Self-Stabilizing Carbon Blacks: The Technological Advantages of Aqueous Ink Jet Systems

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Abstract

New chemical modification processes make it possible to introduce hydrophilic structures to the surface of pigment carbon blacks (pigment CBs). The modification can be done via cyclo additions or radical reactions, for example.

One potential application field for surface-modified pigment CBs is inkjet. The proportion of pigments inkjet inks will steadily grow. Especially self-stabilizing materials satisfy the high demands of this sophisticated technology.

This paper describes comparative analyses between conventional pigment CBs, their physical modification with the aid of polymers, and chemically modified pigment CBs with their wetting-agent free inks. Both pigment properties and ink properties were investigated. To clarify the differences of the pigments EDX-spectra coupled with electron-microscopy was an important method. Dispersion properties were characterized via the zeta-potential, the viscosity, the surface tension, and the particle size distribution of the CB in the dispersion. The results illustrate the benefits of the surface-modified pigment CBs developed by Degussa. In addition to the above-mentioned methods, the inks were tested in brand-name conventional SOHO printers. The dispersant free inks showed superior results with established bubble-jet print heads because the product properties of the surface modified pigment CBs were chemically fine tuned and the ink formulation was simplified.

Introduction

The first printing processes to be called “inkjet” appeared in the early 1960s in conjunction with the growing utilization of computer technologies.[1] The first patents pertaining to bubblejet print head systems, which still represent the largest portion of inkjet printers today, appeared in 1962.[2] This technology use dye-based inks. It was only at the beginning of the 1990s that pigment-based inks, especially inks based on pigment carbon black, were able to establish themselves for inkjet. The advantages and disadvantages of both types of ink are compared in Table 1.

Pigments are superior to dyes in most respects. Pigment carbon blacks have been used as the base for black inkjet inks in the SOHO market for approximately 10 years.[3] Only at that point it became possible to satisfy the high technical requirements. Since their introduction, the proportion of pigmented inks has been rising continuously. In 2003, total worldwide consumption (SOHO + professional sector) amounted to slightly below 50,000 metric tons of ink. An increase to over 70,000 metric tons is predicted by 2009.[4]

Table 1. Dyes and Pigments Compared

Properties	Dyes	Pigments
solubility	soluble	not soluble
stability against chemicals	poor	high
light-fastness	low	very good
line/plot quality	mean	accurate
water-fastness	unsatisfactory	consistent
primary particle size	molecular	> 10 nm

Established Pigment Preparations for Inkjet

By definition, pigments are insoluble in the application medium, and intensive dispersion is therefore necessary for their stabilization. This is primarily accomplished using ball mills. New milling methods, like ultrasonic dispersing machines and high-pressure homogenizers, likewise achieve an effective, fine milling of the pigment dispersions. Compared to other printing procedures, inkjet requires particle size distributions with a maximum particle size less than 500 nm so that the pigment inks can pass through the jets (cross section 10–30 µm).

It is necessary to add wetting agents in order to intensify the interactions of the hydrophobic to slightly hydrophilic surface of the pigment carbon blacks with the dispersion medium water. We shall discuss two principle mechanisms of pigment stabilization by means of wetting agents. Sterically demanding groups or electrostatic forces ensure that the particulate matter will remain irreversibly separated after milling (see Figure 1). One measure for the strength of the electrostatic interaction is the zeta potential of the particles. Simply stated, the more negative the zeta potential, the more stabile the dispersion becomes (in the case of anionic stabilization). Typical polymer-stabilized dispersions feature a zeta potential of -5 to -20 mV.

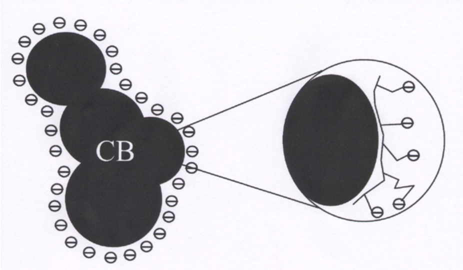

Figure 1. Electrostatic stabilization of CB

In addition to the proportion of wetting agent that is adsorbed on the pigment surfaces, wetting-agent molecules are also in equilibrium in the surrounding solution. This means that the structures that support dispersion are not tightly bound to the pigment particles. If the dispersion is diluted, as could happen in a dye formulation for example, it is possible for desorption processes to occur (dispersion shock). This could ultimately lead to flocculation of the dispersion.

A typical inkjet ink still contains other substances besides the wetting agent, some examples being humectants, biocides, and binders. The dissolved portion of the wetting agent in particular could turn out to be incompatible with other ink additives under unfavorable circumstances, and this would similarly have a negative effect on the stability of the dispersions/inks. The stability of an inkjet dispersion or ink at room temperature over two years is estimated by a time-dependent measurement of the viscosity at elevated temperature (e.g., 30 days at 50°C).

Another disadvantage of using polymeric wetting agents is that they are not shear-stable and thermal-stable in all situations. In the case of bubblejet print heads in particular, the ink must have high thermal stability because short-time temperatures of several hundred degrees Centigrade occur. Pyrolysis of the polymer could cause defects in the heater or encrustations that would lead to failure of the jets in a short time (see Figure 2).

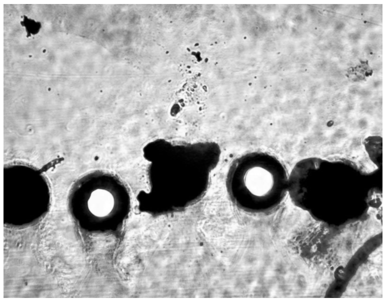

Figure 2. Nozzle clogging after dispersant pyrolysis

At the current time, oxidation is the most commonly used method for generating hydrophilic dispersion-supporting groups on the CB surface. A great variety of oxidation methods have been developed and used in production since the start of the twentieth century. Formation of different oxygen-containing groups in different proportions can be found, depending on the oxidant and reaction conditions. In all cases, numerous structures are formed simultaneously.

A defined production of only one type is not possible.[5] The groups act dispersion-supporting without aftertreatment (e.g., OH, OR) or after neutralization (e.g., COOH → $COO^{\ominus}$). The zeta potential of dispersions based on oxidized CBs is approximately 30 mV. The oxidation proceeds parallel to an enlargement of the surface.[6] Despite the higher hydrophobicity, wetting agents are still necessary for the stabilization of oxidized CBs in aqueous dispersions.

In recent years, the indicated disadvantages in employing most polymeric wetting agents has resulted in stronger efforts to find new approaches to pigment stabilization.

Modified Carbon Blacks via Organic Chemistry

In addition to the oxidation of CB or its direct sulfonation,[7] numerous processes have been developed to selectively change the CB surface by modification via organic monomeric or polymeric substances. Grafting (from or to) is the method that most closely resembles the stabilization of CB in dispersions by means of wetting agents.[8] In contrast to microencapsulation,[9] grafting results in a tight bond to the pigment via covalent bonding.

Meanwhile a large number of processes for surface modification by means of monomolecular modifiers which differ from grafting[10-16] exists. The reagents employed and their respective reaction mechanisms are very markedly different. One example consists of the use of maleic acid derivatives, which can react with the CB surface via ring-closure reactions (e.g., Diels-Alder reaction). A prerequisite for such reactions is the presence of sufficiently reactive double-bond systems on the CB surface (see Figure 3).

In addition, processes in which disulfides (via free-radical reactions) or diazonium salts (free-radical reactions, Meerwein arylation, Gomberg-Bachmann reaction) are used have been described. Moreover, the reaction between CB and cyclopentadienyl complexes, like substituted ferrocene derivatives, is known.

CB modification with dienophiles or radical formers in particular offers the advantage to use a large number of different modifiers, leading to different CB surfaces, because of the wide range of possible substituents. The dienophiles consequently form a type of building block system (see Figure 4).

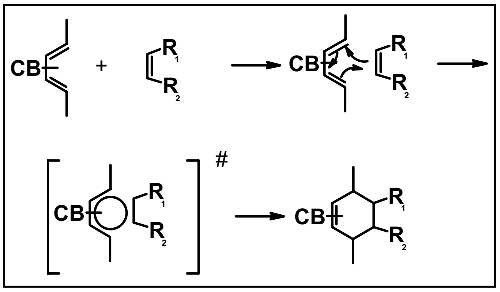

Figure 3. Simplified Diels-Alder mechanism

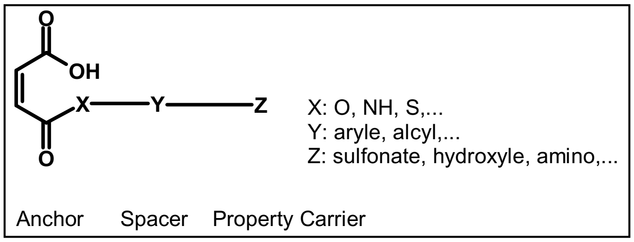

Figure 4. Building block system of the dienophiles

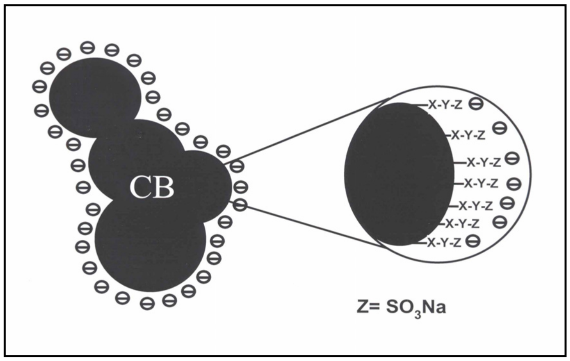

Figure 5. Hydrophilic modified CB

The spectrum ranges from hydrophobic to polar to strongly hydrophilic residues. Their modular structure permits very different combinations, with the possibility meeting the requirements of different conceivable matrices in which the modified pigments could be applied.

For aqueous inkjet applications, the bonding of hydrophilic structures like sulfonate groups is best. In comparison to anionic stabilization by means of a polymeric wetting agent (see Figure 1), the hydrophilic groups are covalently bonded to the CB surface due to its modification. (see Figure 5).

For the professional inkjet sector, in which solvent-containing inks are still often used, aprotic polar or nonpolar CB surfaces may be of interest.

The described methods of surface modification of CB proceed in two major steps.[12-16]

1. Mixing CB and the modifier
2. Activation

Mixing may be performed in different kinds of mixers, with or without a solvent. The critical factor is to obtain an optimum distribution of reaction partners without large aggregates being formed. Under favorable conditions, it is possible to attain a nearly ideal distribution of modifier on the CB surface. The same element ratio is present both in relatively large areas (A in Figure 6) and in the nanometer range (B in Figure 6), a fact that can be proven through X-ray spectroscopy. It therefore follows that there are no separated modifier particles, but rather a coated CB.

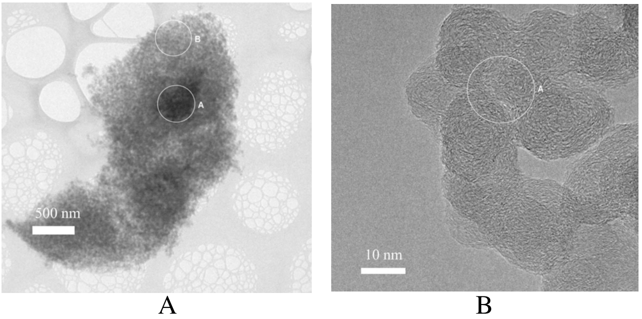

Figure 6. TEM-EDX images of modified CBs

Activation is performed through an energy input, possibly by means of thermal conduction, IR radiation, or microwave radiation, depending on the modifier used.

In most cases, the activation can be carried out without solvents. This is advantageous not only because it permits simplification by process technology, but also because it prevents possible contamination of the modified CBs by solvent residues.

Aftertreatment is no longer necessary once the feed ratios have been properly optimized. The CBs that are obtained can be used as soon as they have cooled. The general processing scheme is particularly advantageous in comparison to modification via monomers or polymers (grafting) and diazonium salts, both of which require solvents. Grafting additionally requires steps to create reactive sites on the CB. To obtain the CBs as a powdery solid in these methods, it is necessary to evaporate the solvents, thereby incurring extra costs and the risk that the product may become contaminated with volatile organic compounds (VOCs).

Dispersion of Hydrophilic Modified CBs

The generating of hydrophilic structures, like sulfonate groups for example, guarantees that the CBs will be easier to stabilize in aqueous systems, in which they are utilized in the SOHO sector. Stabilization in water can be accomplished electrostatically (anionic – sulfonate groups), sterically, or by high solvation (nonionic, e.g., OH or ether groups). The dispersions described below are based only on modified CBs that carry sulfonate groups and that can be dispersed in water without adding a wetting agent.

Dispersion may be carried out with conventional dispersing equipment, such as agitator ball mills, or by ultrasound. Dispersion starts with a 30-minute incorporation phase (e.g., in the Ultraturrax), for generating a homogeneous agglomerate mixture. This is followed by a deagglomeration step for example carried out by 30 min of ultrasonic exposure with 500 W for 500 ml. Due to this surface modification the obtained pigment aggregates will remain stable in the dispersion without wetting agents. After filtration, the maximum size in the particle size distribution (via photon correlation spectroscopy) is usually lower than 500 nm (measured by photon correlation spectroscopy, see Figure 7).

Table 2 shows the most important characteristics of a dispersion based on hydrophilic modified CB compared to an anionic dispersion stabilized with a wetting agent (polymer).

The degree of dispersion was then estimated with an optical microscope at a magnification of 400X.

Directly after production, the dispersion based on modified CB exhibits a lower viscosity. In contrast to the anionic dispersion that is stabilized with a wetting agent, the viscosity does not rise during the storage test (35 days storage at 50°C). Another measure for the stability of ionic dispersions is their zeta potential. For the modified pigment, the zeta potential is much lower than for the combination of an unmodified pigment with an anionic polymer as wetting agent. This might be caused by the equilibrium between adsorbed and dissolved polymer. The bonding of the modifier by means of covalent bonds is irreversible. Moreover, the dispersion of the modified CB displays a higher surface tension. It is advantageous for the surface tension to be as high as possible, especially in respect to flexibility in formulating the ink formulation. Such a dispersion is less sensitive to the additional organic additives (e.g., glycols, binders…), which as a rule greatly lower the surface tension.

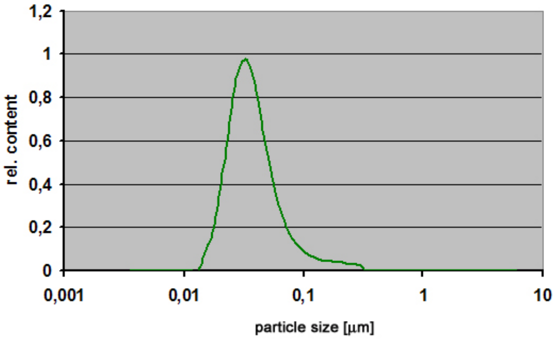

Figure 7. Particle size distribution of hydrophilic modified CB

Table 2. Comparison of Dispersion Properties

Properties	mod. CB	anion. polym. + unmod. CB
Pigment content	15 %	15 %
Mean particle size	55 nm	94 nm
Light optical microscope	homogeneous	visible particles
Viscosity	< 3 mPas	> 10 mPas
Viscosity after 35d/50°C (thermal stability)	< 3 mPas	> 10 mPas
Surface tension	≈ 70 mNm^{-1}	≈ 60 mNm^{-1}
Zeta potential	< - 50 mV	> -30 mV
pH value	> 7	> 7

Inkjet Inks Based on Hydrophilic Modified CBs

Inject printers for the SOHO sector primarily have two types of print heads. The largest share of the printers operate according to the bubblejet process. Whereas the second process is based on piezo print heads. The two processes place different requirements on the ink formulation. For example the surface tension in the bubblejet process is thus usually between 40 and 50 mNm^{-1}, and in the piezo process it is below 40 mNm^{-1}. Furthermore the viscosity of a piezo ink tends to be somewhat higher than that of a bubblejet ink.

The formulation of the test inks is based on the dispersion discussed in the preceding section. All other described additives were carefully added to the dispersion while stirring. Finally, the ink was placed into the printer cartridges. Table 3 summarizes the ink formulations that were used and their properties for both printer systems.

Table 3. Formulation of Inkjet Inks

	mod. CB (bubblejet)	mod. CB (piezo)	anion. polym. + unmod. CB (bubblejet)
Pigment content	4%	4%	4%
Ink additives	15–20%	20–25%	15–20%
Viscosity	< 2–3 mPas	3.0–3.5	> 2–3 mPas
pH	> 7	> 7	> 7
Surface tension	≈ 50 mNm^{-1}	≈ 33 mNm^{-1}	≈ 50 mNm^{-1}

A Hewlett-Packard printer was used as the example for the bubblejet process. An Epson printer was used as the piezo printer.

The inks were subjected to the same test regime. It is possible to analyze and measure divers ink properties through the choice of the printing subject. Such ink properties include the optical density, striation, and the reproduction of details.

The subject was printed multiple times as a function of time and evaluated (refire test). An endurance test (uninterrupted printing) was also conducted. The print quality was additionally determined as a function of the chosen paper grade. Paper grades currently found on the market were used for this purpose. These included uncoated and uncoated copying papers as well as coated papers.

The optical densities (OD) were determined with a SpectroEye™ made by GretagMacbeth™ after the papers had been dried at room temperature for 24 hours. Figure 4 shows the results of the print tests (bubblejet process).

Table 4. Results of the Print Tests

Pigment Paper	mod. CB	anion. polym. + unmod. CB
Content grade	4%	4%
OD of uncoated paper 1	1.52	1.33
OD of uncoated paper 2	1.55	1.41
OD of coated paper 1	1.58	1.54
OD of coated paper	1.62	1.56

The tests on piezo printers were similarly concluded with very good results.

The test inks based on modified CBs are outstandingly printable, even during extensive print orders (endurance test) and after long interruptions (refire test). The printouts feature high optical densities and are very faithful to detail. In particular, their OD, being constantly high even on copying paper, is a prominent advantage. Very high ODs, which are important for deep black, brilliant photo prints, are likewise achieved on coated papers.

The ink based on a dispersion stabilized with a wetting agent delivers much lower and fluctuating OD values, especially on copying papers. Here it is a clear disadvantage of polymeric wetting agents that they evoke deeper penetration of the pigment into the paper. The very strongly negatively charged pigment particles of the modified CBs, on the other hand, penetrated much less into the paper due to electrostatic interactions.

Conclusion

Normally wetting agents are needed for the stabilization of untreated or oxidized pigment carbon blacks. It has been shown that selective and controlled surface modification with organic substances, like dienophiles, disulfides, etc., leads to pigments that exhibit significantly improved hydrophilicity. The modified pigment carbon blacks that we have presented are dispersible in water without adding a wetting agent. After sufficient dispersing, these dispersions are thermally stable and possess outstanding characteristics (high surface tension, extremely low viscosities, excellent compatibility with ink additives). Based on these dispersions, it is possible to formulate inkjet inks that are very well printable on commercial SOHO printers of both common printing systems with very good results. In comparison to polymer-based inks, modified carbon blacks offer greater latitude in ink formulation at a high quality level.

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Biography

Dr. Thomas Lüthge received his Ph.D. in Chemistry from Martin-Luther-University Halle-Wittenberg in 2000. After one year of post-doctoral work with Degussa AG, he joined the staff of Degussa's Application Technology Center, Advanced Fillers & Pigments. The focus of his work is on the detailed characterization of the chemical properties and the tailor-made modification of carbon blacks for NIP applications.