Carbon Black Dispersions For High Optical Density on Plain Paper

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Abstract

As a result of the inherent advantage of pigment based inks over dye based inks, carbon black is now the colorant of choice for black inks in the SOHO market. There is a need for black ink jet inks which give high optical density and excellent print quality on plain paper of varying quality. In this work, a series of self dispersed carbon black dispersions were made using commercially available carbon blacks spanning a broad range of particle morphology. Inks made with these dispersions were printed on a series of 7 plain paper types of varying quality and optical densities were determined. A strong correlation was observed between carbon black particle morphology and optical density.

Introduction

There are literally hundreds of commercial carbon blacks produced today. These materials vary in particle size, aggregate size and shape, microstructure and surface chemistry. It is important to note that these properties are distributional. The primary particle size of carbon blacks may range from 5 to 500 nanometers. The primary particles are spherical and may be porous or nonporous. Surface areas may vary from less than 10 to hundreds of square meters per gram. The primary particles are firmly joined together to form three dimensionally branched aggregates. High structure carbon black aggregates consist of many primary particles and a high degree of branching, whereas low structure carbon blacks consist of few primary particles with little or no branching. The DBP (Di Butyl Phthalate) absorption number is a measure of the degree of structure in the carbon black. Higher DBP absorption numbers are correlated with higher structure of the carbon black. The microstructure of carbon blacks refers to its crystalline nature. High resolution electron microscopy and X-ray structure studies show the primary particles consist of graphitic crystallites arranged concentrically with parallel layers offset laterally and axially rotated (turbostratic structure).[1,2] The choice of carbon black can critically affect the optical density performance of inks. This work examined carbon blacks encompassing a wide range of morphological properties to determine the property region which results in paper independent, high optical density inks.

Experimental

Carbon Black Samples

The carbon black samples used are commercially available materials obtained from Degussa, Cabot, Mitsubishi, and Colombian Chemicals. All materials were used as received. Carbon Black properties reported are those obtained from company literature and so represent typical values, not values determined for specific samples.

Table 1. Carbon Black Properties.

Carbon Black	Surface Area (m2/gram)	Primary Particle Size (nm)	DBP Number (mls/100 grams)
Printex® U	100	25	115
Special Black-4	180	25	110
Vulcan® 6F	110	24	114
Vulcan 9	-	19	114
Special Black -350	65	31	50
Monarch® 400R	96	25	69
Monarch 660R	112	24	64
Printex 80	220	16	100
MA-8	118	24	57
Monarch 880	220	16	112
Black Pearls® 460	84	25	102
Regal® 350	58	46	48
Raven® 3500	379	13	105
Printex 60	115	21	116

Carbon Black Dispersions

The self dispersed carbon black dispersions used here were made by treating the carbon black samples with acidic persulfate at elevated temperature following the method of Kuwahara.[3] The resultant dispersions were treated by ultrafiltration using Koch hollow fiber membranes to remove impurities from the aqueous continuous phase. No additional dispersants or stabilizers were used.

Print Tests

A seven paper test bed was used for the performance evaluation of test inks on plain paper types of varying quality. Papers used were HP Printing (P1), HP Bright White (P2), Kodak Bright White (P3), Georgia Pacific Eureka® Recycled (P4), Hammermill CopyPlus® (P5), Aspen Xerographic (P6), and Xerox 4200 DP (P7). Test inks were prepared using a generic aqueous ink formulation containing 3 weight percent carbon black based on carbon black solids. HP45A ink jet cartridges were filled with the inks and printing was performed using an HP895A ink jet printer. For comparison, a generic ink formulation containing 3 weight percent of the commercially available AcryJet® Black 357 pigment dispersion was also evaluated. Optical density measurements of the printed test sheets were obtained using an X-Rite® Model 500 Spectrodensitometer. The optical density was measured in 10 places on the test sheet and the values were averaged.

Particle Size Measurement

Particle Size measurements of the carbon black dispersions were obtained with a Microtrac® UPA 150 particle size analyzer. Median volume particle size are reported in Table 2.

Table 2. Median Volume Particle Size of Carbon Black Dispersions

Carbon Black	Dispersion Particle Size (nm)
Printex® U	217
Special Black-4	200
Vulcan® 6F	187
Vulcan 9	166
Special Black -350	148
Monarch® 400R	129
Monarch 660R	129
Printex 80	130
MA-8	91
Monarch 880	138
Black Pearls® 460	210
Regal® 350	155
Raven® 3500	137
Printex 60	153

Results

Regression Analysis

Initial print test results indicated both the DBP absorption number (DBP) of the carbon black raw material and the median volume particle size (PS) of the carbon black dispersion strongly affected optical density. Multiple least squares regression analysis for results on a single paper substrate, HP Bright White (P2), was performed with optical density as the response variable and DBP absorption number and dispersion median volume particle size as centered and standardized regressors. The regression model explains 98 percent of the total variation in the optical density of the printed areas on the print test sheet. This is depicted in Figure 1 by a plot of measured optical density versus the predicted optical density. High optical density is favored by using carbon black materials with high structure and carbon black dispersions with large particle size. The ratio of parameter estimates (DBP/PS) show the stronger influence of the DBP absorption number (1.5x larger) than the affect of the dispersion particle size on optical density. (See Table 3)

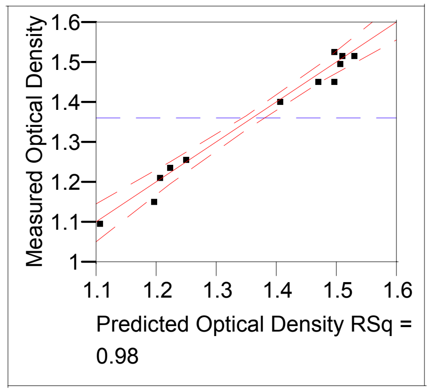

Figure 1. Whole Model – Measured Optical density by Predicted Optical density

Table 3. Parameter Estimates for HP Bright White

Term	Estimate	Std Error	t Ratio	Prob>|t|
Intercept	1.35	0.01	137.93	<.0001
DBP	0.15	0.01	13.20	<.0001
Particle Size	0.09	0.02	4.93	0.0012
DBP *Particle Size	-0.06	0.02	-2.53	0.0351

A scatterplot of optical densities measured over the seven commercial plain paper substrates shows strong correlation across paper types. Rather than fitting individual models for each paper type, we used principal components analysis on the correlation matrix. Our goal was to identify the unique dimensions in optical density variability, extract these unique dimensions and fit a smaller subset of models to the important principal component scores. (See Fig. 2)

Principal Components Analysis (PCA)

Eigen analysis of the correlation matrix is summarized in Table 4 below. The first linear combination of the optical densities (PCA1) explains 97 percent of observed optical density variability. The first principal component scores were saved and are used as a response variable for multiple linear regression. The remaining orthogonal linear combinations account for just 3 percent of total variability and will not be considered further.

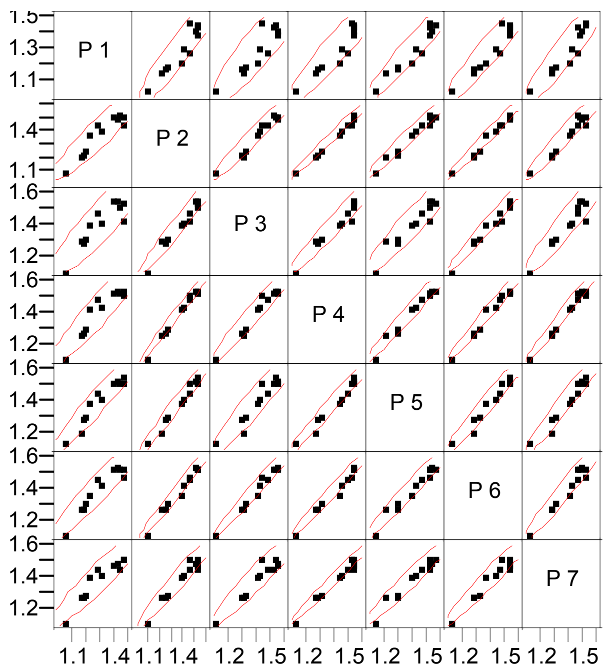

Figure 2. Scatterplot of Optical Densities for Test Inks on Seven Commercial Paper Types

Table 4. Principal Component Eigen Analysis

	Component 1	Component 2
Eigenvalue	6.7867	0.1241
Percent	96.9529	1.7725
Cum Percent	96.9529	98.7254
Eigenvectors		
P1	0.36733	0.78663
P2	0.38110	-0.17370
P3	0.37444	-0.53424
P4	0.38239	-0.12766
P5	0.38046	0.18566
P6	0.38186	-0.12181
P7	0.37794	0.00525

Modeling Optical Density (OD) Across Paper Set

Using the first principal component as a substitute for the complete paper set, we used multiple linear regression to investigate the influence of DBP number and carbon black dispersion particle size on optical density performance. The results of the analysis shown below explained 97 percent of the observed variation in the PCA1 scores. Figure 3 shows the predicted response surface for the optical density system as a function of DBP number and carbon black dispersion particle size. Note the twisting along the margins of the plot which is indicative of a strong interaction between the regression variables. Figure 3 demonstrates that particle size of the carbon black dispersion has a much stronger effect on optical density with low structure carbon blacks than with high structure carbon blacks.

Table 5. Regression Parameter Estimates for OD-PCA Data

Term	Estimate	Std Error	t Ratio	Prob>|t|
Intercept	-0.427	0.217	-1.97	0.0840
DBP	2.126	0.252	8.45	<.0001
Particle Size	2.332	0.394	5.92	0.0004
DBP*Particle Size	-1.296	0.440	-2.95	0.0186

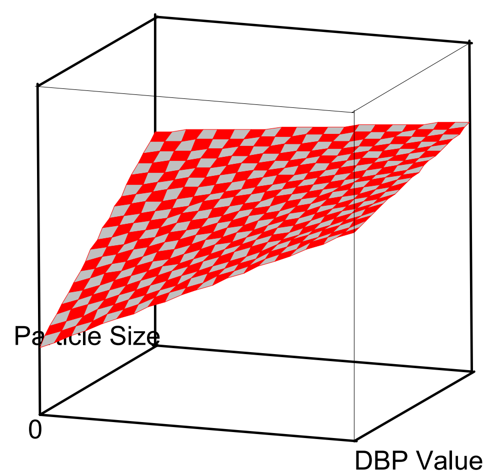

Figure 3. Prediction surface plot for Optical Density System

Optical Density on Different Plain Papers

Table 6 below shows optical density values obtained from two generic inks printed on a range of plain papers. The same generic ink formulation was used for both inks and the carbon black loading was 3 weight percent in each case. One of the inks was made using commercially available AcryJet Black 357 pigment dispersion while the other was made using a self dispersed carbon black dispersion from this study (STR5858EF) chosen to have high optical density. The data show that the optical density obtained with the ink containing the AcryJet Black 357 pigment dispersion is low and depends strongly on the paper substrate used. In contrast, the optical densities obtained with the experimental self dispersed carbon black pigment dispersion have very much higher optical densities that are unchanged across the paper types.

Table 6. Comparison of Optical Densities

Substrate	AcryJet Black 357	STR5858EF
HP Printing	1.02	1.62
GP Eureka Recycled	1.13	1.67
HP Bright White	1.21	1.66
Kodak Bright White	1.28	1.66

Conclusion

The particle morphology of carbon black materials used to make colorant dispersions for ink jet inks has a strong effect on optical density performance obtained with the ink. In particular, high structure carbon blacks and large particle size carbon black dispersions lead to high optical density even on poor quality plain paper. Further, the optical density obtained with colorants based on these carbon blacks tends to be paper independent. Other ink performance considerations restrict the useful range of structure and particle size that can be used in order that acceptable ink performance along all required dimensions is obtained.

References

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Biography

Eric Langenmayr received a Ph.D. degree in Organic Chemistry from the University of Florida in 1980. In 1979 he joined the Rohm and Haas Company where he has worked in a variety of areas including ion exchange resins, polymeric adsorbents, reactive polymers, novel inorganic materials, and latex polymers. His recent work has focused on materials for use in ink jet inks. He is a member of the IS&T and the American Chemical Society.