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An Improvement of the Color Fastness of Ink-Jet Printing Inks by Using the Polymer Coated Pigments

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***Abstract*— To improve the quality of ink-jet printing inks, in this study colored fine particles having structure of pigment cores coated by polymers were prepared by the initiated polymerization of styrene and methacrylate derivative monomers in the aqueous pigment dispersion. At the given conditions most pigment particles are coated by the polymers. The formed polymer covers of pigments have the average thickness of 5.95 nm. The obtained results indicate that the coated pigments are improved dispersion stability in water medium along with a guarantee for the optical color. The size increasing percentage of the coated pigment dispersion after a week is 4.5 %, about fourteen-fold lower than of the original ones. The particles are useful as a coloring material for water-based ink-jet inks. The inks shows excellent water fastness and light fastness meanwhile also be optimized for the important requirements of ink-jet technology such as coloring ability, dispersion and ejection stability.**

Keywords*— *Colored Resin Particle; Ink-Jet Printing Ink; Coated Pigment; Polymerization

I. INTRODUCTION

The color fastness is one of the most important performance indicators of the ink-jet printing ink, and its level directly affects the quality of inkjet printing. Currently, color fixing problem of the ink-jet printing is a major technical task of the development of inkjet printing technology [1]. There are two kinds of inkjet inks on the market: one is a dye-based ink, and the other is a pigment-based ink. Most dye-based ink-jet printing inks suffer from poor water-fastness and poor light fastness properties when printed on common office printing paper. Meanwhile, the use of pigments is faced with some difficulties to reconcile particle size and dispersion stability [2]. Therefore, various attempts to develop colorants capable of an improved color fastness have been carried out. Many means have been proposed to date but not really effective. For example, there is a technique, in which resins are added to the pigment ink [3]. However, with this kind of ink, resin particles and pigments are separately dispersed so that the improvement in pigment dispersion stability is insufficient even when the viscosity of ink is excessively increased. Another technique in which pigment surfaces are adsorbed a resin layer has been proposed. The adsorption is improved by controlling the hydrophobic and hydrophilic moiety of the resin. However, a portion of the resin, which is not adsorbed on the pigment, but suspends, remains in the system, in some cases, may cause some unexpected impairments. On the other hand, a prospective research direction is to replace conventional pigments by pigments covered with film-forming polymers [4-7]. A pigment is added at a stage of a monomer prior to the preparation of a resin, and the monomer is polymerized in the presence of the pigment to coat the pigment with the resin. The coated pigments formed by this way promise a superior performance in color fastness and dispersion stability. However, at present, this technique is still at its initial steps and various problems are left unsolved, such as insufficient optical density and large particle size. Therefore, in this study, the preparation of color particles with the structure of pigment cores coated by polymers will be developed. The polymer shells covering pigment particles will be formed by the initiated copolymerization of styrene and methacrylate derivative monomers. The prepared coated pigment will then be used to produce some ink samples. The color fastness of these inks will be evaluated.

II. EXPERIMENTAL

A. Preparation of pigment particles coated by polymers

An aqueous dispersion of 3% wt. "Microlith Magenta 5B-K" pigment (a product of Ciba Specialty Chemicals Co., Ltd, composed of Quinacridone with concentration of 60% and a vinyl chloride/vinyl acetate copolymer resin), a small quantity of monomers (a mixture of hydroxyl methyl methacrylate - HMA and styrene - ST with the mass ratio 1/1), 0.9% emulsifier and 0.3% initiator Potassium persulfate were polymerized in a vessel equipped with a stirrer, a nitrogen gas inlet tube and a thermoregulator at 80 (degree C). The stirring rate was maintained at 300 rpm throughout the polymerization reaction. The polymerization time was 4 hours.

B. Evaluation of the prepared coated pigment

The formation of the pigment particles covered with polymer layers are observed by TEM (Transmission electron microscopy) technique. The number averaged particle size and the averaged thickness of the polymer layer are computed from TEM images as

$$\bar{d} = \frac{\sum_{i=1} d_i}{N} \qquad \bar{\delta} = \frac{\sum_{i=1} \delta_i}{N} \qquad (1)$$

Where d_i is the diameter of the ith particle, δ_i is the thickness cover of ith particle, N is the particle's number.

- The variation in color of the coated pigment particles compared with initial ones is determined by measuring

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absorptive spectrum based on UV-Visible spectrograph (HP Agilent 8453) USA.

C. Preparation and evaluation of the ink-jet printing ink

The water-based ink sample using the prepared resin particles as colorants was formulated and prepared as the earlier studies [4-6]. The ink was constituted by retaining the dispersed state of the coated pigment in the aqueous medium. The other components were added in order to the produced inks have properties suitable for ink-jet printing. The following characteristics of the produced ink are evaluated.

- Some properties of ink such as viscosity, pH, and surface tension are examined to meet the requirements of ink-jet printing technology.

- Shelf stability: The ink is placed in a container to store it for a month at room temperature (average of 25^0C). The shelf stability is evaluated by visually observing whether or not gelling and/or precipitation occurs

- Dispersion stability: The ink is stored for a week. The variation of the particle diameter is measured by DLS (Dynamic light scattering). The dispersion stability is estimated by increased degree of the particle diameter after every week.

The ink was charged in EPS cartridges of a color Epson printer C-67 that is an ink-jet recording system in which droplets are ejected by the action of thermal energy. Some image samples were printed on plain papers and coated papers to conduct printing quality:

- Ejection stability: The ink is applied to an ink-jet printer, and vertical lines of a dot are printed on the recording papers. Test printing is conducted until the ink contained in the cartridge is consumed. The recording paper sheets are visually observed from a distance 25 cm away to evaluate the printed result by the cartridge at the beginning of use and the printed result by the cartridge right before the end of use in accordance with the standards.

- Color density is measured by an X-Rite 500 densitometer.

- Light fastness: this test is to expose printed samples to sunlight during the summer months with average temperature of 280C and relative humidity of 85%. Exposure tests are made for about 60 days. The fading of the prints is judged by a loss of color density after exposure.

- Water fastness: To test for bleeding in water at room temperature, the printed samples (left to stand for 24 hours) are placed in contact with a damp filter paper for 3 hours or soaked for 5 minutes in a tap water and any bleed or color transfer is noted.

III. RESULTS AND DISCUSSION

As shown in Fig. 1 and Fig. 2 the polymer coated pigments were prepared successfully. Most pigment particles were covered by poly hydroxyl methyl methacrylate – Styrene (PHMA-ST). The average diameter of the coated particles is 121,4 nm and the polymer shells have a uniform thickness of 5.95 nm (Table I). With this polymer layer, the measured absorption spectrum of the pigment dispersion indicates that there is a movement of the maximum absorption wavelength to shorter wavelengths after the polymer covers are formed around the pigment particles (Fig. 3). However, a movement less than 10 nm may be acceptable and it does not cause any significant variation in optical color of pigments [8].

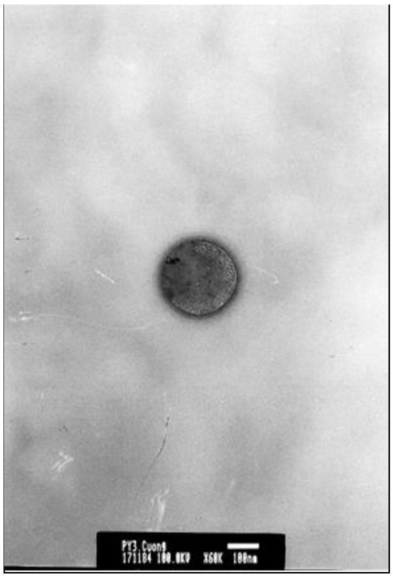

Fig. 1. TEM image of an individual coated particle

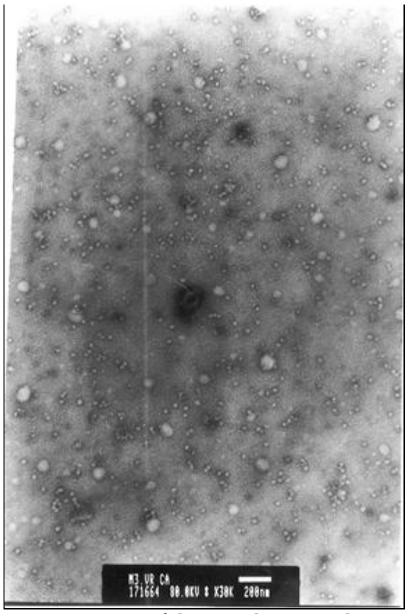

Fig. 2. TEM image of the coated pigment dispersion

TABLE I. CHARACTERISTICS OF THE PREPARED COATED PIGMENT

No	Parameter	Prepared particle	Original particle
1	Average radius (nm)	30.4	24.4
2	Avr.thickness of polymer shells (nm)	5.9	0
3	Time for sedimentation (day)	10	2
	Increasing percentage of particle size with time after a week (%)	4.5	65.4
4	The max.absorption wavelength (nm)	540 - 566	540 - 566

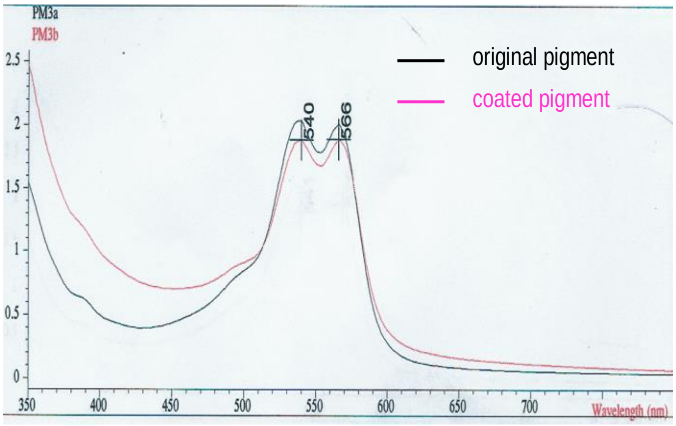

Fig. 3. Spectrogram of the coated pigment dispersion

On the other hand, the polymer shells induce steric barriers between pigment particles to protect the pigment dispersion against coagulation leading to a significant improvement of dispersion stability. No sedimentation sign is observed in the system for months, and the increase in particles size is 4.5% after a week. This increase is fourteen-fold lower than the one at the original system with uncoated pigments (Table I).

The ink sample using the prepared coated particles as colorants was produced. The characteristics of the ink are reported in Table II. The parameters meet the requirements of ink-jet printing technology.

TABLE II. CHARACTERISTICS OF THE PRODUCED INKS

No	Parameter	Value
1	Viscosity (25^{0}C)	5 cP
2	pH	7
3	Shelf stability (storing for a month)	No sedimentation
4	Surface tension	38 dynes/cm

As presented in the section II, the prepared ink was charged in EPS cartridges of a color Epson printer C-67. The printability of the ink was conducted. The ejection stability test was carried on plain paper (360 × 360dpi). The dot lines printed by the cartridge at the beginning of use and by the cartridge right before the end of use were visually compared. No different observation between both proves that the ink is suitable for the investigated apparatus (Fig. 4). The evaluation of color density and color fastness are reported in Table III, Table IV and Fig. 5.

All values of optical density are ranged from 1.0 to 1.7 for the different papers and meet fully the international standard. This confirms that the prepared coated pigments are reliable in color property.

Compared to conventional inks (HP C1700 and HP designjet 800) at the same test conditions it may be sure that the ink obtained in this study allows improving color stability of ink-jet prints. After 40 days exposure, the average percent retention of optical density of the prepared ink is about 20% higher than the compared inks (Fig. 5). On the other hand, in the water fastness tests, there seems to be no noticeable change at the evaluated samples and a contrary is observed at the compared samples printed with the dye inks (Table IV).

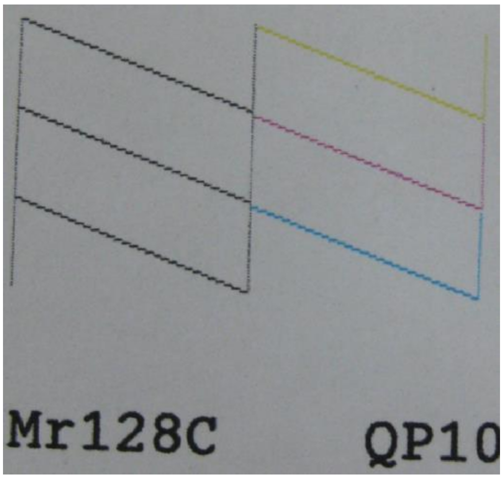

Fig. 4. Dot lines printed by the cartridge (Magenta color) at the end of use

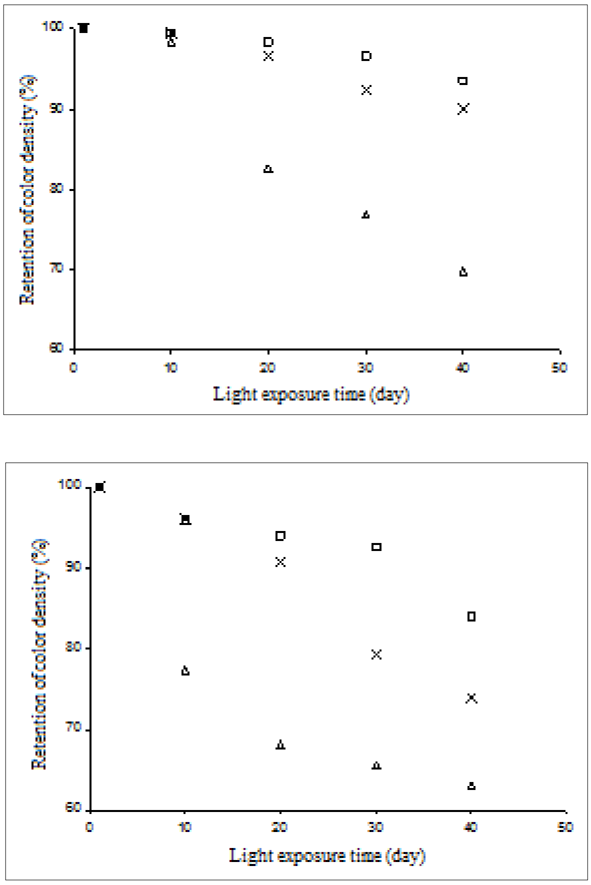

Fig. 5. Light fading of the produced ink (Magenta) on coated paper (above) and plain paper (below) compared to commercial inks (squares: produced ink, crosses: ink of HP designjet 800; triangles: ink of HP C1700)

TABLE III. COLOUR DENSITY OF THE PRODUCED INK

Ink	Optical density on plain paper	Optical density on coated
Prepared ink	0.9	1.70
Compared ink	0.86	1.71

TABLE IV. CHARACTERISTICS OF THE PRODUCED INKS

Ink	Percent retention of optical density after soaking in water (%)
Prepared ink	99
Compared ink	27

IV. CONCLUSIONS

The coated pigment particles which have structure of pigment cores covered with polymers were prepared by the polymerization of styrene and hydroxyl methyl methacrylate monomers in the aqueous pigment dispersion. The polymer layers let to improve dispersion ability of the pigments meanwhile remaining their optical properties. The coated pigments were used to prepare the ink-jet ink and this ink was tested for an ink-jet recording system. The ink exhibits excellent water fastness and light fastness. The results confirm that the polymer coated pigments are considered as a most effective solution to improve the quality of water-based inks.

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