

Polymer Emulsion-Based Ink Jet Colorant and Ink

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

Abstract

The ink jet printing system is becoming popular in the market. There are two varieties of ink in the conventional ink jet ink system. One is water-soluble dye based ink and the other is pigmented ink. Dye-based ink has clear color and high reliability, however it is suffering from insufficiency of waterfastness and lightfastness. Pigmented ink has advantages in waterfast and lightfast, but it has limitation on ink stability, clear color and rub resistance. 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 or pigment. When using polymer emulsion containig water insoluble dye, prints show clear color, waterfastness, and rub resistance properties. And when using polymer emulsion containing pigment, prints show waterfastness, lightfastness, and rub resistance properties. Emulsion-based ink would be a technological breakthrough to improve the durability of aqueous ink jet system.

Introduction

The technology of ink jet printing system progressed very rapidly in these several years. Some printers can print images on the coated media that can not be distinguished from silver halide photographs. Some printers can print text as fast as some personal laser printers. But the progress of colorants seems not so fast in this decade.

The first generation of ink jet ink is composed of water-soluble dye. The most serious drawback of this ink is the lack of waterfastness on the plain paper. The second problem is the difficulties to improve lightfastness from ink composition. Of course water soluble or dispersable lightstabilizers can be used, but these additives do little effect because when it printed the relative concentration of these additives changes on the paper.

As the second generation, pigmented inks were developed to obtain waterfastness and lightfastness. These colorants are stabilized by polymeric surfactants or surface modification methods and their particle size are controlled well.[1,2] These type colorants show good many properties but rub resistace is one week point and, in color colorants, trasparency and small color space are also the problems. Because of its low clearness, pigmented color inks are not used for personal and office printers.

To overcome these problems, emulsion-based ink has been developed for next generation ink jet ink, which provides significant improvement over existing inks. The emulsion colorant is composed of water based polymer emulsion containing water insoluble dye or pigments (schematically shown in Figure 1) and exhibits outstanding dispersion stability, excellent heat stability, fine particle size, high compatibility with ink components, low viscosity and controllable surface tension. Especially dye containing emulsion shows clear color like water-soluble dye and also shows waterfastness like pigments.

Emulsion-based inks were evaluated using some personal ink jet printers (Canon BJC-430J, HP Deskjet 720C and Epson MJ-520C). In this paper we discuss the performances of emulsion-based ink in comparison with the conventional inks.

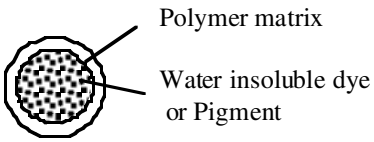

Figure 1. Schema of emulsion colorant.

Colorant Description

Our targeted ink jet ink must satisfy all of the following three performances; reliability, print performance, and print durability. Therefore, we have devised a water based polymer emulsion containing water insoluble dye or pigment to satisfy the above performances. Emulsion colorant was expected to be stable in water and to be fixed on paper tightly, which cause waterfastness and rub resistance along with clear color.

In dispersion type colorant, dispersion stability is essential for print reliability. Since additives such as biocides, chelating agents, humectants and buffers are added to ink jet ink, the polymer emulsion must be stable to these additives. Generally, electrostatic mechanism and steric mechanism are known to stabilize polymer emulsions. And sterically stabilized emulsion is known to be relatively insensitive to ink jet additives. Therefore, emulsions for ink jet inks were preferably designed to stabilized by high steric effect and reasonable electrostatic effect. Moreover, dispersion stability relies on particle size and its distribution. Average particle diameter was controlled to

around 0.1μm and largest particle diameter below 0.2μm (Figure 2).

Kogation is also a big problem in using polymer for thermal ink jet ink. To solve this problem, highly heat stable polymer was desingned not to build up on the heaters.

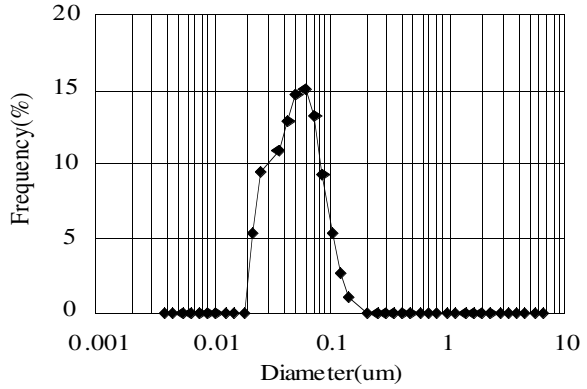

Figure 2. Typical particle size distribution of emulsion colorant.

Print performance comes from how generate images on the substrate having specific properties within a designed range. To eject droplets correctly and to get enough density, ink jet ink must have proper physical and optical properties (low viscosity, controlled surface tension and high absorbance).

Low viscous and high stable emulsion was obtained by controlling the hydrophile-liophile balance of emulsion surface and its particle size distribution. Emulsion colorant was used 5 to 8-wt% in inks. At that concentration, the viscosity of the colorant was 1.3 to 1.6 $mN.s.m^{-2}$ and that of inks showed 2.5 to 3.0 $mN.s.m^{-2}$ (Figure 3).

When using surfactants to stabilize polymer emulsion, it is difficult to get sharp edge print because of the feathering. Soap free emulsion shows high surface tension to get enough ink properties.

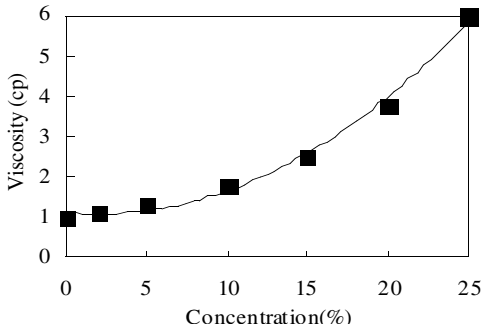

Figure 3. Viscosity vs. concentration.

And to get proper optical density, emulsion colorant has to contain enough amounts of dye or pigment. Previously reported one had not enough dye (up to 25wt%) [3] and have to be used much in inks and that caused the difficulties to get print reliablity. We have developed new synthetic method and get high dye or pigment content polymer emulsion (50 to 75 wt %). Another physicochemical properties are also controlled appropriately (Table 1).

Table 1. Physicochemical properties of emulsion colorant.

Particle Diameter~~A~~vg.	0.08 um
Particle Diameter~~L~~argest	< 0.20 um
Surface Tension	> 50 mN/m (10%)
Viscosity	1.8 ,Ns/m2 (10%)
PH	8.5-9.0
Shelf-life	> 24 months
Stability-60°C	> 3 months
Ames Test	Negative

A lack of print durability was caused by a varieties of external conditions including shear, heat, light, air, water and humidity. Especially water is a weak point to dye based ink for spreading images, and shear is the same to pigmented ink for wearing out images. In emulsion-based ink, these properties can be achieved by film forming mechanism of polymer emulsion. Moreover encapsulation of some stabilizers causes of lightfastness.

Consistency of durability and reliability was also the point for emulsion-based ink. To overcome these problems, we designed polymer molecule to have affinity for not only water but also humectants. When emulsion was company with humectant, ink exhibits high reliability, and when emulsion was apart from humectant on the paper, the resulting print shows good durability. So emulsion-based ink could exhibit high reliability in ink cartridge and high durability when printed.

Runnability of Emulsion-Based Ink

Refilling the initial cartridge of BJC-430J repeatedly, test patterm was printed with emulsion-based ink. More than 100ml of emulsion-based ink were run through without no clogged nozzle and no kogation (Figure 4). Throughout the test, the volume of ejected drops was not changed (Figure 5).

Runnability relies on various ink properties such as anti-kogation, heat stability and anti-clogging performances. Especially anti-clogging property is thought to be most serious problem of emulsion-based ink. But by introducing several kinds of hydrogen bonding functional groups to polymer molecule, which have mutual interaction with humectants, ink could be stabilized well under the dry condition. For example, a drop of appropriatly formulated emulsion-based ink can keep dispersibility on an Aluminium pan over 6 days at 60 °C (Figure 6). But once it was placed on the paper, the humectants were absorbed to paper fiber and, as a result of decrease of ink stability, coagulation of emulsion particle occurred and print durability was achieved.

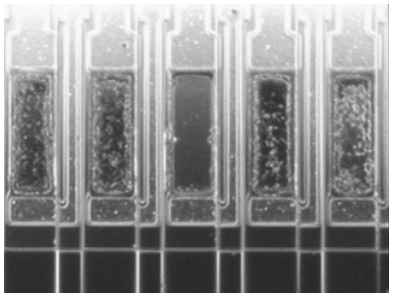

Figure 4. Heaters after printed 100ml emulsion-based ink.

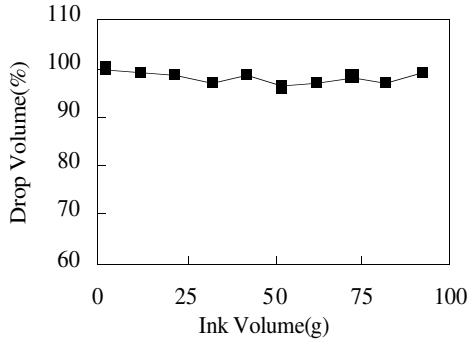

Figure 5. The changes of drop volume throughout the runnability test.

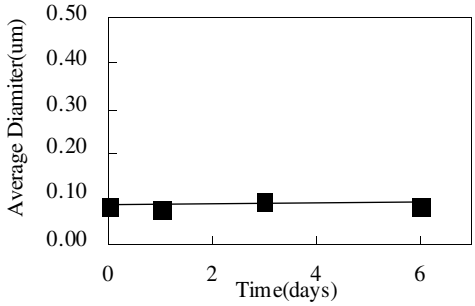

Figure 6. Dipersibility of emulsion-based ink.

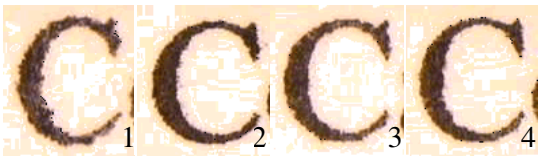

Figure 7. Characters printed from 1) Dye based ink, 2) Pigmented ink, 3) Pigment-containing emulsion based ink, 4) Dye-containging emulsion based ink. (Papar: Xerox 4024 DP)

Print Quality

Figure 7 shows the samll black characters (9pt.) generated from commercially available dye based ink, pigmented ink and developed emulsion-based inks. Although the dye based ink feathered (Figure 7A), the pigmented ink (Figure 7B) and emulsion-based ink (Figure 7C and 7D) did not feather. Dispersion colorants showed enough optical densities irrespective of the kinds of plain paper.

Color Image Quality

It is well known that water-soluble dye based ink has large color space, high brightness and high transparency and pigmented ink has disadvantages in these properties. As shown in Figure 8, dye-containing emulsion-based ink had large color space, high brightness and high transparency. Water insoluble dyes in polymer emulsion showed little melting point in DSC analysis. This suggests that the dyes dissolved in polymer matrix. As a result of that, dye-containing emulsion-based ink developed clear colors and good transparency similar to water-soluble dye based ink.

Pigment-containing emulsion-based ink showed smaller color space on the plain paper, but it showes almost the same color reproductibility as dye based ink on the coated media.

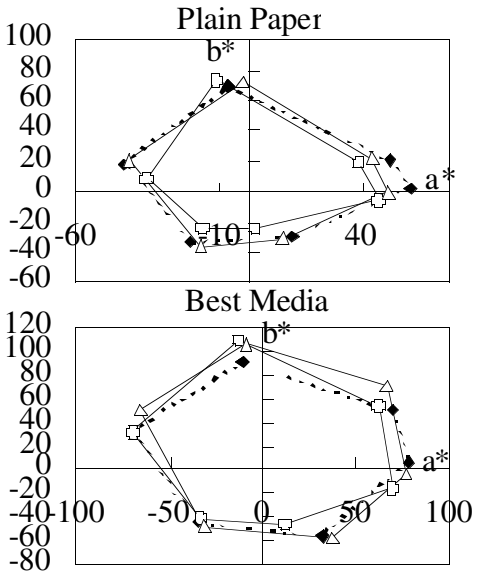

Figure 8. Color space of dye based ink (black square), dye containing emulsion ink (white triangle), and pigment containig emulsion ink (white circle).

Waterfastness

Prints generated from dye based ink, pigmented ink and emulsion-based inks on the plain paper were dried for one hour and then soaked in water for five minutes. Although dye based ink fades, pigmented ink and emulsion-based inks exhibited excellent waterfastness (Table 2).

Table 2. Changes of O.D. in water immersion test.

	Black	Yellow	Magenta	Cyan
Water soluble type	-0.21	-0.04	-0.22	-0.15
Pigmented Ink	-0.01	0	-0.01	0
Emulsion Ink (Pigment)	0	-0.01	0	0
Emulsion Ink (Dye)	0	0	0	0

Rub Resistance

Comparing print durability of ink jet printer with that of laser printer, rub resistance are also needed along with waterfastness and lightfastness. Figure 9 shows the images of characters (12pt.) on the coated media after rubbed three times by an eraser. Conventional dye based ink and emulsion based inks could keep images on the media but pigmented ink came off easily. The difference between these colorants comes from the state of colorant on the media. Water-soluble dye is absorbed in the coated layer but pigment is left on the surface of the media. Emulsions are also left on them but they can form a film by themselves and be settled tightly on the surface. As a result of that, emulsion-based inks showed good rub resistance on any media.

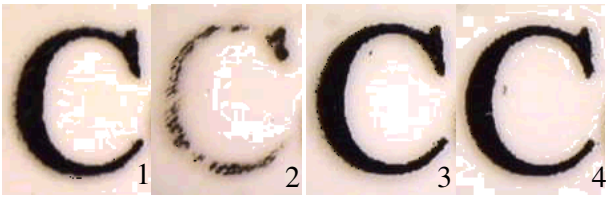

Figure 9. Rub resistance of 1) Dye based ink, 2) Pigmented ink, 3) Pigment containing Emulsion-based ink, 4) Dye containing Emulsion-based ink. (Media: Epson MJOHPS1N)

Lightfastness

Lightfastness of emulsion-based ink was compared to conventional inks using Xenon fademeter. Changes of optical density after 10,000 KJ/m^2 UV irradiation were listed on Table 3. Print of pigment-containging emulsion-based ink showed little change similarly to that of pigmented ink. And print of dye-containing emulsion-based ink changed much than that of water-soluble dye based ink. Lightfastness of colorants depends mainly on the moleculer formula of dye or pigment. But as shown in Table 3, emulsion colorants could improve its lightfastness by containing lightstabilizer along with dye. In these days, some special coated media, which can improve the lightfastness of dye -based ink have been released. But emulsion-based ink has high lightfastness by itself, so we can realize high lightfastness print on ordinary papers.

Table 3. Changes of O.D. after UV exposure.

	Black	Yellow	Magenta	Cyan
Water soluble type	-0.08	-0.09	-0.35	-0.04
Pigmented Ink	-0.02	-0.01	-0.02	0
Emulsion Ink (Pigment)	-0.02	0	-0.03	0
Emulsion Ink (Dye)	-0.1	-0.13	-0.45	-003
Emulsion Ink (Dye with stabilizer)	-0.07	-0.06	-0.23	—

Conclusion

We have developed new type of ink jet colorant made from polymer emulsion containing water insoluble dye or pigment. Emulsion colorants exhibited excellent stability, low viscosity, and controllable surface tension and satisfy all properties to use for ink jet colorant. Emulsion-based ink jet ink had good reliability, enough optical density, high waterfastness, lightfastness, rub resistance and large color values.

Dye-containing emulsion colorant was superior to water-soluble colorants in waterfastness and exhibited clear color. This colorant would be suitable for personal and business printers. Pigment-containing emulsion colorant showed good rub resistance compared with the conventional pigment dispersions and could applicable to highly durable purposes.

Emulsion-based colorant would have the possibilties to replace the conventional ink jet colorants.

References

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Biography

Takehiro Tsutsumi received his B.S. and M.S. in Symthetic 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.