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Evaluation of Some Strategies to Control Fading of Prints from Dye-Based Ink Jet

Suda Kiatkamjornwong* and Kitirochna Rattanakasamsuk
Department of Photographic Science and Printing Technology, Faculty of Science, Chulalongkorn University, Bangkok, Thailand

Hiromichi Noguchi
i-Printer Materials Development Center, Tamagawa Factory, Canon Inc., Japan

The problem of color fading in an ink jet print is a weak point that limits the use of the ink jet prints in outdoor applications. This study investigated the effectiveness of one hindered amine light stabilizer and two UV absorbers on the light induced fading of ink jet ink. The stabilizers (HALS) and UV absorbers were coated on the surface of an ink-receiving layer to form a top layer, which prevents the fading of the ink jet ink. The UV absorber coating on the ink jet substrate can improve the light fastness of dye-based ink jet ink. The type of UV absorber does not strongly affect the light fastness of the dye-based ink jet ink but it affects the background color of ink jet printing substrate. The hydroxybenzophenone type UV absorber causes yellowing of the coated sheets while the benzotriazole type UV absorber does not exhibit this problem. Moreover, the extent of the light fastness of dye-based ink jet is in a direct proportion to the amount of UV absorber in the coated layer. In case of HALS coated sheets, the amine light stabilizer did not improve the light fastness of dye-based ink jet ink across the spectrum, it could only improve light fastness of blue and black colors. Additionally, an ink jet ink receiving layer containing HALS and PVA did not improved fastness ozone-gas induced fading, compared with one containing only a PVA barrier film.

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Introduction

The use of ink jet printers for color printing has increased widely over the last decade. Compared to other printing process, ink jet printing offers some dominant advantages such as a lower cost of printer and wider color gamut. However, an outstanding weak point of ink jet prints is image permanence under either indoor or outdoor conditions, especially low light fastness. Therefore, the light induced fading of ink jet ink printed sheets is a main focal aspect in the recent research. Some workers have studied factors related to the fading of ink jet ink. The fading components can be divided into three composite factors: ink, media, and service environment. The ink jet ink composition plays an important role in the light fastness of ink jet ink. Colorant, binder/resin, solvent and other ingredients exhibit the most impact on the light fastness of the ink. For example, an addition of some types of resins/binders accelerates the photodegradation of dye.[1] Media properties such as pH, chemical composition of the media surface, location of colorant within the media, formulation additives, and the physical form of the colorant affect the light fastness of ink jet prints. Some nitrogen containing polymeric resins such as poly(vinyl pyrrolidone) or PVP and poly(ethylene oxide) or PEO used as the coating media have poor light fastness.[2] The service environment such as source of incident light, light intensity, level of humidity, and presence of oxidative gas affect the image permanence.[3,4] The fading rate under filtered high intensity exposure conditions was 2 to 3 times faster than under filtered low intensity exposure conditions. The photoinduced fading by irradiation light is higher than by fluorescent light, even when solar light intensity equals fluorescent light intensity.

There have been many efforts to increase the light fastness of ink jet prints. The concept underlying light fastness improvement is to inhibit the photodegrading of the colorants. The first method is to modify an ink formula by adding some important additives such as light stabilizers (LS).[5] Second, the laminated sheet containing a hindered amine light stabilizer (HALS) and a UV absorber (UVa) is used as an external filter for absorbing incident light.[6] In this article, we shall modify the ink jet media by coating UVa and/or HALS layer on the surface of an ink-receiving layer to try to evaluate the role of each component.

Experimental

The microporous type ink jet film (HG-201 from Canon Inc., Japan) was used as a base substrate. Benzophenone

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*corresponding author: e-mail: ksuda@chula.ac.th

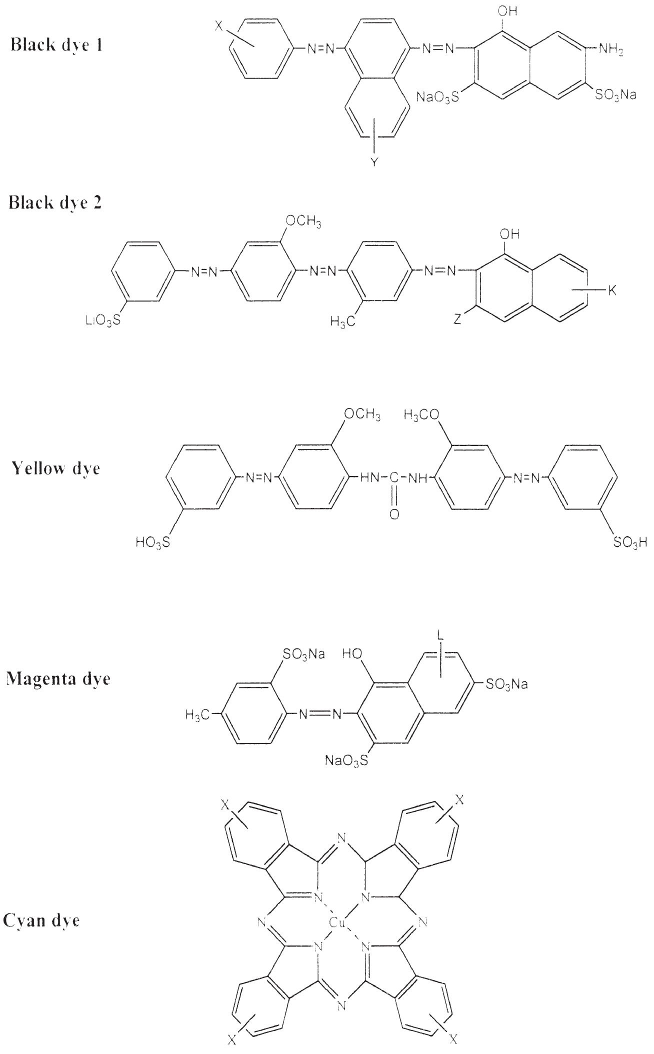


Figure 1. Chemical structures of the dyes used in ink jet ink.

(BP) derivatives (Uvinul MS40 from BASF, Germany) and benzotriazole (BTZ) derivatives (Cibafast W Liquid from Ciba Specialty Chemicals) were used as UV absorbers. A non-aqueous hindered amine light stabilizer (Tinuvin 123 from Ciba Specialty Chemicals (Thailand)) was also used in this research. Polyvinyl alcohol or (PVA) with a degree of hydrolysis of 88 to 89% and a degree of polymerization of 2000 was used. A set of six-color dye-based ink jet inks was supplied from Canon Inc., Japan, and their dye structures are shown in Figure 1.

Preparation of UV Absorber Coated Sheets

Each of the UV absorbers was used for preparing a coating solution containing 0.1, 0.5, 1.0, 2.0, 4.0 or 6.0% by wt. According to the following procedure. The UV absorber was slowly added into methanol and stirred at low speed until it was completely dissolved. A polyvinyl alcohol or (PVA) solution (15%) was separately stirred by a mechanical homogenizer at a speed of 8000 rpm. The UV absorber solution was then slowly poured into the PVA solution. After stirring for 10 min, the mixture was further stirred at a speed of 3000 rpm for another 5 min. The resulting solution was de-bubbled until it was completely homogeneous. The solution was then coated on the HG-201 film and dried at ambient temperature.

TABLE I. Formulation of HALS Coating Solution.

Composition	Concentration (wt %)		
	0 % HALS	2 % HALS	4 % HALS
PVA solution (15%)	60	60	60
Lupasol FG	10	10	10
Tinuvin 123	0	2	4
Toluene	5	4	8
Methanol	25	24	18

Preparation of HALS Coated Sheets

The recipe of the HALS coating solution is shown in Table I. The non-aqueous HALS, Tinuvin 123, (one part) was dissolved in 2 parts of toluene. Methanol was then added into the solution. The mixture was stirred by hand for a rough dispersion. This mixture was then poured into Lupasol FG and stirred for 5 min. To prepare a PVA solution (15%), PVA was separately stirred by a mechanical homogenizer at a speed of 8000 rpm. The HALS mixture was slowly poured into the PVA solution. This mixture was stirred for 15 min. It was then stirred at a speed of 3000 rpm for 5 min. The resulting solution was stored in a desiccator to eliminate any air bubbles until it was completely homogeneous. This solution was then coated on the film substrate. The coating weight was calculated by difference in weight of the film before and after coating of the solution.

Test Chart

The UV absorber coated, HALS coated and uncoated sheets were each printed by Canon BJC 8500 ink jet printer containing a BCI-8 ink set. The test chart was composed of cyan, magenta, yellow, black, blue, red, green and non-printed area.

Testing Condition

a) Light Fastness Testing

The test charts were placed into a Xenon arc lamp weatherometer (Atlas Ci-4000). The condition of the weatherometer is composed of: (1) the back panel temperature at 63°C; (2) the relative humidity of 70% RH; (3) the chamber temperature at 50°C; (4) an irradiation energy of 39 W cm^{-2}. The color value in CIE-L*a*b* color space of each patch was measured after 0, 25, 50, 75 and 100 hr exposure using a spectrophotometer (Gretag-Macbeth Spectrolino).

b) Ozone Fastness Testing

The test charts were placed into the ozone-testing chamber in which the ozone concentration was 3 ppm. The color value in CIE-L*a*b* color space of each patch was measured after 0, 30, 60, 90 and 120 min exposure, using a spectrophotometer (X-rite Color Digital Swatchbook).

The color differences were calculated using the following color difference equation:

$$\Delta E = \sqrt{\left(L_1^* - L_2^*\right)^2 + \left(a_1^* - a_2^*\right)^2 + \left(b_1^* - b_2^*\right)^2}\ , \qquad (1)$$

where ΔE is the color difference, L^* is lightness, a^* and b^* are red-green, and yellow-blue parameters, respectively.

Results and Discussion

Dependence of *ΔE* Values on Exposure Time

The ΔE of color on the uncoated sheet at different exposure times is shown in Fig. 2. It was found that ΔE

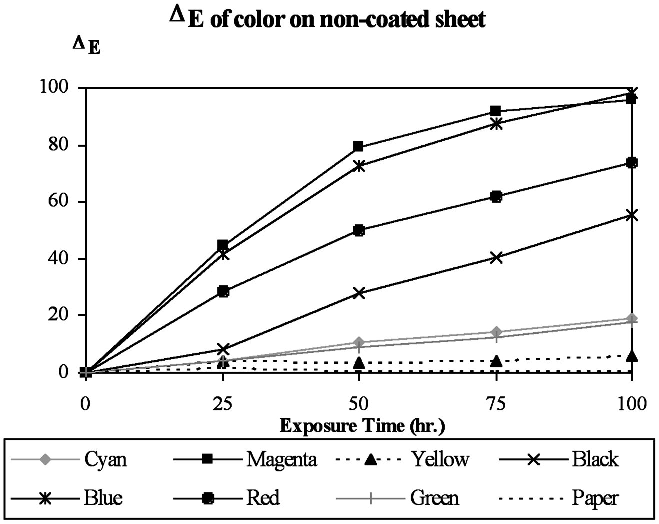


Figure 2. ΔE of dye-based ink jet ink printed on the uncoated sheet.

of each color increased as the exposure time increased. Comparing among each of the colors, the light induced fading of magenta and its secondary color occurred rapidly. Yellow showed the greatest lightfastness. Even when this color had been exposed for 100 hr, Δ*E* was still lower than 10. There was no noticeable difference of yellow color between the non-exposed sample and the exposed samples. The cyan and green colors exhibited a moderate lightfastness. The Δ*E*'s of these two colors after 100 hr exposure were in the range of 20.

The dye molecules on the uncoated sheets can directly absorb the photon energy which causes the dye molecules to be raised into an excited state. In this state, unstable and reactive molecules may dissipate their energy by transferring energy to oxygen molecules, which are thereby excited to the singlet state as shown in the following equations.[7]

$$D + h\nu \rightarrow {}^{1}D^{*} \rightarrow {}^{3}D^{*} \tag{2}$$

$${}^{3}D^{*} + O_2 \rightarrow D^{*} + {}^{1}O_2 \tag{3}$$

$${}^{1}O_2 + A \rightarrow AO_2 \tag{4}$$

The formation of singlet oxygen is a key intermediate in the photooxidation of an azo dye, as shown in Fig. 3.[7] In this research, magenta and black dyes, which exhibit the low light fastness are azo dyes. Very interestingly, the yellow dye, which is also a diazo dye, exhibits good light fastness. This property is possibly attributable to its symmetrical structure. The symmetrical molecule generally shows a higher light fastness than unsymmetrical molecules like the magenta and black dyes. As shown in Fig. 3(a), the azo dye undergoes enol-keto tautomerism. The singlet oxygen degrades such azo dyes to give small fragments of a diazonium salt and, moreover, the photoreduction of an azo dye can also occur in the presence of light and some hydrogen donor.[8] The excited azo dye may accordingly undergo radical formation upon exposure. The radical formation leads, in turn, to the cleavage of the azo bond to yield derivatives of aniline

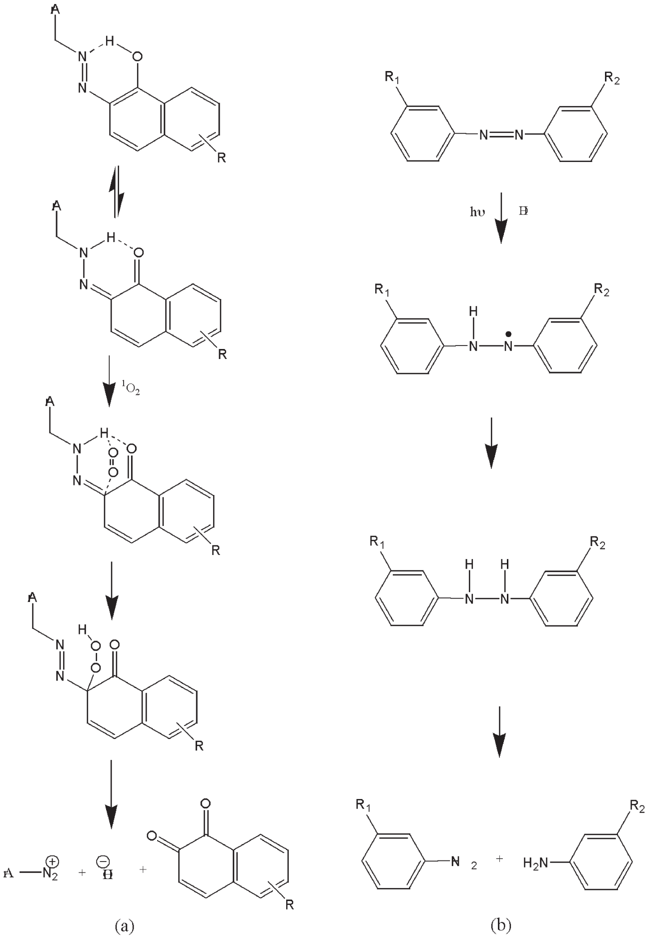


Figure 3. Photodecomposition mechanism of an azo dye (a) oxidative mechanism (b) reductive mechanism.

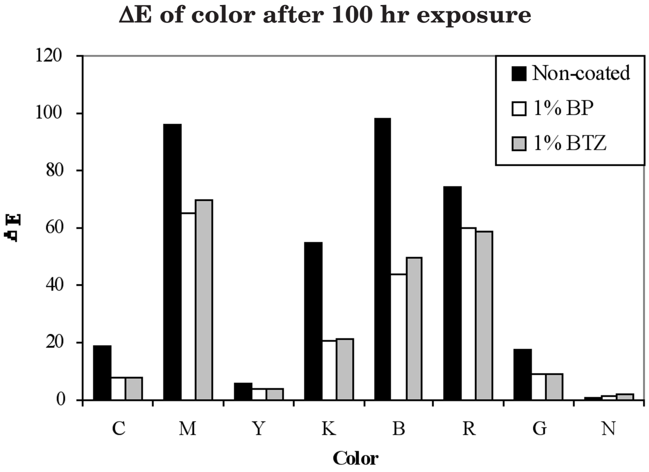
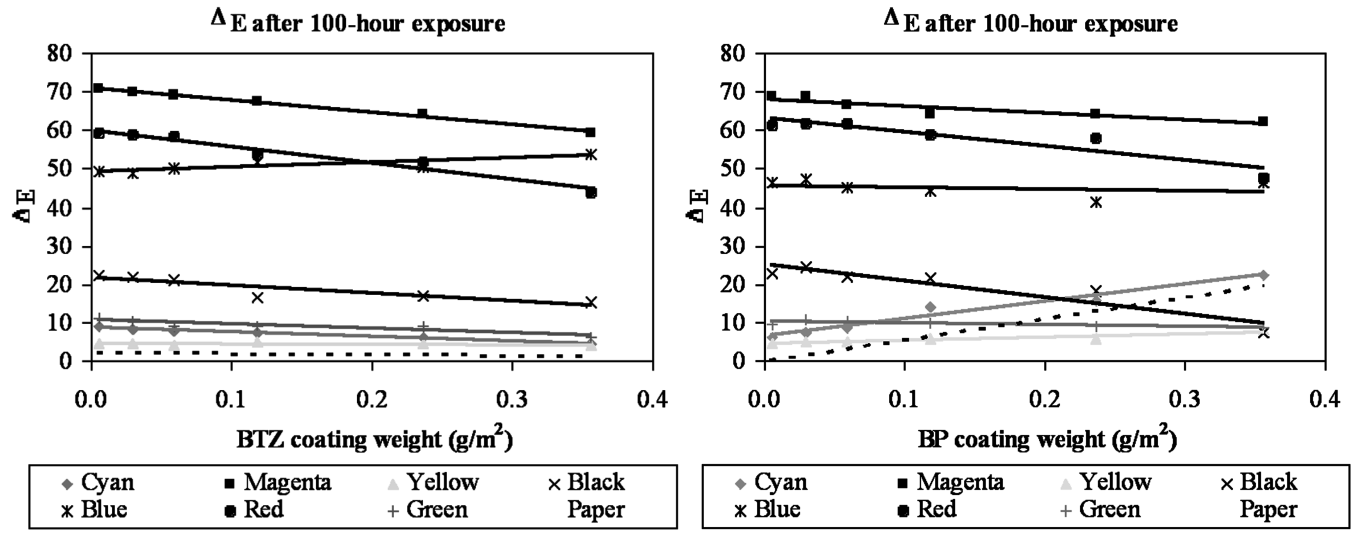


Figure 4. Comparison of *ΔE* of colors after 100-hr exposure on UV absorber coated sheets (coating weight of UV absorber = 0.06 g/m^2, C = cyan, M = magenta, Y = yellow, B = blue, R =red, G = Green and N = no color area).

Effect of UV Absorber on Color Fading

Compared to the uncoated sheet, all of the ink colors, printed on 1% by wt. BTZ coated sheets, exhibited a better light fastness as shown in Fig. 4. The Δ*E*'s of colors



(a) BTZ derivative

(b) BP derivative

Figure 5. Dependence of *ΔE* on the coating weight of (a) BTZ derivative and (b) BP derivative after 100 hr exposure in the Xenon weather-o-meter.

obviously decreased, especially in the magenta, blue, red and black colors. It was found that the fading rates of the colors on the UV absorber coated sheets were significantly lower when compared with those of the uncoated sheet. The UV absorber containing layers partially reduce the transmission of UV radiation, so that the light induced fading of dye caused by the UV absorption does not take place as rapidly. The fading of the various colors will then be retarded. When the type of UV absorber was changed to be the BP type, the results obtained show the same trend as with the BTZ type. There is no significant difference of the color patches on each coated sheet. However, it was found that fading of the less lightfast colors still occurred. We assume that the amount of UV absorber in the coated layer was not sufficient to absorb all the incident UV energy.

When the UV absorber concentration was varied as shown in Figs. 5(a) and 5(b), we found that an increase in the BTZ coating weight in the coated layer could reduce the fading extent of magenta, red and black colors; although the fading of the blue color increased slightly. In case of the BP type, the Δ*E*'s of magenta, red and black colors showed a noticeable decreasing trend with increasing UV absorber coating weight. The Δ*E*'s of cyan and non-printed areas significantly increased however. The increasing Δ*E* could be caused by increases in coating weight of the BP type UV absorber, which additionally absorbs in the spectral region 440–480 nm, to give a yellowish coated layer. This absorption particularly reduces the reflectance of the cyan color. To conclude, an increase in either BTZ or BP type UV-absorber in the coated layer provides more effective improvement in the light stability of dye-based ink jet ink. However, the BP type UV absorber exhibits a yellowing problem at high UV absorber concentration. This yellowing problem causes an unsatisfactory background of the printed substrate. Therefore, a comparison between BTZ and BP type UV absorbers indicated that the BTZ type UV absorber is more useful with respect to both lightfastness and satisfactory print appearance, while the BP type UV absorber provides only good lightfastness.

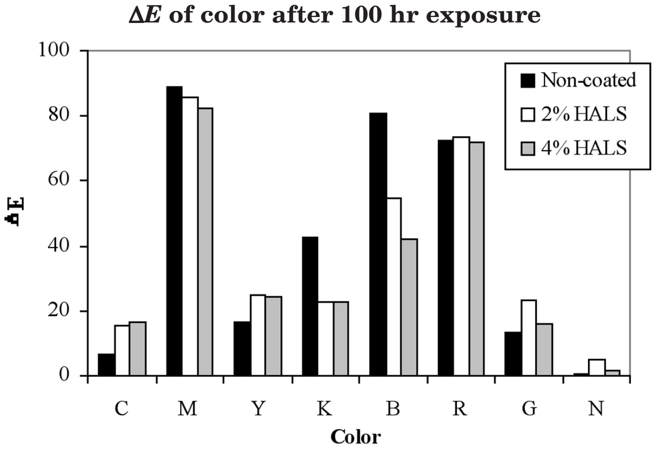


Figure 6. Comparison of Δ*E* of color after 100-hr exposure on HALS coated sheet [coating weight of HALS = 0, 0.12 (2% HALS), 0.24 g/m^2 (4% HALS), C = cyan, M = magenta, Y = yellow, B = blue, R = red, G = Green and N = no color area].

Effect of HALS and Nitrogen Containing Binder

Figure 6 shows the result of the Δ*E*'s of the dye-based ink jet ink on coated sheets and uncoated sheet after 100 hr exposure. It was found that only the light fastness of black and blue colors on the HALS coated sheets were significantly improved; the Δ*E*'s of cyan, yellow, green and background colors on the HALS coated sheets were larger than the Δ*E*'s of these colors on the uncoated sheet. The results imply that the HALS coated layers cannot protect the dye molecules from radiative attack. It is unstable under strong light exposure conditions. Therefore, the binder could possibly be decomposed and free radicals generated. These free radicals may then react with the dye molecules and accelerated the photodecomposition of the dye molecules. Another possible cause for the increase in the Δ*E* of color in the HALS

TABLE II. ΔEs of colors after 120-min ozone exposure.

Substrate	ΔE of color after 120-min ozone exposure							
	Cyan	Magenta	Yellow	Black	Blue	Red	Green	Base
Uncoated	25	3	1	48	26	3	35	1
0% HALS	1	0	0	1	2	1	1	0
2% HALS (0.12 g m^{-2})	1	1	1	1	1	1	1	1
4% HALS (0.24 g m^{-2})	1	1	0	1	0	1	1	1

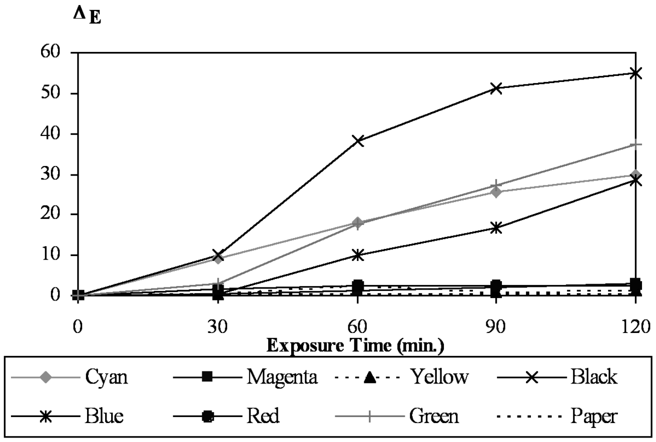


Figure 7. ΔEs of the dye-based ink jet ink on the uncoated sheet under ozone exposure.

coated layer is polyethyleneimine or (PEI). In this research, Tinuvin 123 is a non-aqueous HALS, which cannot be dissolved in the aqueous system. Therefore, PEI is added to stabilize the dispersion of HALS in the coating solution. Some previous work indicated the unfavorable effect of the nitrogen containing binders on ink jet ink prints.[2] The nitrogen containing polymer lowers light fastness of the dye-based ink jet ink, when used as a coating vehicle and binder.

However, in case of the blue color, catalytic fading may accelerate the color change.[7,8] When the magenta color was superimposed on the cyan color, the magenta dye noticeably faded faster than the magenta alone. The phthalocyanine cyan dye could produce singlet oxygen by photosensitization,[9] which then may oxidize the magenta dye. This phenomenon is possibly retarded in the coated layer through interrupting the formation of singlet oxygen from the photosensitization of the cyan dye. Therefore, oxidation of magenta dye by the singlet oxygen in the blue color is delayed.

Ozone-Induced Fading

Apart from the light induced fading of dye-based ink jet ink, some oxidative gases such as ozone, NO_x and SO_x are also a cause of the fading of the ink jet ink in a real world condition. In this work, the ozone induced fading of the dye-based ink jet ink on the uncoated and HALS coated sheets was tested. Figure 7 shows the ΔE's of colors printed on the uncoated sheet after 120 min ozone exposure. The results show that ozone induced fading of black, cyan, green and blue colors occurs rapidly on the uncoated sheets. After 120 min exposure, the ΔE's of these four color patches were above 20. We could explain that these colors, composed of phthalocyanine dye, actively react with the ozone gas. However, the mechanism of this oxidation reaction is not clearly known at present. There are two possible assumptions. The first one is the oxidation of the central metal ion by the ozone gas. The second one is the oxidation of the C=N bond. When the coated sheets (with or without HALS) are compared as shown in Table II, the ozone fastness of these color patches is significantly increased. The ΔE's in the range of 25 – 40 were reduced to the range of 1 – 4. This result implied that the ozone-induced fading of the dyes on the coated sheets did not take place. The reflectance spectra of cyan and its secondary colors (blue and green) after 120 min ozone exposure as shown in Fig. 8 indicated that the maximum reflection of each color was not significantly decreased, regardless of the coating weight of HALS. Therefore, an improvement of ozone fastness is not really related to HALS in the coated layer. However, the increase in the ozone fastness may be attributed mainly to a decrease in air permeability of the ink-receiving layer, because the oxygen permeability of PVA film is very low (5×10^{-8} cm^{-3}/cm^2 s Pa).[10] Therefore, it prevents the ozone gas from penetrating the coated layer and reacting with the dye molecules.

Conclusion

A UV absorber coated on the ink jet substrate can improve the light fastness of dye-based ink jet ink. The light fastness of a dye-based ink jet print is in a direct proportion to the amount of UV absorber in the coated layer. The type of UV absorber does not strongly affect the effectiveness of light fastness of the dye-based ink jet ink, but it does show an effect on the background color of the ink jet printing substrate. The benzotriazole containing UV absorber does not produce yellowing of the coated sheets while the hydroxybenzophenone containing UV absorber exhibits this problem, which causes an unsatisfactory background. Therefore, these two properties have to be compromised. Besides the UV absorber coating, HALS coated sheets did not show an effective improvement in the light fastness of dye-based ink jet ink. The coating of the hindered amine light stabilizer is also not really necessary to protect against ozone induced fading of the dye-based ink jet ink prints.

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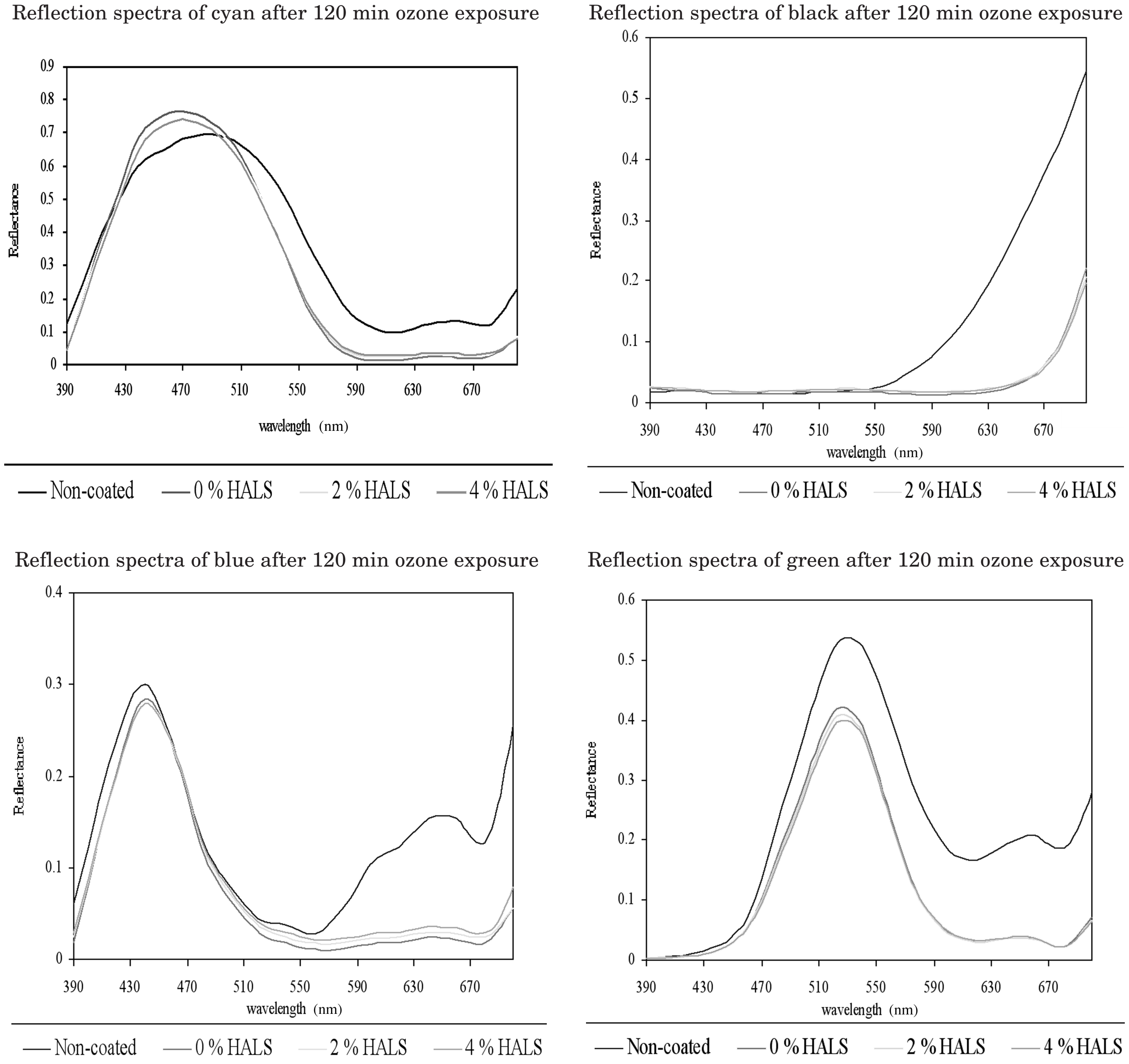

Figure 8. Spectral reflection curves of the colors after 120 min ozone exposure.

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