Encapsulation of Pigmented Inks

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Abstract

The creation of polymer/inorganic (or organic) composite nanoparticles with hydrophobic and hydrophilic surfaces is a very challenging area of research, which is attracting more and more attention. Several approaches utilizing encapsulation technology to create these composite particles will be discussed. One example of encapsulation technology was applied to pigmented inkjet inks as normal dispersants. Inks based on these encapsulated pigment dispersions show a number of advantages, including ink shelf life.

Introduction

Inkjet inks used in various inkjet printers can be classified as either dye-based or pigment-based inks. Dye-based inks can exhibit severe fade deficiency, especially on porous, glossy receivers. Pigment-based inks have been gaining in popularity because of improved color stability. However, in pigment-based inks, the colorant exists as discrete particles. These pigment particles are usually treated with addenda known as dispersants or stabilizers that serve to keep the pigment particles from agglomerating and/or settling out. Pigment-based inks suffer from a different set of deficiencies than dye-based inks.

Robust dispersion technology is critical to good performing inks, particularly in the presence of water-miscible organic solvents (humectants). Pigmented inks can have poor shelf stability. Humectants are used to adjust ink rheology, to maximize ink-jetting performance, and to improve rest-run properties by preventing ink from drying out in the print head. In addition, humectants can be incorporated to lower the ink surface tension and minimize the effect of air-entrapment. These water-miscible organic solvents can have a negative effect on the colloidal stability of pigment particles in an ink formulation. Clearly, there is a need to provide pigmented ink compositions that have improved shelf-life stability.

To develop pigmented inks with good dispersion stability and that eject robustly from thermal head, there are several approaches: the use of polymeric dispersants that generate good dispersions; the addition of polymer into the ink composition as an additive or binder; or the encapsulation of the pigment dispersions. In the latter approach, there are different methods: 1) Dissolve the polymer in an organic solvent and mix with the pigment, then mill and knead the mixture, strip out the solvent and obtain the dispersion; 2) Use micro-suspension polymerization to encapsulate the pigment with the polymers; and 3) Perform polymerization to encapsulate the pigment dispersion in-situ. Each method must be able to produce pigment dispersions that exhibit acceptable ink physical properties including surface tension and viscosity, and they must be able to meet all the additional requirements including ink stability, jetting performance, durability (rub resistance), density, anti-clogging, reliability, and image color-to-color bleed. Encapsulation of pigment particles using polymerization techniques offer some unique advantages over the other methods mentioned. This report summarizes our work on the encapsulation of pigment dispersions.

Experimental

Pigment Dispersions

The process of making the pigment dispersions is described in U.S. Pat. No. 5,651,813. Cyan, yellow, magenta, and black dispersions were produced using, PB15:3, PY 155, and PY 74, PR 122, and PK7, respectfully. Raw pigment was obtained from a variety of vendors including Sun Chemicals Co., Cabot, Degussa, and Clariant.

Encapsulation of Pigments

A stirred reactor containing the above-prepared pigment dispersions was heated to 85ºC and purged with N_2 for 2 hours. Monomers, initiators, surfactants, and other chemicals were continuously added into the reactor, and polymerization was continued until the final product was obtained. The composite colorant particles dispersed in water (composite colorant particle dispersion) were filtered through glass fibers to remove any coagulum. The particles contained both colorant and a polymer phase. Different polymers were used to make the encapsulated pigment dispersions.

Ink Preparation

The above-prepared dispersions were used to prepare inks that contained composite colorant particle dispersions. A typical ink formulation comprises, in addition to the colorant dispersion, 2.5 wt % of Dowanol® DPM, 23 wt % of triethylene glycol, 10 wt % glycerol, and 0.2 wt % of Strodex® PK-90. The final ink pH was adjusted to 8.5 using triethanol amine. The concentration of colorant in the ink is about 2.5 wt% (this being the colorant phase of the composite colorant particles prepared above).

Encapsulated Pigment Dispersion Characterization

The encapsulated pigment dispersions were formulated into inks. Ink stability was tested by measuring the particle size of the fresh inks, and then after the inks had been incubated at 60ºC for one, two, and four weeks. Images were produced by hand coating the test inks onto the different recording media, Epson Premium Gloss, Konica QP, and *Kodak Professional* Inkjet Paper.

Printing Test

The above-prepared inks that exhibited good shelf stability were placed into disposable Epson 440 color and black ink cartridges and loaded into an Epson 440 or 800 printers. Images were printed onto the inkjet receiver substrates listed above, and they all had acceptable image quality.

Results and Discussions

The polymerization process in encapsulation technology is critical in determining the encapsulation efficiency and the properties of the encapsulated pigment dispersions. Therefore, our first studies focused on the reaction process.

Different Process

There are several different processes to encapsulate pigment particles. The following process is similar to the one used above except that no addition polymerization initiator was added to the reactor before the addition of the emulsion mixture.

Process A: In this process, the monomer, initiator, and other ingredients were fed into the reactor continuously and very slowly.

Process B: In this process, the monomer, initiator, and other ingredients were added into the reactors all at once (not continuously).

Process C: This is a process where the surfactant amount in the reaction was the surfactant CMC value.

Results for these samples are summarized in Table 1.

Table 1:

Experiments	Stability in acetone	Stability in ink
Process A	Stable	Stable
Process B	Precipitate	Unstable
Process C	Precipitate	Unstable
Original pigment dispersion	Precipitate	Stable

As the results indicate, different reaction processes for the encapsulation of the pigment particle result in different properties. When the optimum process was used, the ink shelf stability and all of the other ink requirements were achieved. As the reaction process to encapsulate the pigment particle was modified, the resulting encapsulation efficiency varied, resulting in inks with different performance attributes. When process A was employed, the particle encapsulation efficiency was higher than the other processes because of the enhanced monomer diffusion rate and the competing polymerization on the pigment particle surface, rather than the polymerization by micelle-particle nucleation. The results indicate that the polymerization process and the initiator introduction are important factors in determining the encapsulation efficiency and thus the properties of the encapsulated particles. Additional studies were then performed to better understand this process.

Different Temperature and Feeding Rate

Additional reaction parameters were studied to determine if they have a significant impact on the encapsulated pigmented ink properties. Experiments were performed using a similar procedure as above except that the reactions were conducted using different reaction temperatures and feeding rates (i.e., different feed addition time). These experiments are summarized in Table 2.

Table 2:

Feeding time	1.5 hour	2.5 hour	3.5 hour
Sample ID	F1T1 (70°C)	F2T1 (70°C)	F3T1 (70°C)
	F1T2 (80°C)	F2T2 (80°C)	F3T2 (80°C)
	F1T3 (85°C)	F2T3 (85°C)	F3T3 (85°C)

Test results of ink stability and ink-media performance indicated there was no significant difference between these samples. Therefore, based on reaction feasibility, the temperature was chosen to be 80°C, and the feeding rate was chosen to be 2.5 hours.

Different Surfactants

The role of the emulsifier is crucial and multifaceted, enabling the emulsification of the monomer into micrometer-sized droplets and stabilizing the resulting polymer particles during nucleation, growth, and storage of the final latex. Many studies have been done with various surfactants, mixed surfactants, reactive surfactants, and surfactant free (emulsifier-free recipes). Surfactants play a major role in particle nucleation and particle growth during emulsion polymerization. Polymerization rates, particle size and size distribution are all determined by the surfactant. During the post-polymerization processes, including stripping, storage, shipping, and formulation, surfactants play an important role. Our next area of study was the effect of surfactants on encapsulation efficiency, dispersion stability, and ink stability and durability. For these evaluations Pigment Red 122 and the polymer composition P1 were used. Table 3 lists the different surfactants studied, the initiator used, and the final dispersion particle size measured by UPA. The resulting pigment-polymer composite-particle dispersions were formulated into inks, and the properties of these inks were tested. The results are shown in Table 4.

Table 3:

Composite Colorant Particle Dispersion	Surfactant	Initiator	Particle Size (nm)
Control (Pigment)			10
C1	SDS	AIBN	13
C2	Triton 770	AIBN	13
C3	Triton X-100	AIBN	14
C4	Reactive TREM LF-40	AIBN	14
C5	no	AIBN	13
C6	PVA	AIBN	14
C7	OMT	AIBN	13
C8	A-246L	AIBN	12
C9	Triton 770 + Triton X-100	AIBN	14

Table 4:

Ink	Storage stability
Control (pigment only)	excellent
C1	excellent
C2	excellent
C3	excellent
C4	excellent
C5	good
C6	poor
C7	excellent
C8	excellent
C9	excellent

The above results indicate that there was no significant effect on the encapsulation of pigment particles between the different anionic surfactants, SDS, Triton 770, OMT and A-246L. For the nonionic surfactants, Triton X-100 produced similar effects as the anionic surfactants. However, the stability of the pigment dispersion was poor using PVA as the nonionic surfactant, which might be due to bridging flocculation caused by PVA or as a result of the increasing viscosity. When a mixture of anionic and nonionic surfactants was studied, there was no significant difference compared to only using an anionic surfactant. When the reaction did not contain any additional surfactant the final dispersion and ink had desirable properties, which is likely due to the presence of OMT in the pigment dispersion. Finally, when the reactive surfactant TREM LF-40 was added it had a chemical interaction with the polymers, and the final encapsulated pigment dispersion was expected to have better stability.

Different Acid Concentration in Polymers

It was shown in the above studies that acid and crosslinker type in the polymer compositions are important factors in achieving a good dispersion. The acid and crosslinker amounts in the polymer were studied to find the optimum percentage. Pigment Red 122 dispersions were produced using various reaction conditions and the results are shown in Table 5.

Table 5:

Polymer Composition* (wt ratios)	Initiator	Particle Size (nm)	Storage stability
P2	AIBN	11	good
P3	AIBN	13	poor
P4	AIBN	12	poor
P5	AIBN	14	poor
P6	AIBN	56	poor
P7	AIBN	gel	poor
P8	AIBN	12	excellent
P9	AIBN	14	excellent
P10	AIBN	12	excellent
P11	AIBN	14	excellent
P12	AIBN	61	poor

Further studies showed that increasing acid percentage in the polymer composition resulted in pigment inks with good stability, however, if the acid percentage became too high, the pigment dispersion stability during and after the encapsulation decreased. This is likely due to the higher number of water-soluble polymers being formed during the polymerization with higher acid percentages, which might lead to bridging flocculation and/or cause an increase in viscosity.

Crosslinker Concentration

In the design of encapsulated pigmented ink dispersions the crosslinker is a critical component in the polymer composition. Ethylene glycol dimethacrylate has been used as the crosslinker in all of our above examples. Additional crosslinker concentration experiments were performed where the optimized reaction process and conditions were used as described above. Methyl methacrylate and methacrylic acid (20%) were the main components in the polymer shell. In the absence of ethylene glycol dimethacrylate, the ink shelf stability was poor, while excellent stability was achieved using 2.5 – 7.5 wt % ethylene glycol dimethacrylate. At concentrations greater than 7.5 wt %, a coagulum was observed.

Table 6:

Composite Colorant Particle Dispersion	Crosslinker EGDM %	Initiator	Particle Size (nm)
Control (Pigment)			10
1	0	AIBN	12
2	2.5	AIBN	13
3	5.0	AIBN	14
4	7.5	AIBN	14
5*	10.0	AIBN	13
6*	15.0	AIBN	14

Table 7:

Ink	Storage stability
Control (pigment only)	excellent
1	poor
2	good
3	excellent
4	good
5	good*
6	good*

* There is coagulum after polymerization.

Different Crosslinker Series

A series of experiments was conducted where the crosslinker was varied to better understand the effect on the pigmented ink performance. Crosslinkers used in the study included: ethylene glycol dimethacrylate (EGDM), ethylene glycol diacrylate (EGDA), and divinyl benzene (DVB) (all tested using 5% concentration). The optimized reaction process and reaction conditions were used, and experiments were performed as described above. The encapsulated pigment dispersions were characterized, formulated, and tested as described above. The experiments and the results are summarized in Tables 8 and 9. The results indicate that divinyl benzene provides better performance for encapsulated pigment dispersions than ethylene glycol dimethacrylate, while ethylene glycol dimethacrylate gave better performance than ethylene glycol diacrylate.

Table 8:

Composite Colorant Particle Dispersion	Crosslinker	Initiator	Particle Size (nm)
Control (Pigment)			10
1	Divinyl benzene	AIBN	13
2	Ethylene glycol dimethacrylate	AIBN	14
3	Ethylene glycol diacrylate	AIBN	13

Table 9:

Ink	Storage stability
Control (pigment only)	excellent
1	excellent
2	excellent
3	excellent

Summary

Finely dispersed pigment particles with an average particle size of 10 nm were encapsulated with a uniform polymeric shell by performing an emulsion polymerization process in the presence of the pigment dispersion particles in an aqueous reaction medium. By doing so, pigment inks with good dispersion stability can be obtained.

Different reaction processes and conditions were studied, and the resulting encapsulated pigment dispersions and formulated inks were tested and compared. The results indicate that the reaction process, initiator addition mode, and feed rate all influence the encapsulation efficiency.

Many other factors, such as different Tg series, different pigment/polymer ratio, and different preformed polymers, were also investigated, and the optimized conditions were identified for their performance.

References

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Author Biography

Xiaoru Jenny Wang received her BE and MS degrees from Tsinghua University in 1993 and 1995, respectively. She received her PhD from Lehigh University in 2000 and joined Eastman Kodak Company that same year. Her main activities have been in the areas of polymer synthesis, polymer particles technology, polymeric dispersants, inks, overcoats, and media. She has published many patents and papers in those fields.