A Novel Pigment Dispersant and Surfactant For Radiation Curable Waterborne Ink Jet Inks

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Abstract

The development of waterborne radiation curable ink formulations for ink jet applications is challenged by the need for hydrolytic stability. Most conventional waterborne inks are formulated in the basic pH range (pH ≥ 8). In this case, stable waterborne pigment dispersions are formulated with conventional anionic and nonionic pigment dispersants. However, if these same dispersions are used in combination with water-soluble acrylate monomers and oligomers, the basic pH often causes hydrolysis of the acrylic esters. The result is a decrease in pH, changes in viscosity, and poor overall stability. Conversely, if the basic pigment dispersions are added to the acid stable radiation curable monomer and oligomers, the dispersions become unstable, resulting in pigment flocculation and changes in viscosity. To address this dilemma, a novel radiation curable pigment dispersant and a co-functioning surfactant are introduced that yield acid stable pigment dispersions that remain stable when added to the water-soluble acrylate monomers and oligomers. The utilization of these additives is demonstrated in red, yellow, blue and black waterborne radiation curable ink jet formulations.

Introduction

There are an increasing number of radiation curable materials being used to develop jettable ink formulations. These materials react with radiant light to become part of the polymeric film, and are 100 percent solids, which allows formulators to avoid using solvents, and the subsequent regulatory concerns with volatile organic compounds. In order to achieve the low viscosities needed to jet the inks through the tiny orifices within the print head, many low viscosity, mono-functional monomers are used. While these materials effectively reduce the viscosity of the inks, they often are slower curing, have high Draize values, and skin sensitization ratings that make them more challenging to handle safely. One way to avoid using higher amounts of these lower viscosity, slower curing, and more hazardous materials is to use water to reduce ink viscosity. By using water-soluble monomers, oligomers, photoinitiators and pigment dispersions, jettable ink formulations can be made that are less hazardous to make and use.

Waterborne radiation curable inks have successfully been developed for flexographic, and gravure applications. However, one of the most challenging aspects of making these formulations is gaining the necessary shelf stability. The balance of electric charge of the various formulation components and the final pH of the system can be challenging. With radiation curable acrylates, this is made especially difficult since most conventional waterborne pigment dispersions are formulated in the basic pH range. In this pH range, water-soluble acrylate materials are susceptible to hydrolysis. When this occurs, drastic changes in viscosity can result. In addition, pigment dispersions can become unstable resulting in flocculation and/or thixotropic rheology.

This study introduces cationic radiation curable pigment dispersants for waterborne ink jet inks. Pigment dispersions and ink jet formulations will be shown that demonstrate that formulating inks with pH less than 7 provides much improved stability compared to inks that are formulated in the basic pH range.

Materials

The PRO5973 dispersant, PRO6134 surfactant, Polyethylene glycol diacrylate monomer, and 15 mole Ethoxylated trimethylolpropane triacrylate monomer were from Sartomer Company, Inc. The pigments used in this study were as follows: Phthalocyanine Blue 15:3 from Sun Chemical; Arylide Yellow 74 from Magruder Color; Quniacridone Magenta, Red 122 from Magruder Color, and Carbon Black 7 from Cabot. The defoamer Dee-Fo PI-35 from Ultra Additives, and the 1-[4-(2-Hydroxyethoxy)-phenyl]-2-hydroxy-2-methyl-1-propan-1-one photoinitiator from Ciba Specialty Chemicals were used in the ink formulations. The anionic styrene acrylate copolymer dispersion resins were from Johnson Polymer.

Experimental

Viscosities of the inks were measured using a Brookfield DVII+ viscometer with a #19 spindle at 100rpm, at 25°C. PH measurements were performed on a Titralab Tim900 Titration Manager using a PHG201 electrode.

Pigment Dispersion Preparation

The cationic pigment dispersions were prepared using the formulations in Table 1, and the anionic pigments dispersions were prepared using the formulations in Table 2. The liquid ingredients were mixed together in a blender for 1 minute on low speed. In the same blender, at medium mix speed, the pigments were individually added in three increments. The mixer was then turned to high speed for 15 minutes. High shear dispersing was done by charging 25% of the pigment concentrate and 75% 0.8mm YTZ media into an Eiger mill. The mill was then run for 20 minutes at 5000 rpm in re-circulation mode, with a residence time of approximately 10 minutes.

Table 1. Cationic Pigment Dispersion Formulations

Wt. %	Blue	Yellow	Red	Black
Pigment	25	32	35	40
Defoamer	0.42	0.5	0.5	0.54
Surfactant	1.77	2.14	0	2.31
Dispersant	14.38	8	8	8.9
Water	58.43	57.36	56.5	48.21
Pig.:Binder	1.74:1	4:1	4.38:1	4.5:1

Table 2. Anionic Pigment Dispersion Formulations

Wt. %	Blue	Yellow	Red	Black
Pigment	72.3	32	35	37
Styrene Acrylate Dispersing Resin 1	12.5	24.8	25.9	27.4
Styrene Acrylate Dispersing Resin 2	4.1	0	0	0
Ammonia	1.00	0	0	0
Defoamer	0.64	0.5	0.5	0.5
Surfactant	1.25	0	0	0
Water	8.22	42.7	38.6	35.1

Pigment Dispersion Stability Testing

Each of the cationic and anionic pigment dispersions was stored at 25ºC, and the viscosities were measured periodically. When stored for 130 days at 25ºC, no change in viscosity and no pigment settling were observed. The cationic dispersions were also stored in a 49ºC oven, and the viscosity was observed over time. The black and blue compounds were stable for 45 days, the red compounds were stable for 37 days, and the yellow compounds were stable for 22 days before the dispersions became too thick to measure viscosity.

Ink Preparation

The cationic inks were prepared using the formulations in Table 3, and the anionic inks were prepared using the formulations shown in Table 4. In both cases the monomers were blended together with additional dispersant, and water at low shear. The dispersions were then slowly added, and then the inks were mixed for one hour.

Table 3. Cationic Water Borne UV Ink Jet Ink Formulations

Wt. %	Blue	Yellow	Red	Black
Dispersion	20	15.63	14.29	12.49
Dispersant	0	2.75	1.63	0
Polyethylene glycol diacrylate	14	14	14	14
15mole Ethoxylated trimethylolpropane triacrylate	6	6	6	6
1-[4-(2-Hydroxyethoxy)-phenyl]-2-hydroxy-2-methyl-1-propan-1-one photoinitiator	2.4	2.4	2.4	3
Added Water	57.6	59.22	61.68	64.51
Total Water	69.28	67.93	69.72	70.6
Viscosity, cps	7	19	10	5
pH	5.4	6.3	5.8	5.9

Table 4. Anionic Water Borne UV Ink Jet Ink Formulations

Wt. %	Blue	Yellow	Red	Black
Dispersion	13.7	15.63	14.29	13.5
Styrene Acrylate Dispersing Resin 1	2.27	3.88	3.71	3.70
Polyethylene glycol diacrylate	14	14	14	14
15mole Ethoxylated trimethylolpropane triacrylate	6	6	6	6
1-[4-(2-Hydroxyethoxy)-phenyl]-2-hydroxy-2-methyl-1-propan-1-one photoinitiator	2.4	2.4	2.4	3
Surfactant	0.31	0.08	0.07	0.07
Total Water	70.0	72.5	68.8	68.2

Ink Stability

Each sample was stored at 25ºC, and the viscosity was measured periodically. The inks were considered to be stable as long as the viscosity did not change by more than 10cps, and/or the ink began to phase separate. The stability for each of the cationic inks, along with the mode of failure is shown in Table 5.

Table 5. Cationic Ink Stability

Ink Color	Blue	Yellow	Red	Black
Stability	92 days Separation	47 days Thixotropy, separation	85 days separation	>110 days

Table 6. Anionic Ink Stability

Ink Color	Blue	Yellow	Red	Black
Stability	78 hours	4 hours	26 hours	170 hours

In a similar manner, the stability of the anionic inks was measured. The duration and the mode of failure are noted in Table 6.

Ink Film Testing

Films of the inks were drawn down with a number five Mayer rod on both glossy Lanetta Charts and on flat paper. The films were then cured using a Fusion 600 Watts/inch H bulb system. The lamp power output was tested using an EIT Power puck, and the energy needed to cure each color ink film is shown in Table 7.

Gloss measurements were made at an 85-degree angle on each of the films using a BYK-Gardener micro-TRI-Gloss Meter. The values for each color on glossy Lanetta Charts and on flat paper are shown in Table 8.

Table 7. Energy Needed to Cure Ink Films (mJ/cm2) at Various Line Speeds

	Blue	Yellow	Red	Black
	200'/min.	300'/min.	200'/min.	325'/min.
UVC	9.7	6.4	9.7	5.9
UVB	46.3	30.9	46.3	28.5
UVA	66.4	44.2	66.4	40.8
UVV	57.2	38.1	57.2	35.2

Table 8. 85 Degree Gloss Values For Ink Films

	Blue	Yellow	Red	Black
Lanetta Chart	90.6	81.3	83.1	90.8
Paper	5.5	10.3	6.3	6.6

Discussion

Both the anionic dispersions, which were formulated with typical styrene acrylate resins and cationic dispersions, which were formulated with the radiation curable cationic dispersant, were quite stable when tested at room temperature. Both became less stable when tested at 49°C. However, a very significant difference was observed when the dispersions were formulated into inks. While the cationic inks were very stable for 47 to over 110 days, depending on the color, the anionic inks became unstable within several hours. As a result it was not possible to evaluate the film properties of the anionic inks. Conversely, the cationic inks produce bright colored ink films that vary in gloss depending on the substrate on which they were made.

Conclusion

A novel cationic radiation curable pigment dispersant has been developed that yields stable pigment dispersions. These dispersions can then be formulated into cationic radiation curable ink jet inks. These inks are much more stable than inks formulated with anionic pigment dispersions. The cationic inks were stable for 47-110 days, depending on the color, whereas the anionic inks became unstable within hours after being made. Hence it is now possible to formulate radiation curable waterborne ink jet inks.

Biography

William (Bill) R. Dougherty received his B.S. and M.S. degrees in Polymer Science from the Pennsylvania State University in 1982 and 1985, and a Ph.D. in Polymer Science from Lehigh University in 1999. He worked for NL Chemicals from 1985-88, Air Products and Chemicals from 1988-2000, Markem Corporation from 2000-2002, and is currently the Technical Manager of SMA Resins for Sartomer Company, Inc. His work has primarily focused on product synthesis and applications development of 100% solids, solvent borne, water borne, and emulsion products for coatings, inks and adhesive applications. Bill is a member of the Federation of Societies for Coatings Technology, TAPPI, and the American Chemical Society.