Improved Dispersibility of Surface Oxidized Carbon Black Pigments for Inkjet Ink Formulation

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Abstract

Pigment based inkjet inks have assumed a leading market position in desktop as well as wide-format inkjet printing since they provide outstanding light-and water-fastness. The technical requirements on pigmented inkjet inks are tremendously increased by faster printing speed and modern application fields such as commercial inkjet printing. The dispersibility of pigments is one of the key performances to enable the development of such high quality pigmented inkjet inks with tailored particle size distribution and highest optical densities. This technical study focuses on a series of surface oxidized carbon black pigments based on the same carbon black source. Prepared dispersions under the same conditions based on these grades show the strong influences of surface oxidation on carbon black pigments on the dispersibility and the different demand on dispersing additives. Finally, optical densities and long term stability testing of final inkjet inks based on these surface oxidized carbon black pigments were evaluated. The test study shows the advantage of surface oxidized carbon black pigments in regard to improved dispersibility, more economical dispersing processes and higher optical densities for aqueous inkjet ink systems.

Introduction

Surface modified carbon black pigments are of high interest for the development of black pigmented inkjet inks because of the increasing requirement on print speed and print reliability especially for commercial printing applications. Last year we reported that the manufacturing as well as surface oxidation process have an influence on dispersibility of the carbon black pigment as well as the optical density and intercolor bleeding properties of the final inkjet inks [1]. Especially post-oxidized carbon black pigments with a high amount of carboxylic groups on the carbon black surface show excellent dispersibility and applied technical advantages in aqueous inkjet ink formulation.

The main focus of this test study is the impact of a special surface oxidation treatment on the dispersibility of carbon black pigments series. The base black pigment selected for this study is the well known NIPex® 160 IQ. The post-oxidation process has been tailored to obtain high amounts of carboxylic groups on the surface.

Usually, carbon black pigment dispersions for inkjet inks must be dispersed with high dispersing energy to break down the carbon black pigment agglomerates into finely divided aggregates. Additionally and even more important, a high amount of tailored dispersing additives are required for pigment stabilization to guarantee the print reliability of the final inkjet ink. It is obvious that an improvement in pigment dispersibility can improve the economic and technical efficiency in the manufacturing of ink.

A typical manufacturing process of carbon black pigment dispersions and final inkjet inks can be divided in four process steps: pre-dispersion, grinding process, dilution of the mill base and filtration. These four process steps are summarized in figure 1.

Figure 1: *Process steps to prepare carbon black pigment dispersion for inkjet inks*

Improved dispersibility of the carbon black pigment might obtain high cost efficiency on the grinding and filtration process and the demand on dispersing additives. From the technical point of view reduction of dispersing agents or even the absence of dispersing agents may strongly improve the applied technical properties and the flexibility in the formulation of the final inkjet ink. In particular, a tremendous advantage on the optical density on plain papers can be expected from dispersant free self-stabilizing pigment dispersions.

Experimental

This technical study focuses on different carbon black pigments with the same primary particle size.

In test series 1 a commercial carbon black pigment type (NIPex® 160 IQ = CPB-Ref) was progressively post-oxidized to create carbon black pigment types which differ in the degree of oxidation. Volatile matter at 950 °C and a titrimetric method[2] were used to

determine the total amount of functional groups on the carbon black pigment surface as well as the amount of carboxylic groups of the individual oxidized carbon black pigment grades.
In figure 2 the correlation of volatile matter at 950 °C and amount of carboxylic groups of the each individual surface oxidized carbon black pigment sample is shown.

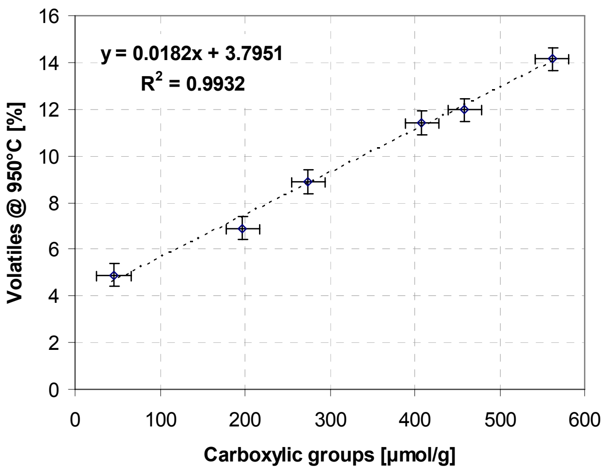

***Figure 2**: Correlation of degree of oxidation measured as volatile matter at 950° C and amount of carboxyl groups of surface oxidized carbon black pigment samples.*

Test Series 1: Pre-Screening and Sample Selection

In a pre-screening test we dispersed each carbon black pigment sample in de-ionized water by the use of ultrasonic dispersing equipment with 500 W power. We did not use any dispersant for the pigment stabilization to evaluate the self-dispersing properties of each post-oxidized carbon black pigment. This pre-test series showed that a carboxyl amount of greater than about 500 µmol/g results in self-dispersible carbon black pigments which can be dispersed to dispersion with very low viscosity and particle fineness and meet inkjet ink requirements. The particle fineness of the dispersion samples was determined with a transmission light microscope at 500-fold magnification. Light microscopic evaluation allows a quick characterization of the dispersion quality and the detection of coarse particles (> 2 µm).
Based on the pre-screening testing we decided to continue a test series 2 with the base black non-oxidized type (CBP-Ref) and two post-oxidized samples, one sample which was not self-dispersible (CBP-ox-1) and a second one with self-dispersible properties (CBP-ox-2) (table 1).

Table 1: Sample selection for the test series

	volatile matter at 950 °C [%]	Carboxylic Groups [µmol/g]	self-dispersible
CBP-Ref	5.3	78	no
CBP-ox-1	9.9	341	no
CBP-ox-2	13.1	512	yes

Test Series 2: Dispersibility

The dispersibility of sample CBP-Ref, CBP-ox-1 and CBP-ox-2 was tested with dispersion formulation 1 (table 2). The pH value of each formulation was adjusted to approximately 8.0 with DMEA. The pre-dispersion and grinding processes were carried out as follows:

Step 1: Pre-Dispersion

De-ionized water and all other components except pigment were filled into the vessel. Carbon black pigment was slowly added while stirring with an Ultra Turrax mixer at low rpm. Once the carbon black pigment was completely wetted, the speed of the Ultra Turrax was increased until optimum homogenization was obtained. Mixing time was 15 minutes.

To prevent evaporation of water and/or solvents and hence crusting of the mill base, all containers were covered during the pre-dispersion process.

Step 2: Grinding Process

The grinding process was carried out in a closed media mill in recirculation mode. Therefore the milling base prepared in step 1 was pumped through the lab media mill Bühler PML-2 (with 0.8 mm Yttrium doped Zirconia beads, rotor speed 1950 rpm) and back to the container with high velocity of circulation. The grinding process was adjusted with maximum limit of specific grinding energy with 200 kWh/t. Within the grinding process samples are picked up at 50, 100, 150 and 200 kWh/t.

The grinding quality of the dispersion was determined by transmission light microscope at 200 fold magnification. The viscosity of each sample was determined with rheometer UDS 200 at 23 °C at shear rate 1000/s.

Table 2: Dispersion Formulation 1

	% by weight
Carbon black pigment	10.0
Anionic dispersant (based on dye)	1.0
Biocide	0.3
De-ionized water	Remaining amount

The evaluation with a light microscope demonstrates the improved dispersibility of the post-oxidized carbon black samples compared with the base pigment black non-oxidized (figure 3): CBP-ox-2 achieves the optimum grinding quality at much lower specific milling energy than the base black CBP-Ref and the sample with lower amount of carboxylic surface groups (CBP-ox-1).

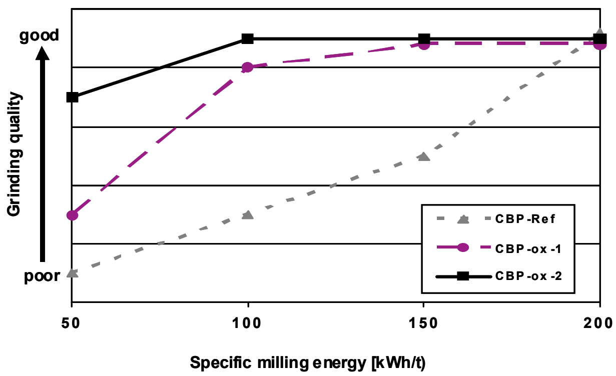

Figure 3: Improvement of the grinding quality by post-oxidation of carbon black pigment samples.

The viscosity of all samples was in the range of 1.7 to 2.3 mPas. Storage stability test at 60 °C for 14 days shows good stability for all post-oxidized samples with at least 100 kWh/t specific milling energy. The dispersion based on CBP-Ref obtained good stability with 200 kWh/t specific milling energy.

Test Series 3: Optical Density

Since the first test study confirmed an significant improvement in dispersibility of the post-oxidized grades (in the same dispersion formulation and dispersing method), an additional test series was carried out using a tailored amount of dispersing additive and dispersing energy for each carbon black sample. A dispersion formulation was selected with a common polymeric dispersant based on styrene acrylate (table 3). The key technical aspects such as the particle fineness of the dispersion as well as the optical density on different paper substrates were determined based on these dispersions. Since we realized in test series 2 (figure 3) that sample CBP-ox-2 showed excellent grinding quality at very low shear rates we also tried to include in this new test series 3 the preparation of sample CBP-ox-2 just dispersed with Ultra Turrax for 30 min at 16500 rpm. We checked the progress in grinding quality by transmission light microscope and stopped the dispersing process as soon as a good dispersibility was obtained. The test results with this new formulation and tailored dispersing process confirmed again the excellent dispersibility of post-oxidized carbon black pigments: CBP-ox-1 with a moderate degree of oxidation could be dispersed with half of the milling energy and a much lower amount of polymeric dispersants as compared to the non post-oxidized reference sample CBP-Ref. CBP-ox-2 with a higher degree of oxidation was self-dispersible without any dispersant additive and resulted in a very fine and narrow particle size distribution if dispersed just with rotor-stator equipment (Ultra Turrax, figure 5).

Table 3: Dispersion Formulation 2

Carbon Black Pigment		CBP-Ref	CBP- ox-1	CBP-ox-2
Bead mill (specific milling energy)	kWh/t	200	100	--
Ultra Turrax	rpm	--	--	16500
Carbon Black Pigment	wt%	15.0	15.0	15.0
Polymeric Dispersant (styrene acrylate type)	wt%	14.0	9.5	--
DMEA	wt%	0.1	0.4	0.7
Biocide	wt%	0.3	0.3	0.3
De-ionized water		Remaining amount		

Table 4: Inkjet ink formulation 1

	% by weight
Carbon black pigment	4.0
2-Pyrrolidone	10.0
1,2 Propanediol	5.0
1,2 Hexanediol	2.0
De-ionized water	Remaining amount

A model ink (table 4), formulated with 4.0 weight % pigment content, was applied to selected plain papers at a thickness of 6 µm. After drying, the optical density of these draw-downs was determined with a commercial spectral photometer (figure 4). The results in optical density showed the tremendous advantage of the post-oxidized carbon black pigments CBP-ox-1 and CBP-ox-2 compared to the reference sample CBP-Ref on each plain paper type selected. The best optical density results were obtained with the self-dispersible carbon black pigment CBP-ox-2. Obviously, the main reason for the improved optical density of the post-oxidized samples is the lower amount (CBP-ox-1) or absence of any dispersant (CBP-ox-2) in the inkjet ink formulation.

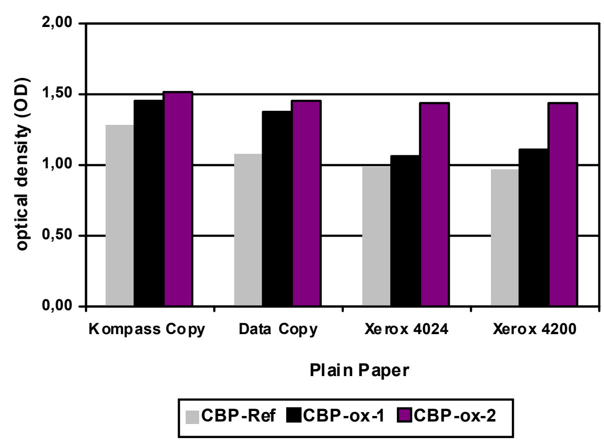

Figure 4: Optical density results of lab model inkjet inks obtained with 6 µm draw downs on critical plain papers.

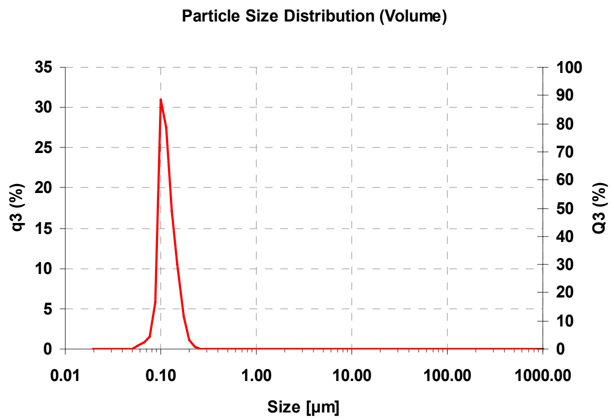

***Figure 5**: Particle size distribution of surface oxidized sample CBP-ox-2 dispersed in de-ionized water with Ultra Turrax for 30 min at 16500 rpm. Measured with Horiba LB-910 without ultrasonic treatment.*

Summary

This study shows the advantages of surface oxidized carbon black pigments with regard to ease of dispersion as well as optical density on representative plain papers. The dispersing process required to manufacture high quality inkjet inks can be streamlined to be much easier and more economical. Additionally, superior optical density results on plain papers can be obtained by the controlled surface oxidation of carbon black pigments. A good correlation can be found between the degree of oxidation (volatile matter at 950 °C) and the amount of carboxyl groups (titration) when the surface oxidation is carried out under defined conditions. It can be shown that a carboxyl group content greater than 500 µmol/g offers self-dispersible carbon black pigments which can be dispersed and stabilized without any dispersant.

A tailored surface oxidized carbon black pigment enables a higher degree of flexibility in inkjet ink formulation by lowering the demand on, firstly, dispersing energy to obtain the right particle fineness and, secondly, dispersing additives. The highest benefit was obtained with self-dispersible sample CBP-ox-2, which can be stabilized in aqueous systems with low shearing energy without any dispersant.

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Author Biography

Gerd Tauber joined Evonik Degussa in 1987 as a chemical engineer for Applied Technology focusing on the use of fumed silicas, precipitated silicas and powdered celluloses in free flow, defoamer and pharmaceutical applications. Since 1997, Gerd has been specializing on carbon blacks for non impact printing applications. He has filed for more than 15 patents.