

Investigation of the Applicational Properties of Carbon Blacks used in Pigmented Ink Jet Inks

Andreas Stübbe, Alfons Karl and Werner Kalbitz
Degussa AG, Frankfurt/Main, Germany

Abstract

In 1992, first pigmented ink jet inks containing carbon blacks were patented [1]. This innovation gives many opportunities to extend the possible use of the ink jet technology into outdoor application or photo realistic prints.

The influence of carbon blacks different in structure, primarily particle size and pH value on the applicational properties of pigmented ink jet inks is part of this paper. Furthermore, the differences between carbon blacks produced using different production proccesses are investigated. Test prints are made on different types of commonly used ink jet paper. Test methods include measurements of the physical properties of the ink jet inks and papers used, evaluation of test prints, and electron and light micrographs of thin cuts of the printed papers.

Introduction

In comparison to dyes, pigments used in ink jet inks have some unrivalled advantages. Mainly named are the lightfastness and weather resistance which make ink jet inks usefull for outdoor applications [2]. The media or print performances like reduction of feathering or the tendency of pigments to remain on porous surfaces [3] are named additionally. Compared to dyes, color pigments have the disadvantages associated with a limited color gamut and being less transparent - demands which are not made on black pigments. At first, partial substitution of the black dyes by the pigment black has taken place. The reasons have nothing to do with the excellent light stability or universal insolubility of carbon blacks. The attibutable reasons are due to the aforementioned media performances. The use of pigment blacks in ink jet inks in both black and white as well as full color printing has been the reality since 1993, when such inks were commercialized for the first time.

The content of this paper is the investigation of the influences of carbon black properties like primary particle size, the carbon black structure and the dispersion properties on the media performances in ink jet application.

Experimental

Pigment Black Characterization

There are two major processes of industrially manufactured carbon. The furnace black process is, as the name indicates, carried out in a closed furnace lined with ceramic. An aromatic hydrocarbon rich oil is atomized and sprayed into a flame generated by the combustion of, for example, natural gas and preheated air. This process produces carbon blacks with high pH values. It is flexible in the variation of the primary particle size and the structure. In the gas black process (not to mix up with the channel black procedure) a large number of small flames impinge against the cooled surface of water cooled rollers. A carrier gas, containing hydrogen, is led over heated oil and, saturated with oil vapors, is fed to burners. In contrast to the furnace black process the gas black process is carried out in a system that is not completely closed and air has free access. This process produces carbon blacks with low pH values. It is flexible in the variation of the primary particle size, however, the variation of the structure is limited. Subsequent treatment is possible for both carbon black types. Furnace blacks are used in the rubber industry and as pigments, while gas blacks are mainly used as pigments, preferably in the coatings industry.

The carbon blacks selected for the experiments are produced by the Degussa gas black procedure and by the furnace black procedure. The gas blacks are listed in table 1, the furnace blacks are listed in table 2.

Table 1

	Primary particle size nm	DBP-absorption ml/100 g	pH value	Blackness Value My
G1	11	105	4.0	285
G2	13	110	4.5	273
G3	20	126	4.5	263
G4	29	115	4.0	248

Table 2

	Primary particle size nm	DBP-adsorption ml/100 g	pH value	Blackness Value My
F1	14	95	9.0	265
F2	15	52	9.5	258
F3	27	123	9.5	239
F4	27	66	9.5	242

The primary particle size is determined by means of electron micrographs and evaluated by a particle size analyser. The DBP absorption is measured in accordance with DIN 53601 C, the pH value is measured in accordance with DIN 53552 and the black value My is measured in accordance with DIN 55979. The carbon black structure correlates with the DBP absorption. The DBP absortions

listed in table 1 are determined on compacted material since due to the very low density of gas blacks the volume of 100g powder is to large for the measurement chamber. The DBP values determined on the non compacted material, like regulated in the standard, are higher.

Paper Characterization

The papers used for the experiments are listed in table 3. All papers are coated and the paper weight is 90 g/m².

Table 3

	Surface Tension mN/m	pH value
P1	57	6.4/7.0*
P2	49	5.1/stabel
P3	32	5.3/stabel
P4	31	6.5/6.9*

To determine the surface tension, the contact angle has been measured by using water, formamid and α-brominenaphtalene. The pH value of the paper surface is measured in accordance with the Zellcheming Merkblatt V/17/80 after 2 and 5 minutes. In Table 4 a visual evaluation made by means of TEM and REM micrographs is given. Particel size and pore size relate to the coating material which consists single or in combination of a silica gel and/or a pricipitated silica.

Table 4

	Particle size µm	Pore size µm	Coating	Coating thickness
P1	ca. 20 2.5-10	2,5 - 5	very compact	dobbel layer 50 µm
P2	2.5 - 18	5 - 10	compact	25 µm
P3	5 - 27	10 - 30	loose	20 - 40 µm
P4	2.5 - 10	5 - 10	loose/uneven	5 - 10 µm

Ink Formulation

From the carbon blacks used a test ink has been made by preparing an aqueous pigment concentration containing 15% pigment black stabilized by using 7% of a non-ionic surfactant and a buffer adjusting the pH value in the range of 8 to 9. The dispersion was made in an Ultra Turrax apparatus for 20 minutes. The pigment concentration then was diluted with deionised water to 5% pigment black. Then 10% triethylene glycol were added. The particle size has been determined by means of photon correlation spectroscopy, the surface tension has been determined by means of the Wilhelmy plate methode (DIN 53914). The viscosities of the inks are in the range of 2 to 4 mPas.

Test Methods of the Applicational Properties

From the inks draw downs have been made on the different papers. The optical density is measured by a Mcbeth RD 918. densitometer. The contact angles are measured by a goniometer from rame-hart, inc., model 100-00. The test results are summarized in table 6. Furthermore light and electron micrscopic investigations have been carried out.

Table 5

Ink no	carbon black	surface tension mN/m	particle size d_{50}, nm
Ink 1	G1	45	92
Ink 2	G2	42	104
Ink 3	G3	41	125
Ink 4	G4	40	185
Ink 5	F1	43	86
Ink 6	F2	44	57
Ink 7	F3	41	167
Ink 8	F4	41	114

Results and Discussions

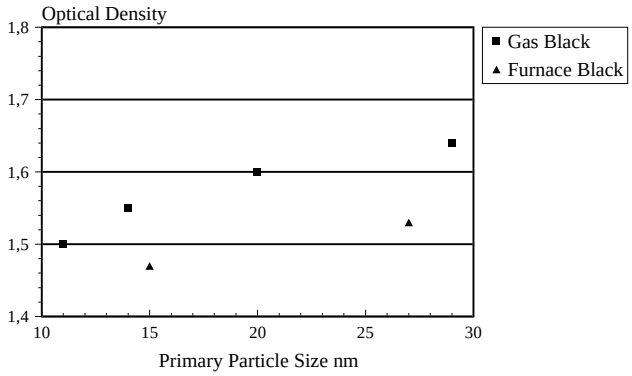
The values arranged in table 5 show that the carbon black influences the surface tension. A main influence is given by the primary particle size of the pigment black and the mean particle size of the dispersion. This trend occured with both, furnace and gas blacks and has an effect on the contact angle given in the table below. More significant is the influence of the different papers on the contact angle. Papers 1 and 2 have good wetting properties which resulted in low drying times. The drop on paper 1 shows, after drying, a gray corona surrounding the deeply black ink piont. This is due to the water which penetrates the top coating and spreads out on the second coating layer. On paper 3 and 4 the contact angles are high and sharp dots are formed with no corona. In particular on paper 3, the drying time is extremly long.

Table 6

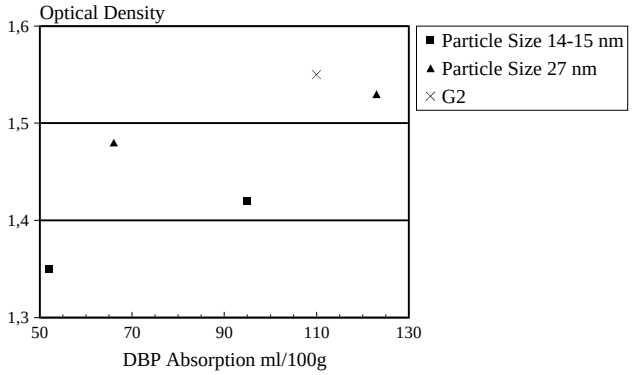
	Contact Angle/Optical Density			
	Ink 1	Ink 2	Ink 3	Ink 4
P1	45/1.50	25/1.55	23/1.55	27/1.50
P2	39/1.51	35/1.53	27/1.58	30/1.62
P3	64/1.29	63/1.29	62/1.35	65/1.32
P4	85/1.50	80/1.55	77/1.60	75/1.64
	Ink 5	Ink 6	Ink 7	Ink 8
P1	12/1.55	12/1.53	29/1.41	16/1.42
P2	39/1.44	30/1.38	29/1.57	19/1.43
P3	65/1.10	63/0.95	58/1.33	60/1.12
P4	76/1.42	86/1.35	75/1.53	74/1.48

Carbon black absorbs up to almost 100% of the visible light and also in the UV- and IR- range of the spectrum. The blackness value increases with decreasing primary particle sizes. The hue varies from blue to brown depending on the type of carbon black, the binder system and the primary particle size. In regards to the light absortion and light scattering properties of a carbon black also the structure has to be considered. A high structure offers the shearforces more points to attack and therefore the pigment is easier to disperse resulting in more single particles which improve the light absorption [4]. The influences of the structure and primary particle size on the blackness value is given in table

1 and 2. In graph 1 the optical density (measured on paper 4), is plottet versus the primary particle size of the gas and furnace blacks. The trend is clear: the higher the primary particle size the higher the optical density. This trend occurs on papers 2 to 4, reflected strongly on the gas blacks. On paper 1 the correlation is not clear or even reversed in the case of the furnace blacks. The influence of the sructure is given in graph 2, in which the optical density is plotted versus the DBP absorption. The latter result is in agreement with the above stated comments, however, the influence of the primary particle size on the optical density is in contradiction to it.



Graph 1



Graph 2

To investigate this phenomenon in-depht, light micrographs have been taken of thin cuts of papers selected from the experiments (see next page). On paper 1 which has a thick coating layer and small pores there is a significant difference between the penetration properties of the ink containing the furnace black (P1/F1) and the ink containing gas black (P1/G3). The furnace black seeps through the coating layer completely, whereas the gas black penetrates only half of the layer. The same penetration behaviour occurs on paper 5 even though the pore size is much larger and the surface tension is relatively low. This explains why the optical densities of furnace blacks are lower than that of the gas blacks since the latter remain more on the suface and therefore develop a higher covering power. There are two possible reasons for it. First, gas blacks with their acidic surface wet the paper coating much better than the basic furnace blacks do. Second, steric effects hinder the penetration of the pigment black. To this possibility micro flocculation must be considered. But since no difference between the slightly acidic and the neutral paper surface occured, this possibility is excluded. The mean particle size of the pigment in the aqueous dispersion has an influence. The values in table 6 correlate with the primary particle size of the pigment blacks and would explain why the influence of the primary particle size is in contradiction to the theory. The ink containing furnace black 3 has a high mean particle size. The corresponding micrograph (P1/F3) shows that the pigment black penetrates slightly into the fine pores of paper 1 but the coverage is irregular and therefore the optical density is unexpected poor. Even though the particle sizes of the inks are significantly lower than the pore sizes of the paper coatings this influence undoubtedly exists but the experiments do not provide conclusive evidence. The comparison of furnace black F1 and F2 (ink 5 and 6 in table 6) leads to the assumption that the pigment black structure must have an influence too. The micrographs P5/F1 and P5/F2 show the different penetration of a high- and a low structured pigment black and the high structured one is penetrated more into the coating pores. To explain the different effects of gas and furnace blacks on the optical densities, transmission electron micrographs were taken from inks no 3 and no 5 dried on glas plates. The TEMs show that in contrast to the furnace black the gas black aggregates grow together during the drying time to a large pigment network which is the most effectiv steric barrier resulting in the extremly high optical densities.

Summary

The Superior print performance of gas blacks in pigmented ink jet inks is a result of the forming of large pigment black network during the drying time which hinder the particles from penetrating into the coating pores.In addition, gas blacks with their hydrophilic surface have good wetting properties to the coatings material. Both result in ink jet inks showing excellent covering power.

References

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4. R. Bode, Pigment Blacks for Plastics, Technical Bulletin No. 40, , Degussa AG, Frankfurt/Main, 4th Edition (1992)
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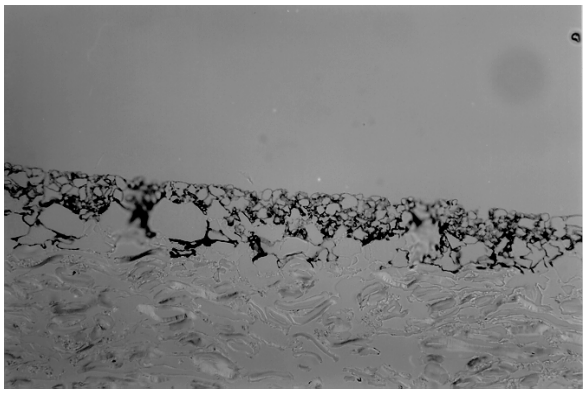
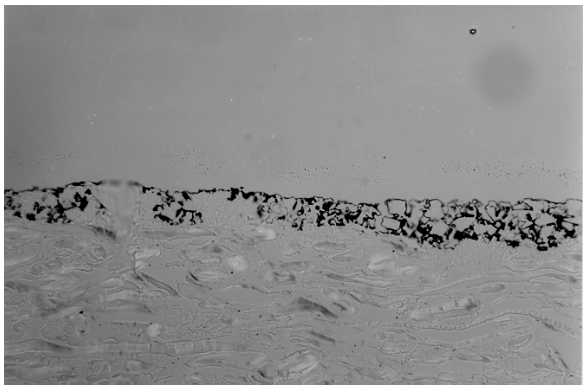
Biography

The author has been in charge of Degussa´s applied technology services for NIP-applications for 14 years. Since June 1998, Mr. Stübbe heads up the newly created global product management for NIP-applications.

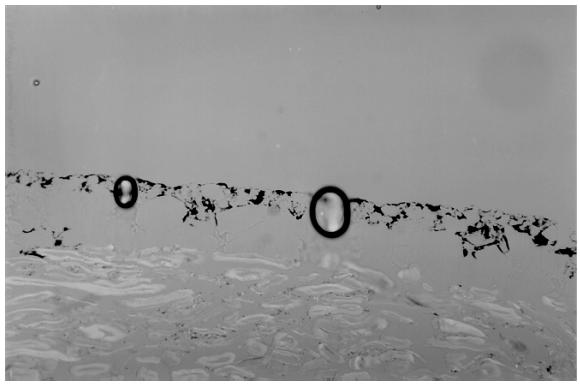
Light Micrographs



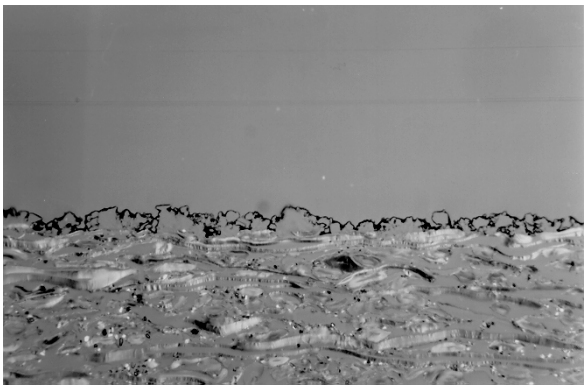
P1/F1



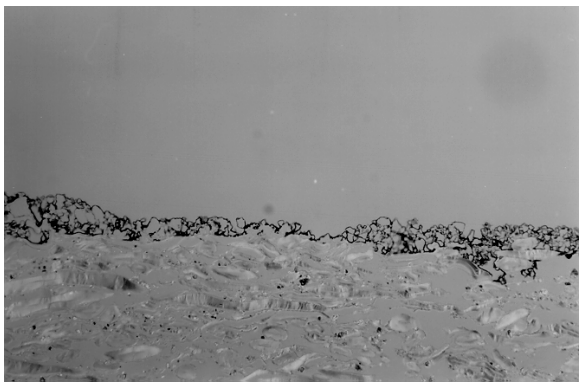
P1/G3



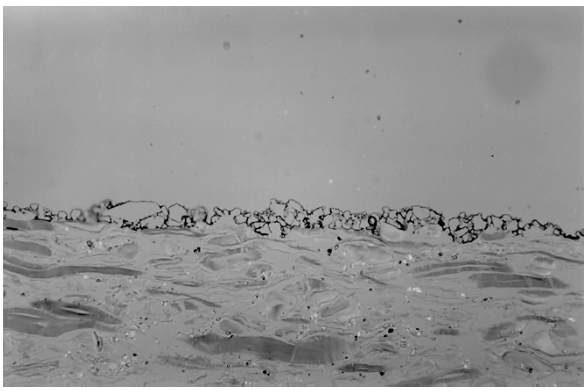
P1/F3



P5/G3



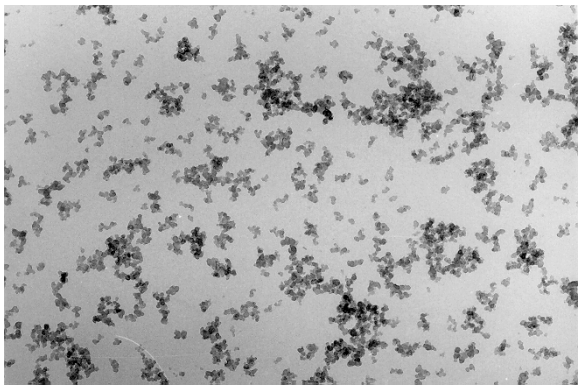
P5/F1



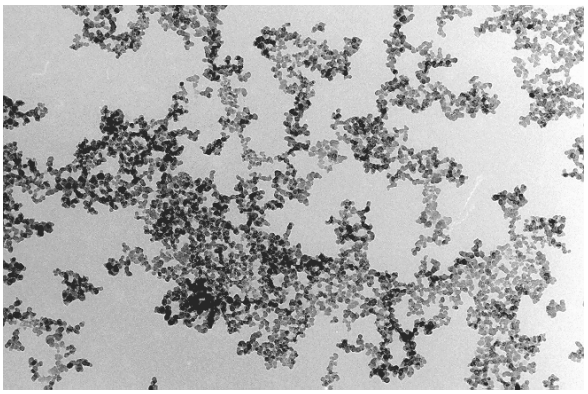
P5/F2

Transmission Electron Micrographs

Magnification 250,000 times



F1. Magnification 250 times



G3