Universal Black Inks Based on New Polymeric Carbon Black Dispersions

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Abstract

Carbon black is well established as the primary pigment in text black inks utilized in small office/home office (SOHO) desktop ink jet printers. Through innovations over the past 10–15 years, inks containing self-stabilized dispersions of surface-functionalized carbon black pigments have evolved as the main technology for such applications. Factors influencing this choice include text density and acuity, paper-to-paper (plain) image quality consistency, and versatility in ink formulation. Although these technologies set the industry standard, important limitations still exist; these include: (1) image smear on plain papers typically used in desktop printing, and (2) the lack of image gloss and durability on coated, glossy papers used for photo printing. These limitations have precluded the broadest use of inks based on self-stabilized pigments. This has been especially true for drop-on-demand thermal ink jet.

This paper focuses on the question of whether it is possible to develop a universal or single black ink based on alternative carbon black dispersion technology that is able to meet the critical requirements of both plain (for text and graphics) and glossy (for photos) papers used in SOHO desktop ink jet printers.

New polymeric dispersions comprising specific carbon black pigments and new polymeric dispersants (terpolymers) have been developed that can provide some of the important performance characteristics of self-stabilized carbon black dispersions used in the ink jet industry. Random terpolymers of benzyl methacrylate (BzMA), an additional hydrophobic monomer containing twelve or more carbon atoms, and methacrylic acid (MAA) have been used as effective dispersants with Black Pearls®700 carbon (Cabot Corporation). Certain inks formulated with these new dispersions were found to be suitable for a variety of ink jet applications and appear to overcome many of the deficiencies currently limiting the more general use of black inks that rely upon self-stabilized carbon black dispersions such as Cab-O-Jet®300 (Cabot Corporation). Several of these new black, pigment-based inks have provided excellent performance when applied to both text and graphics printing (on plain paper) and photo printing (on glossy photo papers).

Introduction

Significant advances in the design and capability of carbon black dispersion technology have occurred since the mid 1990s. Most notable among these advances has been the surface functionalization of carbon black. For example, Belmont [1,2] and Belmont et al. [3] describe the attachment of a variety of functional groups to the carbon surface through diazonium salt reactions, while Nagasawa [4] discloses the direct oxidation of the carbon surface through hypochlorite treatments. Papers by Lüthge et al. [5,6] describe additional methods, such as the Diels-Alder reaction, to attach surface functional groups. The latter paper by Lüthge et al. also describes some of the performance challenges associated with inks based on anionic, polymer-stabilized carbon. A paper by Langenmayr et al. [7] provides further evidence as to the challenges associated with inks formulated with dispersant-based versus self-stabilized carbon. This paper reports that lower optical density and higher paper-to-paper variability are observed with inks formulated from carbon dispersions relying on anionic dispersants as compared to inks based on self-stabilized carbon dispersions prepared through surface oxidation. Langenmayr et al. further indicate, in the case of surface-treated carbon, a strong preference for carbon black of high structure and larger dispersion particle size to ensure the maximum optical density. The ionizable groups in most of the surface treatment methods disclosed in the above references are either sulfonic or, more typically, carboxylic acid resulting in charge-stabilized carbon dispersions suitable for aqueous ink jet systems.

While these self-stabilized carbon dispersions have found increasing application in black, pigmented inks used to print both text and black-and-white graphics they possess some inherent deficiencies that limit their broader use. Conversely, dispersions of carbon black pigments based on either surfactant, oligomeric, or lower molecular weight polymeric dispersing agents have not found utility in black, pigmented inks targeted for such applications. Black inks based on such dispersion technologies apparently lack the density-forming capability of inks based on self-dispersed carbon black dispersions when printed onto the various plain papers used in SOHO printers. However, pigmented inks utilizing dispersant-based colorants have found ever-increasing application in CMYK inks for SOHO printers, especially for photo printing on glossy media and color graphics on all media. The inherent image stability and durability advantages of pigmented inks versus dye-based inks have been the subject of many papers in recent years. To date, self-dispersed CMY colorants have yet to find significant product application. Table 1 compares the performance characteristics of black inks based on self-dispersed and polymerically dispersed carbon black on media types of interest in SOHO printers.

Table 1. Comparison of Performance Characteristics of Black Inks (Self-dispersed vs Polymeric Carbon Black Dispersions)

	Plain papers (ave.)		Photo Papers	
Performance Characteristic	SD	Polymeric	SD	Polymeric
Text density	High	Low- Med.	High	High
Durability	Marg.	Good	Poor	Good
Gloss (photos)	N/A	N/A	Low	High

SD = self-dispersed
Durability refers collectively to image smear, transference, and high-lighter performance

As can be readily seen from Table 1 neither dispersion technology is capable of providing a single black, pigmented ink for SOHO printers that will meet all of the requirements for both plain paper and photo glossy media. The challenge therefore is to create a <u>single</u> technology that can meet the print performance requirements of both media types and can be used in thermal or piezo ink jet printers. In order to accomplish this, the text (or black) density of inks based on polymeric carbon dispersions printed onto plain papers needs to be improved while maintaining all of the existing desirable performance characteristics on both media types.

Experimental Approach and Details

Carbon Black Pigments, Dispersants, and Dispersions

In order to determine the feasibility of creating a single dispersion and ink technology capable of satisfying the above requirements, commercially available self-stabilized carbon dispersion technologies were identified as references. A key consideration was whether the carbon pigment precursor of these industry standards could be obtained in powder form such that direct comparisons could be made to dispersions made from a selection of dispersing materials. It was determined that Cab-O-Jet®200 and Cab-O-Jet®300 were valid industry representations of self-stabilized carbon black dispersions. Black Pearls®700 (BP700), the carbon precursor to these dispersions, is readily available in powder form. These commercial dispersions and various experimental dispersions made from BP700 and Black Pearls®880 (BP880) formed the basis for the investigation. A small molecule dispersant such as KOMT (potassium oleylmethyltaurate) and a random copolymer of BzMA/MAA (benzyl methacrylate/methacrylic acid, MW ~ 7500) were selected as reference dispersants. New random terpolymers comprising benzyl methacrylate, a hydrophobic monomer containing twelve or more carbon atoms, and methacrylic acid were developed. For purposes of this paper they are designated BzMA/X/MAA, where X stands for the additional hydrophobic monomer. These terpolymers had approximately the same MW as BzMA/MAA. Monomer ratios of both BzMA/MAA and BzMA/X/MAA were varied to determine optimum performance for each; for example, the "MAA" content was varied from 20–33 weight percent while the "X" level was varied from 0–30 weight percent. In all instances the polymer remained soluble in water and the dispersions stable in aqueous media, exhibiting zeta potentials of < -40 mv. Polymer neutralization was achieved with KOH.

The experimental dispersions were produced by micromedia milling, optimizing the ratio of dispersant to carbon pigment in each case. The dispersant amounts typically ranged from 24–35 weight percent polymer to pigment. Additional reference surfactant-based or polymeric dispersions of carbon black (unknown dispersant and carbon pigment) were obtained from Clariant Corporation (HostaJet® Black O-PT and HostaJet® Black T-PT) and Degussa Corporation (IDIS®31K and IDIS®40). Table 2 describes the particle sizes obtained at the 50^{th} percentile of each size distribution for the commercial and experimental dispersions. Sizing was done with a Microtrac Ultrafine Particle (UPA) Analyzer 150 from Microtrac, Inc. Polymer monomer ratios/levels for some of the experimental dispersions indicated in parentheses are in weight percent.

Table 2. Particle Sizes of Dispersions Used in This Study

Dispersion ID	Dispersion description	Particle size (nm)
1	Cab-O-Jet®200-sulfonic acid, SD	120
2	Cab-O-Jet®300-carboxylic acid, SD	120
3	HostaJet® Black O-PT	N/A
4	HostaJet® Black T-PT	119
5	IDIS®31K	150
6	IDIS®40	70
7	BP880:KOMT (small molecule)	70
8	BP880:BzMA/MAA (67/33)	70
9	BP880:BzMA/MAA (78/22)	70
10	BP880:BzMA/X/MAA (MAA=22)	70
11	BP700:BzMA/X/MAA (MAA=22)	90
12	BP700:BzMA/X/MAA (MAA=20), Pol/C ratio 1	95
13	BP700:BzMA/X/MAA (MAA=20), Pol/C ratio 2	95

Pol/C ratio = polymer dispersant/carbon pigment ratio

Ink Jet Ink Formulations

Inks were formulated according to Table 3 where the pigment concentration in each ink was 4.0 weight percent and an anionic surfactant was employed. Component levels in Table 3 are in weight percent. Ink viscosities were between 1.6–2.0 cps and static surface tensions ranged from 30–37 dynes/cm.

Table 3. Black, Pigmented Ink Formulations Studied

Ink	PEG400	Glycerol	EG	Surfactant
A	8	----------	5	0.2-0.5
B	3	8	5	0.2-0.5

PEG = Poly (ethylene glycol), EG = Ethylene Glycol

Ink Jet Media (Plain and Photo Papers)

The set of plain papers described in Table 4 was chosen to ensure a representative sampling of commercially available papers used in SOHO printers. In addition, Epson Premium Photo Glossy paper was used as a representative photo paper in order to characterize image performance on a contemporary rapid-drying, glossy receiver. It was felt that one photo paper would be sufficient for this purpose.

Table 4. Plain Paper Set

Paper Designation	Company Source	Paper Brand Name
P1	Xerox	Extra Bright Inkjet Paper
P2	Kodak	KODAK Bright White Inkjet Paper
P3	Hewlett Packard	Bright White (Bright Inkjet) Paper
P4	Hewlett Packard	HP Advanced Paper
P5	Xerox	Premium Multipurpose Paper
P6	Hewlett Packard	Color Inkjet Paper
P7	Georgia-Pacific	Ink Jet Printer Paper
P8	Hammermill	Fore MP
P9	Georgia-Pacific	Multipurpose Paper
P10	Great White(IP)	Great White Multi-Use
P11	Hammermill	Copy Plus
P12	Paris (Burlington)	PrintWorks Multipurpose Paper
P13	Hewlett Packard	Office Paper (Multipurpose Copy Paper)
P14	Hewlett Packard	Multipurpose Paper
P15	Staples	Ink Jet Paper
P16	Georgia-Pacific	Ink Jet Paper

Drop-on-Demand Thermal Ink Jet Printing

A variety of ink compositions were prepared using the black pigment dispersions shown in Table 2 and several of the ink formulations indicated in Table 3. These inks were loaded into empty cartridges available for a Canon thermal ink jet (bubble jet) printer (Canon i960 Photo Printer from Canon U. S. A., Inc.). A stepped target providing uniform patches of ink amounts in 10% increments from 10 to 100% was printed on each of the papers described above. The printer drivers for the CMYK channels were controlled to insure the same printed ink amounts in each channel. Status A Visible (neutral) patch densities were measured using a Spectralino instrument. For each of the papers tested the maximum optical density obtained at the 100% printed ink amount was recorded. For the set of plain papers, an average and standard deviation of all 16 maximum density values for each ink was determined and are reported in Tables 5 and 6. Image smear in Table 5 is a visual measure of how well printed text resists smearing upon rubbing with a finger. The dye ink in Table 5 is the Canon i960 black ink (BCI-6BK).

Results and Discussion

Plain Paper Density and Paper-to-Paper Variability

Described in Table 5 are the average density and density standard deviation of patches printed for each of the dispersions in ink formula A of Table 3 as measured across the set of 16 plain papers. The standard deviation is a good measure of the paper-to-paper variability observed for a given ink and is a figure of merit for a black ink intended to be printed as text or in a B&W graphics mode. Table 6 contains results for a subset of dispersions in ink formula B of Table 3. One of the important performance characteristics for a black, pigmented ink to be printed on plain paper is its resistance to image smear. This resistance to smear is a direct measure of how well the pigment adheres to the paper surface and is important when considering paper handling and paper-to-paper image transference.

It is apparent from Table 5 that the black, pigmented inks based on dispersions of the new terpolymer and BP700 are able to provide density comparable to the inks based on the self-stabilized Cab-O-Jet® dispersions. At the same time low paper-to-paper variability and good image smear resistance can be achieved with the new materials. The density provided by black inks based on these new polymeric dispersions exceed those from internal controls using the small molecule and random copolymer as well those of the commercially available dispersions. The poorer smear resistance associated with the inks made from the two Cab-O-Jet ® dispersions likely results from the fact that the carbon particles reside near the paper surface, unprotected by any type of binder.

Results from Table 6 with ink B provide further evidence that the new experimental polymeric dispersions can provide optical densities and paper-to-paper variability that compare favorably with existing technologies based on self-stabilized dispersions of the same carbon black as well as commercially-available controls.

Table 5. Plain Paper Optical Density, Paper-to-Paper Variability, and Image Durability for Ink A of Table 3

ID	Dispersion Designation	Ave. Density	Std. Dev.	Image Smear
1	Cab-O-Jet®200	1.34	.144	Control
2	Cab-O-Jet®300	1.37	.149	Control
3	HostaJet® Black O-PT	1.18	.231	Improved
4	HostaJet® Black T-PT	1.25	.206	Best
5	IDIS®31K	1.11	.251	Improved
6	IDIS®40	0.96	.037	Best
7	BP880:KOMT	1.06	.114	Improved
8	BP880:BzMA/MAA (67/33)	1.02	.177	Best
9	BP880:BzMA/MAA (78/22)	1.07	.127	Best
10	BP880:BzMA/X/MAA (MAA=22	1.18	.138	Best
11	BP700:BzMA/X/MAA (MAA=22	1.29	.132	Best
12	BP700:BzMA/X/MAA (MAA=20) ratio 1	1.33	.108	Best
13	BP700:BzMA/X/MAA (MAA=20) ratio 2	1.37	.070	Best
-	BCI-6BK (dye ink)	1.30	.041	Best

Table 6. Plain Paper Optical Density and Paper-to-Paper Variability for Ink B of Table 3

ID	Dispersion Designation	Ave. Density	Std. Dev.
1	Cab-O-Jet®200	1.28	.152
2	Cab-O-Jet®300	1.35	.110
3	HostaJet® Black O-PT	1.11	.240
4	HostaJet® Black T-PT	1.14	.231
6	IDIS®40	.093	.043
13	BP700:BzMA/X/MAA (MAA=20) ratio 2	1.33	.049

As a final comparative plain paper assessment, a limited subset of the better performing papers for text density was chosen; this set was made up of papers P1-P5 from Table 4. The optical density results for ink A on this subset are shown in Table 7 to illustrate the high capability of some of the new polymeric carbon dispersions discussed above as compared with key reference materials.

Table 7. Optical Density and Density Variation of Highest Performing Ink A-Paper (P1-P5) Combinations

ID	Dispersion Designation	Dispersant Type	Ave. Density	Density Range
2	Cab-O-Jet® 300	SD	1.47	0.24
7	BP880:KOMT	Small Molecule	1.17	0.28
8	B880:BzMA/ MAA (67/33)	Polymeric	1.22	0.47
13	BP700:BzMA/X/ MAA (MAA=20)	Polymeric	1.45	0.09
-	BCI-6BK (dye ink)	N/A	1.31	0.13

As can be seen in Table 7, on the best-performing plain papers, the black ink based on the polymeric dispersion of BP700 and the new terpolymer exhibits an average density that is very close to the reference ink based on the self-stabilized (SD) dispersion of the same carbon black pigment. These inks easily exceed the average density of the inks based on either the small molecule or random copolymer dispersions of BP880. The black, pigmented ink based on the new dispersion is also seen to have a narrower density range on this set of papers.

Photo Glossy Paper Performance

Image durability and visual gloss (of printed patches) were assessed on the Epson Premium Photo Glossy paper. Those results are described in Table 8 below.

Table 8. Image Durability and Visual Gloss on Epson Photo Paper for Ink A

ID	Dispersion Designation	Image Smear*	Visual Gloss
1	Cab-O-Jet®200	Poor	Low
2	Cab-O-Jet®300	Poor	Low
4	HostaJet® Black T-PT	Good	High
7	BP880:KOMT	Marginal	V. High
8	BP880:BzMA/MAA (67/33)	Marginal	V. High
9	BP880:BzMA/MAA (78/22)	Good	V. High
10	BP880:BzMA/X/MAA (MAA=22	Good	V. High
11	BP700:BzMA/X/MAA (MAA=22	Good	High
12	BP700:BzMA/X/MAA (MAA=20) ratio 1	Good	High
13	BP700:BzMA/X/MAA (MAA=20) ratio 2	Good	High
-	BCI-6BK (dye ink)	Good	V. High

** Resistance to image (patch) smear upon finger rub*

One of the important criteria for a universal black ink is that it should exhibit good durability and high gloss on photo papers. As expected, inks based on surfactant and polymeric carbon black dispersions provide high gloss and marginal/good durability while inks based on self-stabilized carbon dispersions exhibit poor image durability and low visual gloss. The results reported in Table 8 confirm this. Inks based on the new dispersions are able to provide the needed combination of both high gloss and good durability.

Conclusions

Taken together, the results from Tables 5–8 illustrate that black inks based on self-stabilized carbon dispersions provide excellent text/graphics density but less than optimum image durability on plain papers; they also exhibit low gloss and poor image durability on photo glossy media, thus restricting their broader use in SOHO printers. Inks employing a variety of known surfactant or polymeric dispersions of carbon black perform well on photo papers but lack sufficient paper-to-paper density consistency when considered for text and black and white graphics printing on plain papers. Certain inks based on new polymeric dispersions of BP700 were shown to provide average density on plain papers comparable to inks utilizing Cab-O-Jet®200 and ®300 (reference self-stabilized dispersions relying on BP700). At the same time inks based on the new polymeric dispersions performed well on photo glossy papers, thus making it possible to envision a single or universal black, pigmented ink suitable to both thermal and piezo ink jet SOHO printers.

Acknowledgments

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References

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Biography

__Dr. Gary L. House__ is a Distinguished Research Fellow at Eastman Kodak Company.

He received his Ph. D. in Chemical Engineering from the University of Illinois at Champaign-Urbana in 1977. There he studied solid-state science and conducted research on the optical properties of ion-doped II-VI semiconductors at very high pressure. For the past 30 years he has worked in the Research Laboratories of Eastman Kodak Company where research interests have included silver halide emulsion science, color film design, hybrid imaging systems and ink jet technologies. During his career at Kodak he has held a variety of technical leadership and management positions.

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