

Developing Smear-Free Pigmented Inks for Thermal Ink Jet

*Chieh-Min Cheng, Garland J. Nichols, Min-Hong Fu,
and Elizabeth A. Kneisel
Xerox Corporation
Webster, New York*

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 a concept for the development of smear-free pigmented inks by imparting polyurethane resin emulsions into ink jet inks. Inks are prepared by the addition of a polyurethane resin emulsion, and wherein the urethane groups can function as a crosslinking site with carboxyl or hydroxyl functionalities on carbon black colorant or other color pigment surfaces, thereby impart the ink smear resistance, film hardness, and humidity resistance. The addition of polyurethane resin emulsions 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.

Polyurethane resin emulsions useful in ink jet applications are prepared by either processes: (1) polymerizing polyester polyol, polyisocyanate and acid in a solvent, followed by dispersing the mixture in water, or (2) an isocyanate terminated prepolymer is prepared in the melt or in an aprotic solvent, and is subsequently chain extended with a diamine in the water phase in the presence of a neutralizing tertiary amine.

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 from 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 perfor-

mance: 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, many 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.

Waterborne polyurethane dispersions are being used in many industrial coatings applications. They can provide properties such as chemical, solvent, abrasion, and scratch resistance, as well as flexibility and toughness. Waterborne polyurethane dispersions can be prepared by one of two processes: (1) the polyurethane is polymerized in solvent then dispersed in water; or (2) an isocyanate terminated prepolymer is prepared in the melt or in an aprotic solvent, and is then chain extended with a diamine in the water phase in the presence of a neutralizing tertiary amine.

In this paper, we present a concept for the development of smear-free pigmented inks by imparting polyurethane resin emulsions into ink jet inks. Inks are prepared by the addition of a polyurethane resin emulsion, and wherein the urethane groups can function as a crosslinking site with carboxyl or hydroxyl functionalities on carbon black colorant or other color pigment surfaces. In pigmented TIJ inks, the polyurethane emulsions enable better binding of the particulates to the paper or to other particulates through the crosslinkages formed by chemical reaction of polyurethane and active hydrogen groups. Crosslinking of carbon blacks through this interfacial covalent interaction should be able to impart the ink smear resistance, film hardness, and humidity resistance. The addition of polyurethane resin emulsions also develops a list of attributes such as high optical density, good latency, excellent light- and water-fastness, superior black MFLEN, good frequency response, and excellent cool curl and showthrough properties.

Experimental

A. Preparation of Polyurethane Emulsions:

Polyurethane resin emulsions useful in ink jet applications are prepared by either processes: (1) polymerizing polyester polyol, polyisocyanate and acid in a solvent, followed by dispersing the mixture in water, or (2) an isocyanate terminated prepolymer is prepared in the melt or in an aprotic solvent, and is subsequently chain extended with a diamine in the water phase in the presence of a neutralizing tertiary amine¹⁻⁴. Polyurethane emulsions PU-103 and PU-139 were prepared by similar conditions with the change in monomers as exemplified in the following procedure.

Polyester polyurethane resin emulsion PU-103 was prepared as follows:

(1) Preparation of a polyester polyol:

In a 5 liter jacketed glass flask equipped with a mechanical stirrer, 350 grams of phthalic anhydride, 400 grams of isophthalic acid, 1,500 grams of pentaerythritol, and 2,500 grams of soybean oil was heated at 210°C for 5 hours and condensed until the acid number was about 2.5. The resulting polyester polyol had a hydroxyl number of 167.

(2) Preparation of a polyester polyurethane resin emulsion:

In a 5 liter jacketed glass flask equipped with a mechanical stirrer, 800 grams of the above prepared polyester polyol, 60 grams of dimethylolpropionic acid, 200 grams of N-methylpyrrolidone, and 30 grams of triethylamine were homogenized at 5,000 rpm at 80°C for 30 minutes. Then 200 grams of a mixture containing 80 wt% of 1-methyl-2,4-diisocyanatocyclohexane and 20 wt% of 1-methyl-2,6-diisocyanatocyclohexane were added into the reaction flask, and the entire reaction mixture was heated to 110°C. The reaction was continued until NCO groups were no longer detectable by IR-spectroscopy. 15 grams of

IGEPAL CO-850™ (nonylphenol ethoxylate, Rhodia) and 30 grams of tin(II) octanoate were added, and the mixture in the flask was homogenized at 5,000 rpm at 110°C for 15 minutes then cooled down to 100°C. The resulting polyurethane resin solution was sequentially dispersed in 1,250 grams of deionized water at 60°C for 1 hour, then sequentially homogenized at 10,000 rpm at 60°C for 30 minutes. The resulting polyurethane resin emulsion after cooling throughout possessed a weight average molecular weight Mw of 35,000 as determined on a Waters GPC and a volume average diameter for the polymer of 450 nanometers as measured by light scattering technique on a Coulter N4 Plus Particle Sizer. The polyurethane resin emulsion product was comprised of 41 percent by weight of polyurethane resin. Also, the polyurethane resin possessed a hydroxyl number of 84 mg KOH/g, an acid number of 35 mg KOH/g, and a viscosity of 810 cPs at 25°C, as determined by a Brookfield Fluid Rheometer.

Polyester polyurethane resin emulsion PU-139 was prepared by using a polyester polyol of phthalic anhydride, stearic acid, trimethylolpropane, neopentyl glycol, and 1,6-hexanediol. The polyester polyol had a hydroxyl number of 158. The polyurethane resin emulsion was comprised of 42 percent by weight of polyurethane resin, which possessed a hydroxyl number of 79 mg KOH/g, an acid number of 22 mg KOH/g, and a viscosity of 350 cPs at 25°C.

B. Preparation of Inks

Ink PU-103/1 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 Cabotjet 300 (Cabot) carbon black dispersion with water through a graduated separatory funnel. The addition of the 1 wt% of polyurethane emulsion 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 polyurethane resin emulsion, Cabotjet 300 carbon black, sulfolane, 2-pyrrolidinone, nonionic surfactant, and water.

Ink PU-103/3 comprised of 3.5wt% of polyurethane emulsion PU-103. Ink PU-139/1 comprised of 1wt% of polyurethane emulsion PU-139. Ink PU-103/0 was a reference ink which contained no polyurethane emulsion 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 unsmear 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 polyurethane emulsions 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 polyurethane as well as ink with the polyurethane emulsions. The AFM pictures identified high pile height of the polyurethane emulsion 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 polyurethane emulsion 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 polyurethane resin emulsion 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

Inks	Shelf Standing at 25°C			60°C/24 hrs Heat Treatment		
	Viscosity <i>cPs</i>	Surface tension <i>dyne/cm</i>	pH	Viscosity <i>cPs</i>	Surface tension <i>dyne/cm</i>	pH
PU-103/0	2.12	37.3	6.48	2.08	37.9	6.38
PU-103/1	2.10	34.6	6.57	2.06	35.3	6.40
PU-103/3	2.23	35.7	6.36	2.20	36.7	6.21
PU-139/1	1.94	35.1	6.52	1.89	35.9	6.42

The inks exhibited higher optical density as compared to the reference ink without polyurethane emulsion. 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 polyurethane resin emulsion, 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 polyurethane resin emulsion, smear is significant and would transfer during handling of the paper onto fingers, backside of papers), hence productivity is lost.

Table 2. Optical Density and Dry Smear Attributes

Inks	Optical Density		Dry Smear Optical Density	
	Xerox 4024DP	Image Series LX	Xerox 4024DP	Image Series LX
PU-103/0	1.30	1.32	0.18	0.20
PU-103/1	1.43	1.46	0.04	0.05
PU-103/3	1.46	1.49	0.03	0.03
PU-139/1	1.42	1.48	0.04	0.05

The wet smear resistance in Xerox 4024DP and Image series LX papers is significantly improved through the use of the polyurethane resin emulsions. The wet smear OD for inks without polyurethane resin emulsion was about from 0.35 to about 0.36. The wet smear resistance is significantly improved through the use of the polyurethane resin emulsions as the wet smear OD for inks with polyurethane resin emulsions 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

Inks	Wet Smear Optical Density	
	Xerox 4024DP	Image Series LX
PU-103/0	0.35	0.36
PU-103/1	0.05	0.05
PU-103/3	0.04	0.03
PU-139/1	0.06	0.07

Summary

The addition of the polyurethane emulsion into ink jet systems imparts several advantages. Inks are prepared by the addition of a polyurethane resin emulsion, and wherein the urethane groups can function as a crosslinking site with carboxyl functionalities on carbon black colorant or other color pigment surfaces, 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 polyurethane emulsion 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. J. W. Shulman and E. G. Cockbian, Trans. Faraday Soc., 36, 651 (1940).
3. O. Bayer, Angew. Chemie, A59 (1947).
4. J. W. Vanderhoff, M. S. El-Aasser, and J. D. Hoffman, US Patent 4,070,323 (1978).

Biography

Dr. Chieh-Min Cheng is the Manager of the Chemical Toner Pilot Plant in Xerox Corporation. He has worked at Xerox for over 5 years in both the toner design 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.