# Parameters Influencing Ink/Envelope Interaction and Bristow Absorption

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## Abstract

We measure sorptive characteristics of commercial aqueous ink jet inks and several regular and recycled envelopes. Measured properties include ink absorption, critical surface energy, roughness, pore size distribution, and contact angle. There is substantial agreement between measurements of ink absorption by three methods: Bristow absorption, ultrasonic attenuation and Hercules sizing test.

Models of ink absorption based on capillary flow fail to provide reasonable predictions for ink absorption experiments. The Lucas-Washburn capillary speed is the pressure due to the ink-paper surface energy divided by the viscous drag. The resulting theoretical absorption rate is much higher than observed. Effects not taken into account in the Lucas-Washburn theory must inhibit capillary filling.

We propose an ink absorption inhibition mechanism consisting of fast flow between pinning sites and slow, diffusion controlled, depinning. Presence of sizing and penetrants control the balance between capillary flow and diffusion. We describe the time dependence of absorption as an effective time-dependent diffusion system.

## Introduction

Automation of mail sorting by the world's postal services requires machine readable addresses and postal codes. Automatic postage payment verification programs, such as the USPS Information Based Indicia Program (IBIP) and the Royal Mail's Integrated Mail Processor (IMP) extend this requirement to the indicium.

Ink-paper interaction controls print quality, and thus machine readability of information printed in bar codes or characters. Ink jet is the preferred printing method in home offices and small businesses.

We examined[1] properties of aqueous ink jet inks interacting with various regular and recycled envelopes. We measured print quality and readability of two-dimensional bar codes, and found that slow absorption is an important predictor of print quality, while mailers need fast ink absorption to print envelopes at high speed.

Parameters such as pore size, critical surface energy, roughness, coating, and pH characterize paper. Most envelope papers are uncoated. Therefore, critical properties for ink absorption are the structure of the bulk pore system, roughness, fiber and filler type. Type and amount of sizing and water presence dominate surface energetics.

Surface tension, viscosity and pH are critical ink properties, as are differences between true solutions and stabilized dispersions.

Many theories explain aspects of absorption but no model convincingly describes the overall process. The capillary penetration model of Lucas-Washburn (LW)[2] has been used to explain the penetration into paper as a balance between surface tension and viscous drag. LW has limited predictive ability for ink absorption. Other authors[10, 13, 16] propose diffusion as the controlling mechanism.

Various proposed corrections to LW are based on deviation from uniform parallel pores. The pores in paper are short, various sizes, interconnected and not cylindrical. Different authors[3, 4, 5] propose correction factors including tortuosity, discontinuities caused by filler particles and effective pore radius. Kent and Lyne[6] observed that the capillary penetration will accelerate in converging portions of the pore and decelerate in diverging portions.

A homogeneous contact angle measured at equilibrium is an oversimplification[12]. Paper surfaces are chemically heterogeneous due to cellulose fibers with varying amounts of lignin, hemicellulose, organic and inorganic papermaking additives. Sizing agents can be alkaline or acid with different chemical structures and degrees of permanence.

Other papers[10, 11] show that contact angle depends on penetration, porosity, pore size and surface energy. Spreading is enhanced[11] by rough surfaces for liquids with contact angles less than ninety degrees and is inhibited by rough surfaces for contact angles greater than ninety degrees. Effective contact angle with pore walls is not only a function of the dispersive and acid-base chemistry but also of the pore wall geometry. The decrease in apparent contact angle on convergent pores explains absorption in highly sized pores with contact angles higher than ninety degrees.

Swelling liquids, such as aqueous solutions, penetrate capillary walls and enter intrafiber pores. As the fiber network expands, the interfiber pores enlarge and the rate of penetration may increase.

The most widely accepted method of measuring liquid wetting, spreading and penetration is the Bristow wheel apparatus. Many successful studies [14, 15, 17] use Bristow dynamic wetting measurements to predict drying time and print quality. The ultrasonic attenuation technique complements the Bristow wheel test in studying wetting and liquid penetration into paper. The two methods measure the wetting delay found with rough papers and water based inks and the penetration rate. A third method, Hercules sizing time, measures the effect of internal sizing on ink penetration. These three measures of ink absorption are in good agreement and correlate with print quality measured as spread factor [1]. Other properties, such as critical surface energy, mean pore diameter, pore size distribution, and viscosity do not strongly influence the print quality.

## Measurements

Our envelope sample, consisting of ten envelope types, was tested for roughness, air flow porosity, pore size distribution, pH and critical surface energy. We focused on four envelopes, A, B, I, and L which represent extreme characteristics ranging from alkaline recycled to rosin sized regular and recycled envelopes.

We characterized the surface tension, viscosity, pH and contact angle of seven commercially available ink jet inks[1]. Three inks were used for envelope absorption tests.

The ink/ paper absorption was tested by Bristow wheel at contact times from 0.020 to 2. sec., by Hercules sizing test and by ultrasonic attenuation.

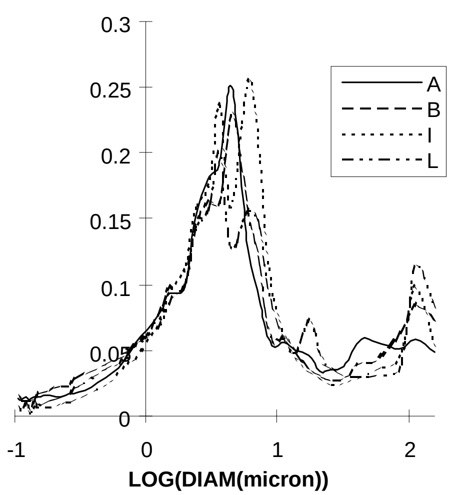


*Figure 1: Derivative of the cumulative pore volume with respect to the log of the diameter vs. pore diameter by mercury porosimetry*

Mercury porosimetry gives information on small pores (few microns). The measurements were done with the Micromeritics Autopore III.

All the envelopes have a similar pore distributions and median pore diameter (4-5μ). Envelopes I and L show a broader range of pore sizes. Envelope L has more pores larger than 10μ. The volume of large pores is a measure of surface roughness. This volume is compared with the data obtained from Parker Print Surf and Sheffield smoothness in Table 1.

| Env | Description | Parker Print Surf(μ) | Shef. Smoothness (ml/ min in$^2$) | Pore volume at 10μ |
|---|---|---|---|---|
| A | 24#white wove | 5.42 | 152 | .226 |
| B | 24# white wove | 6.23 | 145 | .252 |
| I | recycled | 7.68 | 195 | .240 |
| L | Recycled, copier grade | 7.12 | 195 | .297 |

*Table 1: Surface roughness measurements*

Wetting is interfacial adhesion consisting of two major types of intermolecular interactions: dispersive and acid-base[7]. The dispersive and polar components of critical surface energy can be measured using suitable liquid probes and the Zisman or Owens-Wendt theories[8, 9].

The dispersive critical surface energy, according to Zisman's theory, was measured using the following solvent probes: hexane, chloroform, THF, benzyl alcohol, ethylene glycol, diiodomethane, formamide and water. The Owens/ Wendt theory describes the surface energy of a solid as having a dispersive component and a polar component.

| Env. | pH & Internal Sizing | Zisman Surface energy mN/m | Owens/Wendt mN/m | |
|---|---|---|---|---|
| | | | Dispersive | Polar |
| A | 4.9 (rosin) | 35.40 | 39.55 | 0.87 |
| B | 8.4 (alkaline) | 28.28 | 28.75 | 2.28 |
| I | 4.1 (rosin) | 38.87 | 44.17 | 0.41 |
| L | 8.4 (alkaline) | 37.81 | 33.69 | 6.24 |

*Table 2: Zisman and Owens/Wendt critical surface energy*

Envelopes B and L, which have the highest absorption rate, show the highest Owens/Wendt polar component of the critical surface energy.

Measured ink characteristics were surface tension, viscosity, pH and contact angle. These properties are shown below.

| INK | Viscosity (cp) | γ (de Nouy) dyne/ cm | γ (Wilhelm) dyne/cm | pH |
|---|---|---|---|---|
| C | 2.00 | 54.9 | 52.44 | 8.5 |
| F | 1.00 | 42.9 | 41.9 | 8.3 |
| H | 2.9 | 32.6 | 30.17 | 7.8 |

*Table 3: Ink properties*

The contact angle decreases, as expected, from ink C with the highest surface tension to the ink H with the lowest. The ink H absorbs very fast on all the envelopes. The difference between the envelopes A and B in regard to fast absorption may be due to the pH difference of the envelope surface.

| Env. | INK C | | INK F | | INK H | |
|---|---|---|---|---|---|---|
| | t=0 | t=1 min | t=0 | t=1min | t=0 | t=1min |
| A | 81.5 | 66.4 | 56.0 | 0 (30s) | 30.4 | 0 (5 s) |
| B | 82.7 | 74.1 | 73.4 | 65.4 | 36.3 | 0 (5 s) |
| I | 107.0 | 105.6 | 87.7 | 82.9 | 24.1 | 0 (10 s) |
| L | 54.4 | 0 (40s) | 50.0 | 0 (5s) | 10.5 | 0 (5 s) |

*Table 4: Contact Angle*

The Hercules sizing tests correlates with the contact angle. Inks that wet well and contain strong penetrants strike through the paper much faster than the less wetting inks. Papers made of recycled fibers show faster penetration.

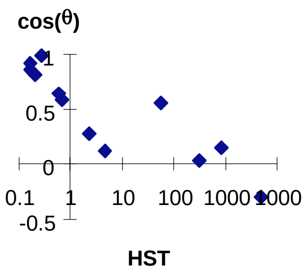


*Figure 2 : cos(θ) vs. Hercules Sizing Time*

Ultrasonic attenuation [19] measures the attenuation of an ultrasound beam across an interface of liquid-paper over a predetermined time period. The various segments of the attenuation curve characterize the wetting and the absorption properties of the paper and the liquid. The measurement depends on the difference in the impedance of air, ink and solid. The ultrasonic attenuation of the various envelopes in contact with the inks were measured by the Ultrasonic Wettability Tester (UWT-3) manufactured by Shin Ei Company, Japan. Measurements correlate to the amount of sizing in the paper and to Bristow and Hercules measurements.

| Env | Ink F | | Ink C | | Ink H | |
|---|---|---|---|---|---|---|
| | $t_w$ (ms) | Slope 1/s | $t_w$ (ms) | Slope 1/s | $t_w$ (ms) | Slope 1/s |
| A | 181 | 1.51 | 1026 | 0.43 | 66.0 | 38.9 |
| B | 133 | 1.60 | 846 | 0.78 | 34.0 | 42.8 |
| I | 541 | 0.62 | 828 | 0.26 | 14.0 | 75.8 |
| L | 63.5 | 29.9 | 170 | 9.99 | 33.0 | 74.7 |

*Table 5: Acoustic wetting measurements*

The wetting times for inks F and C are much longer for envelope I than for L (recycled) and very similar for the A and B. The highest slope is shown for the envelope L which is in agreement with the Bristow test. The difference between the inks follows the contact angle and surface tension values, with ink C having longer wetting time and smaller slope. We can see in figure 3 the correlation between ultrasonic attenuation and the Hercules sizing. Similar correlations exist between the Bristow and ultrasonic attenuation slopes.

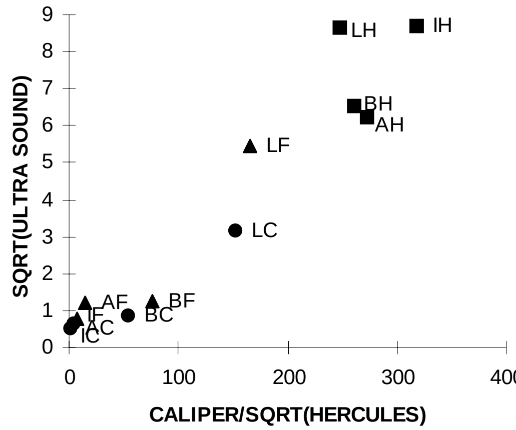


*Figure 3: Correlation between the ultrasound attenuation and Hercules sizing.*

Bristow measurements were performed with the Paprican Dynamic Sorption Tester BA 92. The contact times varied from 20 to 2000 msec.

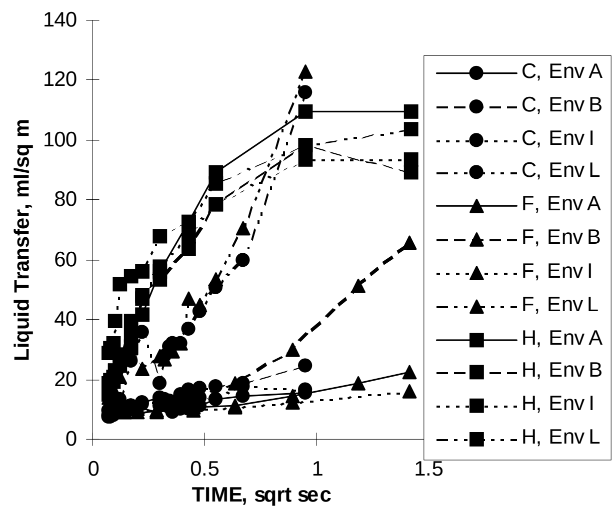


*Figure 4 Liquid uptake for inks C, F and H and envelopes A, B, I and L.*

The Bristow curves show several different patterns:

a)Inks C and F on envelopes A and I show low absorption rates possibly due to rosin sizing. Both inks have relatively high initial contact angle (> 90 for envelope I) and surface tension (> 42 dynes / cm) higher than the envelope critical surface energy.

b)Inks C and F (mainly F) on the envelope B show an initial wetting delay followed by an increased rate of absorption, due to alkaline sizing. The high initial and delayed contact angle are in good agreement with the critical surface energy (lowest for envelope B.

c)Envelope L with moderately wetting inks C and F shows short wetting delays with high absorption rate followed by swelling. This type of behavior results in a high spread factor [1].

d) Penetrating ink H, on all types of envelopes, shows a high Bristow slope without time delays. Saturation starts at short contact times of 0.25 sec.

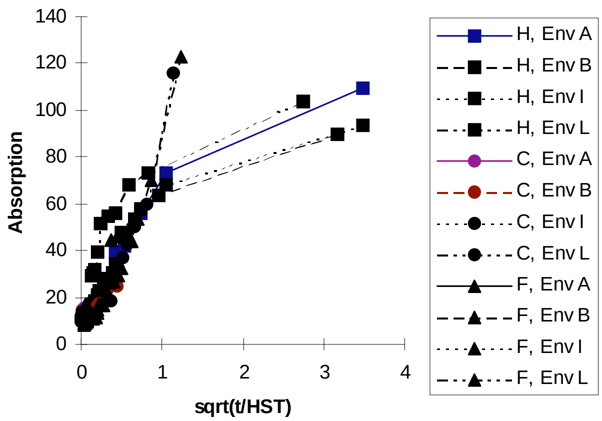


*Figure 5: Normalized Bristow absorption.*

Hercules sizing time measures a characteristic time for ink absorption. Bristow curves correlate well with the Hercules sizing tests, as we can see on figure 5 by plotting the Bristow absorption using time scaled by the Hercules sizing time. The only exception is envelope L which shows swelling.

Lucas-Washburn predicts ink absorption rate as a function of surface tension, contact angle, viscosity and pore diameter. Fig. 6 shows that the calculated LW capillary speed is much higher than the observed speeds.

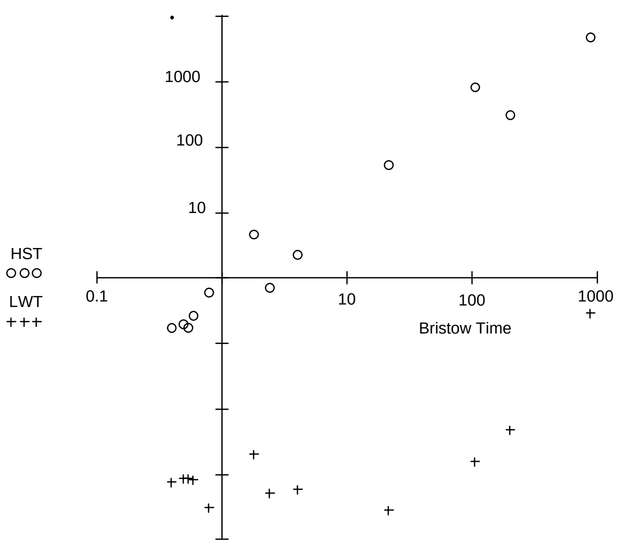


*Figure 6: Comparison of LW calculated speed and experimental times obtained from Bristow and HST.*

Filling must be inhibited by some mechanism. Tortuosity is a possible cause of some inhibition of absorption[4], but tortuosity larger than 3 is hard to reconcile with reasonable models of the pore structure. Small diameter constrictions and large aspect ratio cross sections increase the effective viscous resistance. Poiseuille resistance is minimized for a cylindrical cross-section. Deviations from cylindrical can increase the resistance, but not by the observed factor. Pinning of the motion of the absorption front at the paper-ink-vapor triple line is the most likely controlling factor.

## Model Framework

Capillary pressure is reduced by pinning the fluid surface. Pinning, caused by changes in surface energy, roughness, and changes in pore diameter, delays triple-line motion [18]. The fluid surface can escape from pinning by: decreasing contact angle with time; diffusion into the fiber and filler; flowing through an alternative path around the pinning site; and forming a prewetting film through vaporization.

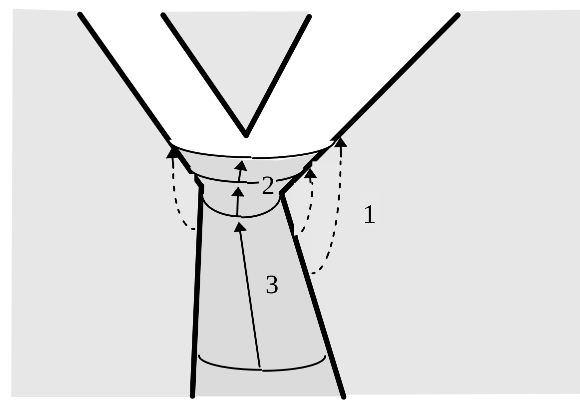


*Figure 7: Ink absorbs by: (1) diffusion past pinning sites (2) and capillary jumps (3) driven by surface energy.*

Pinning times can vary widely. Some locations may pin the flow for a long time. We model the distribution of delay times as a log-normal distribution characterized by a mean and standard deviation (σ) of log(t). A value of (= 2 produces many pinning sites with short delay, and a few with long delays. For (= 1/2 the distribution clusters around the mean with few short or very long pinning times.

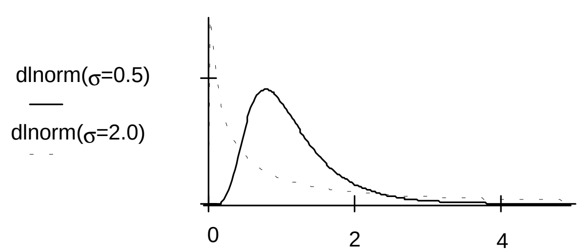


*Figure 8: Pinning time distribution*

For values of (less than 1 and a high density of pinning sites, which is consistent with uniform pinning mechanisms, result in absorption linear in time. Large values of (and small densities of pinning sites can produce an absorption curve approximately linear in square root of t.

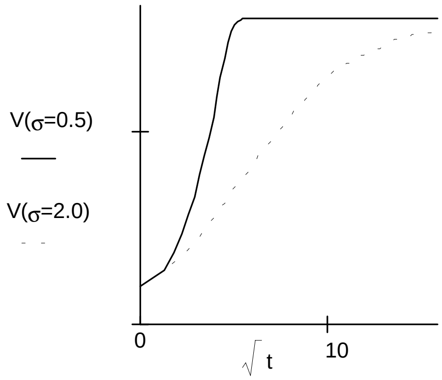


*Figure 9: Monte Carlo calculation of Bristow curves from pinning model with σ of 0.5 and 2.0. The mean pinning time is normalized to 1.*

The pinning will generally not be permanent. The ink-paper surface energy decreases as the ink diffuses into the matrix or reacts with the sizing. Decrease of contact angle with time demonstrates this effect. Ink can find an alternative path around the pinning site, including flow through smaller pores, diffusion through the matrix, modification of the surface in advance of the triple line by a prewetting film, and by condensation of solvent vapor. Whatever the depinning mechanism, the distribution of pinning times controls the advance of ink through the paper. The result, from a macroscopic perspective, is a non-linear diffusion effect.

Ink flow through paper closely resembles the flow observed in diffusion. Even though the mechanism of flow is not expected to be random molecular movement of classical diffusion, the mathematics of diffusion does provide a readily available and understandable framework for characterizing the flow of inks in paper and for predicting flow rates for various initial conditions and concentration profiles. This mathematical model is convenient for analyzing and understanding the basic mechanism involved in Bristow and Hercules experiments. To determine the propriety of the diffusion analogy, we have calculatd the solution of the diffusion equation, taking into account the geometry and boundary conditions specific to the Bristow experiment.

The diffusion coefficient is not a constant, as usually assumed, since the ink motion in the capillary system is inhibited by pinning and the ink flow along the capillary system varies due to various diffusion processes. By measuring the ink absorption as a function of time, a time dependent coefficient can be obtained. As stated earlier in this paper, there are four classes of Bristow absorption curves in figure 4. The difference between these classes is the time dependence of the diffusion coefficient, which can be understood in terms of pinning.

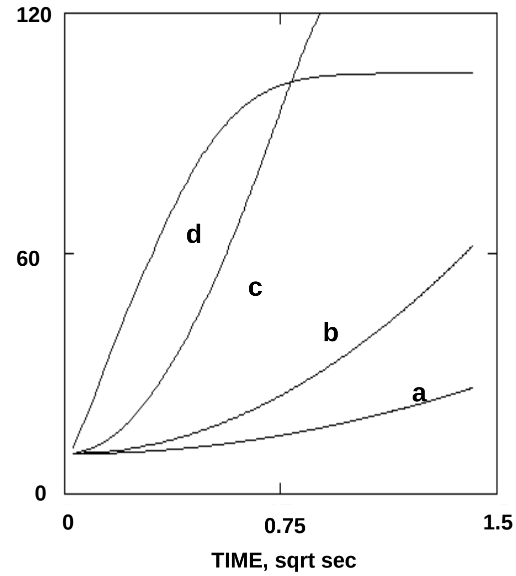


*Figure 10: Liquid uptake calculated Bristow curves of figure 4.*

The parameters of the theory: (diffusion coefficient and time constant) have been determined by fitting the experimental results to an analytical expression. Figure 10 shows the resulting calculated Bristow curves and should be compared to figure 4. Further work on this subject is in progress, but it has to be noted that a simple and precise method of parametrizing the Bristow curves has been found useful to characterize ink paper interactions. Furthermore the same diffusion theory permits to calculate accurately the Hercules sizing time.

The details of evaluating theoretically this diffusion coefficient and the Hercules sizing time will be presented in another communication.

## Summary and Conclusions

The absorption of commercial ink jet inks onto a few envelopes was studied by Bristow, HST and ultrasonic attenuation techniques. The inks and papers were characterized by conventional methods: pore size distribution, roughness, pH and critical surface energy for the papers and surface tension, viscosity and pH for the inks. Correlations between properties such as contact angle, HST, ultrasonic attenuation and Bristow slopes were represented. The calculated HST and Bristow slope from LW equation were compared to the experimental values.

A model describing the inhibited capillary flow by a random distribution of pinning times is invoked. The ink flow into the paper can be interpreted in terms of time dependent diffusion which will be presented in a future communication.

The ink absorption into the selected envelopes follows several patterns according to the degree of absorptivity of both : inks and papers.

a) The strongly penetrating ink shows a clear $t^{1/2}$ dependence with no wetting delays and little discrimination between papers. The tendency to saturate is observed in the earlier stage of the Bristow curve (~.25 msec).

b) The other inks ($\gamma_L$> 40 dynes/ cm) behavior depends on the type of paper. For alkaline sized, recycled paper there is a clear swelling effect at higher contact times. The “wetting delay” varies from very short for alkaline sized paper to very long for heavily rosin sized paper.

This absorptive behavior results in a fuzzy, unacceptable print quality for the case of swelling and well defined edges for the case of slow absorption and long wetting delays.

The main properties that influence the absorption behavior are surface tension, contact angle, type of fiber and internal sizing. All the ink absorption measurements are consistent. Cos(θ) correlates well with the HST time and with the Bristow slope. Ultrasonic attenuation, which measures the presence of trapped air, correlates well with Bristow slope, wetting delay and HST time. Thus, for uncoated paper, the Hercules sizing test provides an alternative comprehensive absorption time scale can be measured more efficiently than Bristow wheel.

The polar component of critical surface energy for the two envelopes with alkaline sizing, B and L, is higher than for the envelopes with acid sizing. The findings from the pore size distribution, critical surface energy, roughness had less direct impact over the ink absorption.

We suggest an inhibited capillary model based on random pinning times followed by a capillary as a general approach to interpret ink absorption. Diffusion controls the time scale depinning process.

The combination of depinning, capillary flow, and bulk diffusion results in an effective diffusion absorption model with time dependent diffusion coefficients. This mechanism can describe Bristow curves with time dependent diffusion coefficients that vary between various ink/ paper systems.

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