

Water-borne Dispersions of Micro-encapsulated Pigments

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Abstract

The application potential of the water-borne dispersions of micro-encapsulated pigments for ink jet inks were described. Our micro-encapsulated pigments have thick acrylic polymers layer with self-dispersion ability on pigment surfaces. Pigments used were carbon black, phthalocyanine blue, quinacridone magenta, and various type of yellows.

These dispersions were very excellent in dispersibility and dispersion stability. The median diameters of dispersions were around 100nm, and the physical and colorimetric properties were maintained over a year under ambiance conditions. Moreover the dispersions showed excellent resistance to water-soluble organic solvents. This characteristic may bring the wide variety of ink formulation.

The inks showed excellent print qualities, i.e., gross, water-fastness, abrasion-resistance, and marking-pen-ink-resistance.

Introduction

Recent improvements of print qualities of ink jet printing are remarkable, and achieve the photo quality. Ink jet printing has been prominent in color printing of consumer use. For industrial application, ink jet printing is used for graphics, signs, labels, textile printing and so on. Because ink jet printing is non-contact printing, it can be applicable for various substances.

Dyes, mainly acidic dyes, are used as colorants for ink jet inks, but they are usually inferior in light-fastness and water-resistance. So, especially for industrial application, pigments began to be used. And in consumer use, carbon blacks are also used.

For ink jet ink application, the dispersions of pigments are required to be excellent in dispersibility and dispersion stability. The dispersion should be stable for more than one year, and particle size of dispersions should be smaller than 100nm in average to be comparable to dyes in color vividness.

Pigments are dispersed in water with dispersants in general procedures, but such dispersions are not always sufficient in dispersibility and dispersion stability. In the process to develop the pigments which are suitable for water-borne systems, we have found that micro-encapsulation technique is excellent to modify the surfaces of pigments for water-borne systems.

In this paper, we report the characteristics of these water-borne dispersions of micro-encapsulated pigments and their application to ink jet inks.

Experiments

Except for the encapsulation polymers, all chemicals were commercially available. Typical examples for pigments were MCF-88(carbon; Mitsubishi), Fastogen Blue TGR(B-15:3; Dainippon Ink & Chemicals (DIC)), Fastogen Super Magenta RTS (R-122; DIC) and Symuler Fast Yellow 4190 (Y-74; DIC), and was SAM1440H (ARCO Chemical) for polymeric dispersant.

Encapsulation polymers were synthesized in laboratory using automated polymerization reaction apparatus(L-2AS; Todoroki).

Dispersions were prepared by means of paint shaker (Toyo Seiki) or beads mill (DCP-SF12; Draiswerke). General procedure was as follows. Pigment, encapsulation polymer (as solution of 2-butanone), base (usually sodium hydroxide), and deionized water were pre-mixed. Then, the mixture was dispersed by means of dispersing apparatus mentioned above. 2-Butanone were distilled off, and diluted hydrochloric acid was added to the dispersion to deposit the polymer on the pigment surface. The mixture was filtered off, and washed several times by deionized water. The filter cake was re-pulped by adding base. Coarse particles were eliminated from the dispersion by centrifuge.

Viscosity and particle size distribution of dispersions were measured by viscometer (RC-500; Toki Sangyo) and particle analyzer (Microtrac UPA150; Leeds & Northrup Instruments), respectively.

For the colorimetric measurements, the dispersions were applied on IJ paper (LC-101; Canon) by wire bar coater (No. 6; Webster). L*, a*, and b* were measured by spectrophotometer (Spectraflash 500; Data Color International).

Ink formulations for evaluation were referred to patent examples. For example, Ink for piezoelectric type printers(represented as piezo type ink, hereinafter) ; referred to JP H07-228808

Dispersion 25parts
Triethylene glycol butyl ether 10parts
Dietylene glycol 15parts
Surfynol 465 (Air Products) 0.8parts
Water 49.2parts

Ink for thermal type printers(represented as thermal type ink, hereinafter) ; referred to JP H06-122846

Dispersion 25parts
Glycerin 8parts
Ethylene glycol 5parts
Ethanol 5parts
Emulgen 120(Kao) 0.05parts
Water 57parts

Results and Discussion

Characteristics of Dispersions

Table 1 shows the dispersibilty and dispersion stability of various micro-encapsulated pigments. The dispersions were prepared by means of paint shaker in encapsulation polymer/pigment ratio of 0.5, and the figures are the median diameters of dispersions in nanometers. Y-138 represents C.I.Pigment Yellow 138, and R, V, B, G are similarly C.I.Pigment Red, Violet, Blue, and Green.

The dispersibility of micro-encapsulated pigments were excellent, and the median diameters of dispersions were around 100nm. Y-138 showed larger median diameter than others. This pigment is designed for paints and plastics, and the primary particles are larger(100-200nm in major axis) compared with other pigments(50-100nm in major axis, except for carbon black). After storage at 50 degrees Centigrade for 7 days, the median diameters of the dispersions were maintained at the same levels.

Table 1. Dispersibility and Dispersion Stability of Micro-encapsulated Pigments

	As prepared	After 50deg. C, 7days
Y-138	201nm	212nm
R-122	130	189
R-177	121	139
R-179	79	74
V-23	125	124
B-15:3	126	138
B-60	85	91
G-36	139	138
Carbon	94	89

The dispersions of carbon and B-15:3 prepared by beads mill were confirmed to be stable after storage for over one year under ambient conditions. The changes of physical and colorimetric properties of the dispersion of B-15:3 were summarized in Table 2.

Table 2. The Changes of Physical and Colorimetric Properties of the Dispersions of B-15:3

	As prepared	After one year
Median diameter	95nm	89nm
Viscosity	4.1mPa s	4.1mPa s
Surface tension	36.7mN/m	36.4mN/m
L*	31.1	31.6
a*	7.9	7.1
b*	33.6	34.8

Table 3. Effect of Encapsulation Polymer/Pigment Ratio on Dispersibility of R-179

Polymer/Pigment	Median diameters
0.05	364nm
0.1	339
0.2	323
0.3	113
0.5	80
1.0	207

In Table 1, R-122 and R-177 seemed to be a little inferior in dispersion stability. These two pigments may be different from others in surface characteristics, so, the dispersion stability can be improved by modification of monomer compositions of encapsulation polymers.

The ratio of encapsulation polymer to pigments also had influence on the dispersibility. Table 3 shows the effect of encapsulation polymer / pigment ratio on median diameters of dispersions of R-179.

As the encapsulation polymers are multifunctional, they may work as flocculant in low polymer/pigment ratio region. The thickness of encapsulation polymers on pigment particles was estimated to be about 1 nanometer at the polymer/pigment ratio of 0.05, when all the polymers were supposed to be uniformly adsorbed on pigment particles. But considering the adsorption equilibrium, the quantity of polymers at this ratio may not be sufficient to cover the surface of the pigment particles completely.

Application to Ink Jet Ink

We prepared inks referred to patent examples. These inks were separately formulated with two types of dispersions, one was the dispersion of micro-encapsulated pigment, and the other was the dispersion of ordinary pigment with polymeric dispersant. We evaluated the dispersion stability during storage under the accelerating conditions.

For the thermal type inks, a little differences of dispersion stability between inks using two types of dispersions were observed. But, for piezo type inks, inks formulated from the dispersions of micro-encapsulated pigments showed excellent dispersion stability compared with inks using the dispersions with polymeric dispersant as shown in Table 4.

Table 4. Dispersion Stability of Piezo Type Inks

	Micro-encapsulation		Polymeric Dispersant	
	As prepared	70deg.C 3days	As prepared	70deg.C 3days
Carbon	99nm	96nm	102nm	357nm
B-15:3	125	123	169	137
Y-138	207	259	198	separation
R-122	136	179	246	gelation

The inks formulated with micro-encapsulated carbon and B-15:3 were very stable. The inks with R-122 and Y-138 were a little inferior in stablity in these cases, but they were improved by modification of encapsulation polymer.

On the other hand, the inks formulated with the dispersions containing polymeric dispersant were inferior indispersibility (larger diameters in as-prepared inks) and dispersion stability. In the case of Y-138, after storage at 70 degree Centigrade for 3days, ink was separated into yellow precipitate and almost colorless transparent liquid. And in the case of R-122, ink was gelled after storage. The viscosity of the dispersions behaved similarly.

We thought these differences of dispersion stability resulted from the differences of the resistance to water-soluble organic solvents. To confirm this, we examined resistance of the dispersions with micro-encapsulated pigments or polymeric dispersant to some water-soluble organic solvents using carbon. Results are shown in Table.5 as the change of median diameters of dispersions. The water-soluble organic solvents were selected from patent examples. In these examinations, the pigment concentration of the dispersions was 15wt% and the ratio of water-soluble organic solvents to the dispersions were 1:9 by weight.

Obviously, the dispersions with micro-encapsulated pigments were excellently stable to every water-soluble organic solvents examined. The dispersions with polymeric dispersant were only stable to ethylene glycol(EG) and 1-methylpyrrolidine-2-one (NMP). This dispersion was not sufficiently stable to even ethanol and 2-propanol(IPA). It seemed that the longer carbon chain of alcohol added, the lesser stability of dispersions. When butoxyethoxy-ethoxyethanol(TEGB) was added, the dispersion was very unstable and showed considerable aggregation of pigment particles after storage.

To evaluate the print quality of inks with micro-encapsulated pigments, we printed graphics and letters. The graphics were excellent in gross, and showed good gamut and color reproduction. The letters printed showed excellent water-fastness, abrasion-resistance, and marking-pen-ink-resistance, even immediately after they were printed.

Table 5. Water-Soluble Organic Solvent Resistance of Dispersions of Carbon

	Micro-encapsulation		Polymeric dispersant	
	As prepared	70deg.C 3days	As prepared	70deg.C 3days
EtOH	84nm	86nm	88nm	110nm
IPA	85	83	102	139
EG	85	82	92	93
EG-E	88	82	97	116
TEGB	84	88	100	894
DMF	88	84	90	111
NMP	84	80	105	98

EG-E : Ethoxyethanol
DMF : Dimethylformamide

Conclusion

The characteristics and application to ink jet inks of water-borne dispersions of micro-encapsulate pigments were investigated. We found;

1. The dispersions were excellent in dispersibility with median diameter of around 100nm.
2. The dispersions were stable over one year under ambient conditions.
3. They showed excellent resistance to water-soluble organic solvents.
4. The inks formulated from these dispersions showed good print qualities and had great potential of applications for ink jet inks

References

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Biography

Masao Tanaka received his B.E. degree in Chemistry from the Tohoku University at Sendai in 1972 and a Ph.D. in Organic Chemistry from Tohoku University in 1977. Since 1977 he has worked in Dainippon Ink and Chemicals, Inc. His work has primarily focused on the pigments, including manufacturing process, new application fields, functional materials such as organic photoconductors. He is a member of the Chemical Society of Japan, the Society of Synthetic Organic Chemistry, Japan, the Japanese Society of Applied Physics, and the Imaging Society of Japan.