The Development of Ink Jet Media for Outdoor Applications

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Abstract

One of the main deficiencies of ink jet printing technology has been the lack of outdoor weatherability of ink-substrate systems. The development of pigmented inks has greatly improved the UV stability of these systems. However, the lack of water resistance has continued to be problematic. Most commercially available ink jet printable coatings have water-soluble binder resins, such as poly(vinyl alcohol) or poly(vinyl pyrrolidone). Even when crosslinked, these highly hydrophilic polymers are still swelled to some degree.

A discussion of a different approach to the development of ink jet printable coatings is given here. Only water-insoluble binder resins are employed in this development. Highly absorbent white pigments are used to give the coating a capacity for ink absorption. The surface energy of the binder resin is used to control the dot spread. When printed with the pigmented "outdoor" inks of Brady ColorPix™ wide format printers this line of ink jet media has an outdoor durability of approximately two years without overlamination.

Introduction

Ink jet has become the dominant printing technology for indoor color images and graphics. It is a cheap, robust, and mechanically simple process. However, the lack of outdoor weatherability of ink-substrate systems has limited its use for outdoor applications. Printed graphics fail outdoors because of insufficient resistance to UV light and water. The development of pigmented inks represented a great advance in ink jet durability, as pigments generally have greater UV stability than dyes and pigments are insoluble in water by definition. Water resistance of ink jet printing substrates, on the other hand, is still generally inadequate. Overlamination, an expensive and inconvenient process, is typically used to give ink jet graphics the required durability for outdoor applications.

One reason for the lack of water resistance of the prior art ink jet recording media is that most of the coatings applied to polymeric film are based upon water-soluble polymers such as poly(vinyl alcohol) or poly(vinyl pyrrolidone). These water-soluble polymers may be crosslinked, but the absorptivity of the coatings suffers if the degree of crosslinking is too great. Even when crosslinked, these highly hydrophilic polymers are still swelled by water to some degree. For an indoor application like an overhead transparency where smudge resistance upon handling is the main issue, the swelling of the coating does not present a major problem. However, for outdoor applications exposure of a swellable coating to rain will result in fading due to liberation of the colorant and will likely also eventually cause the removal of the coating from the underlying polymeric film.

In this paper a different approach to the development of weatherable ink jet coatings is presented. Water-insoluble binder resins are used to create weatherable coatings. Instead of employing a hydrophilic polymer to absorb the ink, absorptive filler materials with large pore volumes are incorporated in a porous coating. The coating must be well above its critical pigment volume concentration (CPVC) in order to give the ink access to enough of the filler particles. The development and some of the properties of BradyJet Vinyl, the first product of this line to be developed, are discussed in the foregoing. All weathering results are for graphics **without overlaminates**.

Test Methods and Protocols

Printing

All media was printed on a Brady ColorPix™ Pro, a 36" wide format inkjet with a piezoelectric printhead. The aqueous, pigmented outdoor ink was used. Test samples were printed at 160 dpi using the fine paper setting.

Accelerated Weathering

All accelerated weather tests were performed on a Xenon Arc Weather-Ometer from Atlas Electric Devices. The reason this instrument was chosen is that it provides the highest correlation with outdoor weathering of all testing instruments that use artificial light sources.[1] The correlation is higher because the spectrum of a xenon are lamp more closely approximates the spectrum of sunlight than the spectra of other light sources such as carbon are lamps and fluorescent UVB 313 nm and UVA 340 nm bulbs. A particular problem with carbon are lamps and UVB 313 nm fluorescent bulbs is the large amount of radiation they produce in the 260 - 290 nm range. This low-wavelength irradiance is often quite damaging to polymers, but since the earth's ozone layer filters out virtually all radiation between 180 and 295 nm, this degradation can result in anomalous weathering results.

The SAE J1960 testing cycle[2] is employed. This protocol calls for a quartz inner filter and a "Type S" borosilicate outer filter for the xenon are lamp. It is a four part cycle:

1. Irradiance for 40 min with a setpoint of 0.55 W/m^2/nm at 340 nm, a dry bulb temperature of 47°C, 50% relative humidity, and a black panel temperature of 70°C.
2. Front water spray for 20 min, same irradiance as (1).
3. Same conditions as (1) for 60 min.
4. Dark cycle for 60 min at 38°C dry bulb temperature and 95% humidity with back water spray.

The test simulates the effects of rain, nightly condensation, and drying concurrent with temperature increase as occurs when a wet surface dries during the morning temperature rise. It is often observed that the cycling of temperature between 38°C and 70°C results in better correlation with outdoor weathering than standards such as ASTM G-26[3] in which the temperature is held constant.

Color Measurements

Several tests were conducted to evaluate the weathered specimens. Reflected color densities were measured with a MacBeth RD-1255 ColorChecker. Color changes were monitored in CIELAB color space with a HunterLab UltraScan Colorimeter using a 10° angle of view, small area of view, D65 illuminant, with specular reflection excluded. A 10% loss in color density and a color change (ΔE) of 10 were used as failure criteria.

Chalking

Many of the experimental coatings chalked significantly. Two tests were developed specifically to assess :he magnitude of this problem. The onset of chalking could be determined with a tape test. A strip of tape with a non-aggressive adhesive was weighed and then placed across a 2" wide weathered specimen. After the tape was rolled five times with a 5 lb roller, the tape was peeled off and weighed again. Once the chalked material began to fall off of the coating this test gave no further information. The long term loss of coating was determined by applying the coating to yellow vinyl and then measuring the yellow color density as a function of Weather-Ometer exposure.

Results and Discussion

Absorptive Pigments

Initial development work was focused on systems containing thermoplastic binder resins known to have good weathering properties and white pigments as absorptive filler materials. Aluminum oxide, boehmite, precipitated calcium carbonate, titanium dioxide, fumed silica, precipitated silica, silica gel, and several types of clays were investigated. Best results were obtained with silica gel, especially the grades with high absorption capacities. An oil absorption value of 60 g oil/100 g pigment was the absolute minimum for which a smear- and bleed-free coating was created. However, a somewhat greater oil absorption value was required if the coating was to meet all of the performance criteria. Thicker coatings, which are required if the filler is not quite absorptive enough, are very difficult to manufacture, as is discussed below.

Silica is the only one of the white pigments mentioned above which is available in grades with oil absorption values greater than 100 g oil/ 100 g pigment. Silica gel is preferred to the other types of silica because of its availability in large particle sizes, which give a more open coating structure, and because the silica gel particles do not break down under shear during mixing operations.

Binder Resin

Only water-insoluble binder resins were considered in this development. The selection of the resin was further constrained by the choice of pressure-sensitive vinyl as the substrate. The sign, banner, and advertising markets have been dominated by vinyl for years, so from a marketing perspective it was desirable to develop a coated vinyl as the first outdoor durable product. Since vinyl has such poor solvent resistance, the resins were restricted to those which are alcohol-soluble or water-dispersible. All themosets which cure above 70°C, the softening point of the vinyl, were also removed from consideration.

The dot spread is determined by the surface energy of the substrate and the surface tension of the ink drop. This may be expressed in terms of the spreading coefficient, S:

$$S = \gamma_{SA} - \gamma_{SL} - \gamma_{LA} \tag{1}$$

where γ_{SA} is the surface energy of the substrate, γ_{SL} is the interfacial tension between the substrate and the liquid, and γ_{LA} is the surface tension of the liquid in air.[4] The liquid will spread on the substrate if S is positive, as this signifies that spreading is accompanied by a decrease in free energy[4]. It is then evident that the surface energy of the solid should be maximized in order to have a large degree of dot spread.

For dye-based inks the dot spread often must be minimized. For ColorPix™ printers with the pigmented ink, on the other hand, the dot spread must be maximized rather than reduced. This serves two purposes. The drop volume of 300 pl is very large, so it is necessary to have a high degree of spreading in order for the ink to move into the pore structure before it is smeared by rollers or the paper bail in the media feed path. A hold-down bar of the original 36" ColorPix™ Pro printer contacts the ink approximately 2 s after printing. This restriction on drying time has been eliminated in the new 54" printer. High degrees of dot spread also maximize the color density, as this results in the covering up of more of the white space between dots.

The preferred binder resins for this line of ink jet media have surface energies greater than 40 dyn/cm. Excellent printing performance was obtained with alcohol-soluble polyamides with surface energies of 45 - 50 dyn/cm. Both high color densities and superior water resistance could be obtained. Waterborne polyamides were also used successfully.

Absorption Capacity of Media

The ink absorption capacity of the coating is controlled by the oil absorption value of the pigment, the pigment to binder (P/B) ratio, and the coat weight. It is critical that the P/B ratio be high enough to put the coating well above the critical pigment volume concentration (CPVC).[5] Below the CPVC the absorptive pigment particles are separated and encapsulated by the binder resin, so the water cannot reach them and the coating absorbs very little ink. Above the CPVC there is not enough binder to fill all space between the pigment particles, so the coating is porous. The pore structure then gives the ink access to some of the absorptive filler particles. The absorption capacity increases with increases in the P/B ratio. However, the P/B ratio is limited by the structural integrity and adhesion of the coating. The transition from a strong, well-adhering coating to an incoherent powder is generally quite sharp.

For a given P/B ratio and oil absorption value a certain coat weight is necessary to have sufficient ink absorption. Below this critical coat weight prints will bleed or smear in areas of heavy ink lay down. As the coat weight is increased above this critical value the color density of images begins to decrease because more of the pigment is hidden beneath the surface of the coating. Consequently, only a narrow band of coat weights gives optimal imaging properties. For a much more in depth discussion of the interrelationships of P/B ratio, oil absorption value, pigment particle size, and coat weight, please refer to the paper presented at this conference by P. Adair.[6]

Chalking

Polyamides are not very common in coatings for outdoor applications. Their UV stability is relatively average for polymers. If not stabilized, polyamides begin to degrade after short exposures to sunlight. The lifetime of polyamide fibers and bulk articles can be extended by a factor of 3 - 10 by various additive combinations.[7,8] On the other hand, the literature has virtually no information on the stabilization of polyamide coatings.

In a porous coating the degradation of the binder resin is manifested as chalking; a friable powder forms on the surface of the pigmented coating as the coating degrades. Highly porous coatings degrade more rapidly than bulk articles, because each pigment particle is only held in position by a few ligaments of binder resin. Thus, only a few polymer chains must be cleaved to liberate a particle.

Efforts to UV stabilize the coating were successful. Tables 1 and 2 show a comparison between an unstabilized coating and coatings containing a UV stabilizer package. Figure 1 illustrates the performance of BradyJet Vinyl, which incorporates the UV stabilizer package in its topcoat. A common failure criterion used at Brady for signs and graphics is a 10% loss in color density (average of CMYK). Table 1 (and Figure 1) shows that UV stabilizers increase the Weather-Ometer exposure corresponding to a 10% loss in color density from 200 hr to 1100 hr, an increase in product life of 5.5 times.

Table 1. Percent Color Density Decrease as a Function of Weather-Ometer Exposure

Coating	168 hr	500 hr	1000 hr
Unstabilized	8.2	29.5	47.5
UV Stabilized (BradyJet Vinyl)	0.0	0.0	8.5

Table 2. Increase in Color Density of Coated Yellow Vinyl Due to Chalking as a Function of Weather-Ometer Exposure

Coating	500 hr	1000 hr
Unstabilized	0.83	0.96
UV Stabilized	0.12	0.33

The data in Table 2 is from lab drawdowns of an experimental coating with and without the UV stabilizer package on yellow vinyl. To put these numbers in perspective, the coatings initially had a yellow color density of approximately 0.5 and uncoated yellow vinyl has a color density of around 2.0. Thus, a color density increase of 0.83 after 500 hr of Weather-Ometer exposure for the unstabilized coating corresponds to removal of half of the coating. It should be noted that yellow vinyl was never coated under production conditions, but was only used in lab-scale developmental work, so no data for this test is available for BradyJet Vinyl.

Figure 1 can be used to estimate the life of BradyJet Vinyl under various conditions. It was noted previously that BradyJet vinyl retained 90% of its printed optical density through 1100 hr of Weather-Ometer exposure. Although the correlation between the Weather-Ometer and actual outdoor weathering is not perfect, Brady uses several guidelines to model weathering behavior. It is believed that one year outdoors in Milwaukee or Chicago corresponds to 300 ± 150 hr in the Weather-Ometer, and that one year in South Florida corresponds to 900 ± 450 hr of exposure. A study in which more definitive correlations will be established is now underway; results should be available in approximately two years.

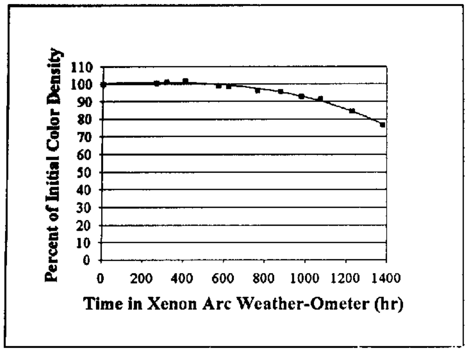

Figure 1. Weathering of BradyJet Vinyl. Color Densities are averages of CMYK

Binder Migration

It should not necessarily be assumed that a coating microstructure obtainable in the lab with slow drying at room temperature in stagnant air can be reproduced under production conditions at an economical speed. Binder migration is a problem which ultimately limits both the coating thickness and processing line speeds. It is defined as the movement of binder resin (usually to the outer surface) during the drying process to create an inhomogeneous microstructure. As the surface of the wet coating is heated, solvent moves up the temperature gradient to the surface where it evaporates, carrying the binder with it in the process.[5]

Binder migration may have several deleterious effects on coating performance. The excess of binder resin at the surface results in poor ink absorption, increased gloss, and often a mottled print appearance. Lack of binder in the bulk of the coating results in poor internal bond, poor scratch resistance, and decreased adhesion to the substrate.

Pan[9] has developed an excellent model of binder migration in a drying coating. Mass and energy balances are readjusted every time the meniscus of the liquid surface in a pore moves. The results of computer simulations with this model show that binder migration may be viewed in terms of competition between the capillary number, Ca, and the Peclet number of the binder, Pe_b.

$$Ca = \frac{\mu V}{\sigma} = \frac{\text{viscous resistance}}{\text{capillary driving force}} \tag{2}$$

$$Pe_b = \frac{WL}{\rho_b D_b} = \frac{\text{bulk mass transfer}}{\text{diffusive mass transfer}} \tag{3}$$

where μ is the coating viscosity, V is the velocity of the air-liquid interface, σ is the liquid surface tension, W is the drying rate, L is the coating thickness, ρ_b is the density of the binder resin, and D_b is the diffusivity of the binder in the solvent mixture. A combination of a low Ca and a high Pe_b results in maximum binder migration to the surface, whereas moderate values of Ca and Pe_b give a uniform distribution of binder. Hence, binder migration may be lessened by increasing Ca or by decreasing Pe_b.

For this system the easiest three variables to change in Ca and Pe_b were the coating viscosity, drying rate, and coating thickness. Consequently, binder migration was controlled by increasing the viscosity of the coating formulation and by optimizing the drying rate and coat weight.

Conclusions

A printable topcoat for ink jet printing with excellent outdoor weathering was developed. In contrast to most film ink jet media, this coating uses a water-insoluble binder resin and relies solely upon a highly absorptive silica gel to absorb the liquid components of the ink. When printed with the Brady ColorPix Pro printer using the pigmented ink, the printed graphics show only a 10% reduction in color density after 1100 hr of exposure in a Xenon Are Weather-Ometer **without overlamination**. A US patent application has been accepted for this ink jet printable topcoat, but has not yet issued.

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Biography

Bruce M. Klemann is a Senior Materials Scientist at Brady USA, Inc. He received a B.S. in chemical engineering in 1987 and a Ph.D. in materials science in 1994 from the University of Wisconsin. His thesis topic was "Thermal, Mechanical, and Fracture Properties of Asymmetric Poly(alkylsilanes)". He researched the mechanical properties and fracture behavior of thin polymer films at The Dow Chemical Company in 1992 and 1993. Since 1994 he has been with Brady USA, Inc. His current research interests include media for digital printing processes, ink jet printing inks, and thermally stable adhesives and coatings.

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