Surface Modification of Black Pigments: A Novel Approach for Advancing Black Pigment Performance In Imaging Systems

Joseph E. Johnson,
Ink Jet Colorants Division,
Cabot Corporation
Billerica, MA

Abstract

Black pigments have had several breakthroughs over the last fifty years that have resulted in improved performance in imaging systems. These events include surface oxidation, tailored surfactants/polymers, and most recently Cabot Corporation's new technology involving the chemical bonding of specific functional groups to the surface of carbon black. The new technology may be applied to a variety of imaging applications where highly stable submicron pigment systems are required, especially for ink jet uses. The unique properties of these new sulfonated and carboxylated black pigments will be discussed and will include specific information on particle size, print quality, waterfastness, and intercolor bleed. Also, the issue of utilizing pigments in ink jet applications will be addressed.

Introduction

Imaging systems have progressed rapidly over the last fifty years due to process and material advances and the merging of polymer, electronic, ceramic and computer technologies. Black pigments, especially carbon black, have also had a profound influence in the imaging area. But despite the progress, imaging systems are now more demanding than ever before. And black pigments have met in the past, and will need to meet future performance requirements.

This paper will review some of the advances in carbon black technology over the last fifty years, with emphasis on an unique and novel technology that Cabot Corporation, the largest carbon black manufacturer in the world, has developed within the last few years. A technology that can meet today's and future needs by modifying the surface of carbon black through chemically bonding of specific functional groups. But first, some general concepts and definitions involving carbon black will be discussed.

General Definitions

Carbon black is the most commonly used pigment for imaging applications, but it is also may be the most misunderstood. The black pigment can be initially classified according to the manufacturing process (e.g., channel black or furnace black) and then to the physical properties (e.g., specific surface area, structure, primary particles size, etc.). With literally hundreds of carbon blacks used in a variety of applications, it is easy to become confused. The confusion is especially compounded when some people (mostly dye chemists) continue to "educate" others by using the misnomer "soot" and carbon black interchangeably!

To lessen the confusion, some basic carbon black terminology will be defined. Carbon black is an industrial manufactured carbon comprised of concentric, circular graphitic layers formed by either the incomplete combustion or pyrolysis reaction of a hydrocarbon(s). The resulting aggregates are spheres that are fused together (chemically bonded) having specific size ranges between roughly ~50 and 1000 nm. Soot is a randomly formed type of carbon having various size ranges, made in an uncontrolled pyrolysis reaction (e.g., a diesel engine or from a chimney fire), which contains a large amount of inorganic and organic impurities. Channel black is a carbon black made by the incomplete combustion of natural gas (flames) impinging, in open air, upon cooled irons containing water. The channel process was discontinued in the United States in 1976 due to economical reasons. Furnace (oil) black, originally invented about fifty years ago,[1] is carbon black formed from the pyrolysis of a mixture of feedstock, air, and natural gas at a particular temperature in distinct reaction chambers, with the quenching of the reaction also being controlled by the injection of water. The oil furnace method now accounts for more than 95% of all carbon black production[2] versus other processes due to the high control of products, higher yields, and (lack of) environmental issues.

Advances In Carbon Black Technologies

Control of Physical Properties

The high control of the physical properties of carbon blacks by the oil furnace process ensured uniform primary particle diameters and structure resulting in pigments having a surface of mostly (>97%,) carbon. The physical properties play a large role in the optical properties of a print and the rheological and conductive properties of an ink.

Surface Oxidation

However, the interaction between the carbon black and the liquid, polymer, or other material in an imaging system (e.g., ink or toner) is dependent on the surface of the pigment. For liquid systems, the interactions are dispersibility and dispersion stability. For dry systems, the interactions are charge and conductivity. The focus in this paper will be on the interactions in liquid systems (specifically surface modification of carbon blacks) although there may be direct applications to dry systems.

Channel blacks were advantageous in having surface oxygen groups (3-11%)[3] formed during the reaction, since these groups aided in the dispersibility and dispersion stability of the pigments in polar media. The groups also enhanced wetting in non-polar media. To improve the dispersion properties of furnace blacks, which had well controlled physical properties, several oxidation methods have been developed using agents such as ozone,[4,5] nitric acid,[6,7] nitrous acid[8,9] and sodium hypochlorite.[10,11] The methods result in the uncontrolled formation of many hydrophilic groups (carboxylic acid, phenols, quinones, lactones, etc.)[12] on the surface of the carbon black, but improve the wetting and dispersibility characteristics. The obvious disadvantages of the oxidation methods are the variation in type and amount of surface groups and reaction byproducts, and the inability to control the process to yield repeatable products.

Traditional Surfactant- and Polymer–Stabilized Dispersions

Another advance in carbon black technology was using adsorbed surfactants or polymers to help disperse and stabilize the carbon black particles in liquid media. A variety of nonionic and anionic surfactants (e.g., alkyl phenol ethoxylates[13] and sodium dodecyl sulfate[14,15]) have been, and are still being, used successively as dispersing aids for carbon blacks. Nonionic surfactants with a HLB (hydrophilic-lipophilic balance) of 14-15 have also been recommended as dispersing agents.[16]

Regarding polymers, at least two different approaches may be used to disperse and stabilize the black pigments. First, two different polymers may be used- one polymer that adsorbs and aids in dispersibility of the pigment, and another polymer that adsorbs at a later time for pigment stabilization. The second approach is to use a block copolymer, containing a hydrophobic (adsorbing) part and a hydrophilic or solvent-liking (stabilization) part. One part of the polymer adsorbs to the black while the other part associates with the solvent and provides stability to the pigment. The main disadvantage using the traditional dispersions is that the ink formulation latitude is severely limited, since an adsorption-desorption equilibrium between the pigment, adsorbed species and the liquid always exists. Another disadvantage is that the properties of the surfactant or polymer may adversely influence the ink (e.g., by lowering surface tension increasing viscosity, or promoting foaming).

Cabot Surface-Modification Technology

Within the last few years, Cabot Corporation has developed an exclusive and new technology that actually modifies the surface of carbon black pigments.[17,18] The technology involves the controlled chemical bonding of specific functional groups to the surface of carbonaceous materials, especially carbon black. Unlike the oxidation methods, only the specific functional group at the desired amount needed will be chemically attached. Unlike the traditional dispersions that require surfactants or polymers, the functional groups are chemically bonded onto the black and will not desorb, foam, or alter the surface tension of liquids. A schematic of the general surfacemodification reaction follows:

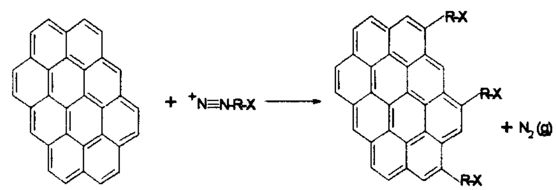

Figure 1: General surface-modification reaction using carbon black.

The advantage of this technology is that the surface of the carbon may be modified with specific functional groups that are compatible with the ink or imaging system (i.e., greater formulation latitude). Some examples of functional species that have been attached to carbon black are shown in Table 1.

Functional Group	**Status**	Name of **Dispersion**
Sulfonate	Commercial	CAB-O-JET™ 200
Carboxylate	Commercial	CAB-O-JET™ 300
Quaternary amine	Experimental	IJX™ 55
Sulfoamide	Experimental	---

Table 1: Typical functional groups that have been chemically attached to carbon black.

Properties of two of Cabot's commercial products CAB-O-JET™ 200 and 300 dispersions. are listed in Table 2.

Property	CAB-O-JET™ 200 Dispersion	CAB-O-JET™ 300 Dispersion
Mean Diameter (μm)	0.13	0.15
100% Diameter (μm)	<0.6	<0.6
Stability		
Room Temperature	>2 years	>2 years
Freeze-Thaw	>3 cycles @-20° C	>3 cycles @-20° C
Heat	>6 weeks @70° C	>6 weeks @70° C
Viscosity	5 cP @ 20% solids	5 cP @ 20% solids

Table 2: Properties of CAB-O-JET 200 and 300 dispersions.

CAB-O-JET 200 and 300 dispersions were also put into several generic ink jet ink formulations and printed using several types of SOHO thermal ink jet printers and one major industrial (waterbased ink; Domino Codebox 2) printer. The inks had reliable printing properties (i.e., no clogging, no change in print o.d. or quality, and no hesitation on start-up occurred). The main differences between the generated prints was that those made from inks containing the CAB-O-JET 300 dispersion were more waterfast and had little intercolor bleed compared to the equivalent inks having the CAB-O-JET 200 dispersion.

Summary

Imaging and carbon black technologies have advanced significantly over the last fifty years. The latter with respect to both physical and chemical (surface) properties. Cabot has developed a unique and new technology to functionalize carbon black with specific groups that can be optimized for particular imaging systems, thus meeting performance requirements. The surface modification allows a greater formulation latitude, in addition to not altering the properties of an ink. Currently, two productss CAB-O-JET 200 and 300 dispersions, are commercially available. These products, when formulated into ink jet ink systems, performed well in common SOHO and industrial ink jet ink printers producing high quality prints.

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