Developing Pigmented Inks for Thermal Ink Jet

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Abstract

Particulate or pigmented inks for thermal ink jet applications exhibit great print quality, far superior to dye based inks. In this paper, we present concept for the development of kogation-free pigmented inks by imparting polymer latex into ink jet inks. Inks are prepared by the addition of polymer latex, and wherein the polymer latex can act as a stabilizer to improve the stability of pigmented ink. The polymer latex can also function as a binder with carbon black colorant or other color pigments, thereby impart the ink smear resistance, film hardness, and humidity resistance. The addition of polymer latex also develops a list of attributes such as high optical density, good latency, excellent light- and waterfastness, superior black MFLEN, good frequency response, and excellent cool curl and showthrough properties.

Polymer latexes are prepared by emulsion polymerization process. Polymer latexes that are useful in ink jet applications include ionic sulfonate polymer latex, epoxy polymer latex, polymer latex with a high glass transition temperature (Tg), or polymer latex with a nonionic surfactant with an HLB (hydrophilic/lipophilic balance) value from 17.5 to 20.

Introduction

Thermal Ink Jet Technology (TIJ) utilizes the direct marking technology to achieve good image quality on media. TIJ has become a forefront in the electronic printing technology as seen by personal printers and other large format printing. The ink design space is wide as demonstrated by many inventors form Hewlett Packard, Canon, and Xerox to name a few. Ink development plays a primary role in the outcome of the printer and its image quality on media. Inks can be designed to achieve many attributes such as waterfastness, intercolor bleed suppression, high chroma, etc. Ingredients such as dyes, pigments provide the colorant, whereas the solvents can provide humectant properties, dye solubility, jetting efficiency, drying attributes, etc. To achieve optimum ink performance: water, colorant, and solvent alone can not provide superior image quality. Additives are essential to enhance the ink properties and performance on paper. A plethora of patents target these additives to provide attributes to satisfy the end user. Additives may include surfactants to aid in dry time, or treat the paper; salts to enhance dye solubility or provide a mechanism for color to color bleed suppression; organics to provide waterfastness, lightfastness, or pH control; polymers to reduce heater deposits, aid in jettison, smear resistance, dispersion stability. A multitude of attributes these additives may provide and cannot be listed here entirely.

Several features such as optical density, line edge raggedness (MFLEN) and intercolor bleed can be controlled by the use of pigments such as carbon black. It has been demonstrated, for example by Hewlett Packard to jet carbon black inks out of 300 and 600dpi printheads to achieve good images. From an ink standpoint, neglecting software or hardware manipulation, the ink chemists can formulate and control most properties of the ink and its behavior on paper. Others have shown the use of additives in the inks to suppress intercolor bleed in the black by adding salts to the color inks, or adding surfactants to reduce feathering between colors. Copolymers, random, blocks etc. have been cited in the patent literature in an attempt to control the ink-paper interactions and ink-ink interactions.

From a polymer standpoint, may polymers have been covered in the literature and to develop new polymers is an enormous task and time consuming. Although leveraging technology from another source such as xerography provides a greater tool and success rate.

Emulsion polymer technology stems from the polymerization occurring between two immiscible liquid phase, an aqueous continuous phase and nonaqueous discontinuous phase consisting of monomer and polymer, a colloidal dispersion. The final product of an emulsion polymerization, referred to as latex or resin emulsion, is often used directly as an emulsion without prior separation of the polymer from the water and the other components. The advantages of this type of polymerization contrast to solution or bulk is the rapid polymerization to high molecular weight and narrow distribution, with ease of heat control. The physical state of the emulsion system makes it easy to control the process. Applications of latexes involve coatings, finishes, paints, and floor polishes.[1-2]

In this paper, we present a concept of the use of polymer latexes for improved and shelf stable inks for thermal ink jet. The preparation of various polymer latexes in pigmented TIJ ink systems is described. The key concept here is the use of latex directly from the result of the emulsion polymerization to the ink system. By utilizing the polymer latex directly without further processing, many advantages are seen. Less processing would result in ease of manufacturing for TIJ inks, as well as less process control systems. The ease of use enables formulation latitude in terms of desired pigment or other additives that will not be subjected to mechanical or thermal means besides simple mixing. By wisely selecting the latex and colorant, non-association or aggregation will occur which enables shelf stability, heat and cold temperature stability, and jettability. A simple metric for severe aggregation would be exemplified by immediate precipitation of the pigment colorant within hours or days. Other metrics can be used such as viscosity changes upon thermal treatment or shelf standing.

Experimental

A. Preparation of Polymer Latexes:

1. High Tg Polymer Latex:

The latex emulsion selected was comprised of 85 wt% of high Tg monomer of methyl methacrylate (a homopolymer with a Tg of 105°C) and acrylic acid (a homopolymer with a Tg of 106°C), and 15 wt% of a low Tg monomer of butyl acrylate (a homopolymer with a Tg of -55°C). The latex polymer generated was comprised of methyl methacrylate/butyl acrylate/acrylic acid terpolymer of 75:15:10 composition using 1.5 wt% of ammonium per-sulfate initiator. The latex was prepared by a batch emulsion polymerization process as follows. In a 500 millimeter jacketed glass flask with a stirrer set at 200 rpm, 1.8 grams of ammonium persulfate, 1.8 grams of sodium dodecyl-benzene sulfonate, 1.8 grams of Triton X-100 (octylphenol polyether alcohol, obtained from Union Carbide), and 232 grams of deionized water were deaerated for 25 minutes. A monomer mixture of 90 grams of methyl methacrylate, 18 grams of n-butyl acrylate, and 12 grams of acrylic acid was charged into the flask and was emulsified for 10 minutes (minutes) at room temperature, about 25°C throughout. The resulting emulsion was then polymerized at 80°C for 5.5 hours in a nitrogen atmosphere. A latex emulsion comprised of 29.7 wt% of solids of poly(methyl methylacrylatebutyl methacrylate-acrylic acid) resin, 0.5 wt% of sodium dodecylbenzene sulfonate, 0.5 wt% of Triton X-100, and 69.3 wt% of water, with an average particle size of 250 nanometers as measured by Coulter N4 particle size analyzer was obtained. The latex polymer possessed a glass transition temperature of 85°C as determined by Seiko DSC, and possessed a weight average molecular weight of 449,000 as determined on a Waters GPC.

2. Ionic Sulfonate Polymer Latex:

An ionic sulfonate latex emulsion comprised of polymer particles derived from emulsion polymerization of ammonium 2-methacrylamido-2-methylpropanesulfonate, styrene, butyl acrylate, acrylic acid, 2/77/23/2 parts (by weight), was prepared as follows. In a 1,000 milliliter jacketed glass flask equipped with a mechanical stirrer, 2.7 grams of ammonium persulfate, 19.2 grams of sodium dodecylbenzene sulfonate anionic surfactant, NEOGEN R™ (20 percent active, available from Kao), 5.8 grams of polyoxyethylene nonyl phenyl ether nonionic surfactant, ANTAROX CA897™ (70 percent active, available from Rhone Poulenc), and 391 grams of deionized water were deaerated for 30 minutes. A monomer mixture of 10.8 grams of AMPS 2411™ (ammonium 2-methacrylamido-2-methylpropanesulfonate, 50 percent active, available from Lubrizol), 208 grams of styrene, 62 grams of butyl acrylate, and 5.4 grams of acrylic acid, and 7.4 grams of dodecanethiol was charged into the flask and the resulting mixture was emulsified for 10 minutes at room temperature, about 25°C (Centigrade) throughout. This emulsion was then polymerized at 80°C for 6 hours in a nitrogen atmosphere. The resulting latex polymer, poly(2-methacrylamido-2-methylpropanesulfonate-styrene-butyl acrylate-acrylic acid) after cooling throughout possessed an weight average molecular weight M_w of 51,500, and a number average molecular weight M_n of 21,600, as determined on a Waters GPC, and a glass transition temperature of 39°C, as measured on a Seiko DSC. The polymer latex possessed a volume average diameter for the polymer of 171 nanometers as measured by light scattering technique on a Coulter N4 Plus Particle Sizer. The latex emulsion product was comprised of 40.1 wt% of poly(2-methacrylamido-2-methylpropanesulfonate-styrene-butyl acrylate-acrylic acid) resin, 0.55 wt% of NEOGEN R™, 0.55 wt% of ANTAROX CA897™, and 58.8 wt% of water.

3. Epoxy Polymer Latex:

An epoxy latex emulsion comprised of polymer particles derived from emulsion polymerization of glycidyl methacrylate, butyl methacrylate, methacrylic acid, 10/84/6 parts (by weight), was prepared as follows. In a 500 milliliter jacketed glass flask equipped with a mechanical stirrer, 1.2 grams of ammonium persulfate, 2 grams of sodium dodecylbenzene sulfonate, 2 grams of triton X-100, and 320 grams of deionized water were deaerated for 30 minutes. A monomer mixture of 8 grams of glycidyl methacrylate, 67.2 grams of butyl methacrylate, and 4.8 grams of methacrylic acid, and 1.6 grams of dodecanethiol and 1.6 grams of carbon tetrabromide was charged into the flask and the resulting mixture was emulsified for 10 minutes at room temperature, about 25°C throughout. This emulsion was then polymerized at 70°C for 5.5 hours in a nitrogen atmosphere. The resulting latex polymer, poly(glycidyl methacrylate-butyl methacrylate-methacrylic acid), after cooling throughout possessed an weight average molecular weight Mw of 36,000, an a number average molecular weight Mn of 11,600, as determined on a Waters GPC, and a glass transition temperature of 38°C, as measured on a Seiko DSC. The polymer latex possessed a volume average diameter for the polymer of 145 nanometers as measured by light scattering technique on a Coulter N4 Plus Particle Sizer. The latex emulsion product was comprised of 21.2 wt% of poly(glycidyl methacrylate-butyl methacrylate-methacrylic acid) resin, 0.5 wt% of sodium dodecylbenzene sulfonate, 0.5 wt% triton X-100, and 77.8 wt% of water.

4. Polymer Latex with a Nonionic Surfactant with an HLB Value from 17.5 to 20:

A nonionic surfactant stabilized latex emulsion comprised of a nonionic polyethoxylated octylphenol surfactant Triton X-705™ with an HLB of 18.7 and polymer particles derived from emulsion polymerization of styrene, butyl acrylate, acrylic acid, 67/30/3 parts (by weight), was prepared as follows. In a 500 milliliter jacketed glass flask equipped with a mechanical stirrer, 0.36 gram of ammonium persulfate, 5.8 grams of polyethoxylated octylphenol nonionic surfactant, Triton X-705™ (70 percent active, available from Union Carbide), and 232 grams of deionized water were deaerated in this 500 milliliter jacketed glass flask for 30 minutes. A monomer mixture of 80.4 grams of methyl methacrylate, 36 grams of butyl acrylate, and 3.6 grams of acrylic acid, was charged into the flask and the resulting mixture was emulsified for 10 minutes at room temperature, about 25°C throughout. This emulsion was then polymerized at 80°C for 6 hours in a nitrogen atmosphere. The resulting polymer latex, poly(methyl methacrylate-butyl acrylate-acrylic acid), after cooling throughout possessed an weight average molecular weight M_w of 660,000, and a number average molecular weight M_n of 163,000, as determined on a Waters GPC, and a glass transition temperature of 55°C, as measured on a Seiko DSC. The polymer latex possessed a volume average diameter for the polymer of 385 nanometers as measured by light scattering technique on a Coulter N4 Plus Particle Sizer. The latex emulsion product was comprised of 34.5 wt% of poly(methyl methacrylate-butyl acrylate-acrylic acid) resin, 1.0 wt% of polyethoxylated octylphenol nonionic surfactant Triton X-705™, and 64.5 wt%of water.

B. Preparation of Inks

Ink LTX-H1 was prepared by the dissolution of a nonionic surfactant in deionized water, followed by the addition of Sulfolane and 2-pyrrolidinone. This organic mixture was then dripped into a stirring mixture of Cabojet 300 (Cabot) carbon black dispersion with water through a graduated separatory funnel. The addition of the 1 wt% of high Tg polymer latex using a graduated separatory funnel was subsequently added to this mixture. The final ink was obtained by the filtration through a 1μm glass fiber syringe filter. The resulting ink comprised of 1 wt% of the high Tg polymer latex, Cabojet 300 carbon black, sulfolane, 2-pyrrolidinone, nonionic surfactant, and water.

Ink LTX-S2 comprised of 1wt% of ionic sulfonate polymer latex. Ink LTX-E3 comprised of 1wt% of epoxy polymer latex. Ink LTX-N4 comprised of 1wt% of polymer latex with a nonionic surfactant with an HLB value of 18.7. Ink LTX-0 was a reference ink which contained no polymer latex in the ink formulation.

C. Ink and Print Quality Evaluations

(1) Physical Properties:

Ink viscosity was measured at 25°C using a Brookfield Model DV-11 viscometer. Ink surface tension was measured at 25°C using a Kruss model K10T plate tensiometer. Ink pH was measured at 25°C using a Corning model 345 pH meter.

(2) Ink Stability:

Inks were placed in a capped bottle and allowed to stand at a temperature of 60°C for 24 hours. The ink physical properties were measured after heat treatment. For comparison, the shelf standing ink was also measured for physical properties. Large changes greater than 0.5 cPs units for viscosity indicated instability. Other physical properties, such as surface tension or pH, were monitored, and changes of 3 dynes/cm or a change in pH by more than about 0.5 would indicate instability. Observation of the ink standing on the shelf at 25°C for settling was also tested.

(3) Optical Density:

An image was printed by an ink jet printer HP855C (Hewlett Packard) on each of the following papers: Xerox Courtland 4024DP and Images Series LX. The optical density of the printed image was measured by an X-Rite densitometer.

(4) Smear Resistance:

(i) Dry smear: The inks were placed in an ink jet printer HP850C. After an image was printed, the image was allowed to stand at 25°C for 24 hours prior to evaluation. The optical density of the solid area was measured prior to smear testing using a densitometer (X-Rite 428). The images were printed on Xerox Courtland 4024DP and Image Series LX paper. A clean sheet of the matching paper was placed on top of the solid area image. Using a rub tester (Testing Machines Inc.), a 4-pound weight was placed on top of the covered image. At a speed of 85 rubs per minute, the image was subjected to 50 rubs at 25°C and 50 percent RH. The area adjacent to the solid area image was measured using the densitometer.

(ii) Wet smear: Same as dry smear evaluation procedure, except an in-house micro wet smear test fixture was used to smear the image with the use of water wetted chisel tips (similar to highlighter felt tips). The saturated tips were assembled into a mechanical pen. The mechanical pen equipped with the wetted tip was traversed across the image at a force of 80 to 100 grams. This procedure was repeated three times across unsmeared regions of the image. The optical density of the area between the printed lines was measured and averaged over at least ten measurements. The optical density of the background of the media was subtracted from the optical density adjacent to the image.

Print Quality Enhancements

To impart print quality enhancements, the polymer latexes that were used in the ink formulations aided in the optical density by agglomerating the pigment particles which are too big to penetrate into the paper fibers, hence an increase in colorant on the surface of the paper. This mechanism was supported through Atomic Force microscopy (AFM) as well as transmission electron microscopy (TEM). AFM monitored the topography of ink without the polymer latex as well as ink with the polymer latexes. The AFM pictures identified high pile height of the polymer latex ink printed on paper contrast to low pile height for the control ink. TEM pictures also exhibited agglomerates rather than loose particles from the pigment.

The inks containing polymer latex exhibit good stability at room temperature and also when subjected to 60°C heat treatment. The inks did not appear to be affected by the addition of polymer latex in the context of instability due to heat treatment or upon standing. The inks were shelf stable with no evidence of settling or precipitation for at least 8 months at about 25°C. The substantially constant viscosity, pH, and surface tension, is maintained despite stressing the ink by, permitting the ink to remain in a bottle at 25°C, then subjecting the ink to heating at about 60°C for 24 hours. Under these stress conditions, the viscosity of the ink does not substantially increase or decrease more than about 0.5 cPs, the surface tension of the ink does not substantially increase or decrease more than about 1 dyne/cm.

Table 1. Physical Properties of the Inks and Stability Testing Measured at 25°C

	Shelf Standing at 25°C			60°C/24 hrs Heat Treatment		
Inks	Viscosity *cPs*	Surface tension *dyne/cm*	pH	Viscosity *cPs*	Surface tension *dyne/cm*	pH
LTX-0	2.12	37.3	6.48	2.08	37.9	6.38
LTX-H1	2.10	34.6	6.57	2.06	35.3	6.40
LTX-S2	2.13	35.7	6.35	2.17	36.4	6.31
LTX-E3	1.94	35.1	6.52	1.89	35.9	6.42
LTX-N4	2.04	35.3	6.54	1.99	35.8	6.45

Table 2. Optical Density and Dry Smear Attributes

	Optical Density		Dry Smear Optical Density	
Inks	Xerox 4024DP	Image Series LX	Xerox 4024DP	Image Series LX
LTX-0	1.30	1.32	0.18	0.20
LTX-H1	1.43	1.46	0.04	0.05
LTX-S2	1.46	1.49	0.04	0.05
LTX-E3	1.42	1.48	0.03	0.03
LTX-N4	1.44	1.49	0.04	0.05

The inks exhibited higher optical density as compared to the reference ink without polymer latex. The smear resistance is evident in the reduction in smear optical density. A reduction in smear resistance enables a more rapid handling of documents by customers. Printing multiple sheets sequentially avoided page to page contact since the image is unaffected or not transferred to the backside of pages. With a polymer latex, the adhesion occurring with pigment to pigment or pigment to resin emulsion enables binding to the paper fibers, and colorant to colorant binding. This enables the performance of a reduction in smear. Without the polymer latex, smear is significant and would transfer during handling of the paper onto fingers, backside of papers), hence productivity is lost.

The wet smear resistance in Xerox 4024DP and Image series LX papers is significantly improved through the use of the polymer latexes. The wet smear OD for inks without polymer latex was about from 0.35 to about 0.36. The wet smear resistance is significantly improved through the use of the polymer latexes as the wet smear OD for inks with polymer latexes was about from 0.03 to about 0.07. Another ink advantage is for highlighter smearing. Since the wet smear test used water, the inks can be used for highlighters that are water based. Fewer smears would enable less transfer when a highlighter pen is drawn across the image, or when liquids are spilled and wiped up.

Table 3. Wet Smear Resistance Optical Density

	Wet Smear Optical Density	
Inks	Xerox 4024DP	Image Series LX
LTX-0	0.35	0.36
LTX-H1	0.05	0.05
LTX-S2	0.04	0.05
LTX-E3	0.03	0.03
LTX-N4	0.06	0.07

Summary

The addition of the polymer latex into ink jet systems imparts several advantages. Inks are prepared by the addition of polymer latex, and wherein the polymer latex can act as a stabilizer to improve the stability of pigmented ink. The polymer latex can also function as a binder with carbon black colorant or other color pigments, thereby impart the ink smear resistance, film hardness, and humidity resistance. The optical density of the pigmented system was enhanced by the relatively small quantity of polymer latex in the ink system. This enhancement is due to the agglomeration of this binder with the pigments, which stay on top of the surface of the paper as supported by AFM.

References

1. G. Odian, Principles of Polymerization, 2nd edition, John Wiley & Sons, New York (1981).
2. R. G. Gilbert, Emulsion Polymerization: A Mechanistic Approach, Academic Press, London (1981).

Biography

Dr. Chieh-Min Cheng is a Principal Scientist and the Manager of the Chemical Toner Pilot Plant in Xerox Corporation. He has worked at Xerox for over 7 years in both the toner design/manufacturing and thermal ink jet technology areas. Chieh-Min received his M.S. in Chemical Engineering and Ph.D. in Polymer Science and Engineering from Lehigh University. He came to Xerox from a scientist position at Polaroid Corporation in 1995.