Fluorescent Nanocolorants Based on Dye-Packaging Technology for Ink Jet Application

Nikolay N. Barashkov, Ronghua Liu
Radiant Color, Richmond, CA/USA

Abstract

The emerging markets and evolving safety regulations for color ink jet printing have placed more rigorous and at times new and specific requirements on ink jet ink designs. A short list of these requirements may include: 1. Larger color gamut (clear color); 2. Archival prints with enhanced image quality; 3. Any substrate or media printing; 4. Rapid throughput (approaching engine limits); 5. All-safe properties.

Colorants available today do not enable the ink design chemists and engineers to meet existing market needs much less the requirements of emerging ink jet markets. This paper provides an example of a dye-packaging technology (DPT) that addresses in-part these same topics. Two disadvantages of DPT materials relative to pigmented materials which include dye-loading and light fastness will be discussed. Both of these parameters are active areas of DPT research and will be greatly improved upon in the near future. We have developed new DPT colorants of fluorescent pigments having uniform particle size, excellent solvent resistance and satisfactory light fastness in aqueous solutions. The DPT colorants containing fluorescent dyes encapsulated within spherical, solvent resistant, polymer particles having a mean particle size below 140 nm show excellent dispersion stability.

Also discussed will be the light fading stability of images made with DPT materials containing fluorescent dyes and images made with water solutions containing the same dyes. Results are quoted as color difference (ΔE) units in CIEL*a*b* color space. Four different DPT fluorescent colorants (yellow, orange, red and magenta) were studied. All investigated colorants are more photostable systems than corresponding dyes.

Introduction

Two major varieties of ink colorants are embodied in conventional ink jet ink systems. One is water- or alcohol-soluble dye based inks and the other is pigmented inks. The coloristic appearance of pigmented inks depends on their molecular and particle properties, e.g. particle size, form or modification, whereas the color of dye based inks is determined solely by the electronic properties of the dye molecule itself.[1] Because of their different nature they differ in applicability profiles too. Pigmented inks distinguish themselves in a good durability, e.g. light fastness, weather fastness, migration fastness, and a high temperature stability, but they are poor in brilliance and color strength. In contrast dye based inks have excellent color properties, e.g. brilliance and a good processibility, but they are poor in durability. The dye-packaging technology is one of the new approaches that can be used to minimize and in some cases, overcome these problems.[2,3]

The bodacious design goal of DPT systems is to separate the color science issues from the printability issues. In so doing, color science design teams may meet market requirements without a dramatic impact on the print engine design. Similarly, the print engine design team is able to optimize for printability without dramatic impact on the color science. Through the separation of these two highly interactive design constraints, less technologically oriented OEM's are empowered to identify and develop new markets for all digital printing technologies. This is particularly viable for the needs of the emerging textile or decorative and applied fine arts markets. Dye packaging promises to provide vehicle blindness over a wide range of ink vehicles and also offers a type of dye receptor for optimal image formation on a wide variety of print media. As packaged dyes, the DPT materials depict color gamut's that are identical to the dyestuff that they are derived. Most importantly, the DPT materials permit the use of otherwise unsafe dyestuff such as Rhodamines thereby providing a kind of all-safe packaging of dyes. As particles, these pseudo-pigments provide holdout and other rheological properties that are similar to their pigment counter-parts. As free polymeric surfaces that may be modified, the DPT materials offer the potential to make systems that are sensitive to the media environment thereby providing a "pre-receptor" component to the colorant.

Experimental

Procedure for preparation of DPT materials is a modified procedure from.[4,5] A 500 ml-capacity three-neck flask equipped with an agitator, a temperature couple and a reflux condenser was added 95 ml of water, 3.2 g of mixture of ionic surfactants and 2.0 g singular watersoluble fluorescent dye or combination of two or three fluorescent dyes, like Rhodamines and Basic Yellow 40. This mixture was purged with nitrogen for 10 minutes while stirring. Then 65 g of styrene, 5.5 g of bifunctional non-polar comonomer and 8.0

g of mixture of two polar monomers were added to the flask to form an emulsion. When temperature was raised to 80 °C, a solution of 0.5 g potassium persulfate in 3 ml water was added. After 4 h at 80 °C, polymerization completed. The resulting fluorescent emulsion was used for particle size analysis and other tests.

Affinity Test

The emulsions were put in 20 mL test tube and settle for 30 days. The degree of suspension stability of the materials in the water was evaluated as follows[6]: E: Suspended very well with no settling, G: Suspended well with a little settling, P: Poorly suspended with a large settling, VP: Completely settled, and F: Floating.

Particle Size Analysis

A laser beam scattering particle size analyzer from Coulter, Model LS230 (range of particle size detection: 0.04 micrometers to 2000 micrometers), was used for the particle size and particle size distribution analysis.

Water Fastness

Images were prepared by making drawdown on copy papers from the fluorescent dispersions and from water solutions containing the same dyes with the same concentration. The dried drawdowns were soaked in water solution for 5 minutes. The changes in optical density of water solution were measured with Hitachi Spectrophotometer U-2010.

Light Fading Stability Test

Evaluation of light fading stability of images made with fluorescent dispersions and images made with water solutions containing the same dyes was performed with LABSPHERE Bispectral Fluorescence Colorimeter BFC-450. Results are quoted as color difference (ΔE) units in CIELAB color space (Table 2). The following equation (1) was used for calculation ΔE:[7]

$$\Delta E = [(L^*_i - L^*_t)^2 + (a^*_i - a^*_t)^2 + (b^*_i - b^*_t)^2]^{1/2} \quad (1)$$

where L^*_i, a^*_i, b^*_i and L^*_t, a^*_t, b^*_t are the CIELAB coordinates before and after light exposure, respectively. The larger the ΔE, the poorer the light fastness of the color.

Results and Discussion

The dyestuffs have been encapsulated into nanocolorants by conventional emulsion polymerization. With the right choice of polar comonomers, we prepared strong fluorescent emulsions without using acrylonitrile monomer, which limits the application of the colorants. The stable aqueous dispersions have a solid content from 15.0 to 36.0 % and have low viscosity. The average diameter of polymer particles that have a spherical shape is below 140 nm with a narrow, monomodal particle size distribution (Table 1). Table 2 shows that the nature of dye has significant effects on the light fastness of the images. At the same dye loading red and orange colorants have almost identical fading rates whereas the yellow is less stable and magenta is least stable.

Table 1. Results of particle size analysis and affinity tests for different DPT colorants

Color	M.D., nm	S.D., nm	Affinity Test
Yellow	130	16	G
Orange	120	15	E
Red	130	17	E
Magenta	137	18	E

Table 2. Light fastness and Water fastness of images generated from DPT materials and images made with water solutions containing the same dyes

Color	Delta E	Water Fastness (Change in O.D.)
Yellow colorant	8.4	0
Yellow dye	21.4	0.06
Orange colorant	2.9	0
Orange dye	6.6	0.08
Red colorant	2.9	0
Red dye	6.5	0.04
Magenta colorant	6.0	0
Magenta dye	15.7	0.1

Conclusion

We have developed acrylonitryile-free fluorescent nanocol-orants with bright color, uniform particle size distribution, excellent water resistance and satisfactory light fastness. The DPT colorants containing fluorescent dyes encapsu-lated within spherical, solvent resistant polymer particles having a mean particle size below 140 nm show excellent dispersion stability.

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Biography

Nikolay N. Barashkov received his PhD and degree of Doctor of Science from Karpov Institute of Physical Chemistry (Moscow, Russia). He came to the US in 1993 and following research appointments at Fermi National Laboratory and Texas Tech University was Research Scientist with the University of Texas at Dallas. He joined Radiant Color in 1997, and his research interests include the chemical and photophysical aspects of polymer-fluorescent dyes interaction. E-mail: nbarashkov@radiantcolor.com