

Polymeric Additives for Emulsion-based Ink Jet Inks

T. Tsutsumi, M. Sawada and Y. Nakano
Kao Corporation, Materials Development Research Laboratories
Wakayama, Japan

Abstract

Polymers are very useful to improve the print durability and already used in many printing systems such as electrophotography. It relies mainly on the property that polymers can make a film to fix the colorants on the media. And polymers are also very useful to control the flow property of the ink fluid. For applying these properties to the ink jet system, the combination of polymer emulsion colorant and appropriate polymeric additives is thought to be efficient. This work was undertaken to study the ability of polymeric additives in the pigment contained polymer emulsion based ink to improve the jetting phenomena holding good print reliability and durability. Several kinds of water-soluble polymer such as polyether, polyamide, polyelecrolyte were added to the pigment contained polymer emulsion based ink, and the change of physical properties of ink was investigated. It was shown experimentally that polyamide and polyethylenglycol derivatives were useful to reduce the kogation and to elevate the drop velocity without deterioration of the print durability.

Introduction

Ink jet printers have made a surprising progress and eject the smaller drop with lower energy at the high firing frequency. So the efficient conversion of the thermal energy into the kinetic energy becomes more important. That is to say, the optimization of the drop velocity of the ink becomes more important for the evolved printers.

Polymer emulsion colorants are thought effective to bring the high print durability to the ink jet system. Comparing with the conventional pigment dispersion, they tend to have some problem about the drop velocity and need optimization of the polymer composition. Besides the polymer composition, the optimization of the total print performances of the polymer emulsion-based ink should be made by the combination of the ink components. The addition of surfactant is the usual technique and was effective to improve the jetting performance. However the lowering of the surface tension of inks tends to lose the print quality. Polymeric additives were thought to be useful for ink jet inks. Previously reported polymeric additives, which were investigated for shortening the ligament and obtaining good print quality, showed the loss of the jetting velocity as a negative character[2,3]. Then the research for other polymeric additives for combining with the polymer emulsion colorant seemed important to obtain good ejection performance and print durability.

Experiment

A model polymer emulsion colorant was prepared as follows. First, 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 = 17,000) and was neutralized with sodium hydroxide. The 25g of the neutralized polymer and 50g of carbon black were mixed with 400g of water. The mixture was dispersed with the beads mill. Then the dispersion was concentrated to 20 %. The physical property of this colorant was listed in Table 1.

Table 1. Physical properties of emulsion colorant.

Viscosity	Surface Tension	Diameter	PH
4.3 mPa.s	48.0 mN/m	120 nm	10.0

In this study, water-soluble low molecular weight polymers were investigated because the elastic property should be minimized. Polyacrylamide (Mw=1500 and 10000), polyacrylic acid (Mw=2000), and Styrene maleic anhydride copolymer (Mw=1600) were obtained from Aldrich Chemical Company and neutralized with sodium or potassium hydroxide. Polyethylenglycol (Mw=400, 1000, 1500, 2000, 4000, 6000) was obtained from Katayama Chemical. Polydimethylacrylamide (PDMAAm) were synthesized in the laboratory by the solution polymerization using mercaptoethanol as a chain transfer agent.

Standard ink for the experiments was made from 6 % of polymer emulsion colorant, 10 % of 2-pyrrolidinone, 5 % of polymeric additive, and water. All inks were filtrated with membrane filter (1.2 μm) just before the experiments. The physical properties of these inks are listed in Table 2.

The process of drop ejection was visualized by the system, which was composed from the flash lamp and the variable delay unit and the CCD camera. The jet images were saved on the videotape and used for further analysis. The print heads of BJC-430 (Canon Inc.) was used standard for the experiments and the printer head of Z-11 (Lexmark International) was used optionally. Kogation test was made under the similar condition of Suga[4] by putting the heater element of BJC-430 without nozzle into a vessel of ink and supplying 5 x 10^6 pulses.

Table 2. Physical properties of the inks.

Additives	Amount (%)	Viscosity (mPa.s)	S.T. (mN/m)
PAA-K(2000)	5	2.72	45.2
PAAm(1500)	5	2.63	42.9
PAAm(10000)	3	2.18	44.1
PDMAAm(900)	5	2.15	45.7
PDMAAm(1200)	5	2.38	46.5
PEG(400)	5	1.96	46.2
PEG(1000)	5	2.11	46.0
PEG(1500)	5	2.16	46.3
PEG(2000)	5	2.39	46.2
PEG(4000)	5	2.53	46.2
PEG(6000)	5	2.89	46.2
PSt/MA-Na(1600)	5	4.35	42.1

Results and Discussion

Drop Velocity

The jetting velocities of the polymer emulsion based inks with different types of polymeric additive were investigated (Figure 1). Four kinds of polymeric additives, PSt/MA, PDMAAm, PAA, and PEG, were found effective to elevate the drop velocity of the emulsion-based ink. PAAm showed no effectiveness about the drop velocity.

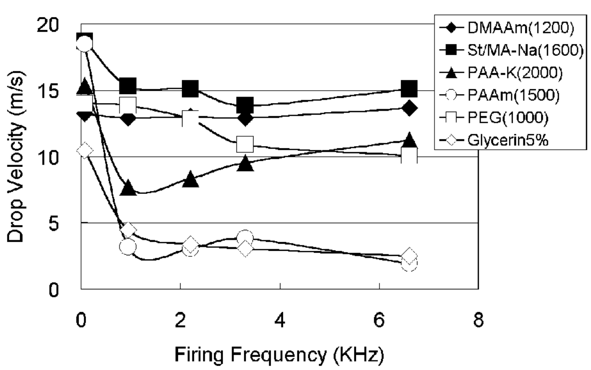

Figure 1. Drop velocity of inks containing different kinds of polymeric additives.

Kogation

Heat stability is the indispensable property of the inks in thermal jet system. So the kogation test of 10 % of polymeric additive solution, colorant dispersion, and inks were investigated with the heater of the bubble jet printer. Table 3 shows the height of the kogation residues on the heater. After the test, the PEG, PAA, and PSt/MA solutions were observed scarce kogation on the heaters but PAAm and PDAAm solution showed small amount of kogation on the edge of the heaters. The reason of these results did not understand well. However the nitrogen atom is subjected to oxidation, so the dissolved oxygen may affect to the kogation of the polyamide derivatives.

Table 3. Height of the kogation residue on the heater.

	Additive solution	Inks
PAA-K(2000)	0.03µm	0.05µm
PAAm(1500)	0.5µm	0.7µm
PDMAAm(1200)	0.3µm	0.2µm
PSt/MA-Na(1600)	0.05µm	0.07µm
PEG(1000)	0µm	0.02µm
Glycerin 5%	-	0.7µm

The tested polymer emulsion colorant showed much amount of kogation. And PAAm and PDMAAm contained inks show almost the same amount of kogation. They had no effect on the kogation property of the colorants. On the other hand, PAA, PSt/MA, PEG contained inks showed almost no kogation residue on the heater. Figure 2 shows the photographs of the tested heater of two inks with or without PEG. Of course, by changing the polymer composition to be stable for the heat, polymer emulsion colorant became to show scarce kogation by itself [1]. However this result suggested that the polymeric additives are useful to reduce the kogation of the colorant and make applicable many kinds of colorants which have problems on the kogation property.

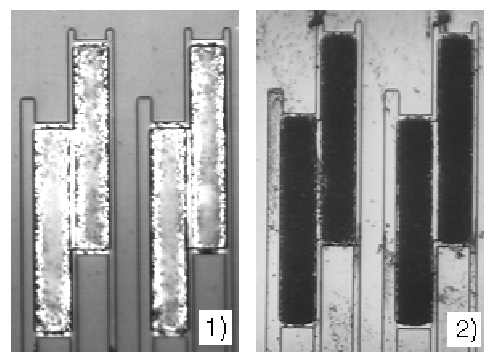

Figure 2. Photographs of the heater surface after kogation test of inks, 1) with PEG1000, 2) without PEG1000

Print Performance

Polymer emulsion colorant has remarkable print durability because it contains a binder with the dye or pigment and can make a film by itself. But when it was used with the water-soluble polymers, the film forming property may be inhibited and consequently the print durability may change. To confirm the influence of the polymeric additives on the print durability, the waterfastness and optical density of the print were investigated.

Table 4 shows the changes of the optical densities when the prints immersed into water for 5 minutes after dried for 1 hr. All investigated water-soluble polymers were not found to affect the waterfastness of emulsion based ink. However only PSt/MA decreased the optical density. This is caused from the low surface tension of the ink brought from the surface activity of PSt/MA.

Table 4. Changes of O.D. in water immersion test (Xerox 4024 paper).

Sample	Initial O.D.	Changes
PAA-K(2000)	1.42	0.00
PAAm(1500)	1.45	0.00
PDMAAm(1600)	1.43	0.00
PSt/MA-Na(1600)	1.28	0.00
PEG(1000)	1.45	0.00

Dispersion Stability

Ink jet additives have not to change the stability of the polymer emulsion based ink. To evaluate the stability of the inks with the polymeric additives, dry stability test was investigated. By using the micropipette, 0.1 ml of ink was weighed in the 2 ml sample tube and dried under 60 °C and measured the changes of the particle diameter (Figure 3).

Two kinds of polyanions, PAA and PSt/MA, reduced the stability of the polymer emulsion-based ink because polyions lower the electric repulsion energy of the emulsion particles. This result suggested that low stability of ink was not necessarily responsible for the low drop velocity. PAAm also reduced the dispersion stability. High molecular weight PAAm is effective for the colloid stabilizer, but low molecular weight seemed inefficient. PDMAAm and PEG did not change the dispersion stability.

From the results of these screening tests about the drop velocity, kogation, and stability, PEG and PDMAAm were thought the suitable polymeric additives for polymer emulsion colorant. Then further examination was made on these two kinds of polymeric additives.

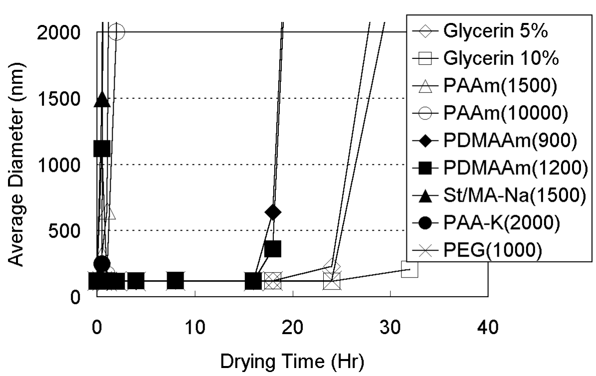

Figure 3. Dispersion stability of inks

Ejection Phenomena of PDMAAm Contained Inks

PDMAAm showed good efficiency to elevate the drop velocity, but they showed some strange jetting phenomenon. The drop velocity of PDMAAm contained ink was increased with the firing counts and became constant after 10^6 drops fired (Figure 4). The reason of this result was not understood experimentally but small amount of kogation residue of PDMAAm would change the condition on the heater surface. The influence of the molecular weight of PDMAAm to the drop velocity was examined after 10^6 drops fired. The drop velocity changed with the molecular weight of PDMAAm (Figure 5). These results suggested that the optimization of the drop velocity with PDMAAm would be difficult.

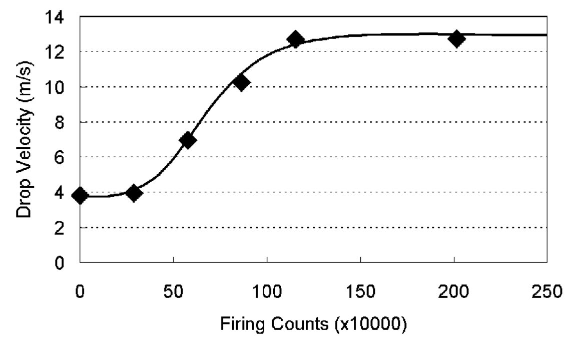

Figure 4. Change of the drop velocity of PDMAAm.

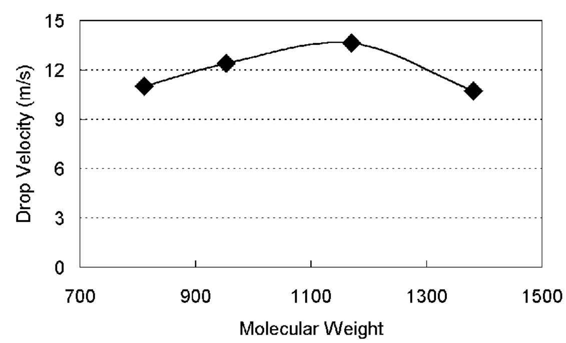

Figure 5. Drop velocity versus molecular weight of PDMAAm.

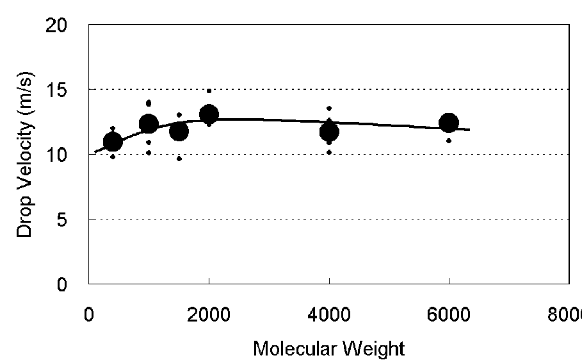

Figure 6. Drop velocity versus molecular weight of PEG.

Drop Velocities of PEG Contained Inks

The influence of the molecular weight of PEG was investigated. It was observed surprisingly that PEG could improve the jetting phenomena independent of the molecular weight and the consequent ink viscosity (Figure 6). This result suggested that the high molecular weight PEG had the nature to improve the jetting phenomenon more effectively than the low molecular PEG. And it also suggested that the modification of PEG molecules had the possibility to obtain the similar effectiveness to the high molecular weight PEG. So we made further investigation about PEG derivatives.

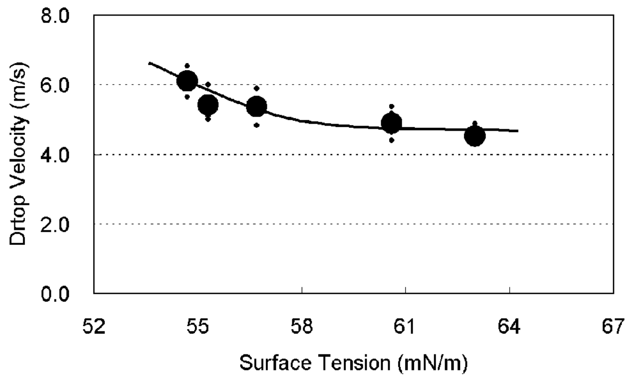

Figure 7. Drop velocity vs. the surface activity of PEG derivatives (Printer head of Z-11 was used) .

PEG has the simple formula and relatively easy to modify chemically. So we made the denatured PEG by changing the molecules with the alkylation or the co-polymerization technology. After the investigation of many kinds of PEG derivatives, the surface activity of PEG derivatives was found a parameter to elevate the drop velocity. Figure 7 shows the drop velocity of the inks containing PEG derivatives versus the surface tension of the PEG aqueous solution (5.0%). The increase of the surface activity of PEG derivatives made increase the drop velocity. On the other hand, the surface activity of additives also has the possibility to decrease the optical density and cause the lack of print quality. In our experimental condition, PEG derivatives did not change the optical density when it's solution have the surface tension above 54 mN/m. Of course, the kind of the most suitable PEG derivatives was supposed to change with other ink components, such as humectants and colorants. Then the careful choice of the ink additives was thought indispensable for obtaining higher print performances. By the combination of suitable PEG derivatives with polymer emulsion colorant, the good ejection performance and good print durability would be achieved.

Conclusion

This paper discussed the combination of the polymeric additives with the polymer emulsion colorant for achieving good ejection performance and print durability. The type and the molecular weight of water-soluble polymer had to be controlled in order to obtaining high drop velocity and dispersion stability. PDMAAm and PEG were found to be the suitable polymeric additives. Especially, the chemical modification of PEG to have little surface activity accelerated the efficiency to elevate the drop velocity. The combination of the suitable PEG derivatives and the polymer emulsion colorant could make the durable print with good ejection phenomena.

References

1. T. Tsutsumi, M. Sawada, Y. Nakano, *IS&T 15th Intl. Conference on Digital Printing Technologies,* 133-136 (1999)
2. J. D. Meyer, A. V. Bazilevsky, A. N. Rozhkov, *IS&T 13th Intl. Conference on Digital Printing Technologies,* 675-680 (1997).
3. C. M. Evans, J. E. Fox, K. P. Hall, P. D. Goodwin, *IS&T 15th Intl. Conference on Digital Printing Technologies,* 78-81 (1999)
4. Y. Suga, T. Eida, S. Koike, *IS&T 3rd Intl. Conference Advanced Non-Impact Printing Technologies,* 285-288 (1988).

Biography

Takehiro Tsutsumi received his B.S. and M.S. in Synthetic Chemistry from University of Tokyo in 1989 and 1991 respectively. In 1991, he joined Kao Corporation and has been engaged in research and development of polymer emulsions. Since 1994, he has worked on ink jet colorants and inks.