Novel Black Pigment For Ink Jet Ink Applications

Joseph E. Johnson and James A. Belmont
Cabot Corporation, Billerica, Massachusetts

Abstract

An innovative black pigment has been developed for water-based inks which provides significant improvements over existing black colorants (dyes and carbon black). Key ink performance improvements include outstanding pigment stability, excellent heat/freeze-thaw stability, fine particle size, and compatibility with water and other ink components. An Ames assay of the pigment was negative. Cabot's new pigments were compared to commonly used ink jet ink dyes for optical properties and fade resistance. Draw downs of the black pigment were found to be darker than those of the dyes, and did not fade when exposured to ultraviolet light. An "ink" was formulated with the pigments and used in drop on demand (Hewlett Packard DeskJet 540 and Canon BJ-200ex) ink jet printers. The optical density and print quality of prints made with pigmented ink were darker and better in quality than that of the ink jet inks that are normally used with the printers. More than 200 ml of a pigmented ink was run through the same cartridge, resulting in no clogged nozzles and no kogation. Cabot's new pigment is a technological breakthrough which improves upon current ink jet ink and print properties.

Introduction

Pigments have several inherent advantages over dyes as colorants including better image durability (waterfastness, rub resistance, and fade resistance), sharper edge acuity, IR (bar code) readability, and heat resistance. Due to these and other benefits, DuPont created a pigmented black ink for use in the Hewlett-Packard (H-P) 1200C ink jet printer three years ago and for the H-P 1600C earlier this year. These products have alleviated most concerns about using pigments in ink jet inks including poor stability, propensity to clog nozzles, and large particle size. However, carbon black still needs to be dispersed and stabilized, usually with the addition of a polymer or surfactant. The resulting dispersion is dictated by the surfactant properties (surface tension <40 dyne-cm, propensity to foam, temperature dependence, stability concerns, etc.). A new type of hydrophilic black pigment has been developed by Cabot Corporation which is non-foaming and stable in aqueous media. The pigmented dispersions have surface tensions and viscosiies similar to those of water. In this paper, optical and light stability properties of Cabot's two new black pigments and four commonly-used ink jet dyes were compared. The optical density (O.D.) and quality of prints made from pigmented ink and ink normally used with D.O.D. printers were also compared. Ink made with one of the pigments was also tested in the printers for nozzle clogging and kogation.

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Colorant Description

In the first study, two Cabot pigments and four commercially available ink jet ink dyes (Table 1) were tested for optical and fade resistance properties. The properties of the dispersions of pigments are shown in Table 2. The high surface tension and low viscosity of the pigmented dispersions may promote stable constant droplet velocity and shorten droplet break-off time[1].

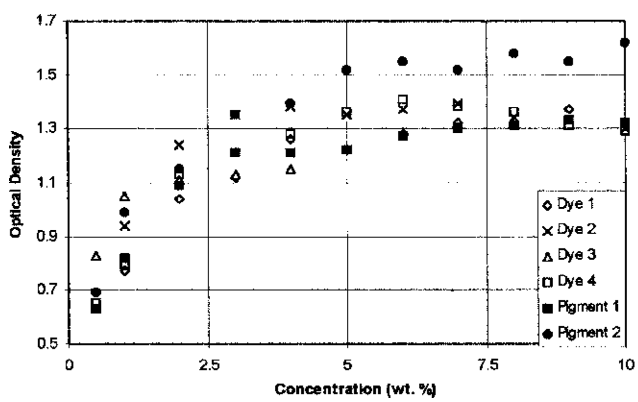

Figure 1. Print Optical Density vs. Colorant Concentration for 3 mil draw downs

Optical Density vs. Colorant Loading

Colorant solutions and dispersions were drawn down at a 3 mil (76.2 um) "wet" thickness on Nashua Dataprint Dual-Purpose Xerographic 20# uncoated paper and al-

Table 1. Colorant Description

Colorant	Description	Type
Dye 1	DUASYN® Direct Black HEF-SF	Direct Black 168-type dye
Dye 2	Basacid® Black X34	Mixture of azo dyes
Dye 3	PRO-JET® Fast Black 2	Azo dye
Dye 4	Bayer SPECIAL BLACK HF	Azo dye
Pigment 1	Cabot Corp. Pigment	Novel Black Pigment
Pigment 2	Cabot Corp. Pigment	Novel Black Pigment

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lowed to dry. The sample concentrations varied from 0.5 to 10% by weight of colorant, except for Dye 3, which was supplied at a 4% solid content. The O.D. readings, determined with a Macbeth 9015 optical densiometer, plotted against colorant concentrations generally showed an initial rise and then leveling off for the colorants (Figure 1). Draw downs of Pigment 1 were similar in darkness to those of the dyes at low and high concentrations. Pigment 2 draw downs exhibited the greatest O.D. of any colorant, at equal concentration, above a 2% loading. The superior optical density of the draw downs of Pigment 2 are probably due to both the colorant adsorbing (laying on the surface) on the substrate, as well as absorbing into the paper fibers. A higher print density is obtained when the colorant remains at the surface of the paper as opposed to being deeply absorbed into the fibers[2].

Table 2. Properties of a 5% (wt.) Pigment Dispersion In Distilled Water

Property	Attribute
Particle Diameter*-Avg.	< 0.10 um
Particle Diameter-Largest	< 0.40 um
Viscosity	1.5 cP
Surface Tension	74 dyne/cm
Density	1.04 g/cc
pH	6.5
Stability- 70 deg. C	> 6 weeks
Stability- Freeze-Thaw	>3 cycles
Stability- Room Temperature	> 1.5 years
Ames Test	Negative

* particle sizing as determined with a Leed's & Northrup Microtrac® UPA instrument.

L*a*b* Values of Draw Downs

L*a*b* readings of draw downs (4% colorant wt.) were determined with a Hunter LabScan II instrument (Table 3). As expected, the L* (lightness) values are inversely proportional to the O.D. readings of Figure 1 (i.e., the lower the L* reading, the darker the draw down). The darkest film, confirmed both visually and by the lowest L* reading, contained Pigment 2. The Dye 1 draw down had a golden-yellow gloss, which is indicated by a high b* value (positive b* representing a yellow color). Dye 2 and 4 draw downs have a blue undertone (negative b* reading), while the Dye 3 film had a bronze-red sheen (positive a* value). The draw down with Pigment 2 has a lower L* value (is darker) compared to that of the glossier Pigment 1. Blackness is a function of both light absorbance and the reciprocal of light scattering (gloss)[3,4].

Table 3. L*a*b* Values of Prints Containing Different Colorants

Colorant in Print	L*	a*	b*
Dye 1	30.7	0.64	5.3
Dye 2	24.9	0.30	-0.12
Dye 3	31.9	4.1	0.18
Dye 4	28.4	-0.52	-0.75
Pigment 1	31.6	0.41	1.3
Pigment 2	24.7	1.0	3.44

Absorption Spectra of Colorants

Absorption spectra of the colorants (diluted with distilled water to 3×10^{-5} g/ml) were obtained using a Perkin-Elmer Lambda-6 UV/Vis spectrophotometer. The pigments absorb throughout the visible and near infra-red region (400-900 nm), while the dyes absorb in limited parts of the visible region (Figure 2). Dye 1 has a strong absorption peak at 485 nm, confirming that the draw down from this dye has a yellow component. Pigment 1 has a higher absorption profile than that of Pigment 2, although draw downs of Pigment 2 are darker than that of Pigment 1. Prints are dependent upon the substrate (paper fibers and voids), the placement of the pigments (into and on the paper), and the interaction properties between light rays and the pigment (absorption and scattering). In a liquid dispersion the scattering of light is governed by the medium (water) and the absorption is controlled by the pigments.

Black pigments are commonly used for making labels for IR and bar coding machines due to their absorption through out the visible and near-infra red regions. A dye may need an infrared absorber (e.g., heavy metal, cyanine, or anthraquinone) to be usable with such machines[5].

Bar codes, made from inks (described later) made from Pigments 1 and 2 using the SCAN-ONE™ Suite system (Vertical Technologies), could easily be read.

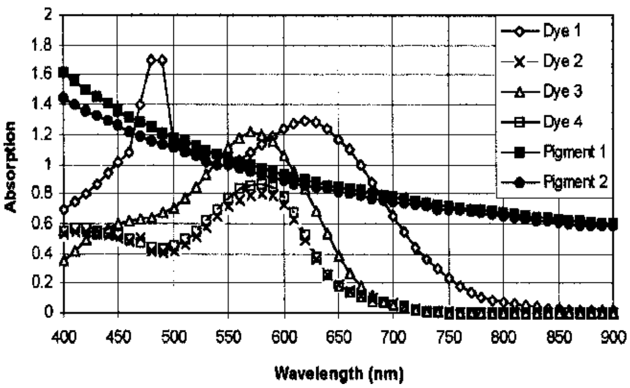

Figure 2. Absorption Spectra of Colorants in Distilled Water at 3×10^{-5} g/ml concentration.

Print Permanence

Print permanence, or light stability, is important for outdoor and office light exposure as well as archival purposes. Draw downs (4% colorant wt.) were exposed to UV-A light using a QUV Accelerated Weathering QUV/SE Instrument (Q-Panel Co.) at an intensity of 0.875 W/m^2/nm (1.25× summer daylight) and a temperature of 60 deg. C. Optical densities of the draw downs were followed as a function of exposure time for fifteen days (Figure 3). The draw downs of both pigments and of one dye retained their original O.D. after the light exposure test. However, films made with the other three dyes faded considerably.

Printing Properties of Pigmented and Common Ink Jet Inks

In the second study, an "ink" (formulation in Table 4) made with Pigments 1 and 2 was used in the Hewlett Packard DeskJet 540 and Canon BJ-200ex printers. Prints made using the dye-based inks (normally used in the printers) were compared to those made with Pigments 1 and 2 for optical density and quality. Hewlett Packard's criteria[6] was used in determining the O.D. and print quality of prints made with the H-P printer. In addition, the Pigment 1 ink was tested for runnability and kogation in the D.O.D. printers.

Table 4. Pigmented "Ink" Formulation, pH 8.5

"Ink Component"	Amount (g)
Pigment	7.0
Triethanol Amine (1 M)	0.5
Ethylene Glycol	10.0
Distilled Water	83.5

Print Optical Density

For the H-P printer, five O.D. values from the prints using the standard test pattern on Nashua 20# uncoated paper, were measured with the Macbeth 9015 densiometer and averaged. The %D, percent difference in O.D. readings was calculated according to Equation 1[6]:

$$\%D = [(O.D._{max} - O.D._{min})/O.D._{min}] \times 100 \qquad (1)$$

The pigmented ink prints were found to be darker and had less deviation in optical density compared to the print made with the recommended ink jet ink (Table 5).

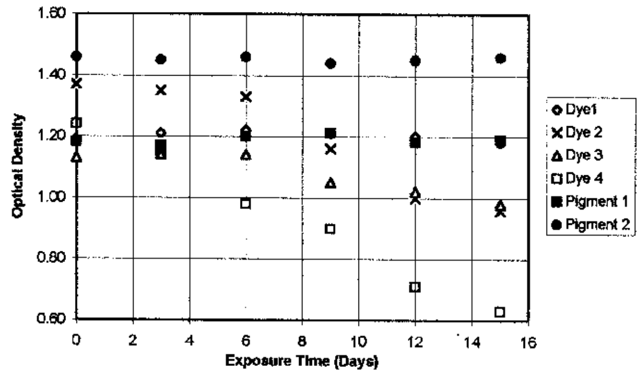

Figure 3. Optical Density of Colorant Draw Downs as a function of UV-A Exposure Time

Table 5. Print Optical Densities and Deviations Using the Hewlett-Packard DeskJet 540 Printer

Print	O. D. (Avg.)	%D
H-P 51626A	1.23	3.3
Pigment 1 Ink	1.29	2.3
Pigment 2 Ink	1.50	2.0

Optical densities of prints made from the pigmented and the Canon ink using the Canon BJ-200ex printer's test pattern were obtained (Table 6). Again, the pigmented ink prints were jetter than those made from the inks that came with the printers.

Table 6. Print Optical Densities From Canon BJ-2ex Prints

Print	O. D.
BC-02 Ink	1.19
Pigment 1 Ink	1.25
Pigment 2 Ink	1.44

Print Quality

Prints made with the H-P printer were tested for quality in accordance with Hewlett-Packard criteria[6]. Wicking, ink flow along paper fibers, causes the characters to have "fuzzy" edges. Spray, the satellite drops, also causes degradation in print quality. Figure 4 shows the characters "Th" generated from the 51626A and both pigmented inks. The characters at 5× magnification have "good" prints according to the wicking standard[6], although the dye-based ink feathers (Figure 4A), while the pigmented inks do not (Figure 4B,C). The 51626A ink also has considerable spray compared to the Pigment 1 ink although, this may also be due to other ink properties (e.g., surface tension and viscosity). The prints generated from the pigments are also narrower than that of the dye—which probably spread on the paper. The characters made from the pigmented inks are better in quality (have sharper edges, don't feather, and have less spray) than those made with the dye.

Figure 4. "Th" characters printed with Hewlett Packard's DeskJet 540 printer using: A) 51626A dye-based ink (top), B) Pigment 1 ink (middle), and C) Pigment 2 ink (bottom)

Runnability of Pigmented Ink

Ink made with Pigment 1 was put in Canon and Hewlett-Packard cartridges and used in the Canon BJ-200ex and H-P DeskJet 540 printers, respectively. Continuous test patterns were printed and the initial cartridges were refilled when the ink was empty. Ten 20 ml cartridge volumes for the Canon printer and seven 35 ml cartridges for the H-P printer were used in the experiment. If the volume of an ink droplet is 50 pl and 200 ml of ink was used, then 40,000,000 droplets were fired per cartridge. The cartridge nozzles did not clog and no kogation was detected since the print O.D. and quality was constant during the study.

Discussion and Summary

Cabot's new hydrophilic, black pigments have excellent properties including dispersion stability in water, and small particle size. The pigments were also found to be Ames negative (non-carcinogenic). Extremely dark draw downs could be obtained using the pigments. The optical density of the pigmented films can significantly exceed those made with commonly-used ink jet dyes. The pigments also do not fade with exposure to UV light. The pigments also absorb through out the visible and near-IR regions. D.O.D. prints and characters made from pigmented inks were darker and more defined than those made with normally-used dye based ink. Copious volumes of pigmented ink did not clog print head nozzles or cause kogation. Cabot's new pigments are a breakthrough in ink jet ink colorant technology and may be used to produce darker, higher quality, non-fading prints.

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