# Surface-Modified Black Pigments For Industrial Inkjet Ink Applications

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## Abstract

Surface-modified black pigments have been developed for industrial inkjet use. Requirements (printer compatibility, print performance, and ink stability) and major concerns will be presented with respect to colorants (dyes and pigments). In order to overcome deficiencies of current colorants, Cabot Corporation has developed new surface-modified pigments. The modification scheme involves covalently bonding specific, functional groups to the surface of carbon black. General properties of the novel pigments and compatibility test results of the colorant with common ink components will be shown. In addition, the pigments were formulated into inks and printed with a continuous, piezoelectric industrial printer. Inks containing currently-used industrial inkjet dyes and conventional pigments, and two commercial, surface-modified pigments from Cabot were printed using a Domino Codebox II printer and compared. The results show that the novel, surface-modified black pigments are very different from conventional pigments and offer significant advantages over currently-used dyes for industrial inkjet use.

## Introduction

Current aqueous inkjet inks used for industrial applications are predominantly dye based. Use of black pigment-based inks in industrial applications has lagged pigment based ink introductions in the small office and home market over the past few years. This lag is mainly due to significant differences in printer technologies. Where industrial printer OEMs have introduced black pigmented inks based on conventional pigment dispersions, concerns with long term stability and running reliability have limited their shelf life claims, or caused them to introduce stirring mechanisms into the printer. As a result, for the most part the industrial market has had to forego the substantial benefits of black pigments (e.g. high optical density, lightfastness, edge contrast, light absorbance and batch to batch consistency).

Commercial products in the office market, and other studies[1] have demonstrated that pigments are superior to dyes (e.g. print quality, blackness, water and rub fastness) and can be used successfully in inkjet printers having small nozzle orifices (<20 microns in diameter) without settling, clogging or kogating. Industrial ink jet printers differ from office printers with their higher print speed, faster dry time, permanent print heads, larger nozzle orifices (~30-60 microns), longer duty cycle (larger volumes of ink jetted through each orifice), a variety of substrates, and differing ink formulations (water or organic solvent based). The means of generating the ink drops also differs with piezoelectric based, drop on demand or continuous printers (the latter which recycles the ink numerous times) predominating. Taken as a whole, the industrial ink jet printer pose significant stability and reliability performance challenges for the colorant. Based upon our evaluations, Cabot's two new surface modified pigments lay to rest stability and runnability concerns that have restricted pigment use in industrial printing in the past.

## Colorant Requirements

Generally, inkjet inks must satisfy three conditions: printer reliability, print performance, and stability. Reliability is absolutely essential! Printer reliability is the behavior of the ink in, through, and exiting from the printer. Reliability includes fast and trouble-free start-up, runnability and shut-down of the printer. Another definition of reliability is *"Does the printer work like it is supposed to?"* Industrial marking and coding printers have the touted attributes of low maintenance costs and "absolute" reliability as key selling points[2]. In addition to the hardware, the ink and ink components strongly influence printer reliability[3]. Key ink parameters include: rheology (viscosity, surface tension, drop break-up), charging, pH (for water-based inks), evaporation time, solubility effects for recycled ink, nozzle build-up and the effects of temperature and humidity. The colorant, in turn, has a substantial effect over the ink parameters. Commercial dyes need to be purified to remove salts and excess organic material which may react with other ink and printer components and adversely affect solubility, nozzle and face plate build-up, pH, charging and flow properties. Of course, with the purification and quality steps additional costs may be generated. Batch to batch variability of dyes creates further problems (and costs) for ink users that are "cleaning" the dye. Additionally, if multiple dyes are used (e.g., a blue and a red dye to form a "black" dye) the variability issue is even further compounded.

Print performance is defined as the generated images on the substrate having specific properties within a designed range. Another way of saying this is- *"Do the images adhere to the substrate and look like they are supposed to?"* Again, the ink and colorant play a large role, as does the substrate, and printer. The main ink parameters are: rheological (surface tension, spreading, penetration, drop-to-drop attraction) , evaporation, absorption and fiber swelling, solubility or dispersibility, film properties (formation, thickness, and adherence)[4-6]. Dyes are known to wick or "feather" along fibers of the substrate causing poor character-edge definition and to penetrate into the porous material resulting in low print optical density[1,6]. The spreading of the dye over the substrate also limits the print thickness and color strength[7], and may result in limited readability of bar codes and other images. The dye must also be compatible with a variety of substrates. Additionally, prints made from water soluble dyes are lacking in waterfastness and lightfastness properties[1,6].

Ink stability is defined as the properties of the ink being constant- *"Is the ink going to change?"*. A disruption in stability could be caused by a variety of factors including ink component interactions, high or variable shear, dye solubility or pigment dispersibility, temperature, pH change for water based inks, humidity and air effects. Dyes having a large amount of contaminants (salts and organic matter) are more problematic vs. pure dyes in causing adverse interactions. Conventional pigments contain adsorbed dispersing agents which may desorb and alter the stability of the ink. In addition, "recycled" inks undergo changes in colorant concentrations, so solubility or redispersibility are necessities.

## Conventional Pigments

Although dyes may be lacking or limited in some respects, they are the most used colorant of choice because they perform better than "conventional pigments". Conventional pigments are defined as pigments that are stabilized by adsorption of dispersing aids (surfactants or polymers). The dispersant is in a dynamic equilibrium adsorbing on the pigment surface while also desorbing off the pigment going into the suspending liquid (Fig. 1(A)). These standard pigments are generally not used in industrial inkjet systems due to deficiencies which include: ink instability, non-uniform jetting characteristics (variance in drop size, high or changes in viscosity, foaming or nozzle clogging, etc.), or solidification at the nozzle or in the printer. Inks with conventional pigments can work in an industrial printer, but usually for a very limited time.

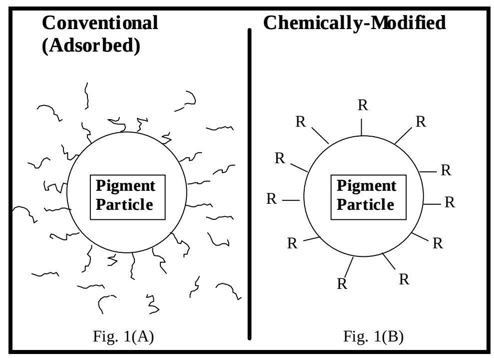


***Figure 1: Schematic of Pigments- 1(A): Conventional Pigment; 1(B) Chemically Modified Pigment (Note: Not to scale).***

## Cabot Pigments

Cabot Corporation has recently developed a new technology that modifies the surface of carbon black pigments without adsorption, but with the attachment of chemical groups[8] (Fig. 1(B)). The technology allows functional moieties to chemically bond to the black pigment. The groups are not in an equilibrium with the suspending liquid, and they do not behave like conventional pigments. The technology involves the controlled chemical bonding of specific types and amounts of functional groups to carbon black. A schematic of the general surface-modification reaction is shown in Figure 2.

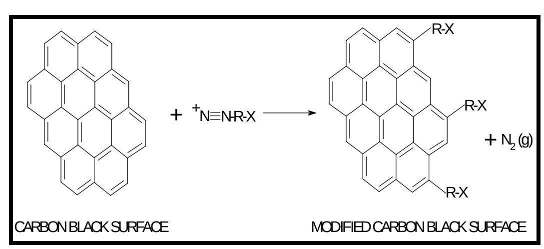


***Figure 2: General Surface-Modification Reaction Using Carbon Black (Note- not chemically balanced)***

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). Cabot has developed two products, (CAB-O-JET™ 200 and 300 black pigments, that are appropriate for industrial inkjet water based applications. Some basic properties of these pigments are shown in Table 1. Essentially, the products are small (colloidal), electrosterically-stabilized pigments.

| Property | CAB-O-JET™ 200 Dispersion | CAB-O-JET™ 300 Dispersion |
|---|---|---|
| Functional Group | Sulfonate | Carboxylate |
| Mean Diameter (μm) | 0.13 | 0.15 |
| 100% Diameter (μm) | <0.5 | <0.5 |
| Viscosity (cP) | 5 cP @ 20% solids | 5 cP @ 15% solids |
| | | |
| Stability | | |
| Room Temperature (Time) | > 3 years | > 3 years |
| Freeze-Thaw (Cycles @ -20/20 °C | >3 | >3 |
| Heat (Time @ 70° C) | >6 weeks | >6 weeks |

***Table 1: Properties of CAB-O-JET™ 200 and 300 Dispersions.***

## Compatibility with Common Inkjet Ink Components

CAB-O-JET™ 200 and 300 dispersions were mixed with common inkjet components and polymers, with the resultant being studied for compatibility. Compatibility is defined as no change in properties (viscosity, particle size and distribution, pH, and surface tension) where applicable. In the following preliminary experiments, common ink components were added to a 5% (final) pigment slurry. A variety of physical properties, (particle size and size distribution, microscopic examination, viscosity, pH, surface tension, etc.), were followed for up to 40% of the additive. Compatible systems are indicated by the shaded lines for each specific component in Tables 2 and 3. The results indicate that the pigments are very compatible with a variety of additives (alcohols, glycols, and glycol ethers) and offer a wide formulation latitude in ink formulation.

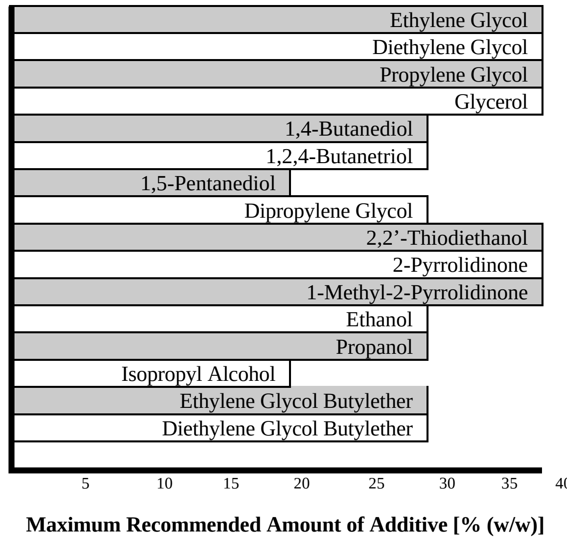


***Table 2. Maximum Recommended Amount of Ink Components to a 5% final (w/w) CAB-O-JET™ 200 in a Water Dispersion***

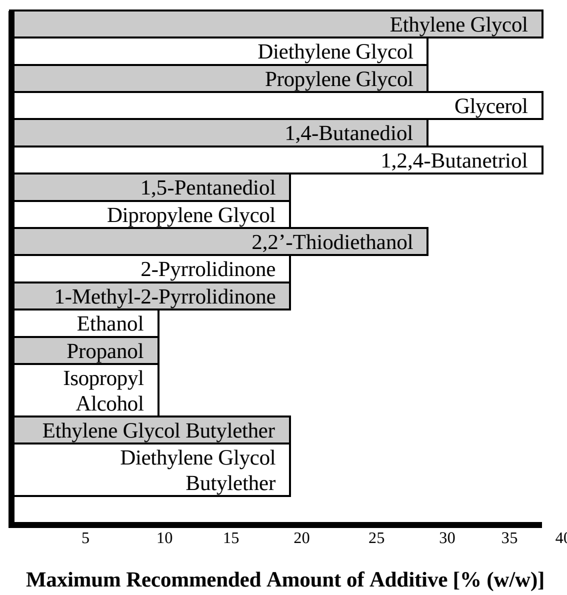


***Table 3. Maximum Recommended Amount of Ink Components to a 5% final (w/w) CAB-O-JET™ 300 in a Water Dispersion***

## Cabot Pigments in an Industrial Inkjet Ink Printer

As noted above, industrial inkjet printers place different demands on a colorant than office printers. To investigate the feasibility of using CAB-O-JET™ 200 and 300 pigments in an industrial printer, the dispersions were formulated into two generic inks and printed using a Domino Codebox 2 printer by Xennia Technology Ltd. The printer, a piezoelectric, continuous printer, was chosen due to its manual diagnostic capabilities of key ink properties and its variation in shear conditions. Printer conditions included a nozzle diameter of 75 µm, stroke rate of 1,800 strokes per second, and 5 µm filters (although the inks, both aged and fresh, were easily filtered to below 1 µm before use). Both freshly prepared and aged (60° C for one month) inks were tested by printing continuously for 24 hours, printing continuously for 48 hours in the recycle mode, and the start/stop mode (overnight shutdowns). Some results of the 48 hour printing study, which were similar to those of the 24 hour printing study, are shown in Table 4. Ink 1 contained the CAB-O-JET™ 200 pigment, while Ink 2 had the CAB-O-JET™ 300 pigment.

| Property | Ink 1: Fresh | Ink 1: Aged for 1 month @ 60$^{O}$C | Ink 2: Fresh | Ink 2: Aged for 1 month @ 60$^{O}$C |
|---|---|---|---|---|
| Modulation Window (V) | 38 | 35 | 33 | 36 |
| Pressure Window (psi) | 19 | 12 | 21 | 11 |
| Foaming | None | None | None | None |
| Jet Break Up | Good | Good | Good | Good |
| Print Quality | Good | Good | Good | Good |

***Table 4: Properties of Inks having CAB-O-JET™ 200 and 300 Pigments Printed With A Domino Codebox 2 Printer for 48 Hours in the Recycle Mode***

The modulation window, or difference between the maximum and minimum applied voltage applied to the piezoelectric element, and the pressure window are indicative of the reliability of the ink. Generally, a modulation window of ≥30 volts indicates that the ink can tolerate printer variations in print head, drive rod, and nozzle designs. The inks satisfied this condition. A 5 psi pressure window is needed so that the system can modulate properly, and also account for print head variability and environmental changes. The pressure window was greater than 10 psi for all inks. These results show that the chemically-modified pigment can be formulated into stable inks which perform well in an industrial printer and be reliable. The inks had excellent (uniform) jet break up and printing characteristics. The inks also did not foam. The 48 hour test demonstrated that the pigmented inks are stable under constant shearing conditions and recirculation. Printer start up was also excellent and without problems. The print quality was good and consistent for all the tests. No foaming was observed. The pigments were easily incorporated into a formulation., and were robust with respect to heat aging, start/stop cycles, and recycling through the printer.

## Comparison of Colorants

Another study was performed in order to compare commonly used (or marketed) water based, industrial inkjet colorants (two dyes and a conventional pigment and CAB-O-JET™ 200 and 300 pigments.) The colorants were incorporated into a model formulation and tested using the above-mentioned inkjet printer and procedures. Active colorant concentration for all colorants, except CAB-O-JET™ 300 which was 6.3%, was 7.2% (w/w). A summary of test results are in Table 5.

| Property | Ink 1 | Ink 2 | Ink 3* | Ink 4** | Ink 5*** |
|---|---|---|---|---|---|
| Jet Break Up | Good | Good | Good | Good | Erratic |
| Gutter Feed | Good | Good | Good | Good | Poor |
| Foaming | None | None | None | Slight | Excess |
| High Voltage Plate Residue | Trace | None | Trace | Modera te | Heavy |
| Print Quality | Good | Good | Good | Good → Poor | Good → Fail |
| Print O.D. | 1.24 | 1.28 | 1.20 | 1.21 | 1.02 |
| O.D.- After 24 Soak | 0.98 | 1.33 | 0.86 | 0.90 | 0.96 |
| O.D.- 72 h dry, 24 h Soak | 1.24 | 1.32 | 0.76 | 0.70 | 1.01 |

***Table 5: Comparison of Properties of Inks having CAB-O-JET™ 200 and 300 Pigments, Dyes, and a Conventional Pigment Printed for 48 Hours in the Recycle Mode***

*Ink 3: Contained LEVACELL® BLACK SP LIQUID; Dye (Bayer AG)
**Ink 4: Contained Pro-Jet® Black OA-PZ Liquid; Dye (ZENECA Ltd.)
***Ink 5: Contained HOSTAFINE® BLACK TS; Carbon Black in Water Dispersion (Hoechst AG)

The results show that Ink 5, containing the conventional pigment, failed to print continuously for 48 hours, which may be due to the foaming and/or the erratic jetting. The same ink produced initial prints with low optical densities (O.D.) on white envelope stock. Ink 4, having a dye as the colorant, also had an issue with foaming, and produced prints with poor quality at the end of the run. Inks 1 through 3, inks that contained Cabot's two pigments and a dye, respectively, were reliable and produced prints of good quality. The O.D. of the prints using Inks 1 and 2 were darker and significantly more waterfast compared to others. In addition, prints made with the pigmented inks are inherently lightfast.

## Summary

Cabot Corporation has developed two commercial products (CAB-O-JET™ 200 and 300 dispersions) which can be used in industrial inkjet printers. The products are very compatible with common ink components and have wide formulation latitude. The new pigments were also incorporated into a model formulation and tested for critical performance properties. Additionally, commonly used dyes and a conventional pigment were also formulated into the model system and tested. Reliability and final print properties for all the colorants were compared. The results show that inks made with the commercial CAB-O-JET™ 200 and 300 pigments offered several advantages over the other colorants including excellent reliability, good print quality, high print optical density, waterfastness, and lightfastness.

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