Ink Jet Coatings for Pigmented Inks

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Abstract

Outdoor-durable media for wide format ink jet printers has become available during the past several years. In its simplest form, an absorptive coating for this application consists of a water resistant binder and a white pigment at some optimum ratio and coatweight. A study was conducted to determine the effect of major formulation parameters on the properties of a model coating system.

Among the variables examined were pigment/binder ratio, coatweight, and silica type. Over 30 silicas of widely ranging particle size and oil absorption were tested. Three important image properties were measured-ink capacity, CMYK densities, and adhesion of the dry coating. The effect of each variable alone, as well as interaction among variables was determined

Introduction

Ink jet media for long term outdoor applications is a fairly recent development. For outdoor use, the ink should be pigmented to minimize photofading and the binder must be resistant to water. There are very few full color sets of pigment-only inks in current commercial use. There are also very few hydrophobic binders in use for ink jet media. Prior to this study, the important formulation parameters for such a system were not well understood by us.

Three important image properties were examined in this study- image density, coating adhesion, and ink drying. 100% CMYK densities were read 24 hours after printing from a standard test target with a MacBeth series 1200 densitometer. Coating adhesions were obtained by laminating a pressure sensitive film to the unprinted topcoat and measuring with a Thwing Albert EJA Tensile Tester. To determine the drying speed, a series of fifty 1cm squares was printed in a test pattern, with the % ink coverage varying from 10-400%. By counting the number of squares exhibiting ink smearing by a media hold down bar, a relative value for ink absorption was obtained.

Four important formulation parameters were selected for consideration. These are the P/B ratio, oil absorption of the silica, silica particle size, and the coatweight of the dried ink absorbing layer.

The P/B ratio is simply a dry weight/dry weight measure of the relative amounts of pigment to binder. For a given silica, higher P/B results in a more porous coating.

Oil absorption values are a commonly reported characteristic of silica gels, defined as the amount of linseed oil (g) required to wet-out 100g of the silica. Depending on such basic parameters as surface area, pore volume, and pore diameter, the oil absorption values (OAV) for common commercial silicas cover the range 80-320 g/100g.

Silica gel consists of primary particles of 2-20 nm which form agglomerates of 2-10 microns. The second value is reported by the manufacturer as particle size, usually measured by a Malvern laser scattering analyzer.

Coatings were made on primed, pressure-sensitive vinyl. Each sample was dried at ambient. All images were printed with a Brady Colorpix^{TM} 36 inch wide printer using outdoor ink and a “fine paper” setting . Coatweights were measured by a cut and weigh technique.

All coatings consisted of a polyamide binder at 20% solids in an alcoholic solvent and a silica. The silica was wetted-out with solvent before adding the binder. A series of 34 silicas with a wide range of oil absorption and particle size was obtained from W.R. Grace and Crosfield.

We address each of the image properties separately in turn. A discussion of the affect of each formulation parameter on the image property alone is followed by consideration of the parameters in combination.

Adhesion

Adhesion of each coating to the primed vinyl was better than the intra-coating adhesion. That is, failure was cohesive rather than adhesive. Adhesion should be affected by those properties which affect the amount of binder between the particles as well as those which affect the strength of the interaction between the binder and particles. Adhesion & P/B. Coatings were made with one silica (OAV 320g/100g)(12g/m^2) and differing P/B ratios. As the P/B increased (Fig.1), the adhesion progressively decreased. This finding came as no surprise. As the P/B increases, the amount of binder decreases and so less force is required to remove the coating. Similar results are obtained with other silica samples, with the position of the curve dependent on the properties of the silica gel.

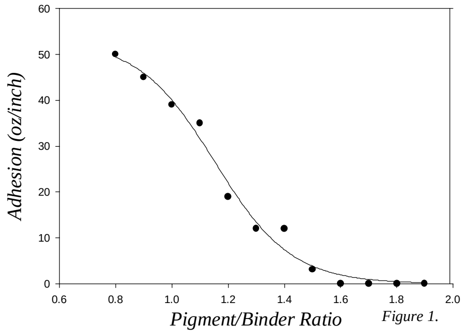

Figure 1.

Adhesion & Oil Absorption. Coatings were made at 12g/m^2 using each of the silica samples at a P/B ratio of 1.1. As shown in Fig. 2, the adhesion for silicas with low oil absorption tended to be much higher than adhesion for high OAV pigments. This seems to indicate that the higher oil absorbing silicas absorb binder, keeping it internal to the pigment particles. Internal binder doesn't help adhesion between particles and so adhesion decreases as the OAV increases. Similar results were obtained for the same silica series at a higher P/B (1.4), with the curve shifted left.

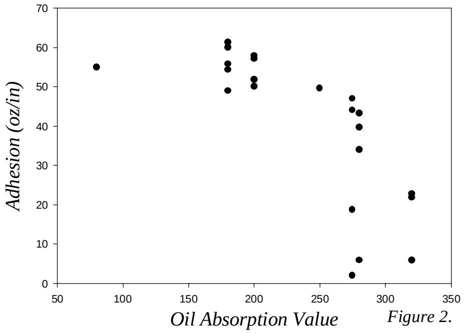

Figure 2.

Adhesion & Coatweight. From 3 to 18 g/m^2, no significant trend was seen for adhesion vs coatweight.

Adhesion & Particle Size. We saw above that, at equal P/B, higher oil absorbing silicas provide lower adhesion. However, there is a great deal of scatter in the data, leading one to suspect a secondary factor affecting adhesion. This was found to be particle size. Silicas of the same OAV but different particle size were coated over a range of P/Bs. A typical set, (275 OAV, Fig. 3), shows that silicas of larger particle size have higher adhesion values at a given P/B.

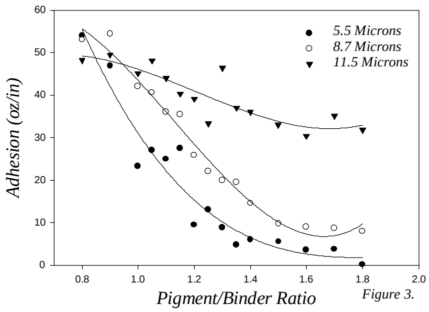

Figure 3.

In comparing large and small silicas, at equal P/B there are larger numbers of the smaller pigment/unit volume than of the larger pigment. There are therefore larger numbers of particle-particle interfaces for the smaller pigment. At equal binder levels, small particles should have less binder at each interface and therefore lower adhesion than large particles.

Ink Absorption

Smear in the test printer is caused by wiping of unabsorbed ink by a media hold-down bar 2 seconds after application. It was originally unknown whether this phenomenon was due to the ink being absorbed too slowly, or to insufficient capacity of the coating.

Ink Absorption & P/B. For a given silica type and coatweight, the ink absorption is very dependent on P/B ratio. A typical plot (Fig. 4) shows that at high P/B, there is no smear. As P/B decreases, a point is reached at which smear just starts. Smear continues to increase smoothly as the P/B drops. At low P/B levels, pores between silica particles are more filled, leading to both more constricted pores and to lower ink capacity/unit area .

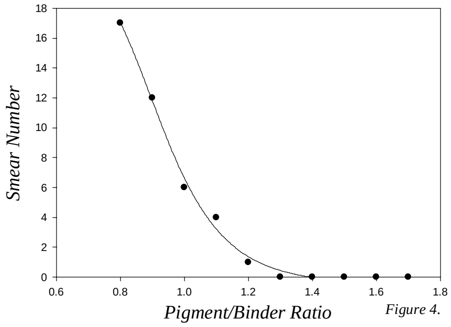

Figure 4.

Ink Absorption & Oil Absorption. Each of the 34 silicas was coated at the same coatweight and P/B ratio in order to isolate the effect of oil absorption value on the ink absorption. For a typical plot (Fig. 5)(1.1 P/B; 12 g/m^2) the higher OAV silicas exhibit less smear than lower OAV silicas. Smear is a fairly smooth function of the pigment OAV.

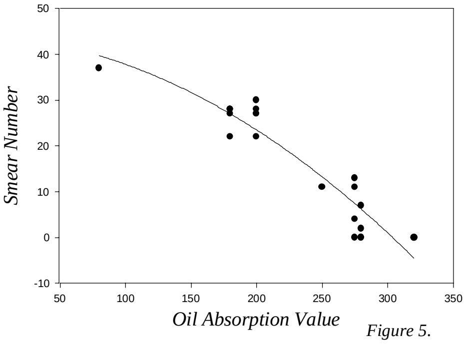

Figure 5.

We believe that the more absorbing silicas tie-up a goodly portion of the binder within their internal pore structure. This leads to larger pores between particles and thus, higher ink capacity and less smear.

Ink Absorption & Coatweight. Ink absorption is very dependent on coatweight. Typical data is plotted below (Fig. 6) in which a silica (OAV 320) was coated at 1.1 P/B over the coatweight range 3- 18 g/m^2. In going from high to low coatweight, a point is reached at which smear begins. Going to even lower coatweights, smear becomes progressively worse. This implies that smear is related to the capacity of the coating rather than the absorbance rate.

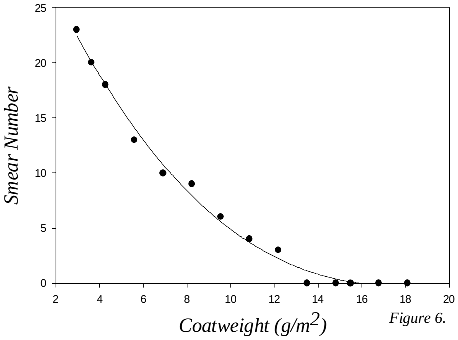

Figure 6.

Ink Absorption & Particle Size. There does not appear to be any effect of particle size on ink absorption over a size range of 3X. This again implies that smear is due to limited ink capacity rather than slow absorbance rate. If smearing was dependent on speed of absorption, one would expect there to be a large particle size effect. That is, particle size should affect the pore size and therefore the rate at which liquid enters the coating. However, particle size does not affect the void volume of packed pigment particles and does not affect the capacity of the coating.

Image Density

Image density is important in determining the acceptability of an ink jet medium. For dye-based inks, a major concern is keeping dot spread to a minimum. For pigmented inks, it is important to allow high dot spread, yet keep colorant near the surface of the coating.

Image Density & P/B. In studies of P/B and density, the density increased with decreasing P/B. This density increase continued up to and slightly past the point at which smearing started. At even lower P/B, smearing yielded somewhat lower densities.

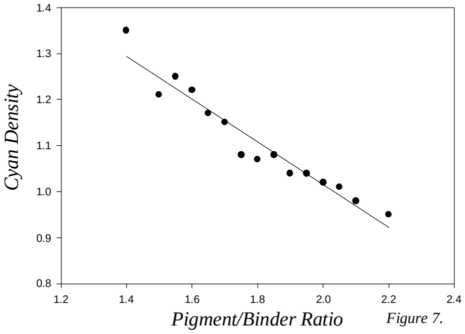

Figure 7.

Image Density & Oil Absorption. When the 34 silicas were coated at the same P/B and coatweight, there was a great deal of scatter in a plot of density vs oil absorption value (OAV). This led us to believe that at least one other important factor, silica size (see below), was affecting the densities. If we separated and plotted density data only for silicas of a given size range, (Fig. 8, 1.4 P/B, 12 g/m^2, 8-9 micron size), a trend was seen of the density increasing with decreasing OAV.

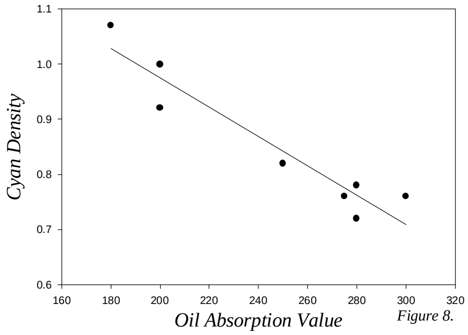

Figure 8.

Image Density & Coatweight. Plots of density vs coatweight exhibited similar appearance for all silica types studied. (Fig. 9) In going from high to low coatweight, the density progressively increased, to the point of smearing. Beyond that point, the density decreases. That is, the highest useful densities are obtained at the lowest non-smearing coatweight.

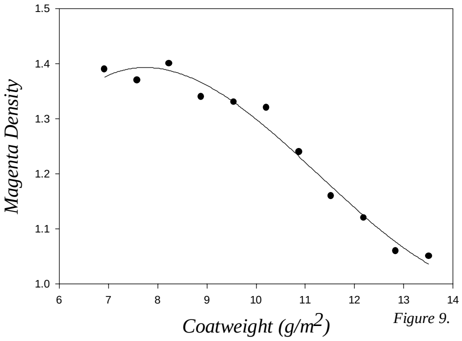

Figure 9.

Image Density & Particle Size. Sets of silicas were examined in which each member of a set possessed the same OAV and differed in particle size. For each of these sets, there was a consistent trend that the silicas of larger average size gave the highest densities. The density advantage of larger vs smaller pigments can be quite large (as much as 0.4 units). Fig 10 shows data from one set of silicas which possess an OAV of 275g/100g and particle sizes of 5.5, 8.7, and 11.5 microns.

What accounts for the effect of size on density? We believe the phenomenon to be an optical one. For silicas at the same P/B and coatweight, the larger silicas should have fewer particles and therefore fewer light-scattering interfaces. Less scattering leads to higher density due to less hiding of colorant.

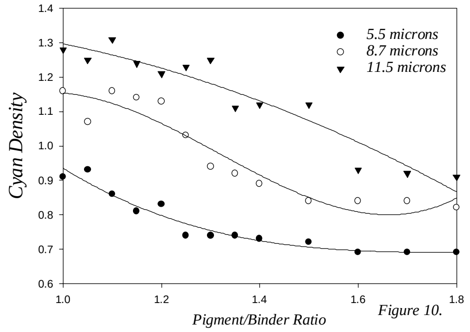

Figure 10.

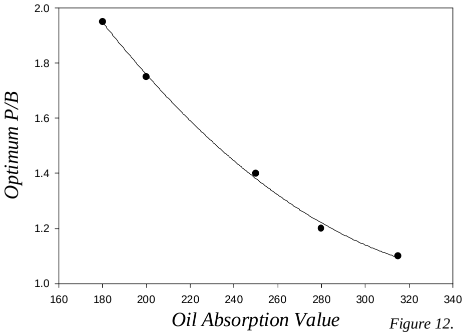

Figure 12.

Interaction of Parameters

We have seen that the formulation parameters do not act independently. For example, P/B, OAV, and coatweight all strongly affect the ink capacity of the coating and therefore both the drying and point of maximum density. This is illustrated by the plot below (Fig. 11) of smear point plotted on axes of P/B and coatweight. There is a direct tradeoff between P/B and coatweight. The densities at the non-smear points are independent of the position on this curve. That is, attainable density at high coatweight and low P/B is the same as that at low coatweight and high P/B. Similar curves are obtained for silicas with differing OAV. Curves for higher OAV silicas are below the curve shown, while those for low OAV silicas are above.

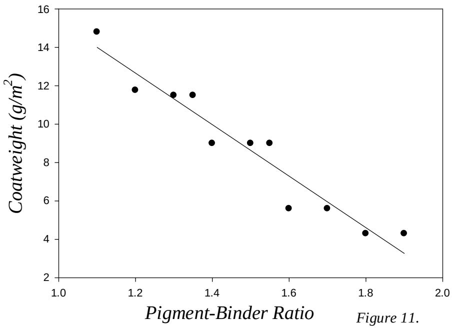

Figure 11.

Another way of examining tradeoffs among the formulation parameters is to consider several different silicas with the same particle size and coatweight but different oil absorbance. A plot of density vs P/B results in a plot similar to Fig.7 for any of the silicas. Silicas with different OAV possess curves shifted from this position. The position of the point at which smearing just starts to occur is a smooth function of the OAV, as shown in Fig. 12 (12g/m^2, 10 micron size). Samples occupying the area below and to the left of the curve exhibit smear.

At the smearing point for each of the silicas, the *adhesion and density are the same for each pigment*. That is, by adjusting the P/B, silicas of similar particle size can be made to yield the same optimal density, absorbance, and adhesion. No functional difference is seen between a high P/B /low OAV coating and a low P/B/high OAV one. Both the oil absorption value and P/B control the amount of binder between pigment particles.

Conclusion

From this study, we found that those parameters which affect the amount of binder between particles affect the adhesion. With other factors constant, low P/B, low pigment oil absorption, and large particles lead to higher adhesion. Coatweight does not greatly affect adhesion.

Those parameters which affect the void volume affect the smearing of the image. With other factors constant, high P/B, high coatweight, and high OAV lead to high ink absorption and thus, low smearing. Particle size does not greatly affect ink absorption.

Those factors which prohibit deep penetration of the colorant particles into the coating-low coatweight, low P/B, and low oil absorption lead to higher densities. Larger, less scattering particles also lead to high densities.

Pigment particle size was found to be very important in determining the coating properties. Use of the largest size possible, consistent with coating roughness and resolution constraints is recommended. There is a tradeoff among the parameters of coatweight, pigment oil absorbance, and P/B ratio. These must be optimized together in order to produce the best possible coating.

Biography

Paul Adair received his BS in Chemistry from Indiana University in 1976 and his Ph.D. in Inorganic Chemistry from the University of Illinois in 1980. His thesis work involved organometallic synthesis. Since that time, he has conducted research and development at Mead, Mead Imaging, DX Imaging, and W.H. Brady. The bulk of his work has centered on the physical and polymer chemistry of imaging systems, including ink jet, photopolymers, and electrophotography. He has also conducted basic and applied research on the photopolymerization of acrylate systems. Paul holds 38 US patents, and has published and presented many papers.

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