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The Development of Receiving Coatings for Inkjet Imaging Applications

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Abstract

A detailed discussion of inkjet media performance requirements as they relate to several coating design parameters is given here. In particular, the image drytime is found to be strongly influenced by the coating material group functionality, environmental humidity at time of printing, ink composition and flux, and receiving coating thickness. In order to reduce the sensitivity of the media drytime performance to change in relative humidity, an inkjet medium with a barrier coating is described. Additional discussion of some user related archivability features is also included.

Introduction

Inkjet technology has become increasingly popular due to the ability of inkjet devices to record multi-color images and text on variety of media with high speed and low noise at a reasonable cost. Tremendous work has been done to improve various printer systems, ink vehicles, and recording media. Short drytime for high speed printing, photo-realistic image quality and good handlability/stability for end users are the ultimate requirements for inkjet recording media.

The development of the image receiving coating for inkjet media requires a detailed understanding of various handling factors and archiving requirements. In addition, knowledge of ink compositions, ink drying processes, ink-medium interactions and the structure-property relationships of polymers and inorganic fillers which are widely used in receiving coating formulations is required. Traditional problems of the recording media designed for inkjet printing, such as feathering, color gamut and many others have been resolved by a combination of improved ink and medium development effort.[1,2] In the following section we will discuss in detail the effect of the coating design on image drytime, and medium handlability and archivability.

Experimental

Sample Preparation

Receptive coatings, containing a variety of water soluble polymers including those illustrated in Figure 1, extenders, fillers and alike, were formulated and coated on different substrates. The coating method varied from Meyer rod to reverse roll to extrusion die and depended on a combination of viscosity and solid profiles which are beyond the scope of this presentation.

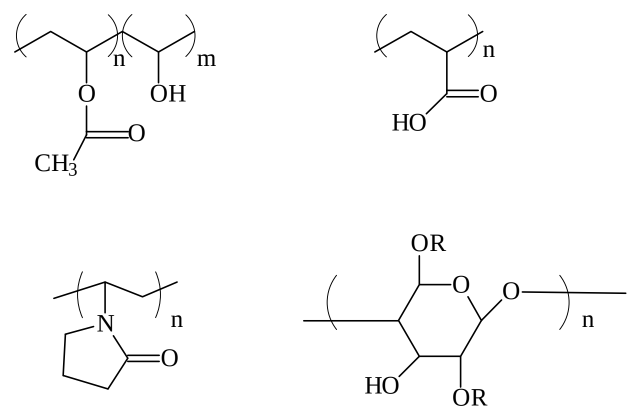

Figure 1 Common resins used in the inkjet receiving coatings.

Water Fastness

The ink receptive coatings were coated on white PET film and imaged on an Epson Stylus 800® color printer. The difference in image density as a function of immersion time is reported as a *dD* according to the following equation:

$$dD = D_i - D_{48\ hours}$$

Distilled water was used as the immersion fluid to test the water fastness of the media.

Drytime Measurement

The prepared media, at a given coating weight, were printed on HP DJ 850C and allowed to dry for certain time. The samples were then blotted with transfer paper under certain pressure. The absolute sample drytime is reported as that no measurable quantity of ink is transferred to the blotting paper as determined by optical density measurements.

Water Uptake

The amount of vaporous water absorbed by typical water sorptive polymers was measured as a function of relative humidity at a constant 23°C. Sample media, at a fixed coating weight, were placed into a controlled atmosphere chamber and allowed to equilibrate for 24 hours. The weight gain of the sample is reported as the moisture uptake.

Light Fade

Samples of the given media were imaged on a Hewlett Packard DJ870Cxi® printer. These samples were allowed to equilibrate at office conditions before testing. The samples were placed in an Atlas SUNCHEX® fadeometer for forty hours exposure with a dosage of 0.35 W/M^2 at 340nm. The change of coloration is reported as a *dE* number by the following equation:

$$dE=((\mathbf{L}_i*-\mathbf{L}_{40}*)^2 + (a_i*-a_{40}*)^2 + (b_i*-b_{40}*)^2)^{0.5}$$

Where: L_i*, a_i*, b_i*; and $L_{40}*$, $a_{40}*$, $b_{40}*$, are the CIELAB coordinates after 0 and 40 hours exposure respectively.

Image Line Growth (Bleeding)

Samples of the given media were imaged at 33°C/80%RH and stored at these conditions for seven days. Base line growth was measured for a 40 mil reference line after the environmental exposure. Line width measurements were made with the assistance of a traveling microscope. Contrast was optimized for each color and is crucial for reproducibility of the data presented here.

Results and Discussion

Image Dry Time

One of the modern technical challenges for inkjet printing is increasing printing speed. The improvement of printing speed relies on both the speed of the printer in putting down drops of ink in a controlled manner and the time for the imaged media to dry. Putting down drops of ink at a faster rate, i.e. head frequency improvements, than can be dried within the image receiving coating will result in poor image quality. Image drytime, for this discussion, is defined as the point in time at which the imaged media will transfer no ink to another surface when placed into contact with it. Today, most ink vehicles used in inkjet printing are aqueous solutions of dye(s) and small amounts of high boiling solvents such as glycol and glycol ethers. Inkjet media must have not only high image resolution but also high water absorptivity to achieve excellent image quality and fast drying rate. Therefore, image drytime is one of the most critical design parameters in inkjet medium development.

Inkjet ink drying mechanisms include absorptive drying and evaporative drying.[3] Furthermore, absorptive drying can be broken down into two components: capillary drying and molecular diffusion. In media with porous structures, like simple sized papers, the absorptive drying process primarily involves capillary movement of the ink droplets from the media surface. In most coated inkjet media, the absorptive drying mechanism involves molecular diffusion of ink vehicle into the bulk media through ink-medium interaction. For evaporative drying, ink droplets are spread on the medium surface and the moisture is removed by air flow over the fluid mass. Unless heat or forced air is provided, the evaporative drying process will be slow and dependent on the equilibrium evaporation of the ink fluid. In reality, ink penetration and evaporation occur simultaneously whereby the dominant mode of ink drying is usually penetration.[4]

Since the ink-medium interaction is the main driving force for molecular diffusion of ink vehicle into the coated media described here, the selection of polymer binders in the design of receptive coating is very important. Water soluble polymers, such as poly(vinyl alcohol)-PVOH, poly(acrylic acid)-PAA, poly(acrylamide)-PAmd and their copolymers, poly(vinyl pyrrolidone)-PVP, cellulose derivatives and others are widely used in the design of inkjet receiving coatings to absorb water and the small amount of organic solvent in the ink vehicle. Obviously, image drytime, which affects printing speed, is dependent upon the water absorptivity of the polymer binders used in the media. The water absorptivity of polymer binders is dependent upon their structure, including the hydrophilicity of the functional groups present, and molecular weight. Furthermore, water itself will hydrate various binders and influence the interaction of polymer binders with both liquid and vaporous water. As shown in Figure 2, at the same coating weight and humidity condition, media made of PAA and Resin A gave much shorter dry time than those made of PVP, PVOH, and a cellulose derivative.

Figure 2 also demonstrates that image drytime was dependent on the coating thickness, or coating weight, of the receptive coatings. For all coatings, the higher the coating weight, the shorter the image drytime. This indicates that the image drying mechanism is dominated by absorptive drying process. At low coating weight, the media do not have enough capacity to absorb all the ink vehicle present. For a coating weight of approximately 8-16 gsm, the image drytime is strongly influenced by the coating thickness. Higher coating weight gives the absorptive layer much higher absorbing capacity. At very high coating weight, in the over 20 gsm regime, no real decrease in drytime is realized at the kinetic limit of the drying process.

Image drytime is also strongly influenced by ink flux as shown in Figure 3. There are three zones in the typical ink flux drytime curves. In the first zone, for low ink flux, the image transfer response, defined here as drytime, is low, indicating quick penetration of ink into the receptive coating. The media have excess capacity for absorbing the ink vehicles in this zone. The second zone in the drytime curve is often short and indicative of a rate change. The image transfer response is occurring longer in this region. Small change in ink flux can result in very large change in the amount of image transferred in this region of the curve. In the final zone the image transfer is essentially infinite. The ink mass used has exceeded the absorbing capacity of the media. Now the ultimate drytime is determined by the slower evaporative drying process, which is much longer than absorptive drying. It is the goal of the media designer to design new media that remain robustly within the first zone, the excess capacity zone, for the full range of possible ink flux. As showed in Figure 3, PAA and Resin A coatings show much longer first zone regions than other media. This is consistent with the higher water absorptivity of the polymers as observed in Figure 2.

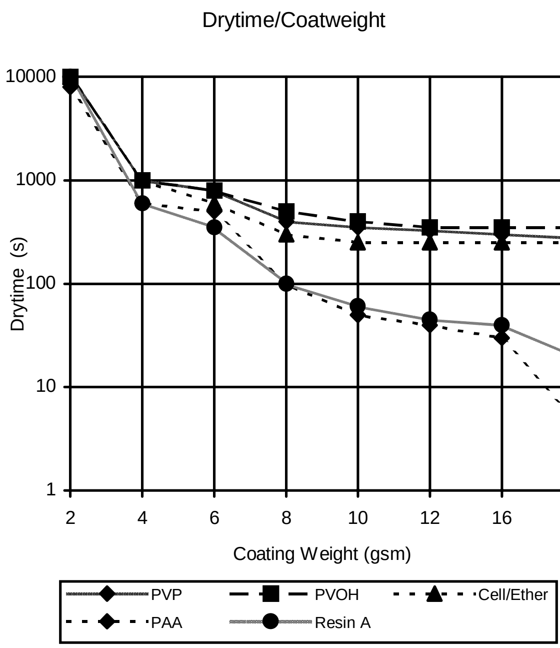

Figure 2 Image drytime as a function of coating weight for selected commercially available and experimental (Resin A) materials.

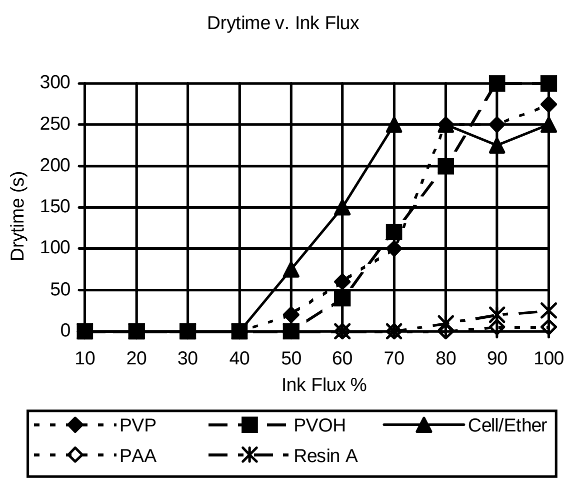

Figure 3 Image drytime as function of polymer binders and ink flux. The receptive coating has coating weight of 12 gsm.

Water soluble polymers are used in most inkjet media. In general, water soluble polymers are sensitive to both liquid water and water vapor. Therefore, the uptake of water from the air, for most water soluble polymers, will depend upon the relative humidity. The water vapor uptake normally increases with the increase of humidity as shown in Table I.

Table I

Water Uptake of Water Soluble Polymers

{Water Uptake(%) $= [W - W_{RH20}]/W_{RH20}$}

Relative Humidity	Methocel A4M®	Resin A
40	1.87	2.09
60	3.63	5.32
80	7.86	12.71

Methocel is a product of the Dow Chemical Company

Much higher water vapor uptake of other water soluble polymers such as (PVP), (PAA), poly(methacrylic acid) (PMAA), (PVOH), and poly(ethylene oxide) (PEO) have been reported in the literature.[4] It was found that PVP has the highest water vapor absorptivity followed by PAA, PMAA, PVOH, and PEO. Theoretically, printing media made of binders with high vapor absorptivity such as PVP and PAA would give very short image dry time at low humidity conditions. Under high humidity conditions, however, the media constructed from these polymers can absorb a significant amount of water vapor before printing. This pre-absorption will reduce the capacity of the medium to absorb the liquid ink vehicle upon printing. Therefore, at high humidity, PVP and PAA are essentially saturated with water and give very long dry time when imaged. The media humidity sensitivity not only prolongs the image drytime but also cause film/image tack and ink bleeding.

In order to minimize the humidity sensitivity of coated inkjet media, a barrier type receptive coating was designed in which an absorptive coating on the substrate is top coated with a thin barrier layer which has little humidity sensitivity. A sketch of a prototypical barrier coating is shown in Figure 4. This type of hybrid system gave much shorter image drytime.

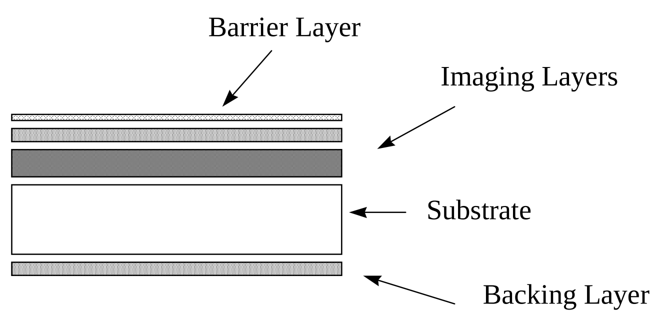

Figure 4 Structure of a barrier coated media. Such a technique can render the media virtually insensitive to the effects of humidity on print quality.

Table II illustrates the impact of a barrier layer coating on image drytime. In materials with only water receptive intercoat (Medium A) or intercoats with non-barrier type topcoat (Medium B), water vapor uptake of the media is high at high humidity conditions. However, the medium with barrier type topcoat (Medium C) shows low humidity sensitivity as expected:

Table II
Effect of Humidity on Water Uptake

{Water Uptake(%) = $[W-W_{RH20}]/W_{RH20}$}

Relative Humidity (%)	Media A	Media B	Media C
40	1.9	5.5	3.4
60	4.1	8.8	6.3
80	18.0	16.6	3.7

Media A=Single Imaging Layer
Media B=Dual Imaging Layers (non barrier)
Media C=Dual Layers-Barrier Coated Product

Image drytime of the barrier type medium and other media is plotted in Figure 5. Consistent with the results shown in Table II, the image drytime of the barrier type medium C is significant shorter and much less humidity sensitive than media A and B at high humidity conditions, even though it is not the fastest drying medium at low humidity condition. With appropriate choice of inter-absorptive layers and modification of the barrier layer, a fast drying medium with no humidity sensitivity can be designed.

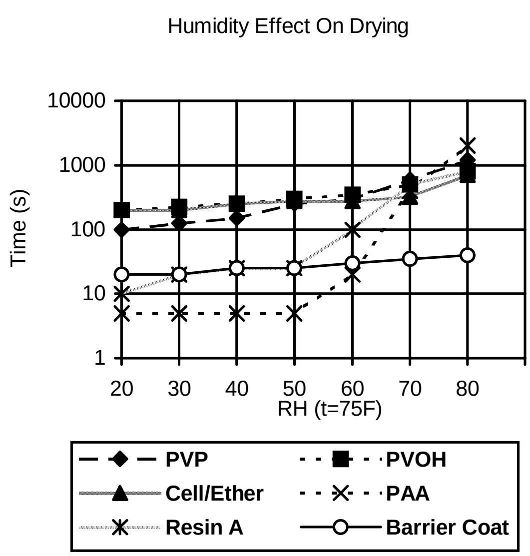

Figure 5 Effect of humidity on image drytime of the media with and without barrier coating.

Handlability & Achivability

With the development of fast, often networkable printers and digital cameras, more pictures will be printed by inkjet printers than ever before. Therefore, media handlability and achivability become more and more important. Image water fastness, smear fastness, light fastness, and storage bleed are the principle concerns for handling and archiving of the inkjet media.

Water fastness can be defined as the resistance to color loss when a printed inkjet medium is immersed in or wiped with water. This is an important property, because the imaged media may be subjected to coffee spills, water spills, or even flooding. Color loss, with resultant loss of image quality, is mostly due to the solubilization of the dyes in the printed image. Any interaction between the various dyes and the ink receptive coating will help to immobilize the dye molecules and improve the water fastness of the printed media.

The most difficult challenge for inkjet medium designers is to develop inkjet waterproof media for outdoor use without relying on post processing such as lamination. Since most inkjet media use water soluble polymers as binder to absorb the nascent ink vehicles, the receptive coatings will swell and be washed away when in contact with water for extended period of time. Therefore, a careful balance between hydrophilic and hydrophobic components in the receptive coating is needed to give both good image and water resistance. Figure 6 shows the water fastness of our specially designed inkjet media for outdoor applications and photo quality imaging application. No color loss was detected after completely immersing the printed image in water for two days.

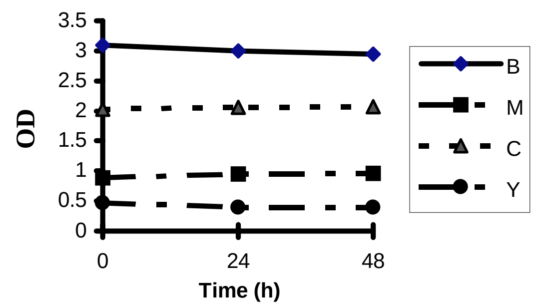

Figure 6 Optical density of the imaged waterfast medium after immersion in water for two days. Little image degradation was noted.

In addition to water fastness, light fastness is a concern for long term stability of the imaged inkjet media. Light fastness can be defined as the resistance of the printed media to degradation by strong light flux. Most applications of inkjet media subject the images to some sources of UV light. In addition, many inkjet dyes will degrade in the presence of visible light. Therefore, light fade of the printed media is often very unfavorable especially for outdoor use such as poster and display signs. The composition of the various polymer binders used in the medium receptive coatings do play an important role in the ultimate light fade resistance of the imaged media. As shown in Figure 7, some polymers are more prone to degradation by light exposure than others. Materials with a high proportion of hydroxyl functionality act as free radical quenchers, which promote light stability. Such is the case for PVOH, cellulose derivatives and others materials.

An additional long term image stability issue is image bleeding. Image bleeding is a very complex problem. High boiling solvents in the ink vehicle, low coating weight, and high humidity conditions can cause image bleeding. High boiling solvents are difficult to evaporate, and tend to remain in the receptive coating where they can act as a dye solubilizer. At low coating weight or high humidity condition, excessive water absorption occurs which results in dye solvation, and coating dissolution. These factors promote image bleeding. To overcome this problem, one must either immobilize the dye molecules by specific interactions such as chelation, or complexation or use high coating weight to achieve excess absorbing capacity. In most cases, dye immobilization for improving water fastness will also improve the light fastness and prevent ink bleeding of the ink jet media. Figure 8 shows the effect of the polymer materials used in the receiving coatings on long term storage bleeding. Complex, often highly specific, interactions between the dyes and polymers or inorganic particles used in the receptive coatings either promote or hinder image bleeding. In particular, PAA may reduce image bleeding through electronic repulsion of the inkjet dyes.

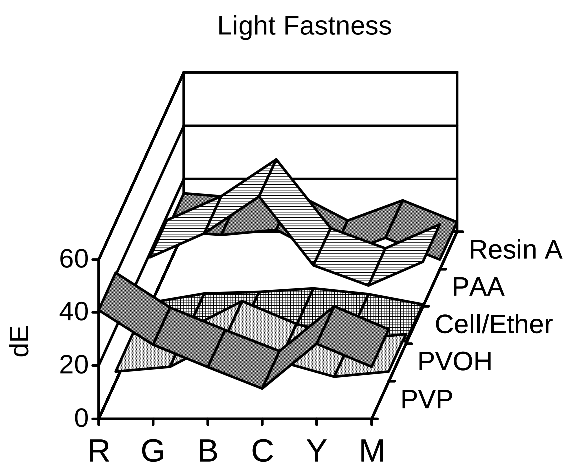

Figure 7 Light fade as function of binder composition in the receiving coatings and dyes in the ink vehicle.

Summary

The design of modern, high performance inkjet media requires a detailed understanding of print quality and storage stability issues. Drytime is the limiting factor in the development of truly high speed inkjet marking devices. Image drytime of the inkjet media products is strongly influenced by the chemical composition, coating weight and ink flux of the inkjet media/ink system. Long term storage issues which impact the utility of inkjet technologies to approach that of traditional photographic systems include water fastness, light fastness and bleeding. These issues are also strongly influenced by the selection of materials used in the receiving coatings of the designed media. It is the goal of the media design engineer to develop systems which optimize the various requirements of modern inkjet recording media.

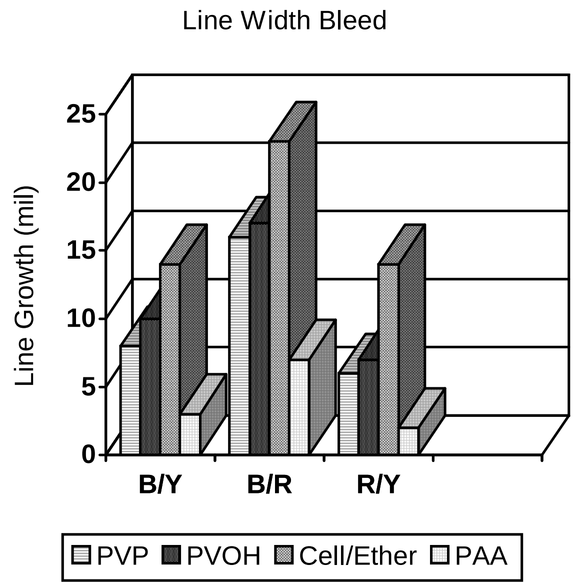

Figure 8 Long term aging bleeding can be significantly influenced by the materials used in the inkjet media. A bleed of 20 mils represents a line growth of 50% in this experiment.

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