

# UV Curable, Aqueous Ink Jet Ink: Material Design and Performance for Digital Printing

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## Abstract

The researches of the ultra violet ray curable aqueous ink jet ink were carried out. Several advantages in adopting the UV system were ascertained by preparing novel materials, which were compatible with ordinary form of aqueous ink jet inks. The aqueous photo initiators and anionic, nonionic, and cationic UV resins were synthesized. The sensitivity in photo polymerization, water fastness of dye base inks on plain paper, fading of dyes by UV exposure, reduction of intercolor bleed by anionic ink and cationic pigment, adhesive force, transparency, and color reproduction in pigmented inks were exemplified with experimental results. All experiments were carried out by using bubble jet color printer loaded low pressure mercury lamps. The aqueous UV inks operated stably on these existing equipments. The main object of loading UV system is to improve the weak points in aqueous pigmented inks. UV system results successfully in the improvements of it. The first key factor to come up the next step is to increase the light sensitivity in colored inks. The performance and future subjects of this technology are discussed.

## Introduction

Ink jet has been received as a simple system which does not use any pre- or post- treatment on printing. From this simplicity today it has got prosperous in the digital printer market. The simplicity has at the same time a difficulty in getting fastness and permanency of the print. The print quality and versatility of ink jet print still has some excuses compared to laser printer or offset printer. In the laser printer dry powder toner is fixed thermally to the paper. In the offset printer transferred inks cure and adhere. The fastness of these system originates in these post-fixing treatment. To get such a reliability to ink jet system from customer it is necessary to get higher quality and permanency of the prints. To satisfy the complex requirements from ink jet system it may be inevitable the ink chemistry to become more and more sophisticated. These inks may become more serious on the real application of these inks. In this study UV curing technique was tested. It is of course the post treatment technique. Aqueous UV curing is not popular in on-demand ink jet systems. The central concern of this study is to overcome the difficulties of aqueous pigmented ink in on-demand ink jet printer. The adhesive force, inter-color bleed, transparency, and color reproduction are examined. This research is intended not to

establish the product design but to get experimental evidences of plus and minus in ink jet digital printing.

## Experimental

### Aqueous Photo-Initiator

There are not the highly water soluble UV photo-initiator for anionic ink jet inks in the market<sup>(1)(2)</sup>. Then, It became necessary to produce a highly water soluble photo-initiator at the initial stage of this research. Two materials were synthesized from Irgacure 2959 (product of Ciba specialty Co.).

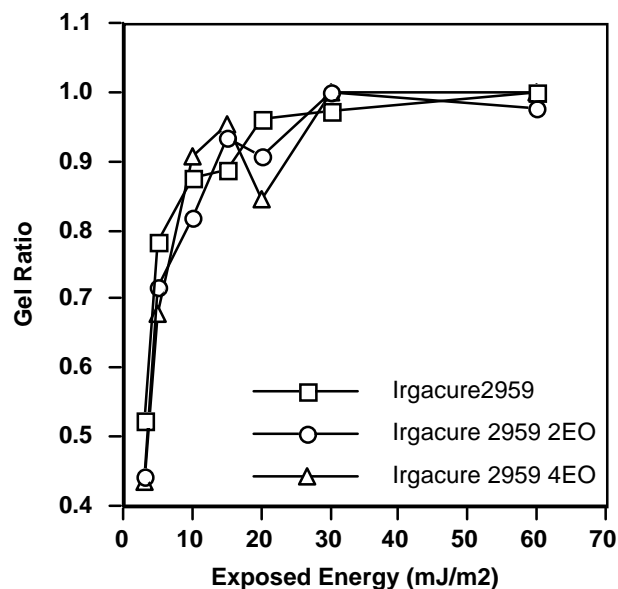
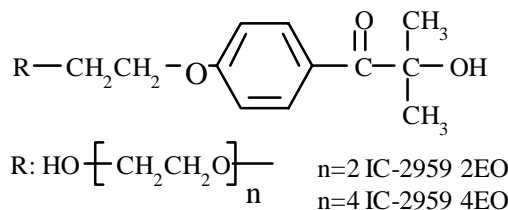


Figure 1. Gel Ratio vs. Exposed UV Energy in Photo-polymerization of Denakol DA0314. PI: 3Wt.% Thickness: 2 mils.



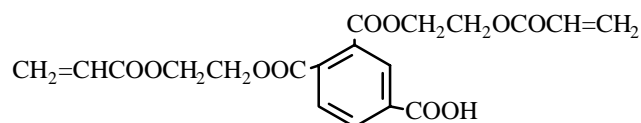
IC-2959 dissolves only slightly in water, but 2EO and 4EO derivatives dissolve quite satisfactorily in water and

solvent composition. The relative photo polymerization speed of IC-2959 and its derivatives are almost same as shown in Figure 1.

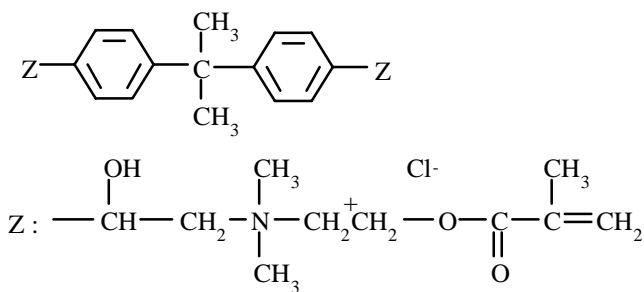
### Water Soluble Oligomer

An anionic, cationic, and nonionic materials were prepared. For an aqueous ink, a highly curable polyfunctional species are necessary. Such materials can be synthesized from the polyhydroxy compounds, which maintain hygroscopic, hydrophilic nature. The examples are as follows:

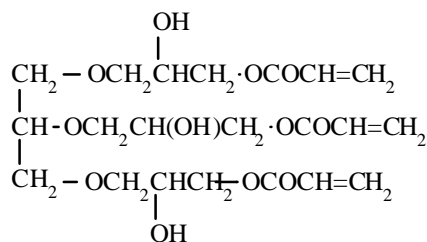
#### Anionic Oligomer : Experimental



#### Cationic Oligomer : Experimental



#### Nonionic Oligomer : Denakol DA-314 (Nagase Chemicals & Engineering Co.)



### Colorants And Ink

The ordinary colorants and solvents could be used if above species were chosen. Nonionic species showed wide compatibility with many colorants. Cationic oligomers are prefer to cationic inks. The weight % of the oligomer in the inks was tested from 1 to 6wt.%. The several inks were formulated to have the viscosity of from 2.0 to 4.5 mPs., and surface tension of from 26 to 50 mN/m. The dyes are typical 1st generation ink jet dyes, and pigments are carbon black, PY-128, PR-122, and PBL-15:3. They were dispersed in aqueous state with polymer dispersants. The polarity of these inks are anionic. Pigmented, cationic black ink was also prepared by using the cationic polymer.

### Equipment

UV lights were laid in front of the printer as shown in schematic Figure 2. The light source is medium pressure mercury lamp (USHIO Electric Co. Japan). The out put energy is 4 mW/m<sup>2</sup> at around 254nm wave length. The UV light was exposed from an upper side of the printed sheet immediately after printing. BJC-465J color ink jet printer (Canon Inc.) was used for these experiments.

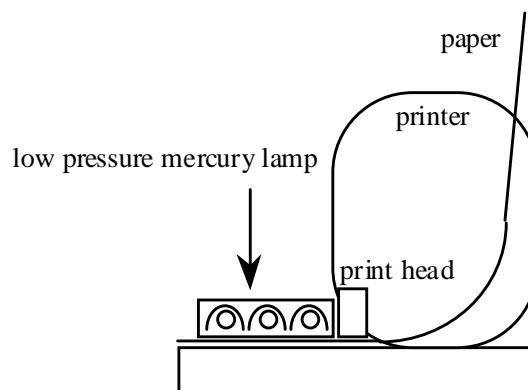


Figure 2. Printer with curing lamp

### Experimental Results

#### Printing on Plain Paper with Dye Based Inks

The remarkable increase in water fastness was obtained as shown in Figure 3. The fastness is not perfect but practically valuable level. The fading on plain paper were quite little.

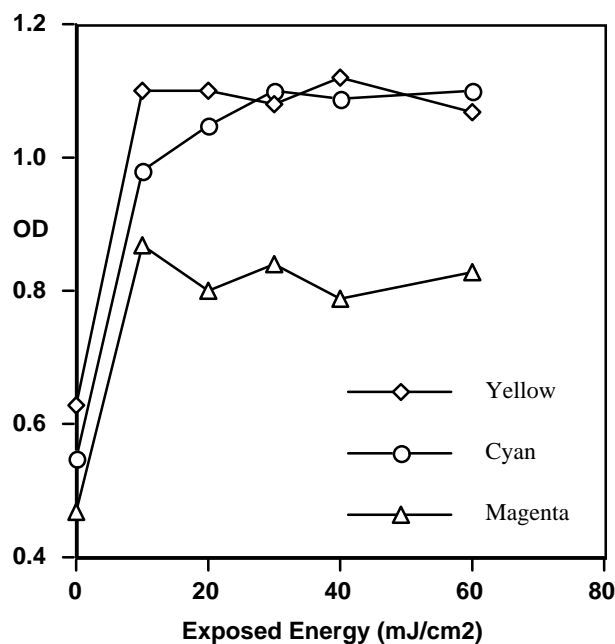


Figure 3. Water Immersion Test after Print/UV Exposure OD values of initial samples are Y:0.93, M:1.00, C:1.08, paper: PB paper (copier paper of Canon).

### Printing on Plain Paper with Pigmented Inks

The anionic and cationic carbon black inks were used with nonionic and cationic UV curable oligomer, respectively. The anionic dispersion of carbon black was made with the anionic polymer<sup>(3)</sup>. The cationic dispersion is made with the cationic polymer and furnace carbon blacks of neutral or basic pH, the precise of which is in the literature<sup>(4)</sup>. The cationic dispersion is rare in ink jet ink. Recent product from Cabot Co. named IJX-55, which is the novel black dispersion of cationic property, will also be used for this object. The oligomers can be selected from the cationic and/or nonionic ones. The rub-resistance by highlighter pen on the plain paper were well improved in both black inks. By using cationic black ink, intercolor bleed between dye based anionic yellow UV inks became quite better than anionic black pigment as shown in Figure 4. The edge sharpness of the character is clear in cationic ink.

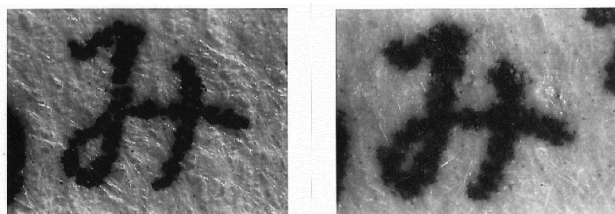


Figure 4. Intercolor Bleed between black pigmented ink and anionic dye based yellow ink on plain paper. left: cationic black pigment; right: anionic black pigment

The rub-resistance of the pigmented ink is affected from the hardness of the cured oligomer. The curable oligomers made from glycols give sometimes soft solid. Therefore the selection of oligomer is important to get satisfactory results. By choosing the oligomer both the intercolor bleed and rub-resistance will be improved at the same time.

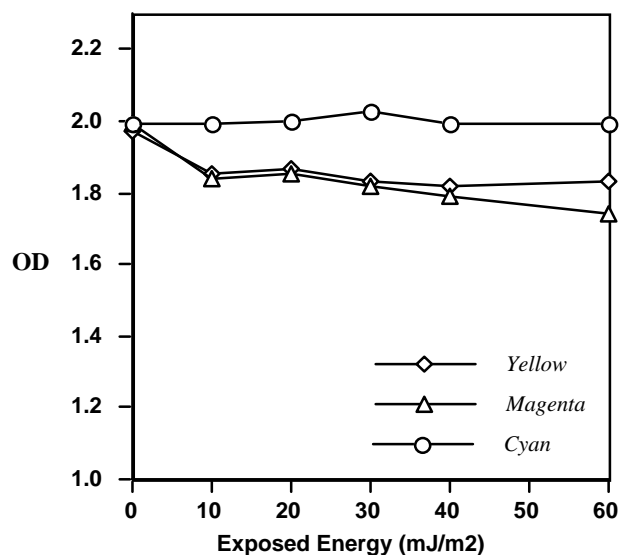


Figure 5. Fading of dyes by UV Exposure on Glossy Paper (GP-201 Canon)

### Fading of Dye Based Color Inks on Coated Paper

Figure 5 shows color fading in case of the glossy paper with dye based color inks. The fading by UV exposure was recognized especially in magenta and yellow dye.

### Print Quality and Drying Mechanism

The print quality on plain paper was not affected at all from an existence of oligomer and initiator. The aqueous oligomers showed small effect on the surface tension because of their high hydrophilicity. We can, therefore, control the quality as ordinary way of ink design. On the other hand, the drying mechanism is quite different from non-UV inks. The drying proceeds as following steps;

- (1) small spreading and penetration in paper
- (2) UV curing (part of the component solidify)
- (3) penetration/evaporation of solvents
- (4) settle down the colorant in a paper

These mechanism let it possible to adopt the high surface tension ink, which ordinary gives sharp image and slow penetration speed. UV printer will make it possible to discharge the printed sheet faster from the printer.

### Adhesive Force on Glossy Paper in Pigmented Inks

The great benefit was recognized in adhesive force of pigmented inks on a glossy paper. By adopting UV system it will become unnecessary to prepare:

- (1) glossy paper for dye based ink and for pigmented ink.
- (2) solid polymeric additives as binder material.

It will become important to find out the most effective timing and intensity of UV light under each condition.

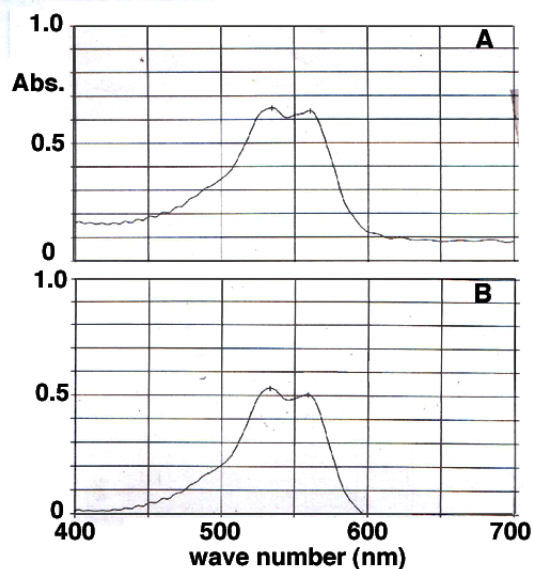


Figure 6. Absorption Spectra of pigmented (quinacridone red) UV ink on PET film A : non-UV ink B: UV ink

### Transparency of Pigmented Inks on Film

The deficiency of pigmented color inks for a desktop printer is lack of transparency when printed on OHP film. It

may be one of the major reasons that the pigmented inks have not been adopted for desktop printer. Figure 6 shows the absorption spectra of the aqueous, UV curable quinaclidone magenta ink on the PET film.

By using UV curing, satisfactorily transparent image was obtained on PET film. The main reason of this result is a presence of curable oligomer, which depress the light scattering through reduction of an aggregation of pigment particles on drying. To get a transparent image with pigment it is of course important to make particle size smaller than wave length of visible light. These transparent image with pigments will get many advantages on various print jobs. By using the transparent print with pigmented color, ink jet printer will get the wider usage as commercial photo print, overlay film, and backlighted showthrough panel etc.

### Color Reproduction

We have frequently encountered the lowering of the chroma of RGB in CMYK pigmented inks particularly in high pigment loading in ink. The main reason of it is opacity and scattering in dispersed pigment particles. Particularly the secondary colors frequently lose the chroma and decline to dark shade. This phenomenon relates to the transparency of the pigments. Figure 7 shows the comparison of UV pigmented and non-UV pigmented inks, whose dispersion and solvent formulation are same except UV resin and photo-initiator. In this case the  $a^*b^*$  color space did not suffer from these effects by reducing the loading of pigment dispersion. On the other hand, the chroma of M and R became higher in UV pigmented inks than non-UV pigmented inks. The combination of magenta dispersion and UV materials chosen gave good result in this case.

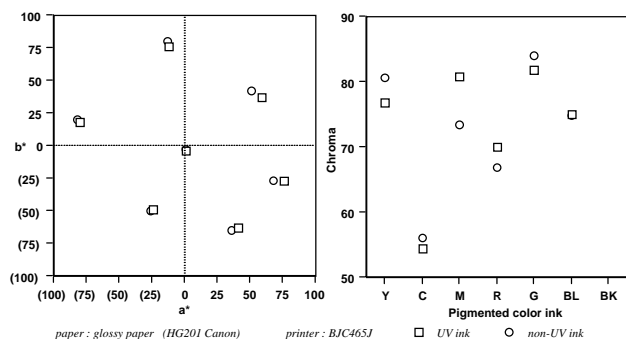


Figure 7. Color reproduction of pigmented inks

### Discussion

The aqueous UV system was surveyed on various aspects by using current office printer. The vital subject of next stage of material design is to increase the sensitivity on pigmented color inks. The UV resins work as a liquid solvent in aqueous ink and work as a binder polymer after printed by becoming solid. To realize more notable effects

for adopting aqueous UV system, following subjects will become important.

From the material design side, it is necessary to produce a low viscous, high reactive, stable, aqueous curable resins. The photo-initiators having a good solubility in aqueous pigment dispersion and higher sensitivity in pigmented formulation are also required. From the print head design side, it is necessary to produce an engine which work stably by using a inks of viscosity up to 5mPs. under driving condition of approximately 6KHz or more and drop volume of from 10 to 40pl. From the equipment design side, the effective UV light source which has a characteristics of best fitted to the photo-initiators selected is necessary.

### Concluding Remarks

Various advantages of aqueous, UV curable ink jet inks were indicated. We can summarize the advantages as;

- (1) water fastness in highly water soluble dyes
- (2) adhesive force on plain paper and coated paper
- (3) reduction of the intercolor bleed by polarity change
- (4) rapid drying on initial stage of print
- (5) getting transparency in pigmented ink

UV system gives many benefits to the printer compared to the non-UV system. The curing system requires the additional equipments to employ the UV light system. The size, cost, and electrical source, and control system must be considered when to optimize each printer. The disadvantages in UV system relate to above items as fading of dyes, odor from UV tube. It is needless to say to consider the environmental aspects, leaking UV light and evolution of  $O_3$ . UV system will be the sure way for the ink jet system to become a long lived printing technology through overcoming these difficulties and getting the quality and permanency like a conventional printing systems.

### References

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### Biography

Dr.Hiromichi Noguchi received Dr. of Engineering from the Tokyo Institute of Technology(polymer science) in 1977. He has worked on R/D of digital imaging materials and joined Canon Inc. in 1985. He has worked in BJ technology on material design of print head, inks, and surface coatings.

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