Rheological, Thermomechanical, and Viscoelastic Requirements of an Ink-Jet Phase-Change Ink for an Offset Printing Process*

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This paper details the development of an ink-jet phase-change ink for a drum-based offset printing process. The offset printing process is based on a page-wide printhead delivering molten ink droplets on demand to a heated intermediate drum surface. The ink is then fused and transferred (transfixed) to the final print medium. The transfixed ink must exhibit sufficient flexibility and durability such that it does not crack or flake off when the print is folded or creased. The ink was formulated to have specific fluidic properties for ink-jet printing. Compression testing was performed on an MTS SINTECH 2/D to tailor the ink formulation for desired compressive and yield stress properties. In addition, dynamic mechanical analyses were carried out to determine the dynamic moduli, glass transition temperature, and tan δ of the ink. The optimized ink represents a formulation customized for high-temperature jetting and an offset printing process.

Journal of Imaging Science and Technology 40: 386–389 (1996)

Introduction

The Phaser® 340[‡] printer was code named "Rogue" during its development. The revolutionary offset ink-jet printing architecture added new technical challenges to the design of the Tektronix phase-change inks.[1] The four phase-change inks, cyan, magenta, yellow, and black, required uniform fluidic properties in order to achieve predictable ink-jet performance in all 352 jets of the page-wide printhead. The temperature variation across the full printhead width required that the inks have matched fluidic properties with the same temperature dependence. This temperature dependence window had to accommodate the typical operating temperature variance of all the manufactured printheads.

After the inks are jetted onto the drum, the inks are fused at an elevated temperature under high pressure and transferred off the drum in a peeling mode onto the print medium. During the hot fusing process, the inks are compressed above their yield stress. It is of paramount importance that the inks not crumble or crack during the fusing process to ensure sufficient mechanical strength for the concurrent transfer step.

Typical offset processes in lithography or electrophotography report, transfer efficiencies near 80%,[2] which means that a cleaning station is required, adding complexity to the printer design and also possibly affecting the printing speed in a continuous printing mode. The usual 80% transfer efficiency was overcome by changing the loci of failure during the transfer step. First, the ink physical properties were optimized to maintain cohesive strength during the fusing and peeling steps. In addition, the drum was coated with a thin layer of silicone oil to lower the surface energy of the drum and to serve as a sacrificial layer to ensure adhesive failure at the drum surface during the transfer step.

After being transfixed onto the print medium, paper or transparency, the ink must possess the hardness needed to prevent blocking when prints are stacked on top of one another. Additionally, the inks must be tough, abrasion resistant, and durable during the normal handling of the prints. To be a practical solution for office color printing, the inks must be flexible enough not to crack when the prints are folded or creased.

Experimental

The ink viscosities 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 (MTS Sintech, Inc), using small cylindrical samples

Original manuscript received March 16, 1996.

* Presented in part at IS&Ts 11th International Congress on Advances in Non-Impact Printing Technologies, October 29–November 3, 1995, Hilton Head, South Carolina.

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‡ Phaser® is a registered trademark of Tektronix, Inc.

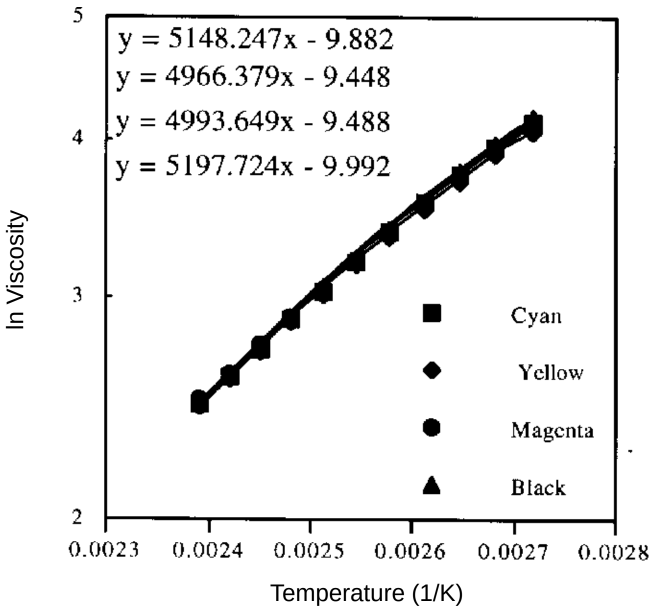

Figure 1. Arrhenius plot [ln viscosity versus $1/T$ (K)] for Phaser 340 printer inks.

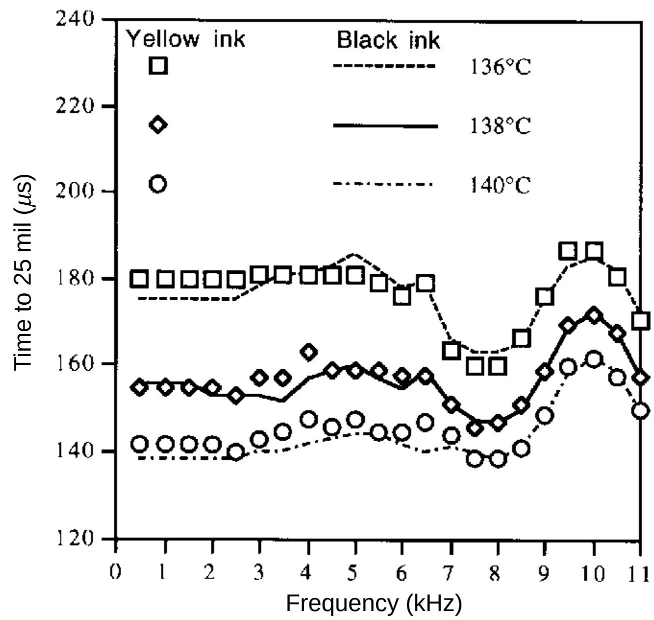

Figure 2. Jetting data as a function of frequency of two primary colors at various jetting temperature.

typically 19.0 ± 1.0 mm in diameter by 19.0 ± 1.0 mm thick. 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 a Rheometrics solid analyzer (RSA lI), using a dual cantilever beam geometry. The dimensions of the sample were about 2.0 ± 1.0 mm × 6.5 ± 0.5 mm × 54.0 ± 1.0 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 ~ 1.0×10^{-5} to ~ 1%. The temperature range examined was ~ –60°C to ~ 90°C.

Results and Discussion

The viscous behavior of most liquids changes 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:

$$\eta = Ke^{E/RT}. \tag{1}$$

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 Kelvin. The activation energy for polymeric fluids is in the range of 5 to 50 kcal/mol. Poly(dimethylsiloxane) has the lowest activation energy known, 4 kcal/mol, due to the great flexibility of the oxygen–silicone linkages. The phase-change ink used with the Phaser 340 printer comprises mainly 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 Eq. 1, the average activation energy (E) for viscous flow of the inks is calculated to be about 10.1 kcal/mol. This value is within the range of values reported for high-density polyethylene, 7.0 kcal/mol, and low-density polyethylene, 11.7 kcal/mol.[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.

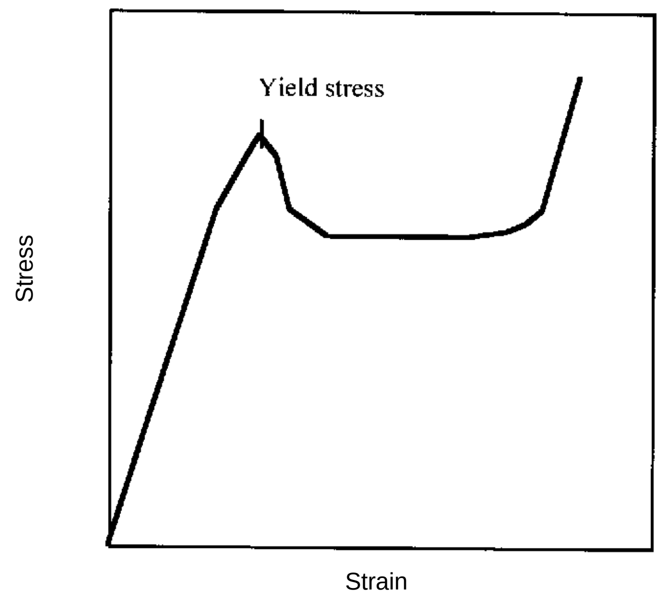

Figure 3. Typical stress–strain curve of an ink coupon in compression.

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 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-shaped coupons. As the temperature increased in the range of ~ 30 to 50°C, the ink still yielded in a ductile manner, but there were appearances of shear bands crisscrossing 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

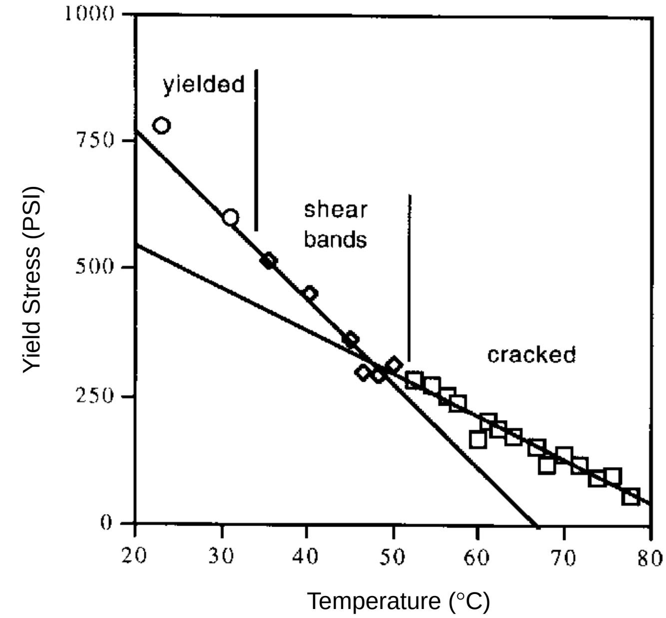

Figure 4. Yield stress as a function of temperature.

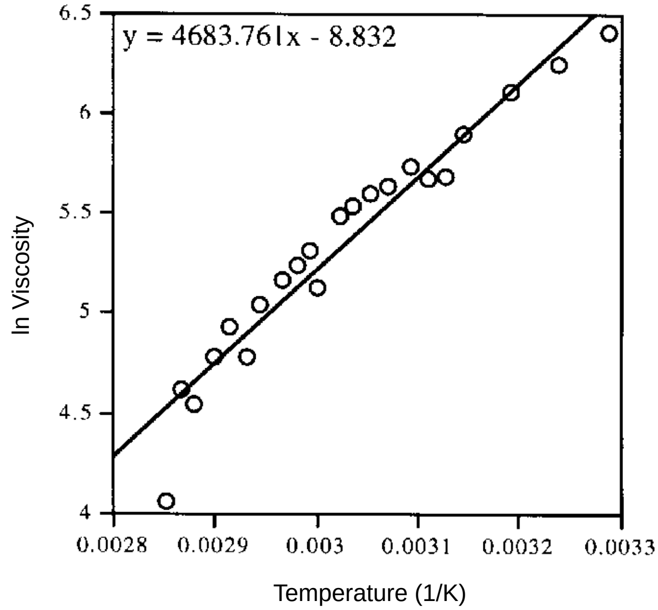

Figure 6. The ln yield stress versus $1/T$ (K)

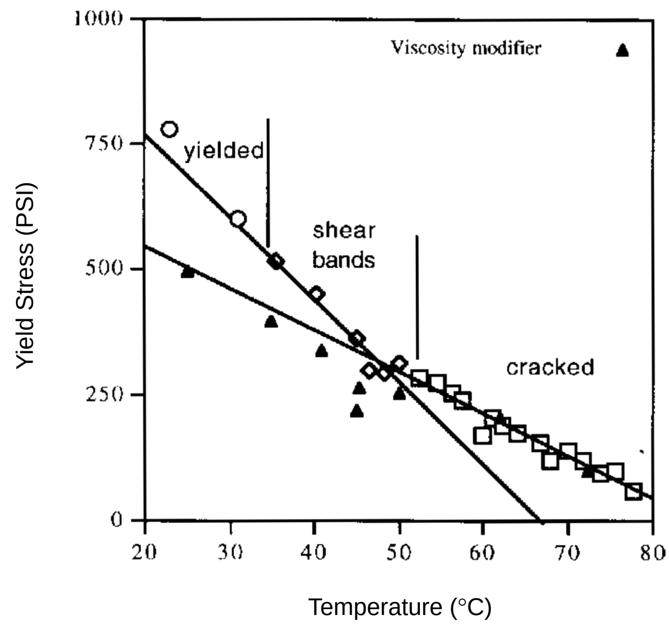

Figure 5. Overlay of yield stress data of the viscosity modifier.

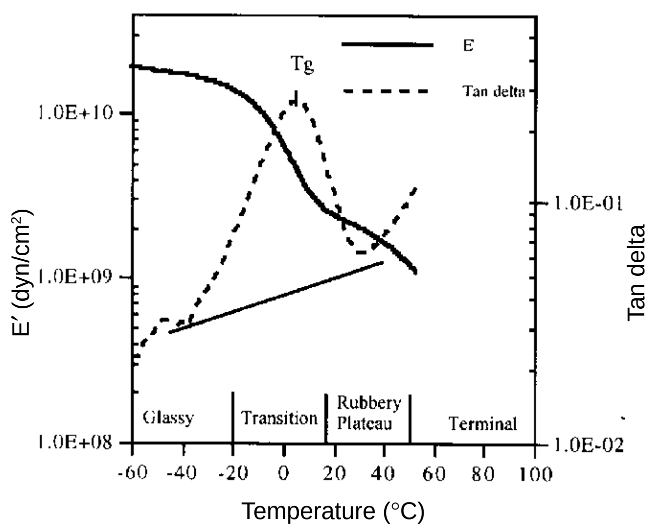

Figure 7. Dynamic viscoelastic data of Phaser 340 printer ink.

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.

Under compression, inks deformed above the yield point will continue to flow without any additional applied stress. This must be because 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:

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

Figure 6 shows a plot of ln σ_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 7 shows a typical dynamic mechanical analysis (DMA) of an ink used in the Phaser 340 color printer. The storage modulus (E') and tan δ are plotted against temperature. The glass transition temperature, T_g, is taken at the peak of the tan δ 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 behavior[7]:

1. *Glassy zone*: $T < T_g$, constant $E' \approx 10^{10}$ dyne/cm^2; motions are mainly due to vibrations of atomic groups.
2. *Transition zone*: $T \approx T_g$; 1 to 3 orders of 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. Tan δ is the ratio of loss modulus (E'') to storage modulus (E'). This ratio indicates the amount of energy a material can dissipate, i.e., toughness. Hence, the area under the tan δ 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:[7]

$$E' \approx \rho R T_g / M_{cr}, \tag{3}$$

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

$$\Delta T \approx 10^2 \, \Delta \log M_n / M_{cr}, \tag{4}$$

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/mol. 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/mol, which is well below the critical molecular weight for entanglement. We therefore hypothesize that the rubbery plateau seen in Fig. 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 refusing 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.

Acknowledgments. The authors wish to thank Theresa Brown, thermal analytical technician at Tektronix Ink Research and Development Analytical Services for performing the critical sample preparations.

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