An Investigation of Blocking Transfer in Phase Change Inks

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Abstract

Conventional blocking test procedures are of the "pass/ fail" type. Unfortunately for the formulation scientist, this criterion provides little guidance in the way of improving an ink formulation. To address inadequacies of a conventional ASTM blocking test method, a new procedure was developed to evaluate printed ink transfer in a phase change ink system using a Sencorp Laboratory Sealer. For phase change ink compositions, blocking behavior is shown to be a function of time, temperature and pressure. At various time and pressure combinations a thermal activation barrier must be crossed before transfer is observed. Moreover, it was shown that this behavior can be derived from the principles of polymer science. Specifically, viscosity and modulus are important factors in the blocking behavior of phase change inks.

Introduction

Blocking can be simply defined as the adhesion between layers of materials such as occurs under moderate temperatures and pressures.[1] Alternatively, blocking is "the undesirable adhesion of adjacent layers of materials in rolls or sheets."[2] Other than the ink formulation itself, factors influencing blocking behavior for printing inks and adhesives are media, pressure, temperature and humidity.

In a typical test method, specimens are placed between plates under small loads for 24 hrs at a specified temperature and humidity.[1] Samples are then judged as pass or fail at the given test conditions. The difficulties associated with this test are several: 1) the time required to complete the test, 2) the subjective nature of the result and 3) the relatively narrow load range applied. Additionally, should some blocking be inevitable, there is little way to quantify the result or link the magnitude of the transfer to the ink composition. For example, a quantitative designed experiment linking blocking transfer to the ink composition could permit the minimization of blocking transfer with respect to the ink formulation.

In the evaluation of a phase change ink composition at Tektronix, slight blocking transfer was observed in printed test samples using conventional test methods. Procedural irregularities such as paper cockling and localized off-set could not be adequately controlled, thereby complicating the analysis. The question as to what degree blocking transfer could be controlled by reformulation was a critical one, but first a more reliable test method was required. The extended time frame of conventional test methods, combined with the procedural complications described above demanded the development for a faster and more quantitative method.

From previous experience, small amounts of color could be readily and accurately quantified using a color measurement device. A standard method to reproducibly induce *some* blocking transfer (threshold blocking) was required whereby test formulations could be compared and optimized with respect to blocking performance. This paper describes the results of an investigation to determine appropriate blocking test conditions and an interpretation of the transfer behavior in terms of the ploymer-like properties of the phase change inks tested.

Description of Test Procedure

Solid fill print samples were prepared on an Phaser® 340 printer. The printed side of the page was covered with a clean sheet of paper and the two sheets were placed between the platens of a Sencorp Laboratory Sealer at a specified temperature, time and pressure. The sheets were then removed and separated from one another. The color transferred to the receiving sheet was characterized using a color measurement device. Transferred color was reported either as ΔE relative to an unprinted sheet of paper or as a ratio of the transferred color to a solid fill section ($\Delta E/\Delta E_{reference}$).

Results and Discussion

Temperature Dependence

During the initial investigation it became apparent there was a strong temperature dependence on blocking transfer of phase change inks. Near ambient temperature no offsetting was observed even after several tens of minutes at 60 psi. Increasing platen temperatures to about 30°C below the melting point of the phase change ink led to transfer of a small but quantifiable amount of color after a few seconds or minutes. The temperature-accelerated transfer led to a reproducible and time-efficient test method. Whereas the previous tests took 24 hours to run, quantitative results could now be obtained in minutes.

Time and Pressure Dependence

Investigations varying time and pressure revealed a complex relationship between the extent of blocking transfer and the test conditions. A plot of transferred color (ΔE) as a function of time indicated the extent of transfer varied with both the applied pressure and its duration. While intuition would suggest that either longer times or higher pressures would lead to greater off-setting, the observed behavior complicated interpretation of the results. For example, the question of which test conditions to use might need to be addressed.

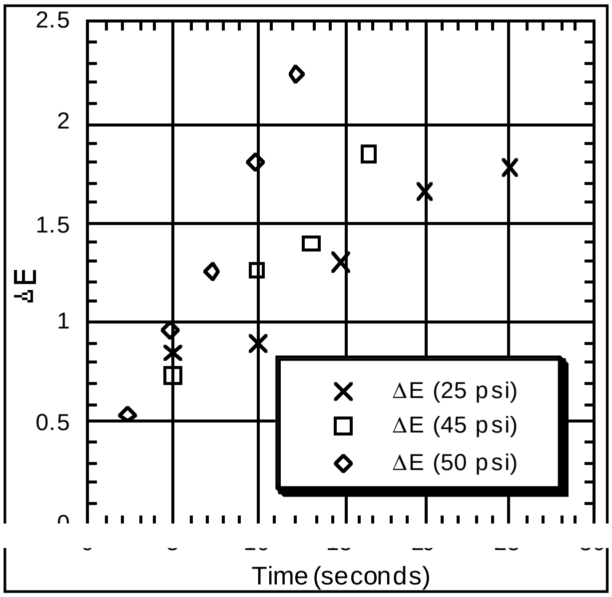

Figure 1. Color Transfer versus Time at Various Pressures (T = 60℃).

A more universal scheme was developed by plotting the extent of transfer as a function of the pressure-time product. (See Figure 2.) This method simplifies the problem of a single test point by representing a wide range of pressures and durations. The slope of the line can be used as the metric of blocking transfer performance with steeper slopes corresponding to poorer blocking behavior.

The observed linear relationship between extent of transfer and the pressure-time product is not entirely unexpected considering possible mechanisms of color transfer. One possible mechanism for the transfer of printed ink between test sheets is viscous flow. In fact, dimensional analysis reveals the pressure-time product to have the same units as viscosity. The polymer-like properties of Tektronix phase change inks have been described previously.[3-4] It is not surprising therefore that extended times and pressures lead to greater blocking transfer.

A comparison of the performance of two phase change inks is shown in Figure 3. Ink 1 contained a relatively low level of plasticizer and was much less susceptible to offsetting relative to the Ink 2. This behavior is consistent with standard printing ink formulation experience.[5] In viscosities terms, the activation energy to viscous flow is lower for Ink 2 than for Ink 1 at the test temperature.

Blocking transfer of phase change inks may be considered as flow of a viscoelastic material from one surface to a second surface under the influence of time, temperature and pressure. Once the activation barrier has been crossed and sufficient flow and deformation have taken place, some portion of the ink will transfer between pages. Indeed, phase change inks used in Tektronix printers such as the Phaser® 340 have essentially polymer-like properties

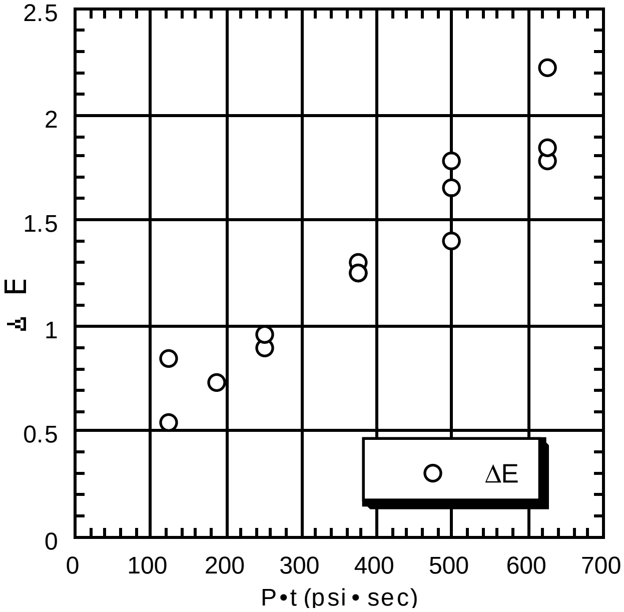

Figure 2. Color Transfer at 60℃ versus the Pressure Time Product

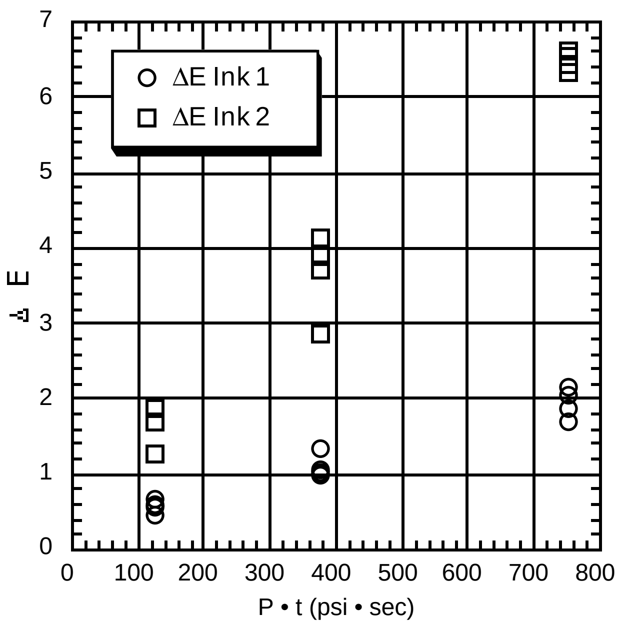

Figure 3. Blocking Transfer Comparison of Two Ink Formulations

which have been described previously.[3-4] Other possible transfer mechanisms such as adhesive failure[6] and thermal phase transition[7] have been described but do not seem to be operating under the test conditions.

For a Newtonian fluid far above the glass transition temperature the activation energy for flow is essentially independent of temperature, following the Andrade Equation:[8]

$$\eta = K\exp[E_a/RT]. \qquad (1)$$

For materials at temperatures less than about 100°C above their glass transition temperatures the Williams-Landel-Ferry (W-L-F) equation holds:

$$E_a = 4.12 \times 10^3 \cdot T^2 \cdot (51.6 + T - Tg)^{-2}. \qquad (2)$$

Under the test conditions described in this paper phase change inks are in the W-L-F regime for polymeric materials. As a result of this relationship, different blocking performance should be expected for phase change inks of differing glass transition temperatures. Ink 2 in Figure 3 has a lower glass transition temperature than Ink 1 and is therefore less resistant to viscous flow under the test conditions. In addition, Ink 2 has a lower elastic modulus (E') than Ink 1 and can be characterized as softer or more yielding. This too, is consistent with the observed transfer behavior.

Temperature Dependence of Blocking Transfer in Other Ink and Printer Systems

The principles described above were applied to other ink and printer technologies. Using the procedure described, blocking transfer of color toner print samples was evaluated. In a limited study, a strong temperature dependence of blocking transfer was observed. Under high time and pressure conditions (1000 psi•sec) and within a narrow temperature range, color toner prints exhibited dramatically different behavior. Virtually no transfer was observed at 70°C and less than 5% transfer was observed at 75°C. However at 80°C, transfer was almost complete at 35%. (It is noted that at equilibrium, half of the toner should be on each sheet, a transfer of 50% would then be a maximum.) The polymeric nature of color laser toner materials is revealed in its blocking transfer behavior.

Print samples from a thermal wax transfer printer were tested with dramatically different results. At low to moderate temperatures (40-60°C) and a range of times and pressures virtually no blocking transfer was observed. Catastrophic failure was observed when the melting point of the thermal wax was reached. This behavior can be understood based on the crystalline nature of the thermal wax system. In the absence of a softening point, the wax remained crystalline up to the melting point where it melted completely into the receiving sheet.

Conclusions

1. Blocking performance of phase change inks was shown to be a function of the product of time and pressure once a thermal activation barrier had been crossed.
2. The test method can be used to provide absolute or relative performance data useful for comparing phase change or polymer-based ink systems.
3. The test method provides a means of performing accelerated tests.
4. The test method may be applied to polymeric systems once the temperature of activation has been determined.
5. The test method is not able to provide direct comparison of greatly dissimilar polymeric systems due to substantial differences in activation energy.

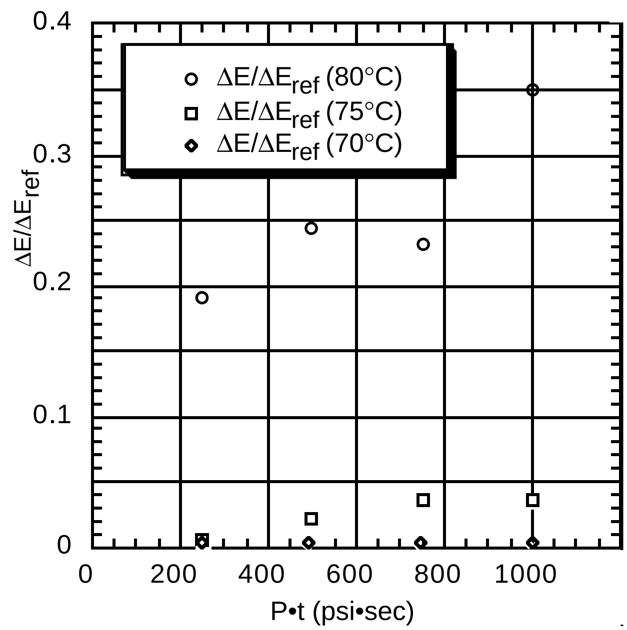

Figure 4. Temperature Dependence of Blocking Transfer in Color Laser Toner Prints

Acknowledgments

The author wishes to thank Janel Velander of Tektronix Inc., Technical Support for providing the thermal wax transfer and color toner prints described in this paper. Also, Drs, Daniel Hahn and Loc Bui of Tektronix Inc., Color Printing and Imaging for helpful discussions.

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