Self-Dispersed Carbon Black for Inkjet Printing Application

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Abstract

Self-dispersed (SDP) carbon black inks have been successfully increased optical density by adding different multivalent metal ions. These selected metal ions cause SDP carbon black particles flocculating on paper surface after printing,, but not affected the stability and jetability of inks.

Introduction

Carbon black is widely applied on inkjet printing because of good chemical durability and light fastness. Self-dispersed carbon black is a surface treated carbon black particle and it can be readily dispersed in water without disperse agents. However, its water like behavior performs inks' penetration on paper after printing and shows poor blackness. This paper tries to improve optical density of ink which came from modified carbon black dispersion.

There are several methods to modify carbon black surface, including oxidation[1], polymerization process[2] and azo reaction process.[3] Successfully exploited oxidation reagents for carbon black surface treatments include ozone, hydrogen peroxide and sodium hypochlorite. Regarding standard half-cell potentials (E^o_{red}), oxidation capability of ozone is stronger than hydrogen peroxide or sodium hypochlorite. (E^o_{ozone} = 2.08 volts > $E^o_{hydrogen\ peroxide}$ = 1.78 volts > $E^o_{Hypochlorite\ ion}$ = 1.64 volts). However, the oxidation reaction is taken place on the gas/solid or liquid/solid interface. The solution of hydrogen peroxide or hypochlorite ion has faster reaction rate than ozone gas. No matter which type is it, there are lots of negative charge on carbon black's surface. These negative charge forms strong electrostatic force to water molecules. Here, we present a special carbon black dispersion treated by sodium hypochlorite and with $-COO^-$ or $-O^-$ groups on pigment surface. (Fig 1.)

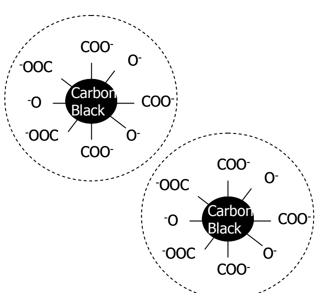

***Fig 1.** The electrostatic force between surface-oxidation pigments*

In image world, people always expect to get higher optical density. General speaking optical density or color strength is proportional to colorant concentration (first-order). However, the first-order approximation fails to account for the phenomena of colorant saturation. Fig 2 shows the real act between colorant concentration and color strength.

A better model for the relationship is as Tollenaar-Ernst equation: [4,5]

$$D = D_{\infty}(1-e^{-my})$$

wherein
D = color density
D_{∞} = saturated color density
y = thickness of ink film (related to pigment concentration)
m = regression coefficient, dependent on the paper and print conditions.

Fig 3 shows adding multivalent ions can increase the saturated color density thus higher optical density.

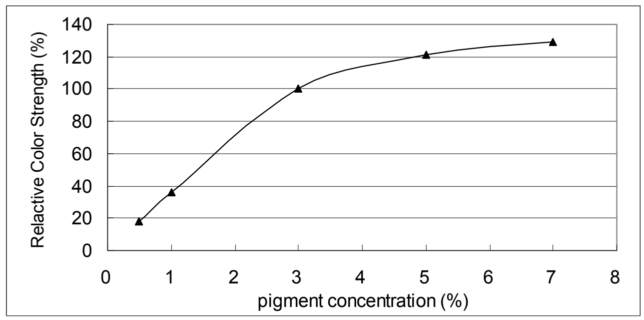

***Fig 2.** The real relationship between colorant concentration and color strength*

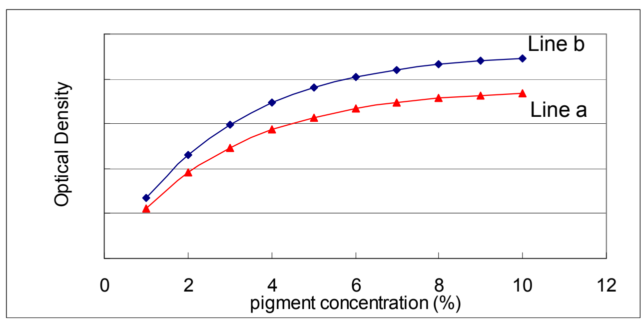

***Fig 3.** Line a is the optical density without multivalent metal ions. Line b is the optical density with multivalent metal ions.*

The present paper relates to a black inkjet ink composition, which comprises: (A) 3 wt% to 10 wt% of black colorant, wherein the black colorant is a carbon black having carboxyl groups and hydroxyl groups on its surface; (B) 0.1 wt% to 20 wt% of humectant; (C) 0.01 wt% to 0.1 wt% of multivalent metal salt, wherein the multivalent metal salt is a divalent metal salt, a trivalent metal salt or a combination thereof, and the water solubility of the multivalent metal salt is 0.1 mole/L or more; and (D) biocide. [6] By adding multivalent metal, the color strength of black ink will be significant improved. That means usage of carbon black can be reduced to get the same optical density or color strength.

Experiment

Preparation of Ink Compositions

Water-soluble pigments used in the table 1 are water-soluble pigments each having on its surface a group terminated with a carbonyl, carboxyl, hydroxyl or other group. This self-dispersed pigment dispersions used here are available from Everlight Chemical Industrial Corporation in Taiwan, under the trade name Evertop Black A-15.[7]

All the multivalent metal salts were dissolved in water with 10% solution by weight. Example 1 were made from 0.5% of glycerol, 2.5% of dipropylene glycol, 10% of triethylene glycol mono-butyl ether, 0.4% of Surfynol 440(Air Product and Chemical, Inc.), 0.2% of Surfynol 420(Air Product and Chemical, Inc.), 0.2% of Proxel GXL, 0.5% of 10% MgCl2 · 6H2O and 42.15% of water. All components were mixing together before adding pigment dispersion. Mixing for 10 minutes, then added 6.6% of Black A-15. Some process applied in Example 2 to 8 and Comparative 1 to 3. All inks were filtrated with membrane filter (1.2μm) just before printing.

Evaluate A : Penetration depth of pigment

To confirm the change of penetration depth by adding multivalent metal ions, we investigated depth picture of pigment in the cross section of paper by microscopy. The microscopy magnified the object 300 times and snapped through digital camera.

Evaluate B :Color strength evaluation

Printing was performed using an Epson T22 printer. The test chart was printed on a plain paper. Color strength measurements were made using an Elrepho type Datacolor 400 spectrophotometer.

Evaluate C : Storage stability test

The example inks are placed at 70° C for one week. The deviation of viscosity was tested under room temperature. The viscosity of each aqueous pigment inks was measured using a cone-plate type viscometer. As the viscometer, DV-Ⅱ+Pro (manufactured by Brookfield Co., Ltd.) was used.

Table 1. Color strength evaluation **(% by wt)**

	Example								Comparative		
	1	2	3	4	5	6	7	8	1	2	3
SDP carbon black	6.6	6.6	6.6	6.6	6.6	6.6	6.6	6.6	6.6	8.5	10
Glycerin	0.50	0.50	0.50	0.50	0.50	0.50	0.50	0.50	0.50	0.50	0.50
Dipropolyene glycol	2.50	2.50	2.50	2.50	2.50	2.50	2.50	2.50	2.50	2.50	2.50
Triethylene glycol mono-butyl ether	10.00	10.00	10.00	10.00	10.00	10.00	10.00	10.00	10.00	10.00	10.00
Surfynol®420	0.40	0.40	0.40	0.40	0.40	0.40	0.40	0.40	0.40	0.40	0.40
Surfynol®440	0.20	0.20	0.20	0.20	0.20	0.20	0.20	0.20	0.20	0.20	0.20
PROXEL GXL	0.20	0.20	0.20	0.20	0.20	0.20	0.20	0.20	0.20	0.20	0.20
$MgCl_2 \cdot 6H_2O$	0.05	0.1							-	-	-
$Ca(NO_3)_2 \cdot 4H_2O$			0.05	0.1					-	-	-
$AlCl_3 \cdot xH2O$					0.05	0.1					
$Fe(NO_3)_3 \cdot 9H_2O$							0.05	0.1			

Results and Discussion

Penetration depth of pigment

Fig. 4 shows cross-sectional images of unprinted plain paper and printed with Example 2 and Comparative1. With the same carbon black amount, Comparative 1 penetrated nearly to the back of the paper but example 2 left pigments anchored at the near-surface. Different thicknesses of ink film were observed. It is also matched with Tollenaar-Ernst equation. Thinker ink film could observe higher optical density or color strength.

Color strength evaluation

Relative color strength is shown in Table 1. With high pigment content (6.6% by weight), the saturated color strength significantly rises by 20~40%. Usually, pigment particles and solvents penetrate into paper when landing on the surface. Normally, solvents are easier to penetrate than pigments. Flocculating the carbon black particles on the surface is happened. When an ink drop lands on the plain paper from printhead, pH and solubility of the ink change. Most plain papers have pH value less than 4. This acid condition of paper lower the solubility of pigment particles due to their double charge layer is disturbed. The pigment crash causes its flocculation. Then, the pigment stops at the surface of a paper.

Adding suitable metal ions could get a similar effect. Here, we choose some soluble salts with alkaline earth metal ions (IIA) and group 3 metal ions (IIIA). When organic solvents penetrate into paper, these metal ions collide strongly with pigment particles. Then pigment is salted out or crashed on the surface of paper. More pigment on the top of paper, more strong reflective lights are observed by naked eyes. Then, we get higher color strength or optical density image.

On the side, we could see the multivalent metal effect is equal or stronger than pigment amount increasing. That means this method also gives a cost-effective advantage.

Storage stability test

Measurements of viscosity of these inks after high temperature storage are shown in Table 3. The storage stability of the ink was evaluated as follows. [8] The viscosity after the test was divided by the initial viscosity. A rating of A was given if the quotient was 1.0 to 1.1, B if over 1.1 but no more than 1.2, C if over 1.2 but no more than 1.5, and D if over 1.5. All eight samples got good results.

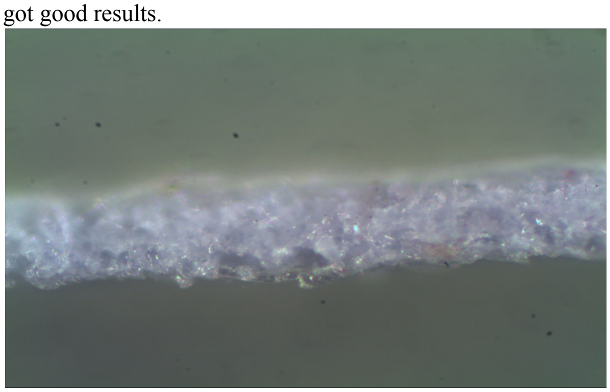

Fig. 4a Cross-sections of plain paper

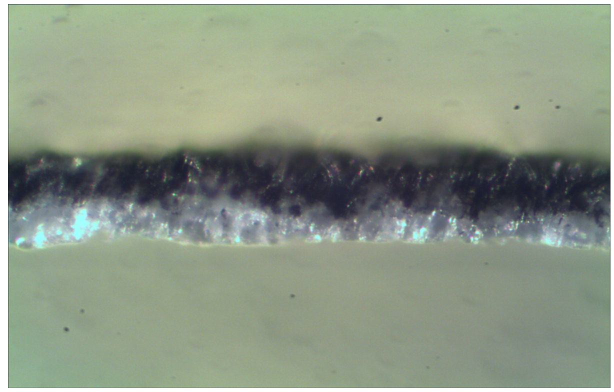

Fig. 4b Cross-sections of Comparative 1

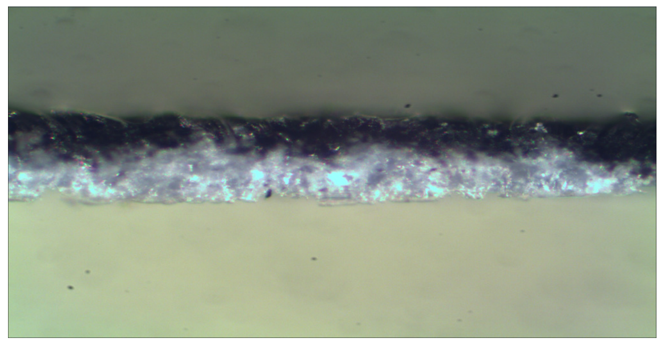

Fig. 4c Cross-sections of Example 2

Table 2. Color strength evaluation

	Example								Comparative		
	1	2	3	4	5	6	7	8	1	2	3
Relative Color strength (%)	132	139	130	133	122	127	121	125	100	111	117

Table 3.Storage stability results

Viscosity (cp@25□)	Example							
	1	2	3	4	5	6	7	8
Initial	2.57	2.56	2.54	2.54	2.64	2.64	2.65	2.63
70° C for one week.	2.57	2.61	2.49	2.53	2.63	2.95	2.62	2.71
Storage stability	A	A	A	A	A	B	A	A

Conclusion

Adding multivalent metal ions can improve optical density or color strength is not new approach, especially in color organic pigments application. But non successful case was present on SDP carbon black dispersion. Here, we supply the special carbon black dispersion to formulate high color strength inks by adding multivalent metal salts.

Reference

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[7] Ueno Shinya; Mori Shiro; Ueda Tsutomu., "Surface-treated carbon black composition and method for producing the same," JP2007084597.

[8] Masahiro Yatake., "Storage stability; mold, bacteria and/or microbe prevention; containing methylisothiazolone and octylisothiazolone antiseptic agents; aqueous nonclogging formulations," U.S. Patent 7,273,898.

Biography

Chien-Wen Lee received his Bachelor and Master Degree from Tam-Kang University (Taiwan), Chemistry Department in 1994 and 1996, respectively. He works at Everlight Chemical Industry Corporation (ECIC) on the disperse dyes development from 1998 to 2002 and special dyestuff for inkjet ink application since 2003.

Hsiao-San Chen received the B.E. and Master Degrees from Fun-Cha University Textile Department from1986 to 1991 in Taiwan. He worked on the reactive dyes synthesis subject in Everlight Chemical Industry Cooperation (ECIC) since 1994. He got a PhD degree from UMIST Textile department U.K. during the working time by company financial supporting. Currently he is inkjet group leader in the R&D department of ECIC.