

Effect of Resin/Binders on Lightfastness of Colorants in Inkjet Inks

Vincent Wing-sum Kwan
Videojet Systems International, Inc.
Wood Dale, Illinois U.S.A.

Abstract

Recent advances in inkjet technology has materialized large format printing in various outdoor and indoor applications. Heavy emphasis has been placed on the precise matching of print media and inks to maximize lightfastness of the colorants used. However, little attention has been paid to depict the use of resin to provide protection against ultra-violet light. This paper describes our effort in identifying useful resins that can provide some ultra-violet light protection. The philosophy of choosing the right resin will be discussed. Examples of using such resins to enhance lightfastness of some dyes or pigments will also be given.

Introduction

Factors affecting lightfastness of colorants have been the subject of intense research in recent years. Components like colorants, media, and ink additives have been investigated.^{1,2} However, the use of resins/binders to increase the lightfastness of such systems has not been addressed. Understanding how the resin/binder system affects the light stability of colorants will enable incorporation of light stability enhancement into the resin/binder used. Consequently, the formulation of inks for outdoor use will be simplified. And formulation of stable outdoor inkjet inks without the use of receptor paper can also be realized.

This paper attempts to answer the following questions.

(a) Does the resin/binder play a role in stabilizing the colorant; (b) What are the structural requirements for an effective resin/binder; (c) Do these resins provide the same stability enhancement for pigment as in dye.

To elucidate the structural requirements of an effective resin/binder, resin/binders with a diversified pool of chemical structures were studied. The first factor of interest is the quantity of aromatic systems in the backbone of the polymer resin. It is envisioned that increasing content of aromatic systems on the polymer backbone will increase ultra-violet absorption, hence protecting the colorants from photo-degradation. The second factor of investigation will focus on resin systems that bear ultra-violet light absorbers as pendant groups. Thirdly, as water is also suspected to be involved in transporting oxygen, which is shown to be one of factors accounting for photodegradation, resins that are not water soluble are also studied to determine whether such resins will improve light stability of the colorants. Though

dyes will be the primary focus of this paper, these factors will be examined with dyes and pigments to determine the relative significance of such factors in these two types of colorants.

Experiment Protocol

In order to solely assess the importance of binder/resin systems in this experiment, the inks formulated will contain a minimal number of components. A typical ink will only consist of a colorant, a binder and a solvent. The ratio of the binder to the colorant will be fixed across the tests. The substrate for the light stability test will also be absent of receptor. The color of the images formed will be measured before and after the irradiation according to the CIELab* scale. The difference in color, which is usually indicated by the delta E value, will be used to assess the light stability of the image. To accelerate the test, carbon arc fadometer is used as the source of ultra-violet light. The period of irradiation is chosen based on the time to observe significant changes in delta E values ($\Delta E > 1.5$). This period was found to be as short as 2 hours, depending on the dye studied. In general, this period is shorter in dyes than in pigments.

Two dyes, one yellow and one red, were used in this study. Both dyes contain azo structure, which represents the most susceptible point of photodegradation. The dyes were formulated into inks with a final dye concentration of 2% (by weight). The low dye concentration is intentionally used to discern any slight effect of the resin/binder on the light stability.

Apart from dye, a yellow pigment - Pigment Yellow 12, was also used for this study. This pigment was chosen for its notorious low resistance to photodegradation.

Results and Discussion

The first experiment concerned the ability of the resin/binders to slow down the photo-degradation of the colorants. Acrylic polymers with increasing quantity of phenyl moieties were used in the experiment. Such results were compared to the control where no polymer was added. The value of delta E for two dyes after 27 hours of ultra-violet irradiation were depicted in Table 1.

The results in Table 1 are quite surprising. When compared to the control panel, addition of resin/binder

bearing phenyl moieties actually accelerates the photodegradation process, even when the ratio of the phenyl group to the acrylic group is as low as 1.5 to 1 in the polymer matrix. Increasing this phenyl/acrylic ratio further magnifies this detrimental effect. This effect is also more prominent in the red dye.

Table 1. Comparison on Delta E Values of Two Inks Using Resins Possessing Various Phenyl group to Acrylic Acid Ratio.

Ratio of phenyl to acrylic acid	Delta E (yellow dye)	Delta E (red dye)
Control (No Resin)	4.4	6.4
1.5:1	10.0	9.9
3:1	9.6	11.5
10:1	7.9	11.9
23:1	9.0	12.0

To reconfirm this observation, Experiment 2 was conducted. In this series of experiments, the actual loading of the polymers bearing the phenyl groups was varied. The ratio of the polymer to dye was studied over a range of 10:1 to 0.6:1, and the results were tabulated in Table 2.

Table 2. Comparison of Delta E Values of Prints Using Inks Consisting of Various Concentrations of Polystyrene-acrylic Acid Resin.

Ratio of Resin to Dye (w/w)	Delta E
0:1	4.4
0.6:1	4.3
1.1:1	6.3
2.3:1	5.5
5:1	5.6
10:1	9.1

Again, Table 2 reconfirmed the findings in Experiment 1. When the concentration of phenyl-bearing polymer was minimized, the photodegradation of the dyes was also found to decrease as revealed in a smaller delta E value.

Though the reasons for such enhanced degradation are not fully understood, it has been suggested that oxygen molecule, under the ultra-violet excitation, will form peroxide radical and subsequent addition product with phenyl groups. Excess phenyl groups in the resin matrix may then react with excited oxygen molecules to form detrimental radicals. Consequently, a polymer with substituted phenyl groups is used to explore this possibility. Polystyrene sulphonate is chosen to be this polymer. The result of this experiment is indicated in Table 3.

Table 3. Comparison Between Delta E Values of Inks Using Poly(styrenesulphonate) in the Two Dyes Studied.

Entry	Delta E
Yellow	3.9
Red	11.3

Unfortunately, adding one sulphonate group onto the phenyl ring does not result in stabilizing the dye. The delta E values for the two dyes are still comparable to that of poly(styrene). More experiments are demanded to elucidate the mechanism for this deteriorating effect of phenyl group.

Apart from copolymers of polystyrene and polyacrylic acids, resin systems containing other chemical functionalities were also used to elucidate the structure requirement for an effective resin system. The other chemical structures studied include ethylcellulose, polyhydroxystyrene, polyhydroxystyrene containing ultra-violet light absorbing pendant groups. These structures are chosen for suggestions that these chemical moieties may provide lightfastness to colorants. Owing to the differences in chemical structures, most of these resins are not water soluble. They are usually dissolved in ethanol. Consequently, the effect of using a non-aqueous resin can also be investigated. The results for such study are given in Table 4.

Table 4. Comparison of Delta E of Prints Using Inks Composed of Different Resin Systems.

Resin Added	Delta E
Nil (Control)	4.4
Poly(styrene-acrylic acid)	9.1
Ethyl Cellulose	33.8
Poly(hydroxystyrene)	33.2
Poly(hydroxystyrene) with U.V. absorbers as pendant group	59.4

In comparison to Table 1, none of these systems provides any protection. On the contrary, these resin systems accelerate the photodegradation as revealed by the large Delta E values. These surprising results command further study into the interaction of these structures with the colorant.

Since pigment is dispersed and not dissolved in the solvent, it enables the use of a vast variety of solvents and hence expands the scope of chemical structures for the testing. Apart from those structures forementioned, structure like pure alkyl group is added to the testing list. The results are depicted in Table 5.

Table 5. Comparison of Delta E of Prints Using Pigmented Inks Composed of Different Resin Systems.

Resin Added	Delta E
Control	32.0
Poly(styrene-acrylic acid)	40.3
Ethyl Cellulose	25.9
Alkyl group	23.1

The results in Table 5 follow similar trend as in Table 1. Resin possessing large portion of phenyl groups was still shown to hasten the degradation process. However, resins bearing two chemical structures did show stabilizing effect when compared to the control. These include pure alkyl and ethylcellulose. Between which, pure alkyl depicts a larger

stabilization effect on this pigment, followed by ethylcellulose. The mechanism for such stabilization is still under investigation.

Conclusion

The nature of the resin/binder employed was shown to affect the lightfastness of the colorants, both in dye and in pigment. Polymers bearing u.v. light absorbers as pendant group, as well as styrene containing polymers, are shown to destabilize the colorants even further. However, polymer containing alkyl groups as well as ethylcellulose did show enhanced stability on the yellow pigment. As the inkjet printing market is approaching receptor-less phase, color protection provided by the resin alone may prove to be vital in realization of such receptor-less application. This is a work made for Videojet Systems International, Inc.

References

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Biography

Vincent Wing-sum Kwan received his Bachelor of Science from the University of Hong Kong, and his Ph.D. in surface chemistry from the University of Minnesota, Twin Cities. He is currently working as a Staff Chemist at Videojet Systems International, Inc. His research interests are in surface modification and formulation of specialty inks.