

A Study on Polymer Coated Colour Pigments for Water-Based Ink

T. K N. Hoang, P. A. Tuan, R. Finsy, and L. Deriemaeker

Abstract—The pigments covered by film-forming polymers have opened a prospect to improve the quality of water-based printing inks. In this study such pigments were prepared by the initiated polymerization of styrene and methacrylate derivative monomers in the aqueous pigment dispersions. The formation of polymer films covering pigment cores depends on the polymerization time and the ratio of pigment to monomers. At the time of 4 hours and the ratio of 1/10 almost pigment particles are coated by the polymer. The formed polymer covers of pigments have the average thickness of 5.95 nm. The size increasing percentage of the coated particles after a week is 4.5 %, about fourteen-fold lower than of the original ones. The obtained results indicate that the coated pigments are improved dispersion stability in water medium along with a guarantee for the optical colour.

Keywords—Aqueous pigment dispersion stability, colored resin particles, emulsion polymerization, water based ink.

I. INTRODUCTION

IN the recent years, water-based ink has been taken as a full environmental solution replacing solvent-based ink in most printing methods. In the conventional water-based inks, water soluble dyes are often used as colorant materials due to their high reliability for dispersion in aqueous medium. However, there are some disadvantages in using dyes, in particular poor water fastness and poor light fastness [1], [2]. In order to overcome these disadvantages, pigments have been used as colorants. Nevertheless, the use of pigments has been faced with some difficulties to reconcile particle size and dispersion stability.

Many means for resolving these problems 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], [4]. 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

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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 [5] – [12]. 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. These problems are relevant to the polymerization [7] - [12]. Therefore, in this study, the preparation of coated pigments will be developed. The polymer shells covering pigment cores will be formed by the initiated copolymerization of styrene and methacrylate derivative monomers. The effect of the polymerization time and the ratio of pigment to monomers will be investigated.

II. EXPERIMENTAL METHODS

A. Preparation of the Coated Pigment

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), an amount of monomers (a mixture of hydroxy methyl methacrylate and styrene with the mass ratio 1/1), 0.9% emulsifier and 0.3% initiator Potassium persulfate was polymerized in a vessel equipped with a stirrer, a nitrogen gas inlet tube and a thermoregulator at 80 (degree C). The detail procedure of this process is reported in ref. [9] – [11]. All chemicals used in the experiments are from Merck Chemicals with purity of 99.9 %. Styrene monomers are purified by vacuum distillation before each experiment.

The experiments were carried out following two series. Firstly, the polymerization time was investigated whereby the mass ratio of pigment to monomers is maintained at a value of 1/10. Secondly, the ratio of pigment to monomers was investigated with the polymerization time of 4 hours.

B. Evaluation of the Prepared Coated Pigment

The formation of the polymer cover and its thickness are determined by TEM technique (Transmission electron

microscopy) [10]. The number averaged particle size of the pigment dispersions and the averaged thickness of polymer covers are computed from TEM images as:

$$\bar{d} = \frac{\sum_{i=1} d_i}{N} \quad \bar{\delta} = \frac{\sum_{i=1} \delta_i}{N}$$

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

- The variation in color of the coated pigment particles compared with initial ones is determined by measuring absorptive spectrum based on UV-Visible spectrograph (HP Agilent 8453) USA.
- The dispersion stability of the coated pigment is evaluated by the dynamic light scattering method (DLS). The dispersion stability is estimated by increased degree of the particle diameter after every week.

III. RESULTS AND DISCUSSIONS

A. Effect of the Polymerization Time

In this part, the coated pigments were prepared according to the above mentioned procedure with different polymerization time in the range 2 hours to 6 hours. The obtained pigments were evaluated by TEM and the results are reported in Table I. Some typical images of the coated pigments are showed in Figs. 1, 2.

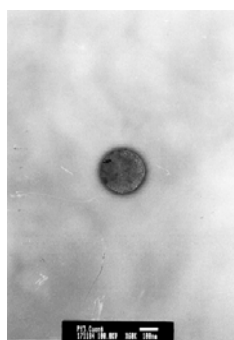


Fig. 1 TEM image of an individual coated particle (sample 2)

Clearly, the thickness of polymer cover strongly depends on the time. The thickness increases with increasing polymerization time (see Table I and Fig. 3). A similar effect is also observed with the number of covered pigment particles. When the reaction time is 2 hours, the cover, even of a particle, is hardly created meanwhile almost particles were coated at the time of 4 and 6 hours.

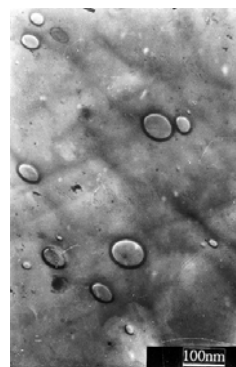


Fig. 2 TEM image of some coated particles (sample 2)

TABLE I
FORMATION OF POLYMER COATED PIGMENTS DEPENDS ON
THE TIME OF POLYMERIZATION

Parameter \ Sample	Time of polymerization (hour)	Number averaged particle size (nm)	Thickness of polymer cover (nm)	Percentage of coated particles (%)
1	2	97.6	0	0
2	4	121.4	5.95	100
3	6	164.0	10.05	100

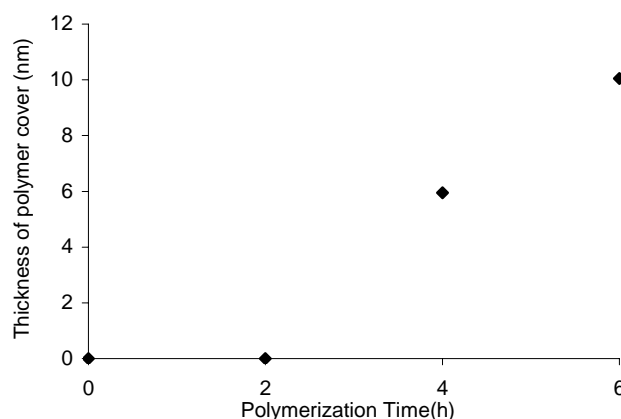


Fig. 3 Average thickness of polymer covers depends on the polymerization time

The polymer shells covering pigment cores induces steric barriers between pigment particles to protect the pigment dispersion against coagulation leading to an improvement of dispersion stability (see Table II).

TABLE II
RATE ENHANCEMENT OF PARTICLE SIZE WITH TIME

Percentage of coated particles (%)	Increasing percentage of particle size with time (%)			Rate enhancement factor (nm/day)
	1 week	2 weeks	4 weeks	
0 (sample 1)	65.4	329.9	580.6	21.03
100 (sample 2)	4.5	9.1	17.4	0.83

At the sample 2 in which all particles are covered by the polymer, a good stability is observed. The increasing percentage of particle size after a week is 4.5 %, meanwhile the correlative value at the sample 1 without the coated particles is about fourteen fold higher. The steric stabilization depends significantly on the thickness of polymer shell and the number of protected particles. Some experimental works report the preferred value of thickness is ranged from 5 – 15 nm [7, 9]. A cover less than 5 nm is clearly not effective to protect pigment but a larger (than 15 nm) one may cause a negative effect on the stability due to an acceleration of sedimentation of pigments. Moreover, it might reduce the color density of pigments (see Table III). The measured absorption spectrum of the pigment dispersions indicate that there is a movement of the maximum absorption wavelength of pigment dispersions to shorter wavelengths after the polymer covers are formed around the pigments. The larger thickness the farther is the movement. A movement less than 10 nm may be acceptable and it does not cause any significant variation in optical color of pigments [7].

TABLE III
OPTICAL COLOUR PROPERTY OF THE PIGMENT DISPERSIONS

parameter Sample	Time of polymerization (hour)	Thickness of cover (nm)	Maximum absorption wavelength (nm)	
			Original pigment	Coated pigment
1	2	0	540 - 566	N/A
2	4	5.95	540 - 566	540 - 566
3	6	10.05	540 - 566	509 - 550

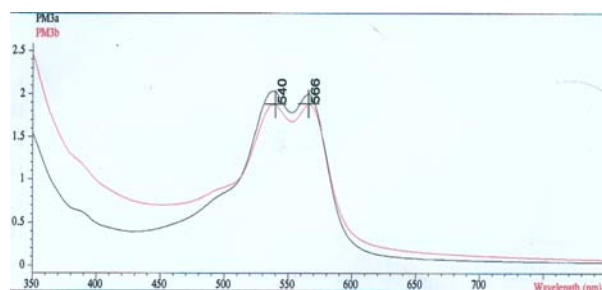


Fig. 4 Light absorbance of the coated pigment system (sample 2) in comparison with the original one

At the reaction time of 4 hours, 100 % of pigment particles are covered by polymer covers with averaged thickness of 5.95 nm (see Figs. 1, 2). These polymer covers let the pigment system improve the dispersion stability meanwhile still guarantee their optical color (Fig. 4).

C. Effect of the Ratio of Pigment to Monomers (P/M)

The coated pigments were prepared according to the above mentioned experimental procedure with the polymerizations time is maintained at 4 hours and the ratio pigment/monomers changing from 1/3 to 1/10. The experimental results reported in table IV and Fig. 5 indicate that the mass ratio of pigment to monomers has a significant influence on the formation of polymer films covering pigment cores.

TABLE IV
FORMATION OF COATED PIGMENTS DEPENDS ON
THE RATIO OF PIGMENT TO MONOMERS

Parameter Samples	Ratio of pigment to monomers	Thickness of polymer cover (nm)	Percentage of coated pigment particles (%)
1	1/3	0	0
2	1/5	11.2	75
3	1/8	11.7	100
4	1/10	10.5	100

The number of particles which are covered by polymers decreases with increasing the ratio pigment/monomers. At the ratio of 1/3, the formation of polymer shells is not even observed although the polymerization take a much longer time than preferred value (Fig. 6). Meanwhile, at the ratios pigment/monomers of 1/8 and 1/10, the formation of polymer cover is observed at almost all pigment particles (Fig. 7). To get a possible explanation for these results, two ways of the formation of polymer shells are referred. Firstly, monomers can adsorb on the pigment surfaces and then the polymerization will take place thereon. Secondly, polymers are formed first in the medium and then they will encapsulate on the pigment surfaces. The latter may be closer to the experimental results. By this way, we can explain that when the ratio pigment/monomers is decreased (e.g. monomers concentration in the medium is increased), the polymer which are formed in solution will be increased. This leads to increase amount of pigment particles coated by the polymer. However, this way hardly explains for the phenomenon in which the thickness of polymer cover seems to be decreased with decreasing the ratio pigment/monomer from 1/5 to 1/10 unless we suppose that this decrease is an acceptable fluctuation. Furthermore, the former seems reasonable if we see the results of the fourth experiment. At the ratio of 1/3, the amount of monomers after complete coverage of the pigment surfaces is not probably enough to form polymers with a sufficient molecular weight so that the formation of polymer cover is not observed.

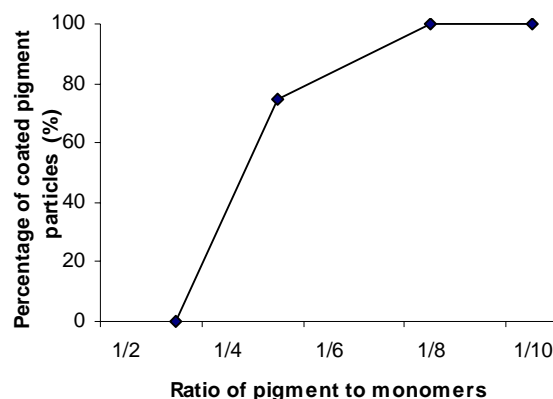


Fig. 5 Percentage of coated particles depends on the ratio of pigment to monomers

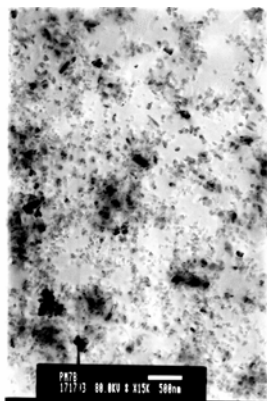


Fig. 6 TEM image of the uncoated pigment (sample 1)

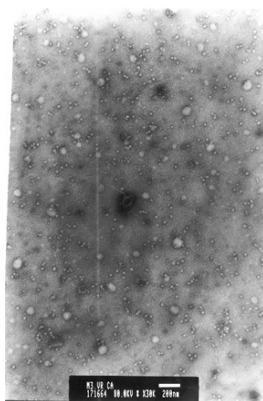


Fig. 7 TEM image of the coated pigment (sample 3)

So it is able to think that the formation polymer cover process may be the combination with two mechanisms. This is a logical conclusion, if we understand the essence of monomers which participate in the polymerization. HMA monomer is water-soluble and its polymerization is the bulk polymerization. This reaction prefers to happen following the first way. On the contrary, Styrene monomer is insoluble which will participate in the emulsion polymerization and the poly-styrene precipitates on the pigment surface by a copolymer reaction. When the monomer concentrate is small, HMA monomer is the decisive factor of the polymer cover process. Otherwise is the role of styrene monomer. This thing also indicates that the mass ratio between two kinds of monomers is the important factor which need be investigated.

IV. CONCLUSION

The coated pigments 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 dispersions. The effect of the polymerization time and the ratio of pigment/monomers on the formation of coated particles were investigated. The obtained results indicate that the average thickness of polymer covers and the number of pigment particles coated increase with increasing the time and with increasing the ratio of pigment/monomers. On the other hand, the increase of the thickness may vary the optical color of pigments and influence on dispersion stability of the coated pigment. The preferable time and ratio pigment/monomers for the polymerization is 4 hours and 1/5. At this value, almost pigment particles are covered by polymers. The formed polymer covers will protect pigments against coagulation that without any significant effect on their color. The results also confirm that the monomers, the pigments and the polymerization conditions used in this study are appropriate for the production of polymer coated pigments which are considered as a most effective solution to improve the quality of water-based inks.

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