Effects of Glycine Derivatives in Dispersed Colorant Based Inks

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Abstract

Recently, pigmented inks became popular for personal and office printers. They have advantages in waterfastness and lightfastness, but they have limitations on clear color, rub resistance and jetting reliability. Therefore, new inks have been required to overcome these problems.

We have developed new emulsion colorant in order to solve these problems. The colorant is water based polymer emulsion containing water insoluble dye. The emulsion colorant based inks show clear color, rub resistance like water soluble dye based inks and waterfastness, sharpness like pigmented inks. But the emulsion colorant based inks cause clogging at the nozzle of print head, and by this clogging jetting reliability are fallen off.

To solve this problem, we investigated various humectants suitted to the emulsion colorant. As the result, we found that addition of glycine derivatives improved jetting reliability of the emulsion colorant based inks sharply, and that glycine derivatives were useful humectant for pigmented inks, too.

Introduction

Ink jet printing systems have been developed as a target getting print quality of silver halide photographs. By developments of jetting smaller drop, coating media, and water soluble dye based inks, ink jet printers became to be able to achieve high level print quality over silver halide photographs. But when using water soluble dye based inks, print qualities on plain paper are insufficient in waterfastness, lightfastness, sharpness and optical density. To overcome these problems, pigmented inks have been developed.[1,3] The pigmented inks are used to wide format printers and some personal printers, but they (especially color pigmented inks) don't become popular inks for ink jet printers by lack of clear color, optical density, rub resistance and jetting reliability.

We have developed new emulsion colorant[2] in order to solve these problems. The emulsion colorant is composed of water based polymer emulsion containing water insoluble dye and it shows clear color, rub resistance like water soluble dye based inks, waterfastness, sharpness like pigmented inks and high optical density over these inks. But the emulsion colorant based inks cause clogging at the nozzle of print head and by this clogging jetting reliability are fallen off.

We evaluated various humectants (alcohols, ethers, amino acids and their derivatives etc.) to improve jetting reliability. As the result of this investigation, we found that addition of water soluble amino acids and their derivatives, especially glycine derivatives improved jetting reliability sharply. In glycine derivatives, N-methylglycine, N,N-dimethylglycine, N,N,N-trimethylglycine are very effective.

In this paper, we show effectiveness of glycine derivatives in our emulsion colorant based ink system and our pigmented ink system.

Experimental

Materials

The model emulsion colorant was prepared by next two steps.

1st step : Synthesis of water insoluble polymer
2nd step : Preparation of polymer emulsion containing water insoluble dye

<1st Step : Polymer Synthesis>

The copolymer of styrene, lauryl methacrylate and methacrylic acid was prepared by the solution polymerization in 2-butanone (St/LMA/MAA = 40/40/20 wt%, Mw = 20,000, solid contents=50%)

<2nd Step : Preparation of Polymer Emulsion>

60g of the polymer, isolated from the polymer solution by drying under reduced pressure, and 40g of Vail Fast Blue 2606 (produced by Orient Kagaku K.K.) were dissolved completely in 300g of toluene, and 24g of a sodium hydroxide aqueous solution was added to the solution to partially neutralize the salt-forming groups of the polymer. Then, 600g of ion-exchanged water was added thereto, followed by stirring, and the mixture was emulsified in supersonic wave emulsifier for 30 minutes. Toluene was completely evaporated from the resulting emulsion at 60°C. Under reduced pressure, and part of water was also removed to give an emulsion of fine polymer particles containing Vail Fast Blue 2606 (Figure1 and Table 1).

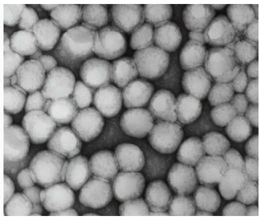

Figure 1. TEM photograph of the emulsion colorant

Table 1. Physical Properties of the emulsion colorant

Solid Content	20%
Average Particle Diameter	92 nm
Surface Tension	57 mN/m
Viscosity	2.1 mPa・s
p H	8.6
Stability (60°C)	> 3 months

<Preparation of Test Ink>

The components listed below were formulated, and the resulting dispersion was filtered through a 0.2 μm filter to remove dust and coarse particles to obtain aqueous ink.

Polymer emulsion	60g
Glycerin	10g
humectants	10g
Acetylenol EH	1g
Ion-exchanged water	19g

* Base ink: ion-exchanged water 10g instead of screening humectants

Ink and Print Quality Evaluations

Printing was carried out using the test ink on a commercially available ink jet printer, Color Mach jet printer "Model EM-900" manufactured Seiko Epson Inc. Optical density, waterfastness and rub resistance of prints were evaluated in accordance with the following methods.

<Optical Density and Waterfastness>

Optical density: Plain paper (Xerox 4024 DP) was printed with the ink (100% duty) and dried spontaneously for 24 hours in a room. Optical density of the print was measured with a Macbeth densitometer (RD918, manufactured by Macbeth).

Waterfastness: After measured optical density of the print, 10 drops of ion-exchanged water was droped to the print with syringe and oozing level of the print was observed with the naked eye to evaluate waterfastness.

<Rub Resistance>

Glossy paper for ink jet printing (MC glossy paper, produced by Epson) was printed with the ink (100% duty). The printed surface was reciprocally rubbed 5 times with an eraser set at a fixed incline of 45° with a load of 1 kg thereon, and the condition of the rubbed printed surface was observed with the naked eye to evaluate rub resistance.

<Jetting Reliability>

Anti-clogging property: Alphanumerical letters were continuously printed for 10 minutes by EM-900 (Epson). The printer was stopped and allowed to stand uncapped at 40°C. and 25% RH for 2 weeks. After the standing, printing of alphanumerical letters was resumed. The number of movements for restoration from clogging (cleaning) that were required to obtain prints of the same quality as that obtained before standing was examined.

Drying resistance: A few drops of the ink were dropped in an aluminum cup and were dried at room temperature. The time (hours) required for forming a dried film was measured. The drying resistance thus measured is one of indications of anti-clogging property.

<Ink Dispersion Stability>

The ink under evaluation was allowed to stand in a thermostat set at 50°C for 1 month. The particle size distribution of the ink was measured with a Coulter counter before and after the standing, and the ink dispersion stability was evaluated according to the following rating system.

Result and Discussion

Additional Effects of Alcohols and Polyols to Ink Performance

We investigated addition effects of alcohols (ethanol, iso-propanol) and polyhydroxy compounds (polyols : ethylene glycol, diethylene glycol, trimethyrolpropane, glycerin) as humectants. Table 2 shows the result.

Table 2. Additional Effects of Alcohols, Polyols in the Ink

Hemectants	Base	EtOH	IPA	EG	DEG	TMP	Gly.
Optical Density	1.06	1.08	1.05	1.04	1.05	1.09	1.05
Waterfastness	◎	◎	○	○	○	○	○
Rub Resistance	○	○	○	◎	◎	○	◎
Drying Resistance	1>	1>	3	15	18	10	20
Anti-Clogging	X	X	X	Δ	Δ	Δ	Δ
Stability	◎	◎	◎	◎	◎	◎	◎

In the base ink that humectants are not added, stability of the ink and waterfastness of the print used the ink were very well. Optical density of the print was high, rub resistance of it was good. But drying resistance of the ink was insufficient, therefore anti-clogging property was poor. To improve drying resisitance and anti-clogging property of the base ink, we tried addition of alcohols as humectants in the base ink, but their addition was not effective.

Addition Effects of Ethers, 2-Pirrolidine, Glycine and Their Derivatives to Ink Perfomance

We investigated addition effects of ethers (triethelene glycol monobuthylether, diethylene glycol monobutylether) and 2-pirrolidone, glycine and glycine derivatives (N-methyl glycine, N,N-dimethyl glycine, N,N,N-trimethyl glycine, glycyl glycine,). Table 3. and Table 4. show the result.

Table 3. Additional Effects of Ethers, 2-pirrolidine and Glycine in the Ink

Hemectants	TEGMBE	DEGMBE	2-pirro.	Glycine
Optical Density	1.05	1.03	1.08	1.08
Waterfastness	◎	◎	○	○
Rub Resistance	○	○	◎	◎
Drying Resistance	2	3	15	>24
Anti-Clogging	X	X	Δ	○
Stability	Δ	X	◎	◎

Table 4. Additional Effects of Glycine Derivatives in the Ink

Hemectants	MG	DMG	TMG	Gly.-G
Optical Density	1.10	1.10	1.12	1.08
Waterfastness	◎	◎	◎	○
Rub Resistance	◎	◎	◎	◎
Drying Resistance	>24	>24	>24	>24
Anti-Clogging	◎	◎	◎	○
Stability	◎	◎	◎	◎

Addition of ethers was not effective to improve of drying resistance and anti-clogging property. Moreover, ink stability became worse by addition of ethers. But sharpness of the print with these inks were improved by quick penetration into plain paper.

On the other hand, additions of glycine and glycine derivatives, especially N-methylglycine, N,N-dimethyl glycine, N,N,N-trimethylglycine were very effective for improvement of drying resistance and anti-clogging property. The print with the ink added glycine derivatives exhibited optical density and rub resistance higher than the print with the ink without glycine derivatives. This result suggests that remaining of the ink in plain paper increased by additions of glycine derivatives.

Effects of N,N,N-trimethlglycine concentration

Figure 2 shows the effect of N,N,N-trimethlglycine concentration on anti-clogging property of the ink.

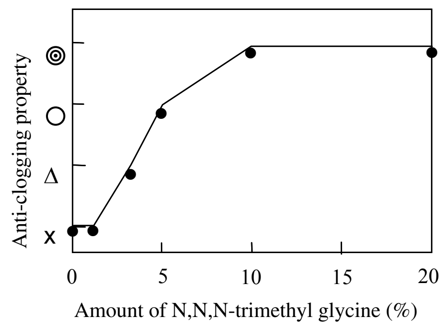

Figure 2. Amount of TMG vs. anti-clogging property

Anti-clogging properties of the ink added different amounts of N,N,N-trimethlglycine to the base ink were investigated (concentration = 1%, 3%, 5%, 10%, 20%). Improvement of anti-clogging property was sufficient by addition over 10%, but waterfastness of the print with the ink added 20% of N,N,N-trimethl glycine was fallen off slightly.

Figure 3 shows the photograph of jetting behavior from nozzles of printer head after anti-clogging test of the ink added 10% of N,N,N-trimethlglycine. Jetting behavior was very good.

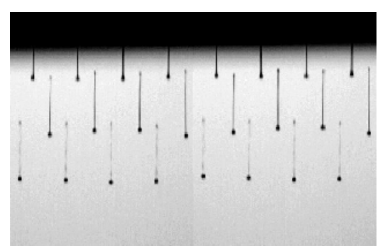

Figure 3. Jetting condition of the ink added TMG

Additional Effects of N,N,N-Trimethyl Glycine for Pigmented Ink

Additional effects of N,N,N-trimethylglycine to pigmented ink was investigated. The pigmented ink was prepared in the following method.

<Preparation of Pigmented Ink>

The same polymer mentioned above was prepared by the solution polymerization and was neutralized with sodium hydroxide. The 30g of the neutralized polymer and 70g of pigment (CI No. Pigment Blue 15:3) were mixed with 500g of water. The mixture was dispersed with the beads mill. Then the dispersion was concentrated to 20%.

Inks for this study were made from 5% of pigment in the colorant, 10% of glycerin, 10% of N,N,N-trimethyl glycine, 1% of acetylenol EH and the rest of ion-exchanged water. The ink was filtrated with membrane filter (1.2 μm) just before the experiments. Table 5 shows the result.

Table 5. Additional Effects of TMG for Pigmented Ink

Hemectants	None	TMG
Optical Density	1.11	1.15
Waterfastness	◎	◎
Rub Resistance	○	○
Drying Resistance	1>	>24
Anti-Clogging	×	◎
Stability	◎	◎

We found that addition of N,N,N-trimethylglycine for pigmented ink was very effective to improve drying resistance and anti-clogging property similarly to the addition to emulsion colorant based inks.

Conclusion

We mentioned that additons of glycine derivatives, especially N-methlglycine, N,N-dimethyl glycine, N,N,N-trimethlglycine were very effective to improve jetting reliability not only for our emulsion colorant based ink, but also for our pigmented ink. And in the case of N,N,N-trimethlglycine, additions over 10% were necessary. Moreover, additions of glycine derivatives were effective to heighten optical density and rub resistance.

In the near future, ink jet printers will become main printer in the office by improvements of the print quality for plain paper and print speed. Therefore, it is necessary to use dispersed colorant based ink. The result of this study will be useful for managing dispersed colorant based ink.

References

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Biography

Michitaka Sawada received his M.S.in Polymer Science from Osaka University in 1986 and joined Kao Corporation in Materials Development Research Laboratories in Wakayama, Japan in 1986. Since 1989, he has been worked on polymer materials and ink jet colorants and inks. E-mail: sawada.michitaka@kao.co.jp