Reactive Ink System for Aqueous Ink Jet Printer

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Abstract

The adhesion of the ink dots on the printing materials is primary subject for the commercial printing applications of ink jet printers. This paper deals with the novel, reactive binder system for aqueous ink jet printer. The inks contain the two groups of liquid material in the different inks, which react each other and changes to solid polymer after mixed on the surface of the receiving material. The reaction is based on the Michael Addition Reaction. The reaction breaks out spontaneously under ambient temperature. The initial gelling is fast and overall reaction finishes with getting out of solvents. The both group of materials are hygroscopic, low viscous, and colorless. The polymeric materials born adheres the colorants to the surface of the receiving sheet and protects from the liquid and gaseous materials from the environments. The polymeric binder gives the various advantages on the fixing of the colorants, such as the smear resistance, water fastness, image migration, and ozone fading. The paper selectivity on printing will become smaller by adapting this system.

Introduction

The major mechanism of fixing in ink jet printer today is an absorption into the receiving materials. It is difficult to use the inks containing enough solid binder on current ink jet print heads because of viscosity rise, clogging, or kogation. The printed materials made with ink jet paper and an aqueous inks are ready to be suffered from many effects from the environments. Many ideas to load the binder material in an ink have been presented to improve the above condition. Table 1 shows the examples of the reactive system.

Table 1 Reactive Ink Systems in Ink Jet Inks

System	Reaction Principle
P-POP (Canon)	coagulation of dye and mordant
reaction of ink components and materials in paper	1; esterification with acid anhydride 2; condensation with alkoxy silane 3; addition to epoxide
UV curable ink	photo polymerization
Michael Addition	Addition of amines to acrylate

Principle of Michael Addition Reaction

The Michael addition reaction has been used in two package paint system.(1) The addition reaction scheme of unsaturated acrylic material and amine is as in Fig. 1.

The compounds having the electrophilic group X at α position of unsaturated bond (monomer A) can react with primary amines (monomer B) spontaneously. The aqueous system of this scheme has become possible by preparing the suitable set of compounds. The crosslinked polymeric layer does not dissolve any more in water and immobilize the colorants in receiving sheet.

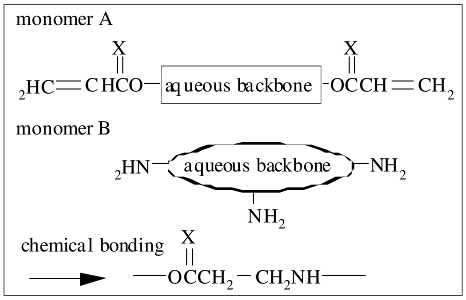

Figure 1. Reaction Model of Michael Addition Reaction

Experimental

1:Aqueous Acrylic Compounds (monomer A)

The aqueous acrylic compounds are prepared from hydrophilic polyepoxides, which are the same category of materials in UV curable ink.(2) The materials prepared are highly water soluble and satisfactorily low viscous.

Table 2 Basic Properties of Aqueous Acrylic Compounds

	n	Viscosity(mNm)	pH	Acid Value
CNJ-21	2	75	5.8	3
CNJ-22	2	65	6.8	3
CNJ-23	2	70	6.0	3
CNJ-31C	3	2800	6.7	1
CNJ-32	3	8800	6.0	4

n: number of acrylate substituent in each molecule; measuring condition of Vis.and pH : 25C

The Figure 2 shows the evaporation rate of 50 : 50 aqueous mixture of acrylic compounds. The evaporation of water reduced by the presence of the acrylic compound. These materials are quite resemble to aqueous solvents for ink jet inks. The Figure 3 shows the viscosity of aqueous mixtures of monomerA and B. The viscosity of the aqueous solutions are satisfactorily low. From these properties concentration of ordinary solvents can be decreased in reactive system.

2. Aqueous Amino Compounds (monomer B)

The aqueous amino compounds for this system can be selected within the commercial materials. They are the lower molecular weight polyethylene imine, polyarylamine, and primary amino derivative of polyols. The molecular weight and number of branches are significant to the gelling speed and solid properties.

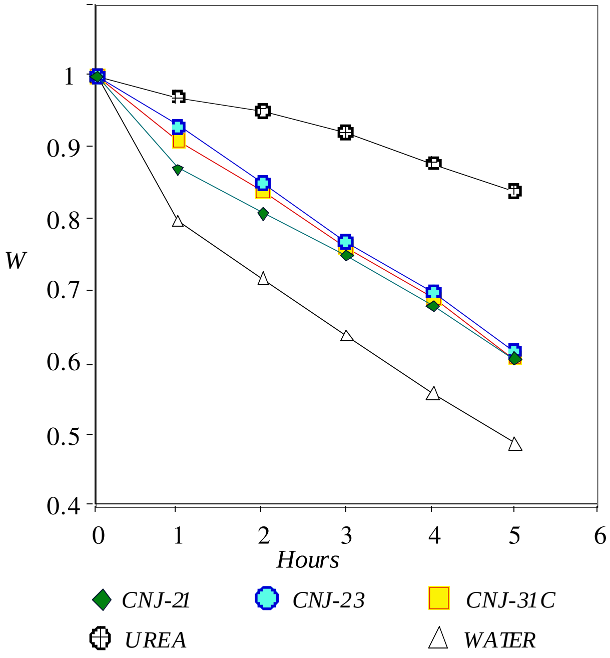

Figure 2. Evaporation of water from monomer A solution under room temperature, monomer : water=50:50 W : Relative Weight of the Solution

3. Ink System

The combination of the reactive material and colorants are chosen from the stability of the inks. Though the acrylic compounds are acidic to neural, they show wide pH range of stability. Therefore the acrylic oligomers can be used both in anionic and cationic ink. As the monomer B are strong base, it is necessary to examine the compatibility with the colorants. Normally the acidic ink is preferred. The concentration of the reactive species in inks are permitted from 5 to 30% by weight. On formulating the ink set, it is better that either A or B is tri-functional. The crosslinking rate, fastness, and hardness are affected from the number of functional group. When both A and B is bi-functional, the reaction product frequently keeps solubility in water, the reason of it is probably the reaction product has the linearly linked structure.

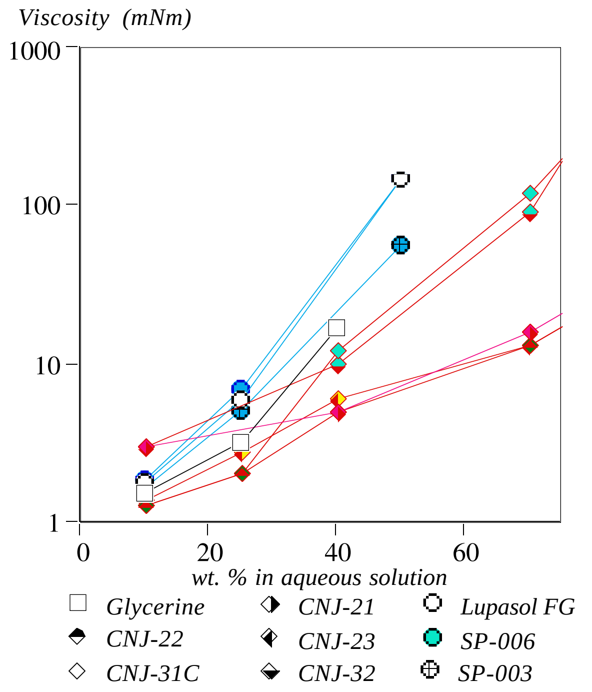

Figure 3. Viscosity of aqueous solution of monomer A and B

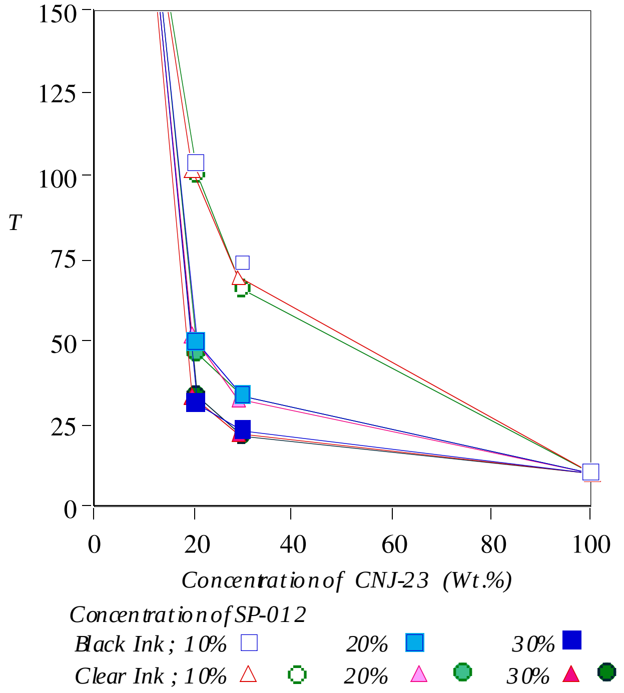

Figure 4. Gelling Time T (sec.)

4. Reaction Rate

The measurements of reaction in testing tube were carried out and shown in Figure 3. The initial gelling means the time changing to viscous gel when mixed in testing tube. As seen in Figure 4 the initial gelling occurs within 2 min. after mixing. The temperature of the mixed liquid raised rapidly. The real reaction on printing may occur faster than in testing tube with the evaporation or diffusion of the solvents.

5. Solidified Ink Layer

Figure 5(a) (b) shows cross sectional view of the glossy paper made by ordinary black pigmented ink and its reactive ink. In case of ordinary ink the pigment dispersion placed near the surface of the paper. The surface layer of the ink is not flat. On the other hand the reactive ink flattened the layer and covered the surface region uniformly. The deep penetration of pigment particles was backed up by ejecting the extra base ink (monomer B clear ink).

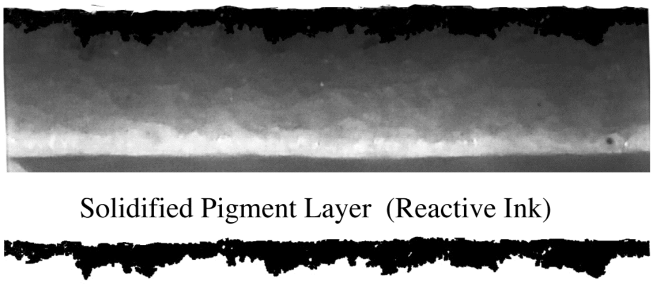

*Figure 5(a). Cross section of Glossy Paper Printed by Reactive ink A containing carbon black(*Cab-O-Jet™-300*) and 15% of CNJ-22 and ink B containing 15% of Lupasol FG.*

*Figure 5(b). Cross section of Glossy Paper Printed by non-reactive ink containing carbon black(*Cab-O-Jet™-300*).*

Applicational Performance

1. Smear Resistance

The smear resistance is improved by adopting the reactive system in pigmented inks. Cab-O-Jet™-300 was used for this tests. The pigment particles in Figure (a) were placed deeper than Figure (b), and the layer of it was flatter than in Figure(a). The reason of higher smear resistance is a swelling of coating layer by the monomer B and the filling up by particles by the born polymer.

2. Water Fastness and Migration

The water fastness of dye based inks were improved by the reactive ink. Direct blue-199, acid red-52, and acid yellow 23, direct yellow 132 printed on the plain paper were tested. The water fastness is determined ordinary by the solubility and dissociation of dyes. The migration is a diffusion of dye molecules promoted by the residual solvents and/or humidity from environments. The highly crosslinked polymer matrix suppressed the diffusion of dye molecules. The soluble dyes are trapped in the cage of the polymer network produced by reaction. The base material (monomer B) might bind also the dyes by ionic interaction. The drop volume ratio and mixing between colored ink of monomer A and clear ink of monomer B has critical importance to get high water fastness.

3. Fading Resistance from Ozone

The Figure 6 shows results of the accelerated ozone fading test. The typical dyes for ink jet were tested. As seen in Figure 5 the reactive ink remarkably improves the fading of these dyes on glossy paper. The most of the glossy paper are suffered seriously from gaseous materials. This effect relates to the fading of ink jet pictures under in-door conditions. The small pores were filled up by the polymer matrix born on reaction. The higher drying rate of the glossy papers are guaranteed by these micro pore structure. The polymer precursor in inks cover them after printing.

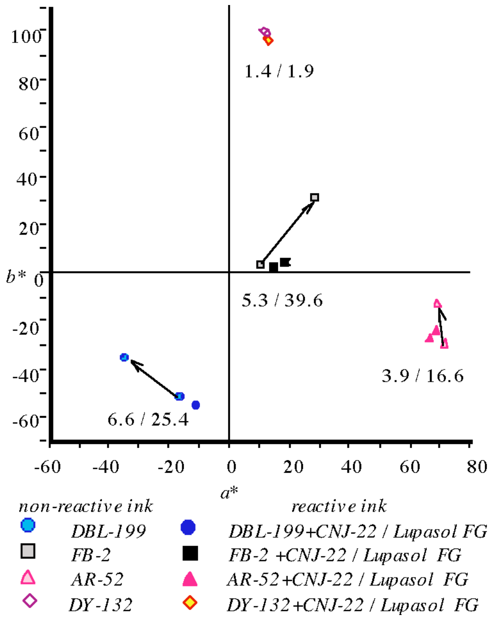

Figure 6. Ozone Fading Test concentration of ozone : 3ppm. Duration : 2hours under RT paper : ink jet glossy paper , arrow denotes the direction to change.

Discussion

1. Addition Reaction

The Michael addition reaction in ink jet inks is faster in nonaqueous system. This fact means we are able to get more effective benefits in non-aqueous ink system. It means also that the molecules of water and solvent reduces the reaction by their ionic property. The total reaction finishes with the evaporation of the solvents. Therefore it is necessary to receive the facts that the total reaction in aqueous system requires the longer time on real printing application. This phenomenon possibly originates in the hydration. The hydrated amine (monomer B in aqueous condition) may be protected by surrounded water molecules from reaching closely to the vinyl molecules.

2. Development of Materials

The principal materials for Michael reaction are (1) vinyl compound and (2) molecules having the primary amine. The former materials are used also in aqueous UV curing ink system. It is necessary to prepare the wider variety of the monomer compounds for this system. Unfortunately the aqueous materials are limited because of the clear waterborne system is not popular even in coating technology. Though the aqueous system in future will become major in coating and ink technologies, the safety regulation and risks in producing the new materials on the world limits the wider, faster developments.

3. Light Fastness

The reactive ink system require the materials to raise the light fastness of print made with dye based inks. The ozone fading has been overcome already. If we get the materials to prevent the effect of the light the reactive ink system will give large advantages on printing with non-coated printing papers.

4. Reaction with Colorants

If the colorants have an ability to react with these monomers, the performance of the reactive ink system will become more effective. The surface modification of pigments to get such a reactivity is one of the ways.(3)

Conclusion

The novel reactive system was tested and the advantages were ascertained. The reactive materials played like aqueous solvents. The inks penetrated deeply into the paper and changes to polymer. The borne polymer was a good binder for the aqueous ink of dyes and pigments.

References

1-1. EP-A 0672538 E.I.Du Pont De Nomours and Company

1-2. A. Noomen *Progress in Organic Coatings*, **17** (1989) 27

2. Hiromichi Noguchi, *IS&T International Conference on Digital Printing NIP14* (1998) TORONTO p109-110

3. Tsubokawa et al. Reactive & functional Polymers **37**,(1998),75-82

Biography

Hiromichi Noguchi received his Dr. of Engineering from the Tokyo Institute of Technology (polymer science) in 1977. He worked in DIC for 7 years and joined Canon Inc. in 1985. He has worked on R/D of digital imaging materials in BJ technology.

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Satoru Fujii received his MS degree in organic synthesis from the Osaka University in 1984 and joined Nagase Chemicals Ltd. Now he is the assistant general manager of the research & Development Division of Nagase Chemicals Ltd.. He has worked in R&D of functional polymer for coating and their printing applications.

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