

Effects of Mordant Type and Placement on Inkjet Receiver Performance

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Abstract

We have investigated the effect of two common dye mordants, poly(vinylbenzyl trimethyl ammonium chloride) (PVBTMAC) and poly(diallyldimethyl ammonium chloride) (PDADMAC) on the image stability of inkjet prints generated by two Hewlett Packard inksets. The effect of mordant placement in the coated structure (top, bottom, or throughout) was studied using optical cross sectional micrographs and correlated with the stability data.

Experimental

Poly(diallyldimethyl ammonium chloride) (Aldrich Chemical Co.) was used as received. An aqueously dispersed crosslinked latex of poly(vinylbenzyl trimethyl-ammonium chloride) was prepared as described in reference [1], such that the molar ratio of vinylbenzyl trimethyl ammonium chloride: ethylene glycol dimethacrylate was 93:7. Each mordant material was combined with non-deionized lime process ossein photographic quality gelatin (Eastman Gelatine) in a ratio of 90:10 and coated from a 10 weight % solution in water onto corona discharge treated polyethylene-resin coated paper. The films were chill set at 40 degrees F, then thoroughly dried by forced air heating to yield coatings with a total dry coverage of 8.6 grams/square meter.

Where the mordant is specified as being distributed throughout the film, the 90/10 binder/mordant composition comprises the entire layer. If the mordant is specified as residing in the top half only; the bottom 4.3 grams/square meter are gelatin only, while the 90/10 binder/mordant composition is used only to coat the top 4.3 grams/square meter. When the mordant is located in the bottom half, the opposite sequence is coated. In either case, the two layers are coated simultaneously by a slide hopper technique.

Prints were made on the films using a Hewlett Packard Photosmart printer (C3844A and C3845A cartridges)) or a Hewlett Packard 722 or 890 printer (C1823A cartridge). Targets were generated using CorelDRAW software specifying 100% cyan, magenta, or yellow.

Lightfastness was evaluated by exposing the printed samples to 50 KLux daylight radiation for 7 days. Lightfastness is recorded as % retained optical density.

Waterfastness by soaking was evaluated by immersing the printed samples in room temperature deionized water with light agitation for 5 minutes. Retained optical density is recorded. Values of retained optical density of 100% are indicative of dye immobilization; below 100% indicate that dye is dissolved out of the receiver, and values over 100% indicate that while the dye is confined in the layer, bleed occurs.

Dripfastness was measured by placing printed samples at a 45 degree angle to the horizontal, and dripping one drop (about 0.1 mL) of deionized water on each color patch. The prints are inspected and a qualitative evaluation of dye movement is made. A rating of poor indicates a large amount of dye movement, fair indicates that some dye is moved, and good indicates that no dye movement was detected.

Optical densities of the as-printed samples were compared, but no significant variations were observed with changes in mordant placement or type.

Offset was evaluated by printing patches of solid ink, holding the prints for 2 hours, then interleaving them with bond paper and stacking them under pressure. After 24 h, they were unstacked and the bond paper inspected for evidence of offset. In general, there was very little evidence of any offset and no difference between any of the samples.

In an attempt to gain insight into the mechanisms of the observed trends, printed areas were cross sectioned and examined by optical microscopy.

Results

In order to better understand the mobilities of the various dyes, chemical analysis of the cyan, magenta, and yellow inks were performed.

HP Photosmart Inks

Chemical analysis of the cyan, magenta, and yellow inks in the C3844A and C3845A cartridges indicates that all the ink sets have nearly identical humectant mixtures, consisting of 8.0-9.0 weight % 1,2-hexanediol.

HP 722/890 Inks

The C1823A cartridges yielded the following information, which confirms the information in ref. [2].

Ink	pH	Humectant mixture (by weight)
Cyan	7.9	8% 2-pyrrolidone; 8.6% 1,5-pentanediol; 7.7% 2-ethyl-2-(hydroxymethyl)-1,3-propanediol
Magenta	6.8	similar to cyan
Yellow	6.2	4.2% 2-pyrrolidone; 4.3% diethylene glycol; 8.2% 2-ethyl-2-(hydroxymethyl)-1,3-propanediol

While the yellow ink contains only one dye, two distinct dyes were detected in each of the cyan and magenta inks.

While both the Photosmart and 722/890 inks contain anionic dyes, the analysis of the dye structures indicates that with the exception of the cyan dye, they are different from each other.

Effects of Mordant Distribution on HP Photosmart Performance

The placement of the mordant within the layer has a marked effect upon the distribution of the dyes in the layers. This is particularly apparent in the case of the magenta and yellow dyes, which are apparently strongly enough attracted to the mordant species that they are practically absent from the top half of the layer when mordant is present only in the bottom. The cyan dye, while obviously attracted to the mordanted bottom half of the layer, still remains substantially distributed in the upper portion of the film.

All the inks have similar solvent mixtures, so no differences in solubility or swellability of the layers should be observed for the different inks. Instead, such differences may be partly explained by taking into account the molecular size, and hence mobility, of typical anionic inkjet dyes. While magenta and yellow dyes are generally fairly small molecules, cyan dyes often belong to the bridged phthalocyanine family and are of a higher molecular weight and larger size, inhibiting their ability to travel as freely throughout the swollen inkjet receiver layers.

The observations above can be helpful in understanding the stability data below, which show the lightfastness and waterfastness of the two mordants in various positions.

Waterfastness (Soak Test)

Mordant	Where	C	M	Y
None		78	35	50
PDAD MAC	Through	113	87	99
“	Top	101	96	96
“	Bottom	100	101	99
PVB TMAC	Through	105	100	102
“	Top	106	101	87
“	Bottom	93	96	88

The waterfastness data clearly shows an improvement in dye retention and bleed resistance when either of the mordants is introduced. There are slight differences in retention depending upon where the mordant is positioned, however, they are not as dramatic as one might expect from the cross-sectional dye distributions. In particular, the behavior of the cyan dye is surprisingly independent of whether the dye is actually in contact with the mordanting species. When the mordant is located solely in the bottom layer, and the cyan dye does not appear to reach it, the waterfastness is only slightly different from when the mordant and dye are both located in the top layer. It is possible that with the soak test method of measuring waterfastness, the ink receivers are sufficiently swollen so that dyes can migrate further into the layer, perhaps reaching the mordant-containing regions.

In contrast, the dripfastness test, while much less quantitative, does provide a means for differentiating water resistance of the various receiver/mordant combinations. For the case of PDADMAC, the following observations were made:

Qualitative Dripfastness

PDADMAC Location	C	Y	M
Top half only	Good	Good	Fair
Bottom half only	Fair	Fair	Poor

Confining the mordant to the top half of the receiver obviously is advantageous over locating it in the bottom. For the case of the PVBTMAC latex, the effect was somewhat less obvious:

Qualitative Dripfastness

PVBTMAC location	C	Y	M
Top half only	Fair	Good	Poor
Bottom half only	Fair	Fair	Poor

Lightfastness

Mordant	Where	C	M	Y
None		91	97	90
PDAD MAC	Through	93	76	89
“	Top	98	60	90
“	Bottom	97	70	92
PVB TMAC	Through	98	76	95
“	Top	97	75	95
“	Bottom	95	76	93

The lightfastness data shows a substantial decrease in magenta lightfastness when either mordant type is introduced into the system. In the case of the latex mordant, there is no change in magenta lightfastness regardless of where the mordant is located. Since there is only half as much mordant present in the systems where it is present only in half the film, we would expect there to be less of an effect on lightfastness. However, since the magenta dye migrates preferentially to the areas containing mordant as discussed above, presumably every dye molecule is associated with and destabilized by a mordanting species.

In the case of the solution polymer, PDADMAC, we see a small effect of mordant placement on magenta lightfastness, with placement of the mordant in the bottom half of the film resulting in an improvement in lightfastness over locating it in the top half. Since there is a substantial amount of magenta dye remaining in the top half of the film, where no mordant is available, it is not adversely affected by exposure to light.

The yellow dye is distributed much like the magenta dye in the layers, but is apparently not destabilized by the presence of either the latex or PDADMAC mordants. As a result, we see no difference in the stability of the yellow dye between the samples. The cyan dye is not partitioned through the layer to the extent that the other dyes are, and as a result its distribution is not as dependent on mordant presence or location.

Effect of Mordant Distribution on HP 722/890 Performance

Unlike the HP Photosmart magenta, the HP 722/890 magenta dyes to not tend to migrate to the bottom of the layer when the mordants are concentrated there. The cyan dye acts similarly to the magenta, remaining near the top surface regardless of the mordant location. The yellow shows more evidence of migration to mordant-rich areas of the film.

Comparison of the yellow and magenta ink compositions shows a difference in humectant type and amount, which may influence the distribution of the ink and therefore dye within the coating.

Waterfastness

Mordant	Where	C	M	Y
None		89	90	25
PDAD MAC	Through	139	105	124
"	Top	141	121	125
"	Bottom	151	135	122
PVB TMAC	Through	119	121	106
"	Top	118	127	115
"	Bottom	137	134	115

The waterfastness data confirms the microcopic evidence that the yellow dye reacts strongly with the mordants evaluated. However, as observed with the Photosmart inks, there is surprisingly little dependence of dye loss or bleed on where in the structure the mordant is located. Even when dyes are not distributed well into the portions of the film that contain mordants, waterfastness is improved over the cases when no mordant is present.

Changes in water resistance measured by the dripfastness test were less conclusive than for the case of the Photosmart inks described above. In general, there were very slight improvements observed in dripfastness when the mordant was located nearer the free surface.

The lightfastness data shows a dramatic effect of mordant presence on magenta and yellow dye fade, and little effect on the cyan dye. The magenta lightfastness shows an interesting effect. When the mordant is located in the bottom half of the film, most of the magenta dye never reaches it, and the lightfastness is improved over the cases of having PDADMAC throughout the entire layer or in the top half. The same trend is observed for the latex mordant, again indicating that the dye and mordant must be in contact in order for the degradation to proceed.

Lightfastness

Mordant	Where	C	M	Y
None		77	81	81
PDAD MAC	Through	70	49	36
"	Top	70	55	42
"	Bottom	75	72	47
PVB TMAC	Through	68	56	42
"	Top	67	55	58
"	Bottom	73	81	56

Conclusions

Optical Density and Offset

For the ink sets studied here, optical density and offset performance were not affected by mordant presence, type or placement. These observations were somewhat unexpected, since introduction of a mordanting species would be expected to reduce offset by limiting dye mobility and hence probability of transfer to a contact sheet. It is possible that the particular solvent mixtures used in these inksets allow the dyes to penetrate sufficiently that such surface effects become negligible. The optical densities would be expected to increase measurably if the dye is held mainly near the free surface of a given receiver. However, in these cases, no difference was observed whether the dye was held deeply within the layer at the top of the layer. One explanation is the high degree of transparency of the ink receiving layers studied here, so that light is not scattered significantly in the top part of the layer when the dye is confined to the bottom.

Waterfastness

All the mordants improve waterfastness performance as measured by a soak test, as expected. However, this improvement is observed whether or not the dye is in contact with the mordant before the soak test starts. It is postulated that the soak test lasts sufficient time that much of the dye can travel in the receiver so that it encounters a mordanting species if it is not already mordanted. In contrast, waterfastness as measured by a drip test shows results more consistnet with expectations, with dripfastness degrading when the dye and mordant are not in direct contact in the layer.

Lightfastness

All the mordants studied here had an adverse effect on at least one of the dyes in each of the ink sets tested. The mordants and dyes must be in contact within the layer in order for the dye fade to occur. In the examples where the dye is confined to the topmost layer, but the mordant confined to the bottom most layer, dye fade was reduced substantially. By carefully altering dye mobilities through molecular weight or humectant choice, layers can be provided such that the dye species most susceptible to light fade do not contact the mordant-containing regions, while all others do. In such a way, waterfastness and lightfastness could be co-optimized.

Acknowledgements

Barb Rawleigh, Bob Guistina, and Scott Derry all contributed greatly to the analytical data discussed here.

References

1. R. N. Kelley and G. A. Campbell, “Silver Halide Element with an Antistatic Layer”, US Patent 4,070,189.
2. L. E. Johnson, H. P. Lauw, N. E. Pawlowski, J. P. Shields and J. M. Skene, “Thermal Ink-Jet Inks having Reduced Black to Color and Color to Color Bleed”, US Patent 5,536,306.

Biography

Lori Shaw-Klein received her B.S. and M.S. in Materials Engineering from Rensselaer Polytechnic Institute in 1983 and 1985, respectively. She joined Bausch and Lomb in 1985 working on optical thin film deposition, and received her Ph.D. in Materials Science from the University of Rochester in 1992. Since 1992, she has been at Eastman Kodak Company, where she currently works on ink jet media development.

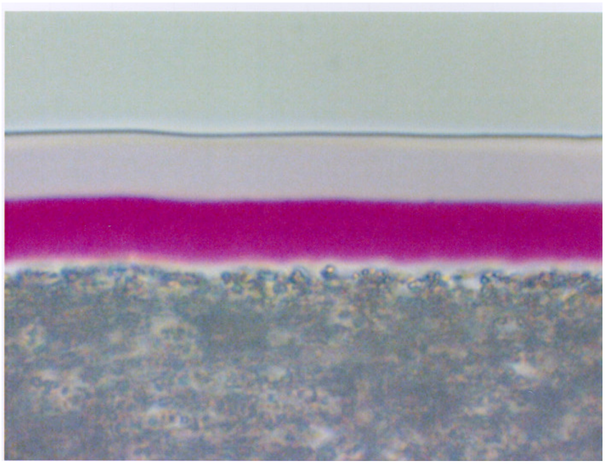

Figure 1. HP Photosmart magenta dye distribution with PVBTMAC concentrated in bottom half of receiver

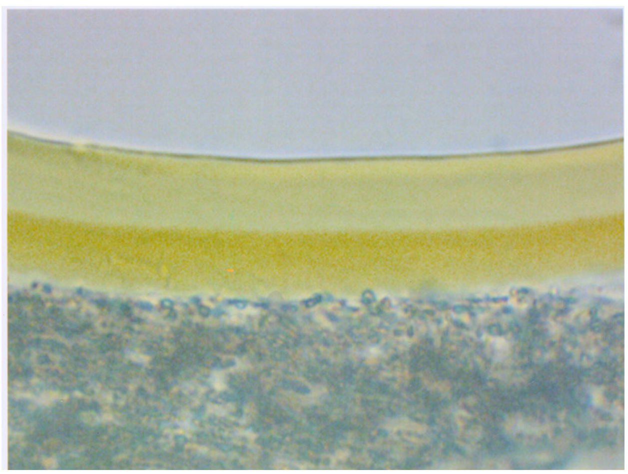

Figure 2. HP Photosmart yellow dye distribution with PVBTMAC concentrated in bottom half of receiver

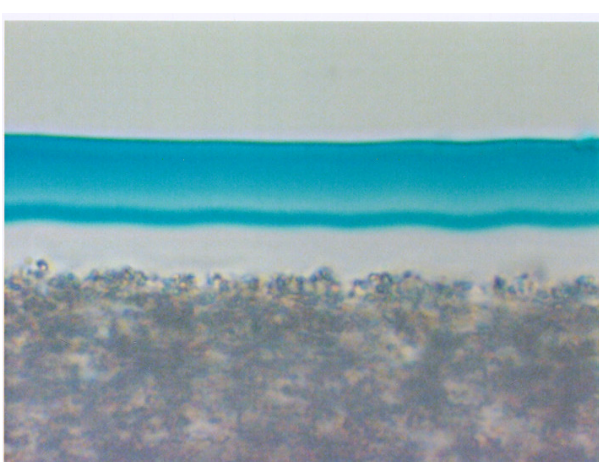

Figure 3. HP Photosmart cyan dye distribution with PVBTMAC concentrated in bottom half of receiver

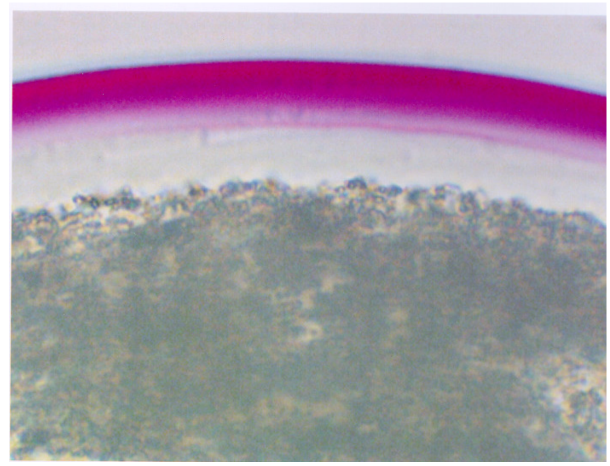

Figure 4. HP 722 magenta dye distribution with PVBTMAC latex concentrated in lower half of receiver

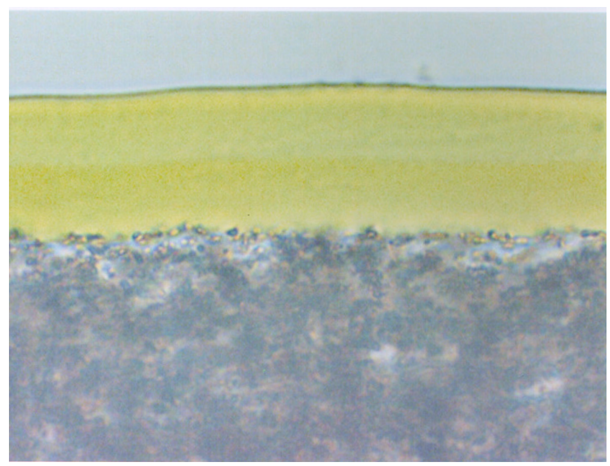

Figure 5. HP 722 yellow dye distribution with PVBTMAC latex concentrated in lower half of receiver

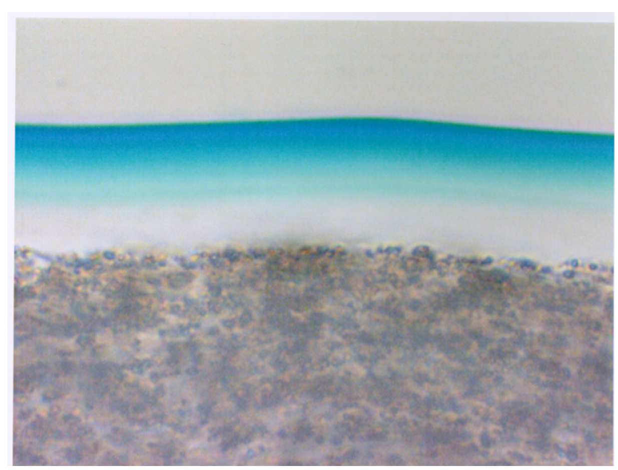

Figure 6. HP 722 cyan dye distribution with PVBTMAC latex concentrated in lower half of receiver