Thermodynamics of the Digital Transfer Printing Process

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Abstract

The digital transfer printing process is divided into two steps: i) the digital print of an image on the transfer paper and ii) the thermal transfer (sublimation process) of the printed image onto the textile or other polymer substrates.

Based on the sublimation model the thermal transfer process is explained and the critical physical parameters are evaluated: affinity of the dye to the paper and sublimation enthalpy of the dye.

Analyzing the spectral behavior of transfer dyes transferred at different temperatures the activation energy for the transfer printing process is evaluated and compared to the sublimation enthalpy of the dye.

The spectral behavior of transfer papers before and after transfer show a dramatic change in shade. This clearly indicates a fixation of the transfer dye on / in the paper surface. As a conclusion to evaluate the whole transfer printing process it is necessary to take the distribution equilibrium between the paper and the substrate into account: The higher the affinity of the paper to the dye, the lower is the color strength on the substrate.

Based on the physical properties of transfer disperse dyes the consequences on color generation and reproducibility are discussed.

Introduction

The total textile printing production is about 24 billion square meters per year. In traditional analogue printing approximately 8000 printing machines are used world wide dominated by rotary screen machines. In traditional printing the fibers that are printed cover the complete spectrum with cotton (>50%), Rayon / Viscose (~14%), Polyester (18%) and Polyester / Cellulose mixtures (~12%) being the major types.

The colorants used have been developed over the last 120 years to achieve the technical application and color fastness requirements demanded by the industry.

The majority of textile printing is carried out by direct printing, followed by processing of the printed textile to achieve fixation and washing to achieve end users' fastness requirements. The textile printing technology used is both capital intensive and requires a high worker skill base.

A second approach to printing is to use "Vapor Transfer printing ", where an image is printed with specific disperse dyes onto paper and then transferred to the polyester by a heat transfer process.

Vapor Transfer Printing was developed commercially in 1965 by Sublistatic SA of France, being based on an earlier French Patent (1).

Currently, textile thermal transfer printing accounts for approximately 6% of all textile printing, which means a third of all polyester is printed by this route.

The use of ink jet in thermal transfer printing with disperse dyes was first proposed in 1977(2). Currently digital transfer printing is used for sample printing as an integral part of the design selection and production process. Also for certain industries which have small run production requirements, such as the flag/banner and sportswear industries, digital transfer printing is increasingly being used for small production runs.

As industrial production ink jet printers become increasingly available in the future, increased production printing of transfer paper will be carried out by digital printing.

The Transfer Printing Model

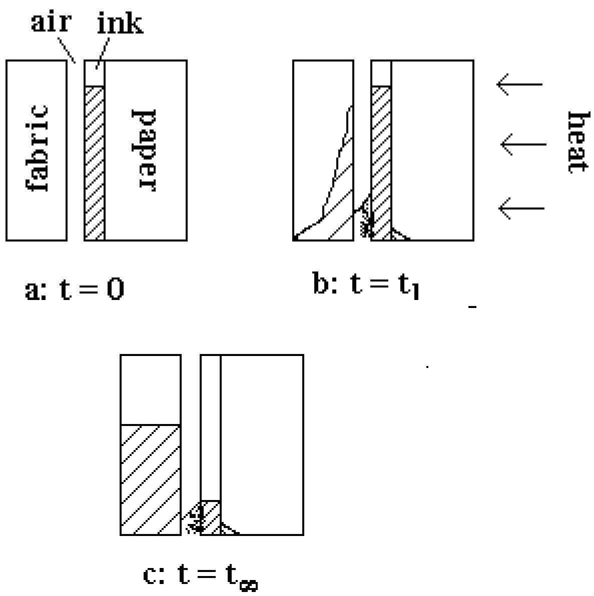
The first detailed studies of the Vapor printing transfer process was by Fenoglio and Gorondy (3) and Griffiths and Jones (4) in the 1970's.

Based on their models (Figure 1) three phases are involved in the thermal transfer process:

i) the dye layer printed on paper,
ii) a vapor phase transfer of the dye
iii) the polyester textile as the receiving substrate.

There are three physical processes involved in the transfer process:
i) the vaporization of the dye,
ii) the diffusion of the dye across the air gap
iii) dissolving the dye in the polyester substrate.

Fig 1: The Thermal Transfer model



Step 1

In the first step the dye has to vaporize. The available concentration of the dye, proportional to its partial pressure p, in the Vapor phase is described by the equation of Clausius -Clapeyron (5,6):

$$\frac{dlnp}{dT} = \frac{\Delta_v H}{R\ T^2} \qquad (1)$$

Transfer of the available dye at a constant temperature in the gas phase is constant as long as sufficient dye is available in the ink layer and assuming that there is no or only a slight solubility of the dye in the ink layer or paper.

The partial pressure of the dye is determined by the heat of vaporization $\Delta_v H$ and of the transfer temperature, T.

Step 2

The transport of the dye across the air gap is controlled by a diffusion process (5,6), which can defined by Ficks 1st Law of Diffusion.

$$\frac{\dot{N}}{F} = D\ \frac{\delta c}{\delta x} \qquad (2)$$

As long as there is enough dye in the ink layer the concentration of dye vapor at the paper surface is constant. Therefore the diffusion step controls the time needed for the transfer. The transfer itself is conducted to a first approximation at constant temperature and pressure. Assuming that the transfer temperature of the polyester/printed paper combination is reached much faster than the transfer time a steady state has to be expected with a defined partial vapor pressure at the surface of the paper and a defined partial vapor pressure of the dye at the textile surface.

Step 3

At the transfer temperature the polyester textile is above its glass transition temperature (Tg) Therefore, as soon as the dye reaches the polyester surface it is immediately dissolved in the polyester by a “solid solution” mechanism (7). Because the dye is not absolutely insoluble in the paper / ink layer, according the Distribution Law of Nernst, an equilibrium between the concentration of the dye in the paper / ink layer and the polyester (5) has to be taken into account:

$$K = \frac{c_{dye\ polyester}}{c_{dye\ paper}} \qquad (3)$$

This equilibrium determines the amount of dye transferred.

The temperature dependence of K (the dye distribution ratio) is given by the following equation (5):

$$\frac{dlnK}{dT} = \frac{\Delta_L H}{R\ T^2} \qquad (4)$$

Here, K is the distribution coefficient between the two phases, T the temperature and $\Delta_L H$ the differences of the enthalpy of solution for the dye in the two different phases. This distribution between the two phases is temperature dependent if $\Delta_L H$ is different from zero, otherwise a temperature independent equilibrium state is observed. The temperature dependence on K increases the higher the differences in $\Delta_L H$.

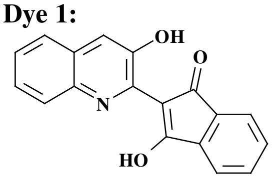
In this model the time needed for establishing this equilibrium should be determined by the diffusion process and the available concentration of the dye in the vapor phase.

Experimental Work

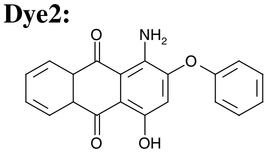
For the investigations of the transfer behavior four disperse dyes were evaluated (Table 1).

Table 1: Structures of Four Disperse Dyes Studied

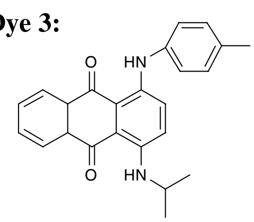
Dye 1:



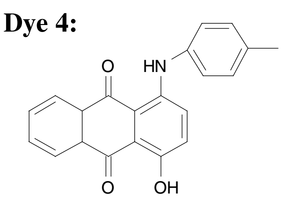
Dye2:



Dye 3:



Dye 4:



The dyes were formulated as inks and then printed with an ENCAD Novajet III (thermal drop on demand) on two types of paper. The printed papers were then transferred with a heat press to the polyester textile (the applied pressure was 6 bar).

Two different papers were used: i) a specially developed paper for vapor phase digital transfer printing, and ii) a standard high quality coated ink jet paper for photo quality printing.

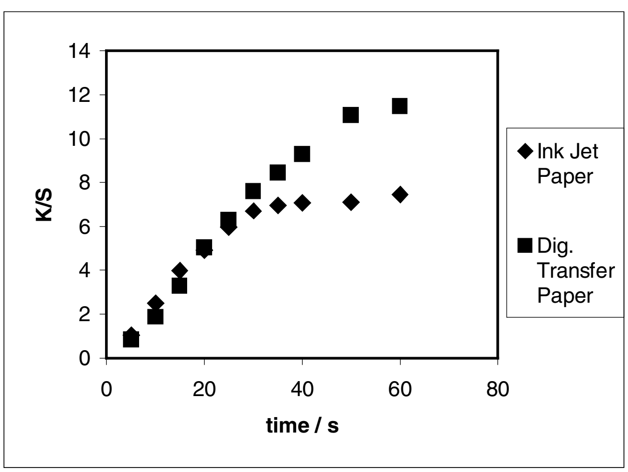
To evaluate the effect of temperature, the printed papers were transferred at three temperatures: 170°C, 190°C and 210°C. The amount of dye on the printed paper and the remaining dye on the transferred paper, was determined by extracting the dye in a soxhlet extractor with toluene and determining dye amounts by spectroscopic methods. The dye transferred to the textile was calculated from the difference between the amount of dye printed on the paper and the remaining dye on the paper after the transfer. The dye transferred to the polyester was then correlated with the reflectance data of the printed polyester using Kubelka Munk theory.

To evaluate the effect of transfer time the printed paper were transferred up to 60 seconds in steps of 5 and 10 seconds at a constant temperature of 210°C. the resultant color depth was evaluated by reflectance data.

Results

The influence of the transfer time for the two different papers on the resultant color strength is displayed in Figure 2. Two regions are observed: At low transfer times a continuous slope, identical for both types of papers, is observed. At high transfer times the curve levels out to an equilibrium state were any increase in transfer time does not increase the color depth.

Figure 2: Color Strength of Dye 3 at 640 nm versus Transfer Time in Seconds



According to the model we observe a linear increase of K/S on the polyester in accordance with Kubelka Munk theory (i.e. K/S is proportional to the concentration). This is consistent with a diffusion controlled transfer process of the disperse dye. Interestingly, the slope for both types of paper is the same, indicating that there appears to be no influence of the paper on the rate of diffusion. This indicates that the vapor pressure of the dye at the boundary is the same for both types of paper. Therefore, it seems that the dye particles in the ink are placed on the surface of the paper and, in the main, do not penetrate into the paper during the ink jet printing process.

In Table 2 the distribution coefficients (K) of the dyes between the paper and the polyester are shown. The distribution coefficient (K) is calculated according to Equation 3. It is clearly seen that the two different papers have different " retaining power" for the disperse dyes.

Table 2: Distribution Coefficients K of the dyes between paper and polyester textile

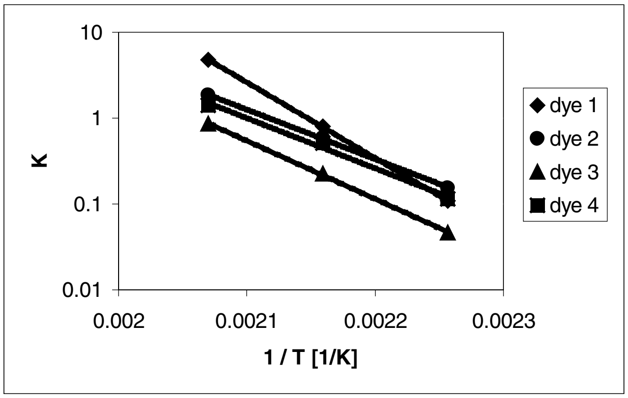
	Photo Quality Ink Jet Paper	Digital Transfer paper	Ratio of K (Digital) to K (Coated) papers
Dye 1	4.80	21.25	4.56
Dye 2	1.85	9.42	5.09
Dye 3	0.85	4.19	4.93
Dye 4	1.41	6.20	4.39

This is also consistent with Figure 2. The color strength levels out, indicating that there is no further transfer of dye to the textile i.e. an equilibrium of the dye between the polyester substrate and the paper / ink layer has been reached.

A ratio of the distribution coefficients for the two types of paper for each of the 4 different disperse dyes gives a very consistent result, indicating that the specific paper has a similar effect on each of the 4 disperse dyes, even though they have different chemical structures and vapor pressures.

In Figure 3, the distribution coefficient K between the polyester textile and the ink jet photo quality paper is plotted against the inverse of the absolute temperature.

Figure 3: Distribution coefficient K as a Function of temperature for Dye 1 to 4 on photo quality ink jet paper



There is clear exponential increase of K with temperature consistent with the expected behavior according to Equation 4.

The slope of the curves is a measure of $\Delta_L H$. As $\Delta_L H$ is very similar for this selection of four dyes, this implies that if any these dyes are used in combination to obtain a specific new shade then we would obtain a uniform color build up of shade. Furthermore, the shade will also be consistent even if there were small temperature changes that can occur in a production heat transfer press.

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In Figure 4, the distribution coefficient K between the polyester textile and the digital transfer paper is plotted against the inverse of the absolute temperature

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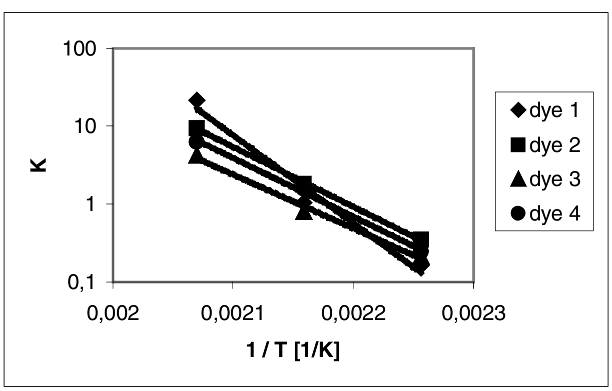
Figure 4: Distribution Coefficient (K) as a Function of temperature for Dyes 1 to 4 on Digital Transfer Paper

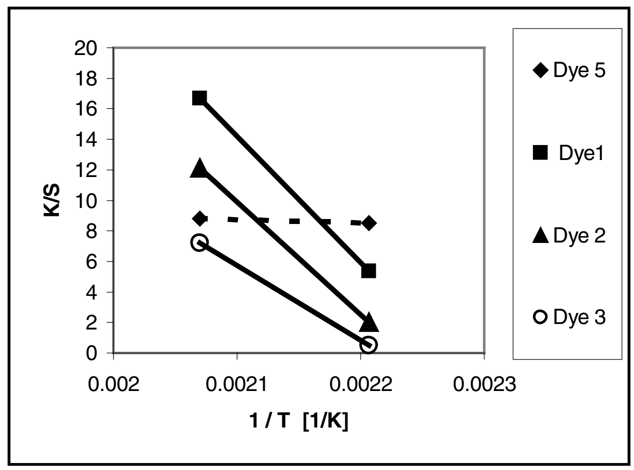


The same behavior for the dyes on the digital transfer paper is observed. Because the distribution coefficients (K) are very much higher for the special digital transfer paper it is clear that the equilibrium is more pronounced on the side of the polyester for this digital transfer paper than for the ink jet photo quality paper. This gives color yields very much higher than normal photo quality ink jet papers. i.e. color depths can be achieved at very much lower dye concentration in comparison with papers not designed for digital vapor phase transfer printing

Also, the slopes of the curves (a measure of the $\Delta_L H$) are all similar, the color build up would also be uniform and would have the same robust performance under production heat transfer conditions .

To compare the behavior in color strength with the temperature dependence of the equilibrium constant K, the spectral data (K/S) is plotted against the inverse of the absolute temperature (Figure 5)

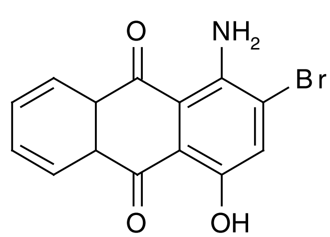
Figure 5: K/S at maximum wavelength for Dyes 1 to 3 and Dye 5 as a function of temperature



For the Dyes 1 to 3 there is also a strong temperature dependence of K/S (measure of the color depth at maximum wavelength) as there is for the distribution coefficient (K).

Due the linear relationship between K/S and concentration at maximum wavelength, the plot of K/S against the temperature provides a simple and qualitative method to measure the temperature dependence of K (the distribution coefficient).

Fig. 6: Structure of Disperse Dye 5



With Dye 5 replacing Dye 4, the temperature dependence in K/S differs completely to the other disperse dyes. If Dye 5 was used in combination with any of the other disperse dyes (dyes 1 to 4) to obtain a specific shade, we would obtain different color shades at different transfer temperature. Also, small variations in production transfer temperatures would produce very different and non-reproducible shade variations under actual production processing conditions.

Conclusions

The digital transfer printing process is characterized by three steps

i) the vaporization of the dye either from a solid or a liquid state
ii) a diffusion process over the air gap
iii) Dissolving of the dye in the polyester fabric.

Using the "Transfer Printing Model" and determining from experimental data, some fundamental relationships of the disperse dye, paper and processing conditions, a reliable method of determining the most compatible disperse dyes and transfer paper combinations can be obtained.

The present paper has shown that the highest amount of transferred dye is determined by the distribution equilibrium (K) between the paper and the polyester fabric. The distribution coefficient is strongly temperature dependent. By choosing the disperse dye and paper combinations with the highest distribution coefficients the color depth will be maximized.

Also, under industrial production conditions, equally important is to obtain both a uniform color build up and small variation to shade changes with temperature in combination shades. By using methods outlined in this paper the most reliable disperse dye/paper combinations can be chosen.

BASF, have used these methods in evaluating and developing BAFIXAN® disperse dye inks for transfer printing using ink jet printing. These disperse dye inks are now being used in both piezo and thermal based ink jet printers. Equally, the transfer paper to be used is important and is not simply a question of using any paper; the correct selection is always required to obtain optimum performance under production transfer conditions. By using combinations of compatible thermal transfer disperse dyes and specifically developed transfer papers a reliable and reproducible process for industrial conditions can be produced.

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Biography

John Provost is with the Global Ink Jet Marketing Team of BASF AG in Ludwigshafen, Germany.
John Provost has been involved in Textile Printing for over 28 years with Courtaulds, ICI, Zeneca and BASF and for the last 15 years has been active in researching textile ink jet printing solutions.
He is the author of over 50 Papers and Patents in digital and analogue textile printing and has made many presentations at International Printing Conferences.
John Provost graduated with a B.Sc. Honours degree in Colour Chemistry and a PhD Research degree in Colour Physics from Bradford University (UK). He is also a Fellow of the Society of Dyers and Colourists in the UK. .

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