Surface Oxidized Carbon Black Pigments for Improved Inkjet Ink Performance

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Abstract

This technical study focuses on two production processes - namely the widely used furnace black process and the gas black process. These pigment blacks types were then subjected to three different gas phase, post oxidation processes to alter the surface chemistry. The influence of these changes was evaluated in dispersion and inkjet ink form to gain a better understanding of their impact on a range of physical properties related to inkjet print performance.

Besides the general physico-chemical analysis of these samples, advanced techniques like X-ray photoelectronic spectrometry (XPS) and titration methods are used to characterize the surface chemistry. Pigment dispersibility and particle size were determined. Finally, optical densities and inter-color bleeding properties of two formulated inkjet inks, based on these surface oxidized carbon black pigments, are evaluated. The test studies show distinct advantages of a surface oxidized carbon black pigment for improving dispersibility of aqueous systems as well as the influence of the oxidation process on critical print qualities such as optical density and inter-color bleeding.

Introduction

Carbon black has historically been used as the preferred colorant in conventional and digital printing processes. For inkjet inks, it is an ideal pigment to deliver the high optical densities essential for printed text. Due to the increasing demands for faster print speeds and greater print reliability - especially for commercial printing applications, surface modified carbon black pigments are of high interest to the print industry. Modifications to the carbon black process can increase the hydrophilic surface groups to improve dispersibility of carbon black pigments in aqueous systems. Additionally, its fractal structure and surface properties influence some of the key performance attributes of inkjet inks, including their optical density and inter-color bleeding properties. Surface modifications can be accomplished via post-oxidation processes leading to a broad variation in surface chemistry as shown in Figure 1. It is common to measure the degree of oxidation of a carbon black pigment in terms of its volatile matter (at 950 °C) according to DIN 53552. In the case of non-oxidized furnace blacks, the degree of oxidation is usually < 1.5 % while in the case of non-post-oxidized gas blacks the range lies between 4 to 6 %. The post-oxidation process can increase the degree of oxidation to > 20 %.

The two important carbon black manufacturing approaches are the gas black and the furnace black process [1]. Due to differences in these processes, a wide range of distinctly different black pigments can be produced. The key differences of these black pigments as produced by the gas black and furnace black manufacturing processes are summarized in Figure 2.

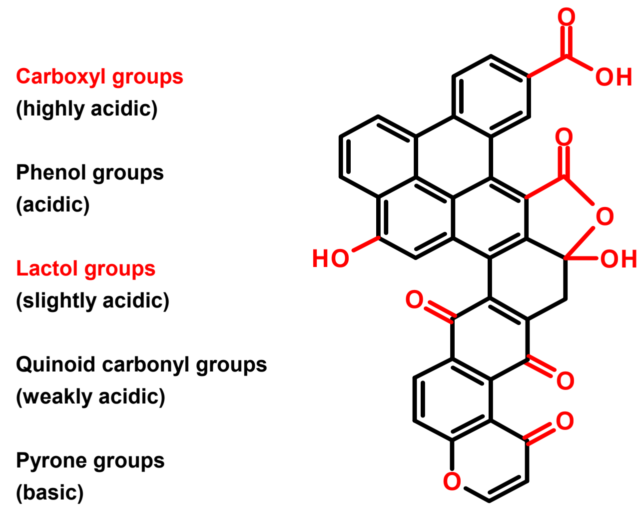
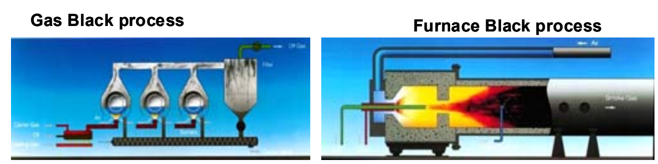


Figure 1: *Surface functional groups on carbon blacks*



Open oxidizing atmosphere	Process	Closed reduced atmosphere
Very high but loose structure	Structure	Variable
Many acidic groups	Surface oxides	Few basic groups
Acidic (3.5 - 4.5)	pH value	Basic (9 - 10)
Hydrophilic, polar	Water wettability	Hydrophobic, non-polar

Figure 2*: Key differences between gas blacks and furnace blacks*

The gas black process derives its name from the fact that the feedstock is vaporized and fed to the combustion chamber by means of a carrier gas. This vaporization step prevents the carbon black pigment from being contaminated with feedstock residues and also results in formation of a low ash product. During the burning phase, the presence of oxygen ensures a high degree of oxygen-functional groups on the pigment surface. These polar groups account for the acidic nature of all gas blacks.

The furnace black process uses liquid hydrocarbons as feedstock. The feedstock is injected into a refractory-lined furnace, which is heated by the combustion of natural gas and pre-heated air. After the carbon black pigment is formed, it is quenched by water, cooled down and separated from the gas stream. Furnace blacks usually carry a small amount of basic functional groups on their surface and therefore exhibit a hydrophobic, non-polar character, and have a pH value above 7.

Characterization of Pigment Black Surface

Different methods are available to characterize the carbon black pigment surface [6]:

- pH value
- Volatile matter at 950 °C
- Titrimetric determination of acid and basic surface oxides [2]
- Spectrometric methods by means of X-ray photoelectron spectrometry (XPS) [3]

The pH value of a carbon black pigment is a good indicator of the type of surface groups present. Low pH values point to acidic groups while high pH values are due to basic groups.

More detailed information about the presence and concentration of functional groups on a carbon black pigment surface is obtained by measuring the weight loss when heated to 950 °C (% volatiles). The functional groups decompose in the temperature range of 300°C to 950°C to form CO, CO_2, H_2O and H_2.

Quantitative methods to determine the acid and basic surface oxides are obtained by titrations with sodium hydrogen carbonate, sodium carbonate, sodium hydroxide solution and sodium methylate [2].

The surface oxides may be subdivided by their acidity into four groups of different acid strengths. Such titration methods are still very time consuming and XPS measurements are a preferred technique to determine the different surface groups. XPS detects the surface groups selectively and the measured signals originate solely in the uppermost atomic layers. XPS measurement beds covering an area of 1cm^2 are measured integrally which permit a comparative analysis of the surface oxygen fraction. [3]

In our test study we used a combination of these test methods to characterize the degree of oxidation of different surface oxidized carbon black pigments.

Experimental

This technical study focused on a series of carbon black pigments with a primary particle size of about 25 nm. A commercial gas black type (GB-Ref.) as well as a furnace black (FB-Ref.) were used as reference samples. Three different gas phase post-oxidation processes designated with A, B, C were applied to produce post oxidized samples GB-A, GB-B, GB-C and FB-A, FB-B.

Volatile matter at 950 °C, pH value, XPS-measurements and a titrimetric method to determine the amount of carboxylic groups were used to analyze the surface chemistry of the various carbon black pigment samples in this study. The test results show that the choice of oxidation agent has a tremendous influence on the surface chemistry of the carbon black samples. Oxidation agent B resulted in the highest concentration of carboxylic groups for the gas black as well as the furnace black. Both the titrimetric method and the XPS measurements on the surface oxidized gas black samples, GB-A and GB-B, confirmed the highest amount of carboxylic groups present. While there isn't a large difference between GB-A and GB-B in volatile matter at 950 °C, the XPS method reveals sample GB-B has the greater quantity of acidic polar groups.

Table 1: Characterization of Surface Groups
(* Titrimetric method, ** XPS method)

	pH	Volatile Matter at 950 °C [%]	Carboxylic Groups [µmol/g] *	Surface Oxygen Fraction [Area%]**	Polar C=0 Groups [Area%]**	Acid -COOH Groups [Area%]**	Ratio Acidic to Polar Groups**
GB-Ref	4.5	5.0	13	1.9	0.7	1.1	1.58
GB-A	3.0	15.3	467	6.9	3.2	3.3	1.03
GB-B	2.6	13.8	587	15.0	5.4	8.2	1.52
GB-C	4.0	10.6	152	4.2	1.6	2.1	1.28
FB-Ref	9.5	0.8	0	0.3	0.1	0.1	1.56
FB-A	3.7	2.0	33	1.8	0.6	1.0	1.65
FB-B	3.1	2.6	61	3.7	1.1	2.3	2.09

Dispersibility of Surface Oxidized Carbon Black Pigments

An examination of a dispersion sample using a transmission light microscope at 500X magnification allows for a quick characterization of the dispersion quality since coarse particles can easily be detected. Further valuable information on the dispersion quality and particle size distribution can be obtained by static laser light scattering measurements. These measurements are also useful to evaluate the dispersibility of carbon black pigments. In a simple standard test procedure, a pre-defined quantity of carbon black pigment is stirred into de-ionized water.

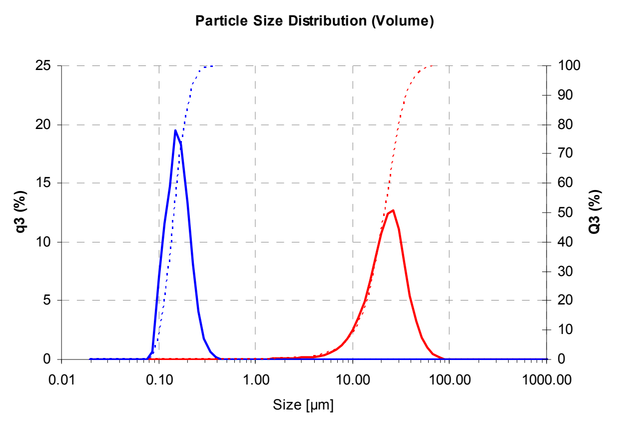


Figure 3: Particle size distribution of surface oxidized sample GB-B (blue) in comparison to non-oxidized GB-Ref (red). Measured with Horiba LA-910 in water without any surfactant (1 min US).

The particle size distribution can be measured as a function of time, with and without ultrasonic treatment. Such a test is beneficial for estimating the dispersibility of carbon black pigments. Figure 3 shows there are significant differences in particle size distribution profiles between the non-post-oxidized gas black (GB-Ref) and the surface oxidized sample (GB-B). The finer particle size and narrower distribution of sample GB-B is directly attributed to the higher concentration of surface oxides.

Optical density

The paper coating quality is one of the prime determinants for the optical density values achievable with an ink. The paper coating can prevent the penetration of pigment particles thereby forming a layer of pigment particles at the paper surface allowing the development of high optical density values. This situation is different for uncoated papers as the finely dispersed carbon black pigment particles easily penetrate into the voids and pores of an untreated paper thus decreasing the optical density of the printed text or image. Preventing this penetration of carbon black pigment into an uncoated paper is the challenge for ink formulators.

It is common for inkjet inks to contain additives possessing good wetting properties (e.g. dispersants), to stabilize the ink. These dispersants will also accelerate the intrusion of the pigment into the paper resulting in lower optical density values.

In our laboratory testing, a model ink (Table 3) was tailored for a bubblejet (thermal print head) printer. The ink was formulated at a concentration of 4.0 % based on the pigment weight. The ink was applied to a variety of inkjet and plain papers at a thickness of 6 µm. After drying, the optical density of these draw-downs was determined with a commercial spectral photometer (Table 4).

In preparing carbon black pigment dispersions, the large agglomerates must first be broken down into the finer aggregates by grinding. Pigment dispersions can be produced with a variety of dispersing equipment and techniques. Bead mills are one of the most commonly used piece of equipment in the manufacture of carbon black pigment dispersions.

In our lab test series we dispersed the carbon black pigment samples according to the dispersion formulation described in Table 2 by using a shaking mixer (Lau type BA-S 20K). The dispersing time was 2 hours. 0.8–1 mm zirconium oxide beads were used to increase the input of grinding energy.

The test results confirm that the choice of pigment has a significant effect on the resulting optical density values: All gas blacks obtained much higher optical densities than any of the furnace blacks - on both plain and coated papers. The primary reason accounting for greater optical densities achieved by the gas blacks are the network-like re-agglomeration at the substrate surfaces. It is the very high structure of gas blacks that minimize the intrusion of the pigment into the paper pores and voids[4].

These results indicate the surface chemistry of the carbon black pigment does not have a significant impact on the optical density. However, we tested the influence of the surface chemistry of the carbon black pigments on the optical density in another dispersion formulation to confirm the above mentioned test results. The main difference in this dispersion formulation 2 (Table 6) was the use of a non-ionic dispersant as opposed to the anionic type used in initial ink formulation.

Tables 2 through 7 provide detail on the pigment dispersions, ink formulations and optical density values achieved on the various papers.

Table 2: Dispersion Formulation 1

	% by weight
Carbon black pigment	15.0
Acid Black 1 (anionic dispersant) [4]	1.0
Biocide	0.3
De-ionized water	83.7

Table 3: Inkjet Ink Formulation 1

	% by weight
Carbon black pigment	4.0
2-Pyrrolidone	12.0
1,2 Propanediol	5.0
Glycerol	3.0
1,2 Hexanediol	1.2
De-ionized water	74.8

Table 4: Optical Densities on 6 µm Draw Downs (Inkjet Ink Formulation 1)

CBP sample	Plain Paper 1	Plain Paper 2	Inkjet Paper
GB-Ref	1.42	1.46	1.55
GB-A	1.40	1.45	1.55
GB-B	1.41	1.45	1.54
GB-C	1.42	1.47	1.57
FB-Ref	1.16	1.19	1.31
FB-A	1.14	1.19	1.31
FB-B	1.15	1.18	1.31

Table 5: Dispersion Formulation 2

	% by weight
Carbon black pigment	20.0
Tego Dispers 760W (nonionic dispersant)	16.0
DMEA (Dimethylamino ethanol)	0.2
Biocide	0.3
De-ionized water	63.5

Table 6: Inkjet Ink Formulation 2

	% by weight
Carbon black pigment	4.5
Dipropylene glycol	3.0
1,2 Propanediol	6.0
1-Methoxy-2-Propanol	5.0
1,2 Hexanediol	1.6
De-ionized water	79.9

Table 7: Optical Density on 6 µm Draw Down (Inkjet Ink Formulation 2)

CBP sample	Plain Paper 1	Plain Paper 2
GB-Ref	0.93	0.95
GB-A	1.05	1.04
GB-B	1.38	1.47
GB-C	0.95	0.97
FB-Ref	0.96	0.94
FB-A	0.96	0.92
FB-B	0.98	1.03

Due to the lower surface tension of inkjet ink formulation 2 it was not surprising that the optical density results were lower than with inkjet ink formulation 1 (see Table 7). However, gas black sample GB-B was the only carbon black pigment obtaining acceptable optical densities on both plain paper samples.

Inter-color Bleeding

Two test methods were used to evaluate the influence of the surface chemistry of the carbon black pigment on the inter-color bleeding properties of final inkjet inks. The first test method is based on determining the flocculation tendency of the carbon black pigment as soon as the black pigmented inkjet ink comes in contact with a dye based ink (yellow). In theory, a rapid flocculation rate of the carbon black pigment reduces its mobility resulting in less intermingling (e.g. inter-color bleed) of the inks.

A small droplet of the inkjet ink sample (Table 6) is placed on a microscope slide close to a drop of color dye based inkjet ink. A cover slide is carefully placed onto the two drops without any pressure. The flocculation tendency of the different inkjet inks was evaluated by light microscope at 200X magnification.

The test results for flocculation tendency show a broad range based on the oxidation level of the carbon black used in the ink. The gas black sample GB-B, an oxidized gas black type with the highest carboxylic groups, has the strongest flocculation tendency with yellow dye based inks.

Figure 4: *Light microscopic images (200x) of the transition from a black to a yellow ink drop. The flocculation tendency (from left: strong: GB-B, moderate: GB-A, no: GB-C) correlates with inter-color bleeding properties after printing.*

In a second step a print test was carried out with inkjet ink formulation 2 using a bubblejet (thermal) printer. The carbon black pigment samples showed significant differences in inter-color bleeding properties which clearly correlated with the flocculation tendency (Table 8).

Table 8: Inter-color Bleeding and Flocculation Tendency

CBP Sample	Flocculation Tendency	Inter-color Bleeding
GB-Ref	No	Strong
GB-A	Weak	Moderate
GB-B	Strong	No
GB-C	No	Strong
FB-Ref	No	Strong
FB-A	No	Strong
FB-B	Weak	Moderate

Summary

This study shows the advantages of tailored surface oxidized carbon black pigments for specific inkjet ink performances in regard to optical densities and inter-color bleeding effects. It demonstrates that the manufacturing process (gas black or furnace black) as well as the oxidation process are key parameters to adjust the dispersibility and the inkjet ink performances of surface oxidized carbon black pigments. The XPS method is beneficial for quantitatively determining the surface oxides of carbon black pigments. A high concentration of carboxylic groups on the carbon black surface features technical advantages for increasing optical density values and for reducing inter-color bleeding.

As ink formulators know in designing a specific ink, there are always trade-offs to be made between ink stability (choice of the right dispersant) and printing properties (mainly optical density and inter-color bleeding). A surface modified carbon black pigment with tailored carboxylic group density offers additional degrees of freedom for the ink formulator, e.g. to lower the amount of polymeric dispersants etc. The significant improvements made to dispersibility, showed in the case of GB-B (compared to GB-ref), benefit the dispersion process and allow greater flexibility for a higher quality ink to be formulated - resulting in enhanced print performance.

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Author Biography

Leo Nelli joined Evonik Degussa in 2004 and is a Senior Scientist for Applied Technology, specializing in technical support for Non Impact Printing media and inkjet inks. His present efforts involve identifying new uses for fumed metal oxides, precipitated silicas and pigment blacks for the paper and printing industry. Leo has over 20 years experience in the paper and printing industry and has been granted two US patents and filed for more than 10 patents.