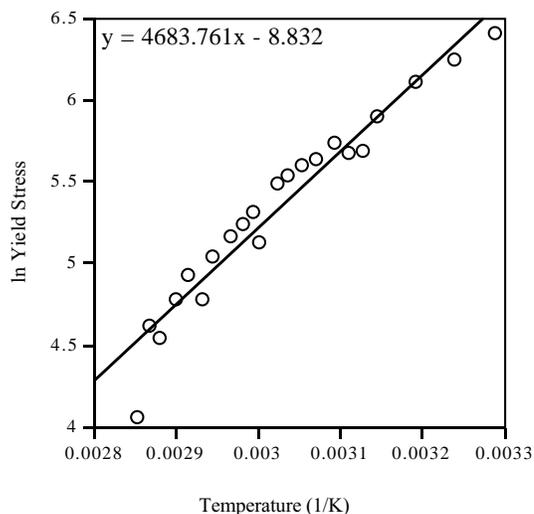


Figure 6. In yield stress vs. $1/T$ (K).

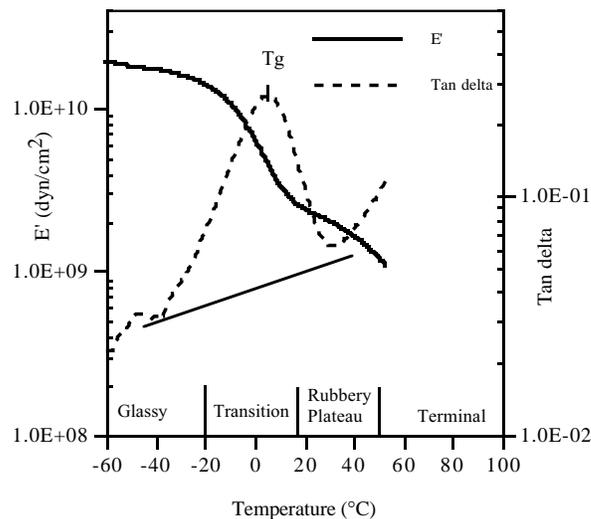


Figure 7. Dynamic viscoelastic data of Phaser 340 printer ink

Figure 7 shows a typical DMA curve of the ink used in the Phaser 340 color printer. The storage modulus (E') and $\tan \delta$ are plotted against temperature. The glass transition temperature, T_g , is taken at the peak of the $\tan \delta$ curve. The glass transition temperature is the temperature at which an ink goes from a glassy state to a tough, leathery state. The curve of storage modulus versus temperature can be subdivided into several zones of elastic behaviour:⁷

1. Glassy zone: $T < T_g$; constant $E' \approx 10^{10}$ dyne/cm²; motions are mainly due to vibrations of atomic groups.
2. Transition zone: $T \approx T_g$; 1-3 order magnitude drop in E' ; motions are due to short range diffusional motion.
3. Rubbery plateau: $T > T_g$; characterized by a slightly negative E' slope; motions are due to rapid short range diffusional and retarded long range motions.

4. Terminal zone: $T < T_m$; a second big drop in E' ; motions are due to slippage of long range entanglements and configurational changes.

The glass transition temperature of the ink is well below room temperature. This is of critical importance to ensure that the ink, once printed on the page, remains flexible and does not crack or flake off when being folded at ambient temperature. The $\tan \delta$ is the ratio of loss modulus (E'') to storage modulus (E'). This is a ratio of the amount of energy a material can dissipate, i.e., toughness. Hence, the area under the $\tan \delta$ curve is a good measure of toughness. The higher the value the more energy the ink can dissipate. The length of the rubbery plateau is marked by the two softening temperatures of the ink. The first softening transition occurs in the transition zone, and the second softening transition occurs in the terminal zone. The rubbery plateau of the ink represents a window of usage temperature for the ink. Van Krevelen has found that for amorphous polymers the storage modulus can be correlated as follows:

$$E' \approx \rho RT_g/M_{cr} \quad (3)$$

while the length of the rubbery plateau, ΔT , may be approximated by the equation:

$$\Delta T \approx 10^2 \Delta \log M_n/M_{cr} \quad (4)$$

where, ρ is the density, M_{cr} is the critical molecular weight for entanglement, and M_n is the number average molecular weight. The M_{cr} for high polymers is typically in the range of 4 to 35×10^3 g/mole. However, the molecular weights of the waxy components of the Phaser 340 printer ink are in the range of 0.5 to 3×10^3 g/mole, which is well below the critical molecular weight for entanglement. It is hypothesized that the rubbery plateau seen in Figure 7 for the Phaser 340 printer ink formulation arises from intermolecular hydrogen bonding.

Conclusions

A phase change ink was developed for high temperature jetting and for subsequent offset printing. The high temperature rheology of the ink was formulated to have uniform fluidic properties at jetting conditions. Yielding behaviors of the ink were characterized to optimize the hot fusing process, without inducing cohesive failure in the ink. Dynamic viscoelastic properties of the ink were examined to ensure the final toughness and flexibility of the ink on paper.

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