CHAPTER 4

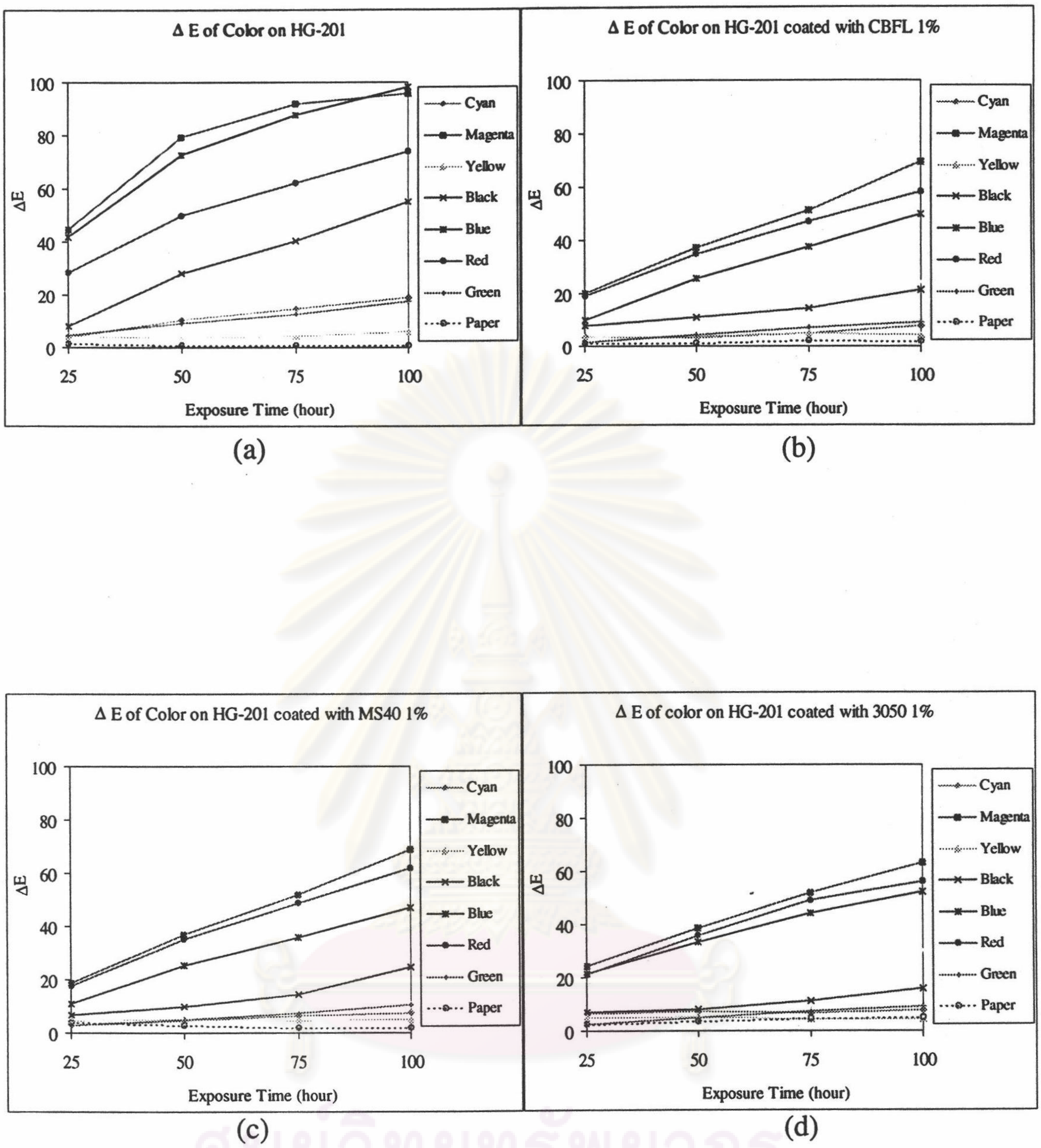
RESULTS AND DISCUSSION

In this research, the term "light fastness" is referred to the stability of a color under light exposure. It can be exhibited in terms of color difference (ΔE),[5,13] which can be calculated from Equation 3-1. The ΔE of a color is usually inversely proportional to the fastness. The higher the ΔE value of a color, the lower the fastness of a color.

4.1 Effect of UV absorber on light fastness of the dye-based inkjet ink

The dye-based inkjet ink was printed on the non-coated microporous inkjet film. After exposure in a Xenon weather-o-meter, the ΔE of each color at different exposure times was shown in Figure 4-1 (a) and the color patches on the non-coated sheet were shown in Figure 4-2 (a). It was found that the ΔE of each color increased when the exposure time increased. Comparing among each color, the light induced fading of magenta and its secondary color thus occurred rapidly. Yellow color showed the highest lightfast property. Even this color had passed the 100-hour exposure, the Δ E was lower than 10. There was no noticeable difference of yellow color between the non-exposure sample and any exposed samples. The cyan and green color exhibited a moderate lightfast property. The ΔEs of these two colors at 100-hour exposure were in the range of 20.

It can be explained that the dye molecules on the non-coated sheet can directly absorb the photon energy. This phenomenon causes the excitation of the dye



Δ E of Color on HG-201

Δ E of Color on HG-201 coated with CBFL 1%

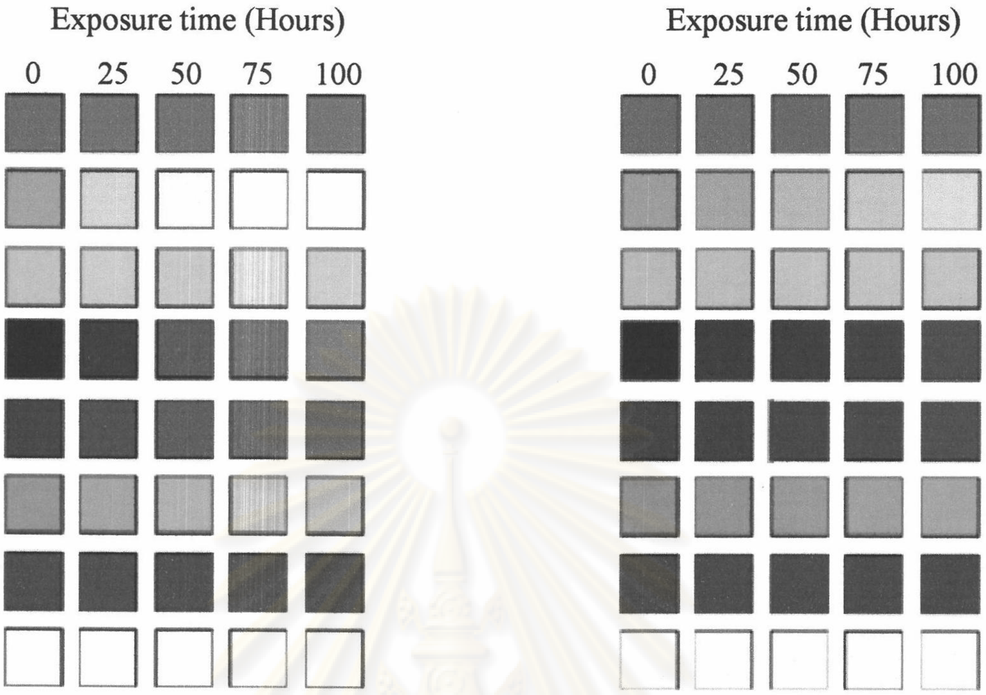
(a) (b)

Δ E of Color on HG-201 coated with MS40 1%

Δ E of color on HG-201 coated with 3050 1%

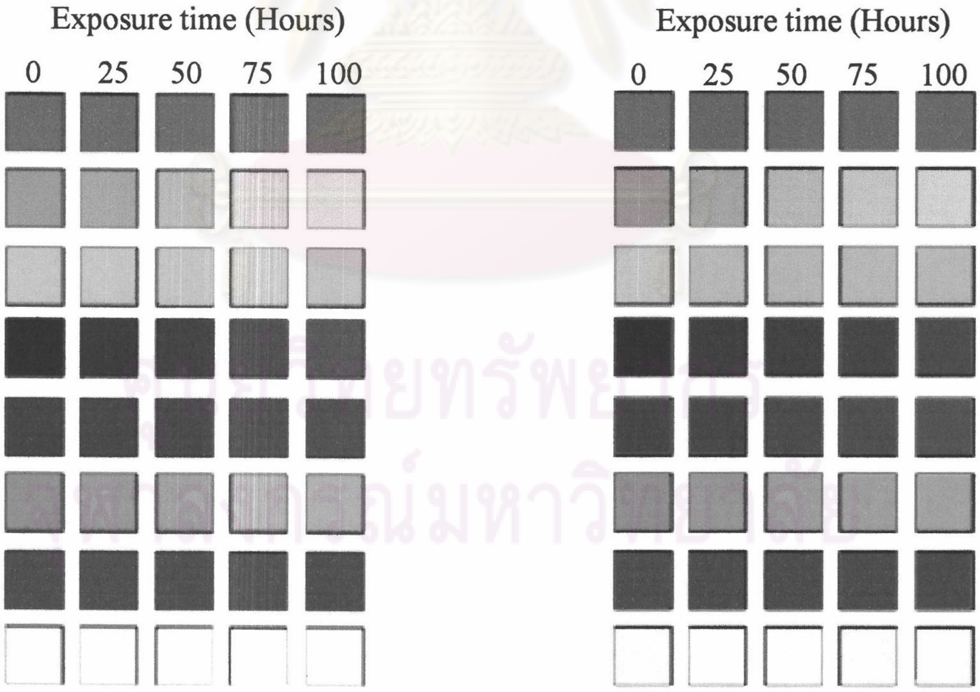
(c) (d)

Figure 4-1 ΔE of dye-based inkjet ink printed on different substrates: (a) HG-201; (b) HG-201 coated with 1% of BTZ containing UV absorber; (c) HG-201 coated with 1% of BP1 typed UV absorber; (d) HG-201 coated with 1% of BP2 typed UV absorber



a) Non-coated sheet

b) 1% BTZ coated sheet



c) 1% BP1 coated

d) 1% BP2 coated sheet

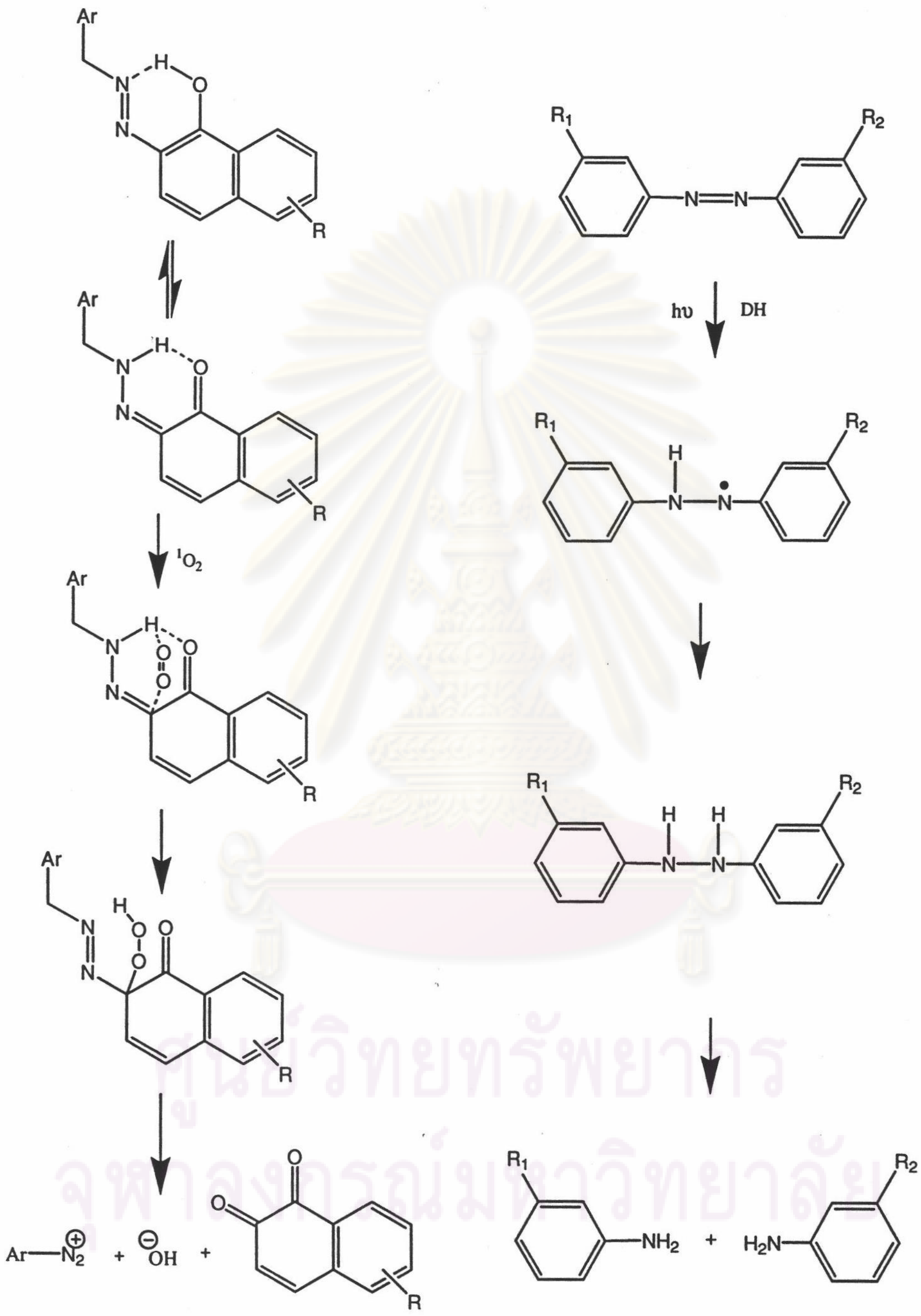
Figure 4-2 Color patches of dye-based inkjet ink on different substrates molecules to be in an energy-rich state. At this state, the unstable and reactive molecules have possibly to dissipate their energy by transferring energy to the oxygen. Oxygen in a triplet state is therefore changed to be singlet oxygen as shown in the following equation.[31]

$$D + h\nu \rightarrow {}^{1}D^{*} \rightarrow {}^{3}D^{*} \tag{4.1}$$

$$^{3}D^{*} + O_2 \rightarrow D + {}^{1}O_2 \tag{4.2}$$

$$^{1}O_2 + A \rightarrow AO_2 \tag{4.3}$$

The formation of singlet oxygen is a key intermediate in photooxidation of an azo dye. Some former works have presented the role of singlet oxygen in a photofading of the azo dye as shown in Figure 4-3(a).[32] Moreover, the photoreduction of an azo dye can also occur in the presence of light and some hydrogen donor as shown in Figure 4-3(b).[33,34] In this research, yellow dye was di-azo dye, its structure is shown in Figure 3-1. It was found that the yellow dye had a symmetrical structure. This symmetrical molecule generally shows the higher light fastness than the unsymmetrical molecule like the magenta and black dye.[35] In case of magenta, which shows the worst light fastness, its chemical structure was mono-azo dye, its structure as shown in Figure 3-1. When an azo functional groups in the magenta dye was decomposed, the molecule transforms to be a non-azo molecule, which is colorless (Figure 4-4). In contrast to the black dye, it contains the mixture of di-azo and tri-azo dye. When an azo functional group in these dye molecules was broken down, the decomposed product still retained one or two azo functional groups in their structure (as shown in Figures 4-5 and 4-6). These molecules can exhibit the color. Therefore, black color was changed to be reddish black after exposure as shown in Figure 4-2 (a).



(a) (b)

Figure 4-3 Photodecomposition of an azo dye (a) oxidative mechanism (b) reductive mechanism

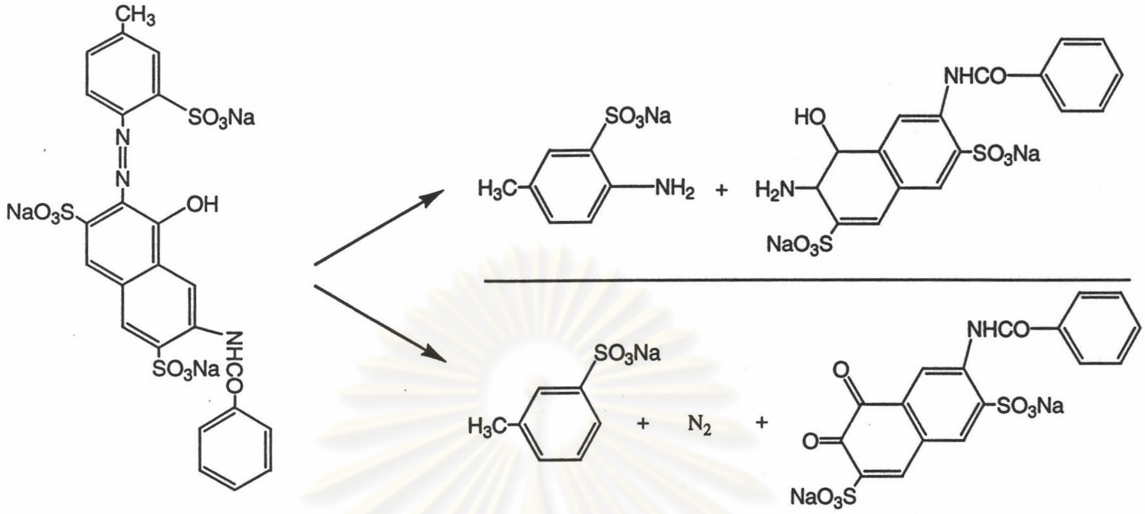


Figure 4-4 Photodegradation of magenta dye

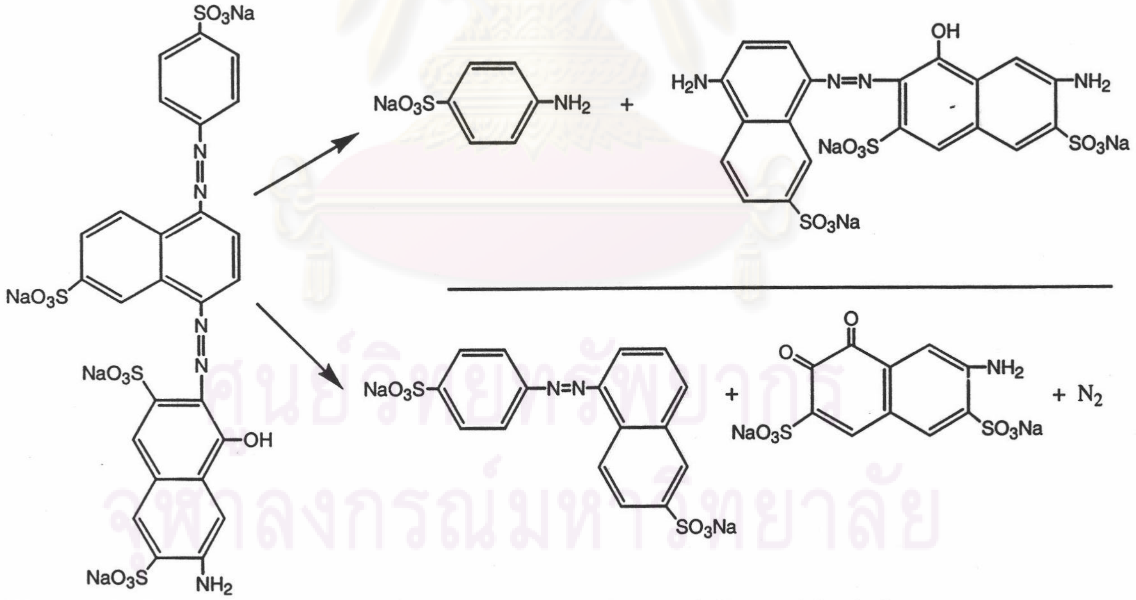


Figure 4-5 Example of photodecomposed products of di-azo black dye

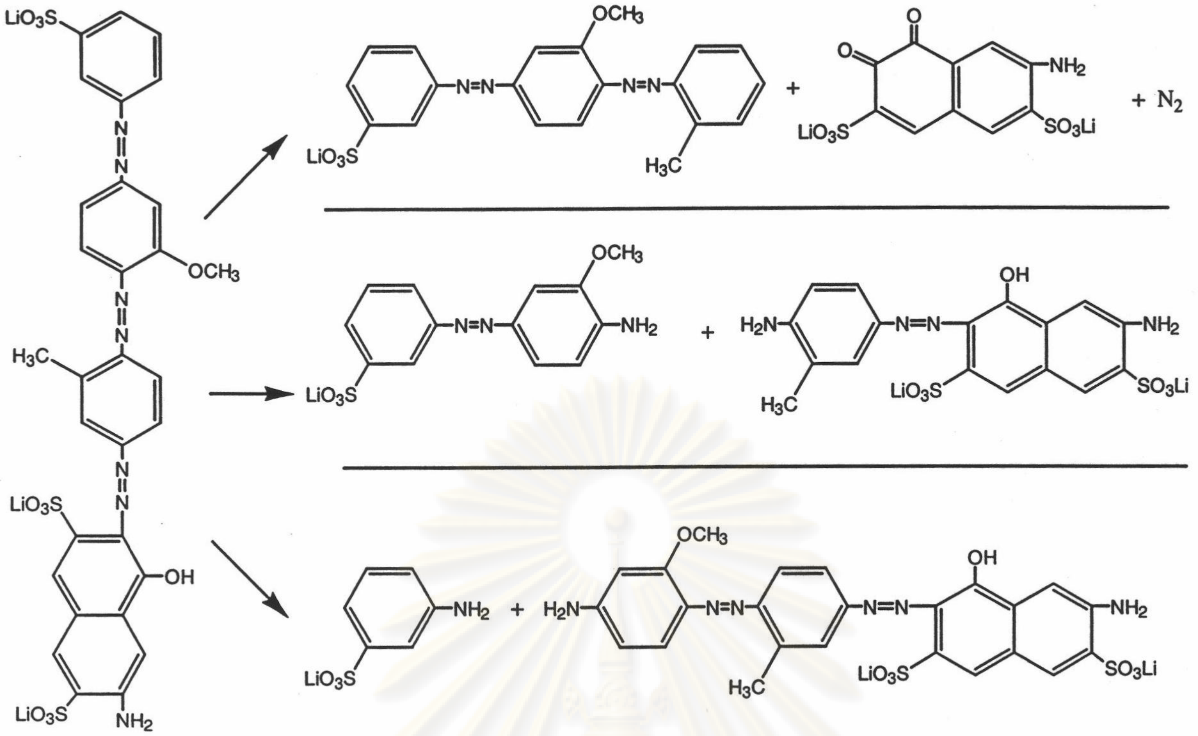


Figure 4-6 Example of photodecomposed products of tri-azo black dye

Table 4-1 Comparison of fading rate of color

Substrate	Apparent fading rate of colors ($\times 10^{-3}$)						
	Cyan	Magenta	Yellow	Black	Blue	Red	Green
Non-coated	0.18	9.98	1.70	14.86	7.79	29.09	2.00
BTZ 1%	-0.07	3.13	-1.63	7.11	1.82	24.34	0.19
BP1 1 %	-0.37	2.54	-1.45	8.49	0.42	24.82	0.16
BP2 1%	-0.13	3.35	-1.65	4.91	1.27	22.58	0.14

On the contrary of the non-coated sheet, all of the colors, printed on 1% w w^{-1} benzotriazole (BTZ) derivative type of the UV absorber (Cibafast W liquid) coated sheets, exhibited a better light fastness as shown in Figures 4-1(b) and 4-2 (b). The Δ Es of colors obviously decreased especially in the magenta, blue, red and black color. Moreover, when the type of UV absorber was changed to be benzophenone (BP) derivative type (Uvinul MS40 (BP1) and Uvinul 3050 (BP2)), the results so obtained also showed the same trend as the one from BTZ derivative type of UV absorber. There is not quite different of the color patches on each coated sheet. Figures 4-1 (c) and 4-1(d) show the ΔEs of colors printed on 1% w w^{-1} Uvinul MS40 coated HG-201 and 1% w w^{-1} Uvinul 3050 coated HG-201, respectively. Table 4-1 exhibits the comparison of apparent fading rate which, was calculated using the following equation:

$$\text{Fading rate} = d[\ln(R)]/dt \qquad (4\text{-}1)$$

Where R = Reflectance

t = exposure time (hour)

It was found that the fading rate of the colors on UV absorber coated sheet was significantly low when compared with the non-coated sheet. This can be described that the UV absorber coated layers can partially reduced the transmission of UV light as shown in their transmission spectra in Figure 4-7. When the high energetic photon was partially inhibited to bombard the dye molecules, the light-induced fading of dye, which is caused by the UV energy absorption of dye molecules does not rapidly take place. The fading of colors will also be delayed.[1] However, it was found that the fading of the low lightfast color still occurred. This was assumed that the amount of UV absorber in the coated layer is not sufficient to absorb all incident UV energy and cannot protect the dye molecules for the long time exposure. Moreover, BP2 coated layer shows absorption in the visible range between 380-400 nm. This is an evidence of the yellowing of coated layer which will be discussed later.

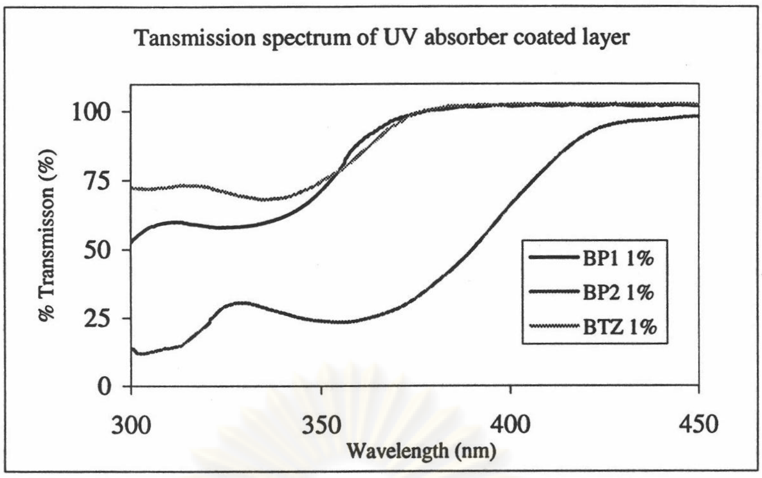


Figure 4-7 Transmission spectrum of UV absorber coated layer (Coated on PP film)

In summary, comparison of the three UV absorbers was shown in Figure 4-8. ΔEs of these coated sheets after 100-hour exposure were obviously lower than the non-coated ones. It can certainly be indicated that UV absorber coated sheets can improve the light fastness of dye-based inkjet ink on the microporous type inkjet film. However, the type of UV absorber does not strongly affect the fading reduction of the dye. The ΔE between the BTZ and the two BP types of the UV absorber coating is slightly different.

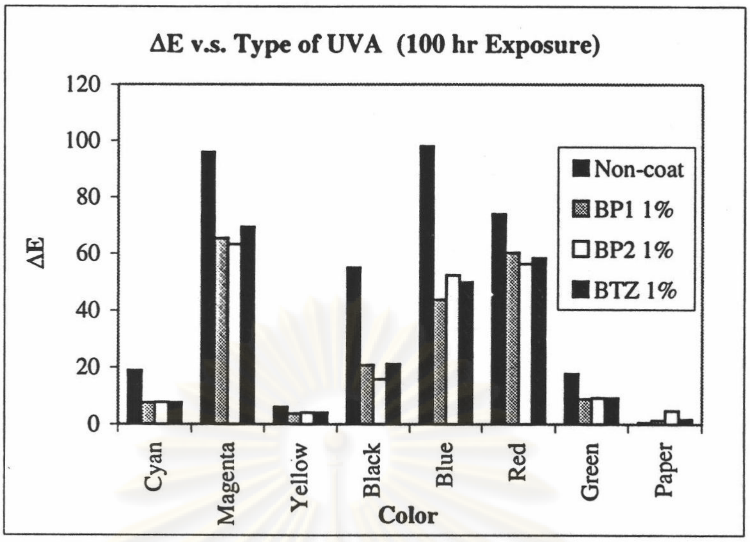


Figure 4-8 ΔEs of color patches printed on different substrates after 100-hour exposure in the Xenon weather-o-meter

4.2 Dependence of light fastness of the dye-based inkjet ink on UV absorber concentration

Based on the Lambert-Beer Law (Equation 2.1), a parameter which influences the effectiveness of UV absorber is the concentration of UV absorber. Therefore, variation of the UV absorber concentration in the coated layer is tested. Figure 4-9 shows the dependence of the light fastness of dye-based ink on BTZ containing UV absorber concentration in coated layer. The color patches on the BTZ containing UV absorber were also shown in Figure 4-10. The light fastness of magenta, red and black color at 100-hour exposure increased when the BTZ containing UV absorber concentration increased. Cyan, green and yellow color, which exhibited a good lightfast property were stable at any UV absorber concentrations, but the fading of blue color was unexpectedly increased when the concentration of BTZ containing UV absorber was increased.

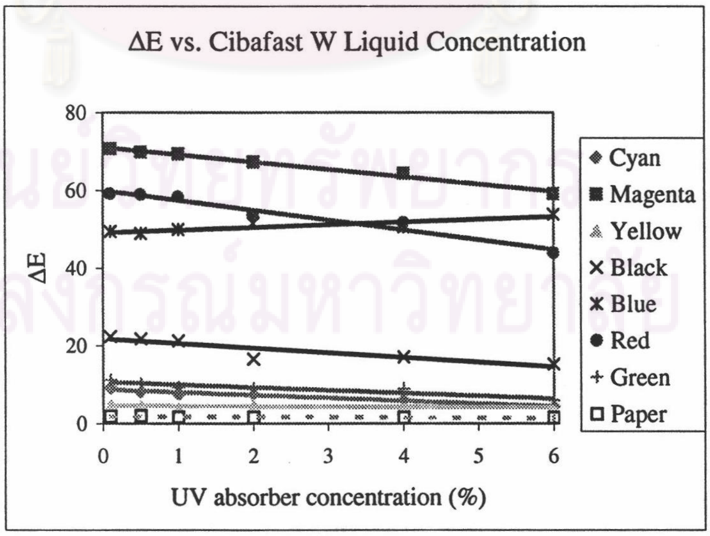
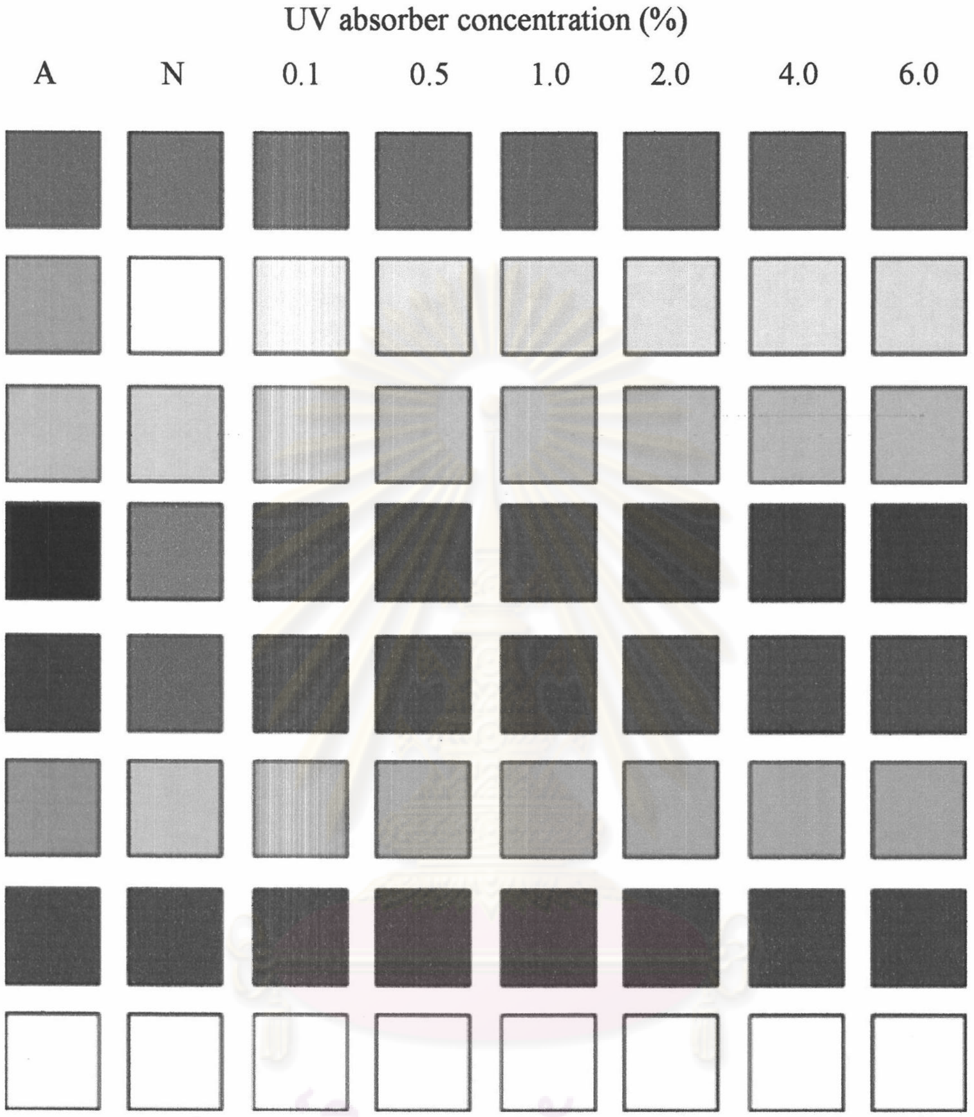
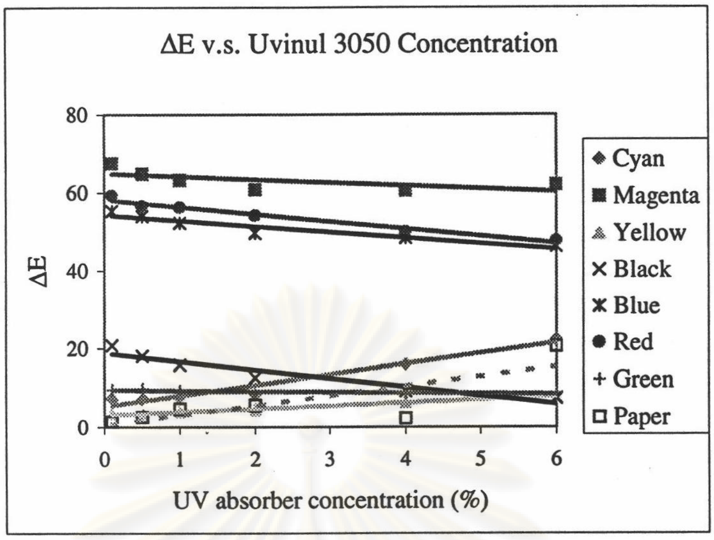


Figure 4-9 Dependence of ΔE on the concentration of BTZ containing UV absorber after 100-hour exposure in the Xenon weather-o-meter

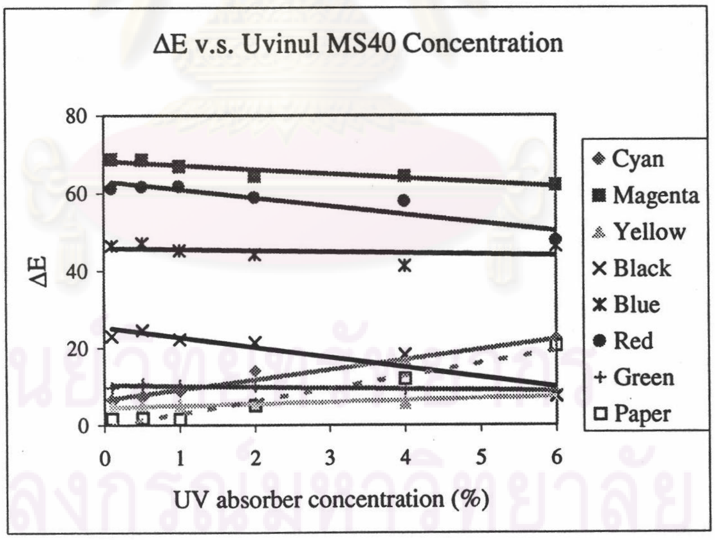


A = non-coated sheet before exposure; N = non-coated sheet after 100 hour-exposure

Figure 4-10 Color patches of dye-based inkjet ink on BTZ coated sheet after 100-hour exposure

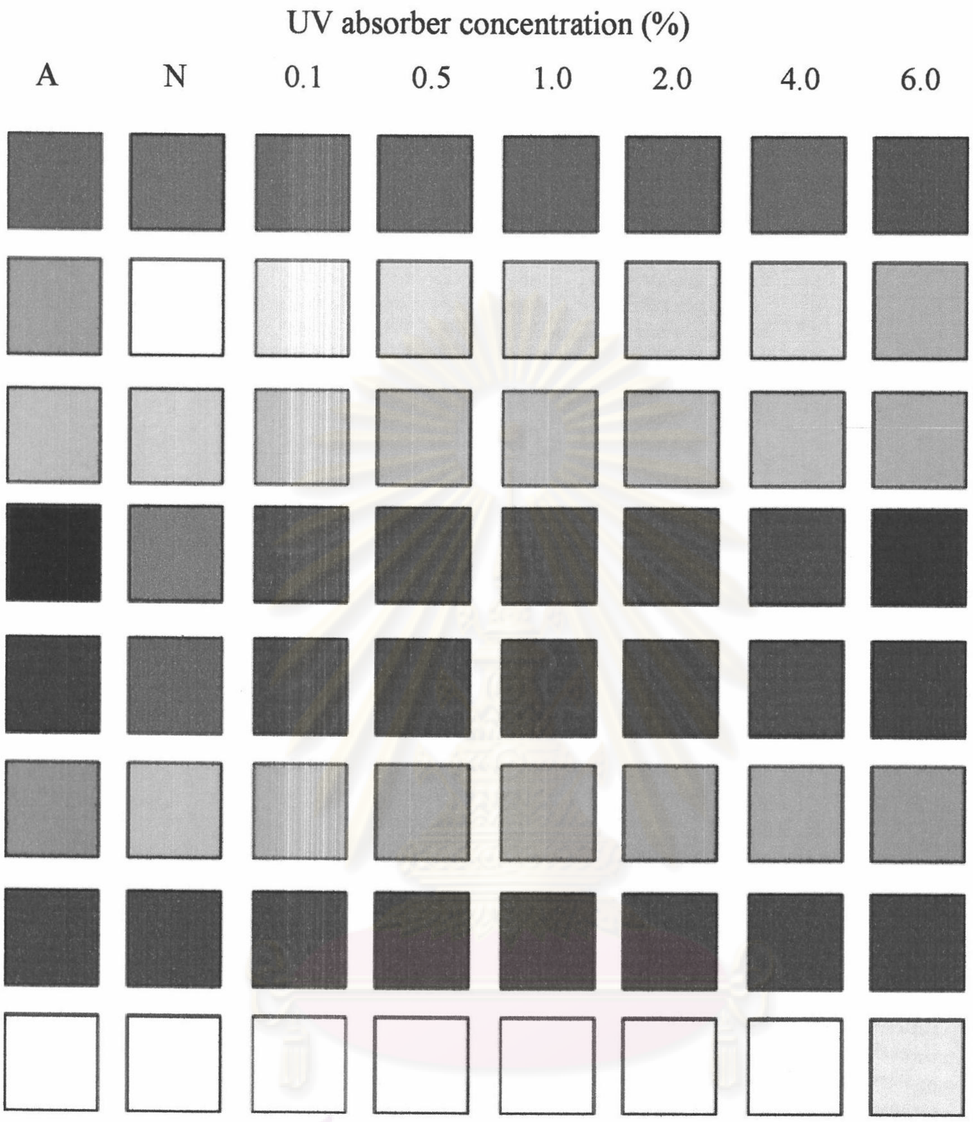


(a)



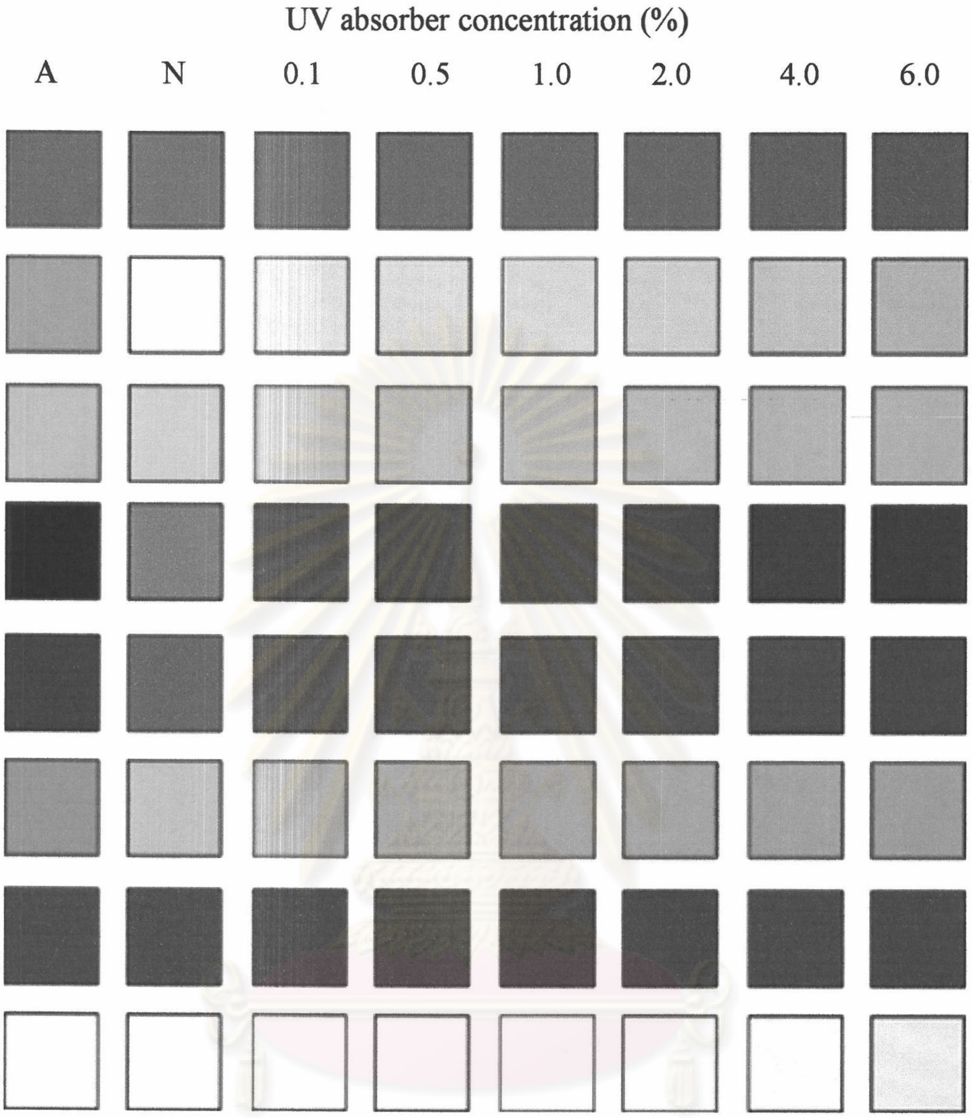
(b)

Figure 4-11 Dependence of ΔE on the concentration of BP containing UV absorber after 100 hour exposure in the Xenon weather-o-meter (a) BP1 (Uvinul MS40) and (b) BP2 (Uvinul 3050)



A = non-coated sheet before exposure; N = non-coated sheet after 100 hour-exposure

Figure 4-12 Color patches of dye-based inkjet ink on BP coated sheet after 100-hour exposure



A = non-coated sheet before exposure; N = non-coated sheet after 100 hour-exposure

Figure 4-12 (continued) Color patches of dye-based inkjet ink on BTZ coated sheet after 100-hour exposure

In case of the BP containing UV absorber, the relationship between the ΔEs and UV absorber concentration was shown in Figure 4-11 and the color patches on the BP coated sheets were shown in Figure 4-12. The trend of the ΔE of color on BP1 coated sheets was similar to the trend of the ΔE of color on BP2 coated sheets. An increasing concentration of BP containing UV absorber significantly affected the reduction on the ΔE of red and black color. It, however, slightly decreased the photofading of magenta color. Yellow and green colors, which were stable to the light exposure were not affected by the amount of UV absorber on the coated layer. However, the trend of the ΔE of blue color on the BP1 coated sheets was different from the trend of ΔE of blue color on BP2 coated sheets. The former was constant while the later was slightly decreased. The results obtained also indicated that both of the coated sheets exhibited an increasing ΔE value of cyan and non-printed areas when the amounts of BP containing UV absorber in the coated layer were increased.

In order to describe this phenomenon, a color of the coated layer, which can be represented by the color of non-printed area was considered. Figure 4-13 shows yellowing of the coated layer, which is represented in the value of CIE-b*, at 0 and 100 hour exposure. The coated layer, which has the value of CIE-b* above 0 can be detected by eye. In case of BP1 UV absorber (Uvinul MS40) coated sheet, it was found that the yellowing of the unexposed coated layer at any concentration is not clearly noted. When the coated sheets were exposed, the yellowing of non-printed area is directly proportional to the UV absorber concentration in the coated layer. The yellowing can be detected by eye at the concentration of 2 % w w^{-1} or above. The BP2 UV absorber (Uvinul 3050) was significantly different from BP1. Even though the coated sheets have not been exposed, the yellowing of the coated layer still occurred even the UV absorber concentration is only 0.5 % w w^{-1}.

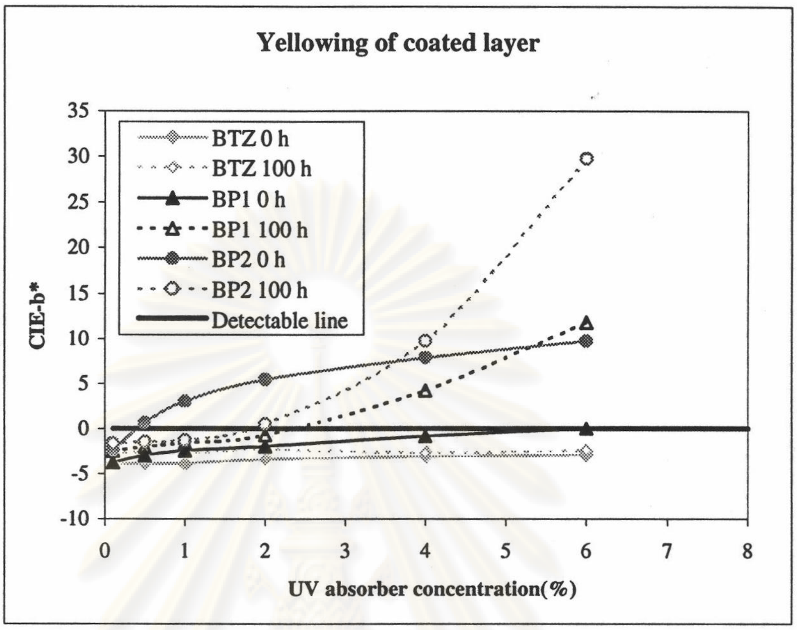


Figure 4-13 Yellowing of the coated layer

The increase in yellowing of the coated layer is the only reason for the color change on the non-printed area. Therefore, the ΔE of the non-printed area on the coated sheet with high UV absorber concentration is large. This phenomenon directly involves in the increasing ΔE of the cyan color. As shown in Figure 4-14, spectral reflectance of the yellowish non-printed areas is distinctly different from the spectral reflectance of the colorless non-printed areas. A partial absorption of spectrum is found at 420-480 nm. This additional absorbing region strongly affects the reflection spectrum of cyan color. It can be seen that the maximum reflection wavelength (λ_{max}) of cyan color is then shifted from 480 nm to 500 nm. Therefore, the color measurement of cyan color on the yellowing substrate is not precisely correct.

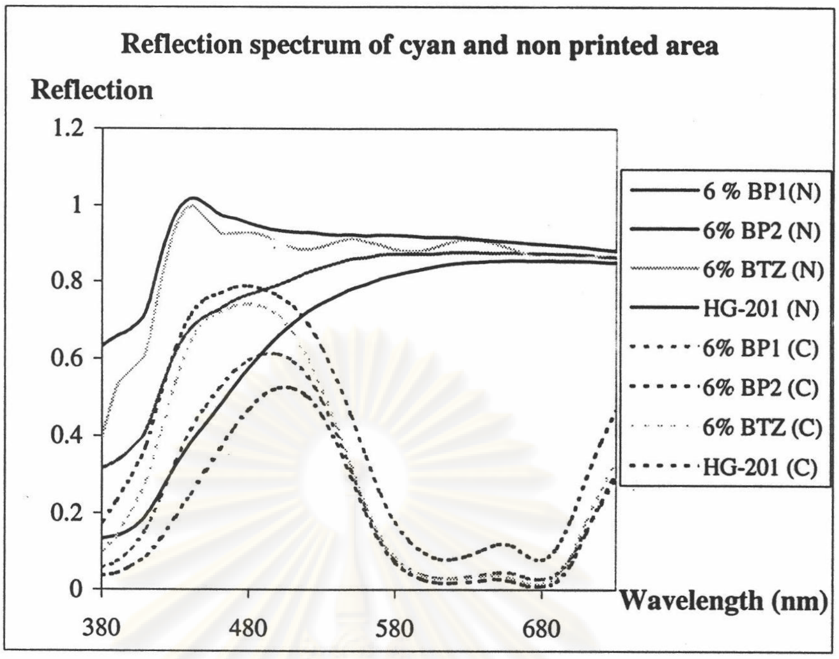


Figure 4-14 Reflection spectrum of cyan (C) and non-printed area (N) of the printed substrate after 100-hour exposure

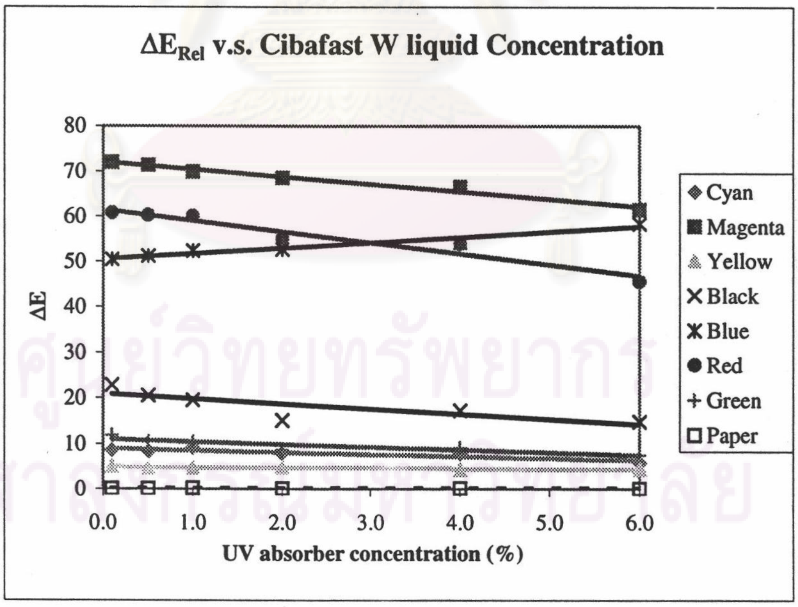
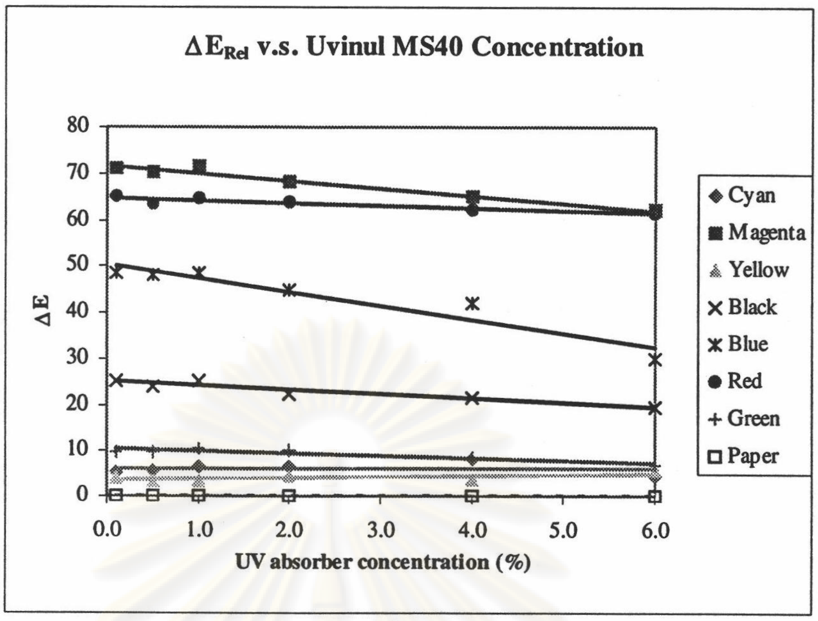


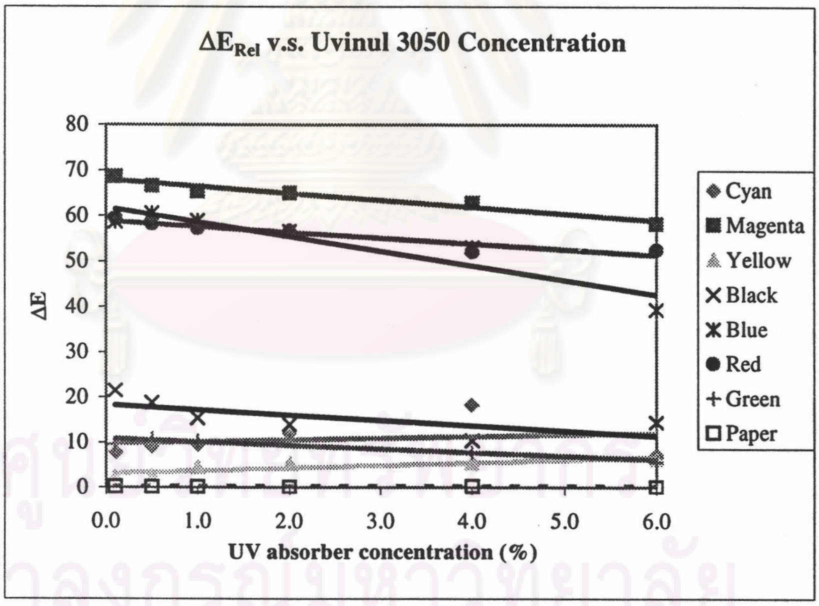
Figure 4-15 Dependence of ΔE measured in relatively white point mode on the concentration of BTZ typed UV absorber after 100 hour exposure

In order to eliminate the effect of yellowish background, the color value of all the printed samples were re-measured in the relatively white point mode. In this mode, the color measuring device is re-calibrated with the non-printed area on every sample. Figure 4-15 shows the dependence of the ΔE measured in a relatively white point mode on the BTZ containing UV absorber concentration. As clearly shown in Figure 4-15 that the trend of ΔE did not significantly changed. Furthermore, the color values measured either in an absolute or relatively white point mode are also not significantly different.

Figures 4-16 (a) and (b) show the relation of UV absorber concentration and the ΔE measured in the relatively white point mode. The trend of the ΔE of cyan color on both BP types of the UV absorber shows more steadily. This result indicates that increasing BP containing UV absorber does not influence the fading of cyan color. On the other hand, it can be assumed that the light fastness of cyan color on the UV absorber coated layer is not affected by the UV absorber concentration in the coated layer. Moreover, there are also some observations about the trends of other colors. The blue color shows higher light fastness when the UV absorber concentration is increased, while the red and black colors show less effect of UV absorber on their light fastness.



(a)



(b)

Figure 4-16 Dependence of ΔE measured in relatively white point mode on the concentration of (a) BP1 and (b) BP2 UV absorber after 100-hour exposure

Figure 4-17 shows the dependence of fading rate on the UV absorber concentration. In case of BP containing UV absorber, the fading rates of cyan and yellow color are not affected by the amount of UV absorber in the coated layer. The fading of cyan, magenta, black, blue and red is dependent on the type and amount of UV absorber. The amount of BP containing UV absorber in the coated layer shows more influence on the fading rate of those colors. The higher UV absorber concentration, the lower fading rate. This trend is similar to the fading rates of black and red color when BTZ UV absorber is used. However, unlike the BP containing UV absorber, when the amount of BTZ containing UV absorber was increased, the fading rates of cyan, magenta and blue color are slightly changed.

To conclude, an increase in both BTZ and BP containing UV absorber in the coated layer provides the more effectiveness on the improvement of dye-based inkjet ink. However, BP containing UV absorber exhibits a problem of yellowing of the coated layer at the high UV absorber concentration. This problem causes an unsatisfactory background of the printed substrate. Therefore, comparison between BTZ and BP containing UV absorbers indicated that the BTZ containing UV absorber is more effective in both lightfast property and satisfactory prints while the BP containing UV absorber provides only a good lightfast property.

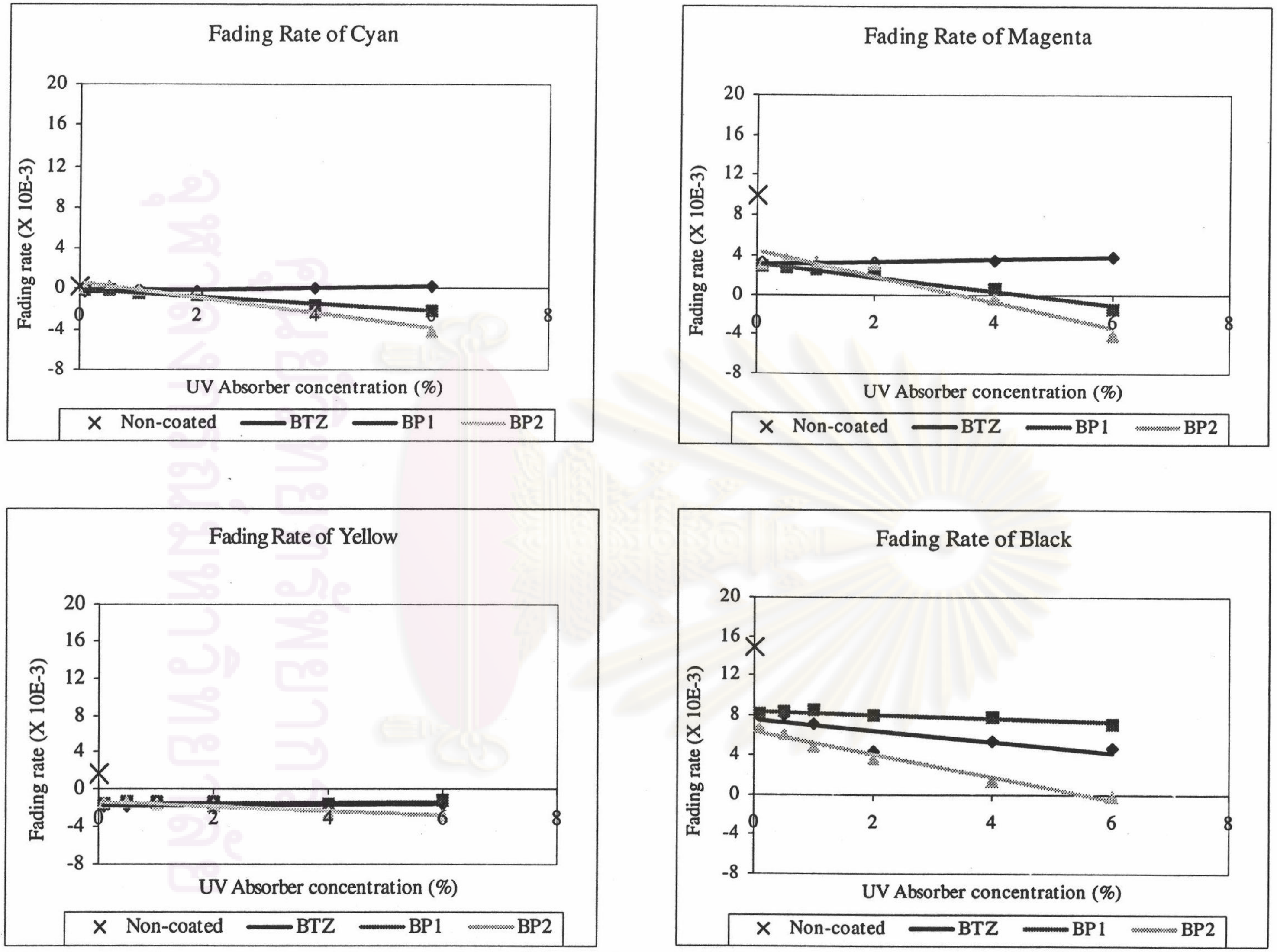


Figure 4-17 Dependence of fading rate on the UV absorber concentration

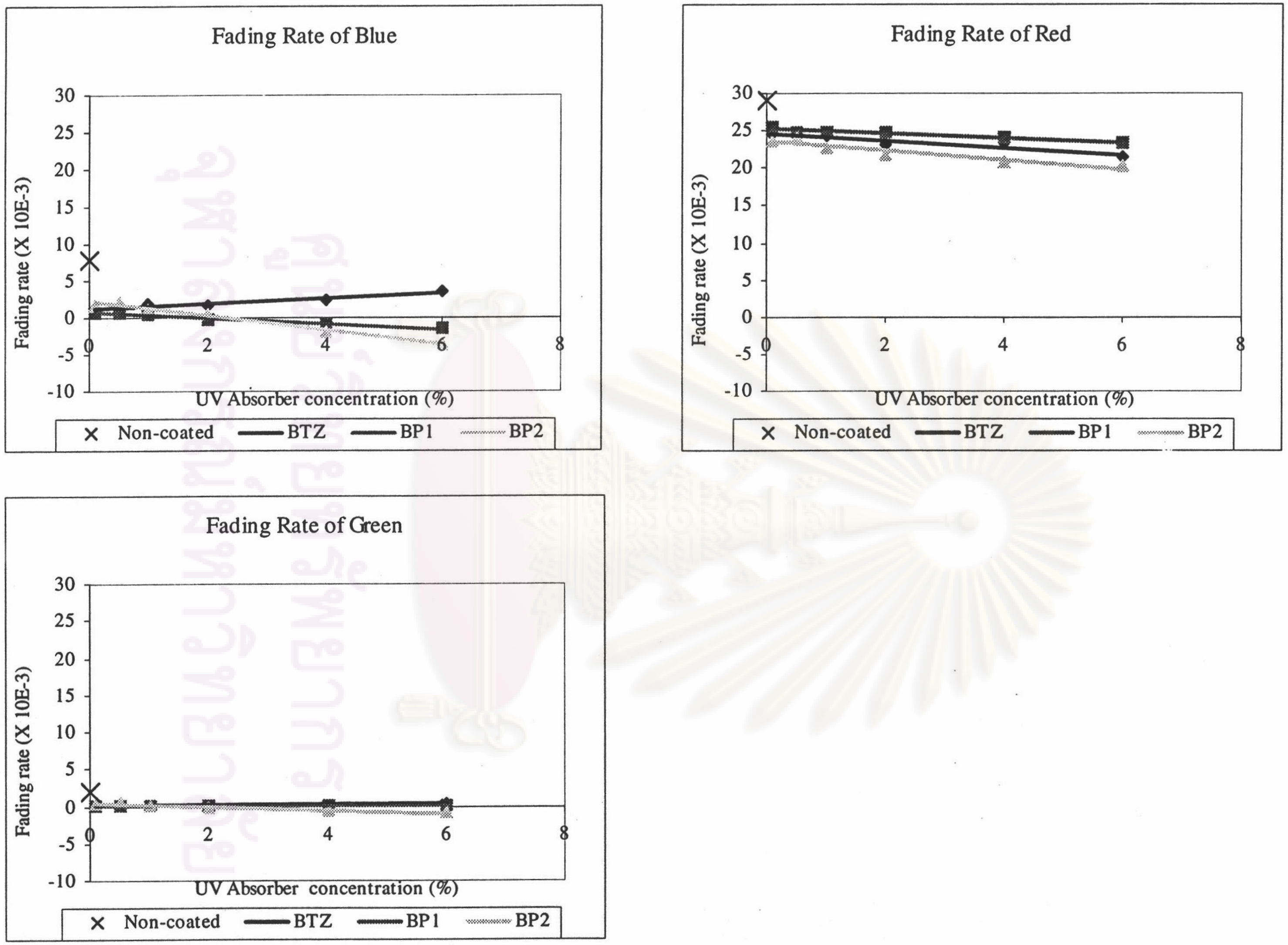


Figure 4-17 (continued) Dependence of fading rate on the UV absorber concentration

4.3 Effect of hindered amine light stabilizer (HALS) on light fastness of dye-based inkjet ink

Apart from the UV absorber, A hindered amine light stabilizer (HALS) is generally used in the light stabilization of various materials. Therefore, the effect of HALS on light fastness of the dye-based inkjet ink was evaluated to develop the light fastness property.

Then 0, 1, 2 and 4 % w w^{-1} of HALS coating solution was coated on the microporous inkjet film. After drying at the ambient temperature, the coated sheets were printed and exposed in the Xenon weather-o-meter. A non-coated sheet was used as a reference.

Table 4-2 ΔE of dye-based inkjet ink after 100-hour exposure

Substrate	ΔE of color after 100 hour exposure							
	Cyan	Magenta	Yellow	Black	Blue	Red	Green	Base
Non-coated	7	89	17	42	81	73	13	1
0 % HALS	20	87	27	28	52	75	20	4
1 % HALS	14	86	27	21	50	73	19	3
2 % HALS	16	86	25	23	55	73	23	5
4 % HALS	17	82	25	23	42	72	16	2

Table 4-2 shows the result of the ΔEs of the dye-based inkjet ink on coated sheets and non-coated sheet after 100-hour exposure. It was found that only the light fastness of black and blue color on the HALS coated sheets was significantly improved. However, the ΔE of magenta color was slightly decreased, but the ΔEs of cyan, yellow, green and background color on the HALS coated sheets were larger than the ΔEs of these colors on the non-coated sheet. Comparison among the coated sheets, it was found that when the HALS concentration in the coated layer was increased, the ΔEs of color tended to decrease slightly.

The above results can imply that the coated layers cannot protect the dye molecules from radiation attack. It is also unstable under strong light exposure. Therefore, the binder is decomposed and the free radicals are generated. These free radicals then react with the dye molecules and accelerate the photodecomposition of the dye molecules. On the other hand, when HALS is added into the coated layer, the ΔEs of color decrease. This can be explained that some free radicals are eliminated by the reaction mechanism of HALS, which is generally called "Denisov cycle" as shown in Figure 4-18.[11] The decomposition of dye molecules is partially inhibited. The higher the amount of HALS, the lower the decomposition. Nonetheless, the unused amount of free radical is still high enough to accelerate the dye decomposition. Therefore, the ΔEs of HALS coated sheets are still higher than the ΔEs of non-coated sheet even though the HALS concentration is as high as 4 %. Another possible cause of the increase on the ΔE of color on the HALS coated layer is the poly(ethylene imine)[PEI]. In this thesis, Tinuvin 123 is a non-aqueous HALS, which cannot be dissolved in the aqueous system. Therefore, PEI is used to stabilize the dispersion of HALS in the coating solution. From the previous work, there was some results indicated the unfavorable effect of the nitrogen containing binders.[20] These binders cause the lowering of light fastness of dye-based ink on those binder coating media.

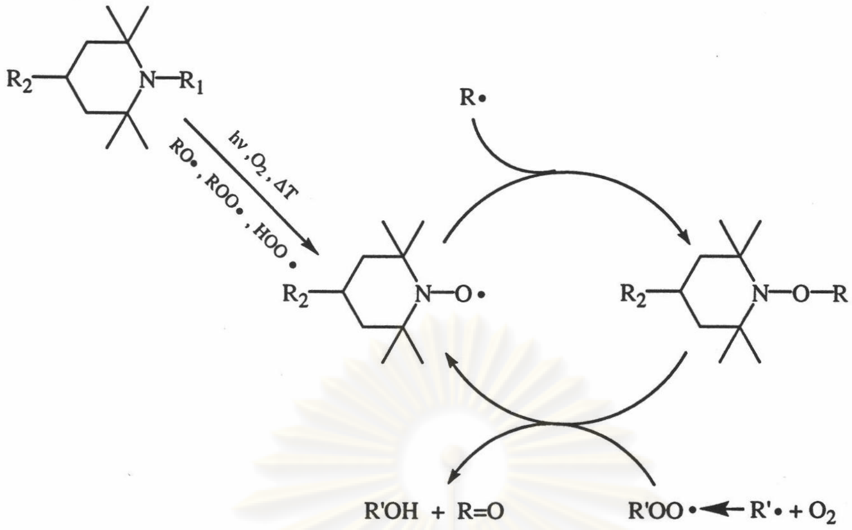


Figure 4-18 Modified Denisov cycle

However, in case of the blue color, catalytic fading accelerates the color change.[34] When the magenta color superimposed the cyan color, the magenta dye is noticeably faded faster than the magenta alone. The phthalocyanine cyan dye can produce singlet oxygen by photosensitization,[21] which then proceeds to oxidize the magenta dye. This phenomenon is possibly retarded by the coated layer through interrupting the formation of singlet oxygen from the photosensitization of the cyan dye. Therefore, the oxidation of magenta dye by the singlet oxygen in blue color is delayed.

Apart from the light induced fading of dye-based inkjet ink, some oxidative gases such as ozone, NO_x and SO_x are also a cause of the fading of the inkjet ink in real world condition. However, NO_x and SO_x are reported from a few work, to be a cause of fading. Therefore, ozone induced fading is now the focal aspect in gas-induced fading. In this thesis, ozone fastness of the dye-based inkjet ink on the non-coated and HALS coated sheets are tested.

Figure 4-19 shows the ΔEs of color printed on different HALS coated sheets after 120-minutes exposure in the ozone testing chamber. The comparison of cozone induced fading was also shown in Figure 4-20. The condition of ozone testing chamber was 3 ppm ozone concentration and 40% RH. It was found that non-coated sheets exhibited the poor ozone fastness of black, cyan, blue and green color. After 120-minute exposure, the ΔEs of these four colors are above 20. When the coated sheets were compared, the ozone fastness of these four colors was significantly increased. The ΔEs were in the range of 1-4. Increase in the ozone fastness is caused by a decrease in air permeability of the ink receiving layer by PVA film as a good gas barrier. Therefore, ozone gas cannot penetrate through the film to react with dye molecules.

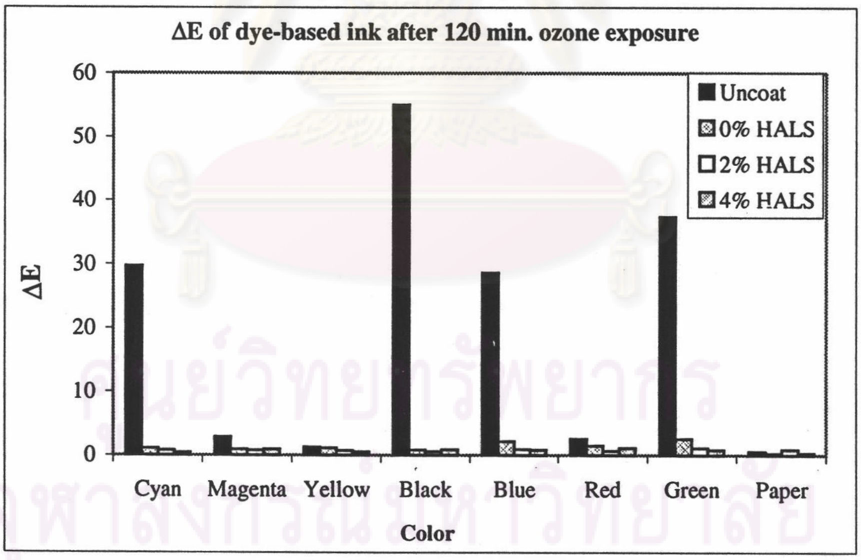
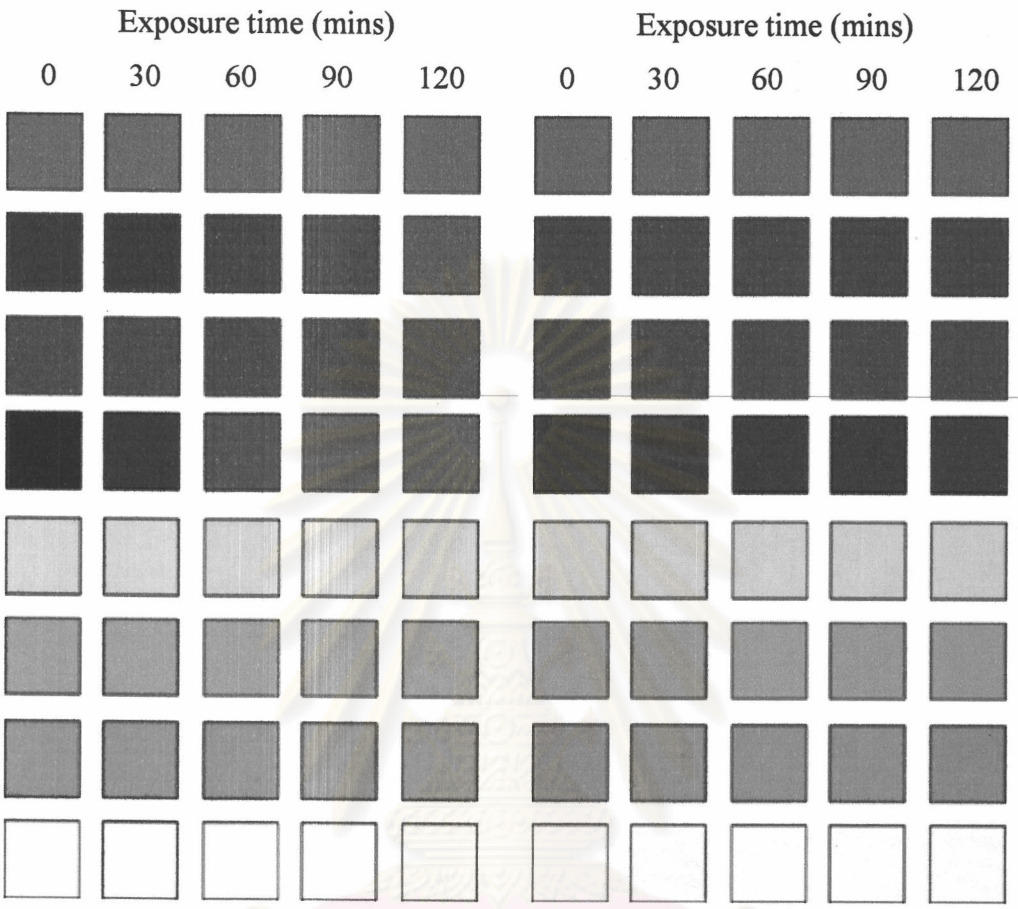


Figure 4-19 ΔEs of color patches printed on HALS coated sheets after 120-minute ozone exposure



a) Non-coated sheet **b) 2% HALS coated sheet**

Figure 4-20 Ozone induced fading of color patches on different substrates

4.4 Effect of UV Absorber and HALS in double-layered coating on light fastness of the dye-based inkjet ink

The results from Sections 4.1 – 4.2 indicated that the UV absorber coated sheet shows an improvement on light fastness of dye-based inkjet ink. Unlikely, the results from Section 4.3 indicated that the HALS coated sheets do not show effective results to improve the light fastness of the dye-based inkjet ink. However, there is an evidence of improving the light fastness of dye-based inkjet ink by a synergistic effect of the HALS and UV absorber in the lamination method. Figure 4-21 present the schematic diagram of laminated sheet of the inkjet prints. The comparison of the light fastness of dye-based inkjet ink on the laminated sheet and non-laminated sheet was presented in Figure 4-22.[36] It was found that the light fastness of the dye-based inkjet ink on the laminated sheet was highly improved. The ΔEs of magenta, red, black, blue and, yellow color, which were higher than 30 on the non-laminated sheet were below 20 when these colors were laminated on the sheet containing HALS and UV absorber layer.

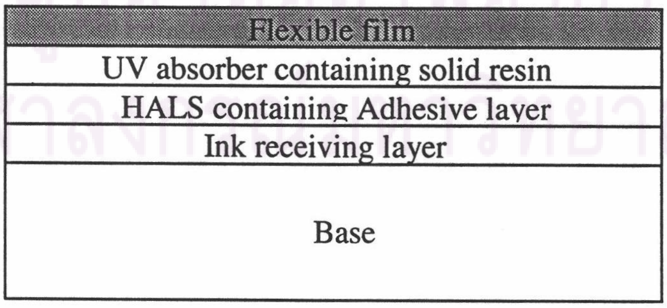


Figure 4-21 Schematic diagram of a laminated inkjet print[2]

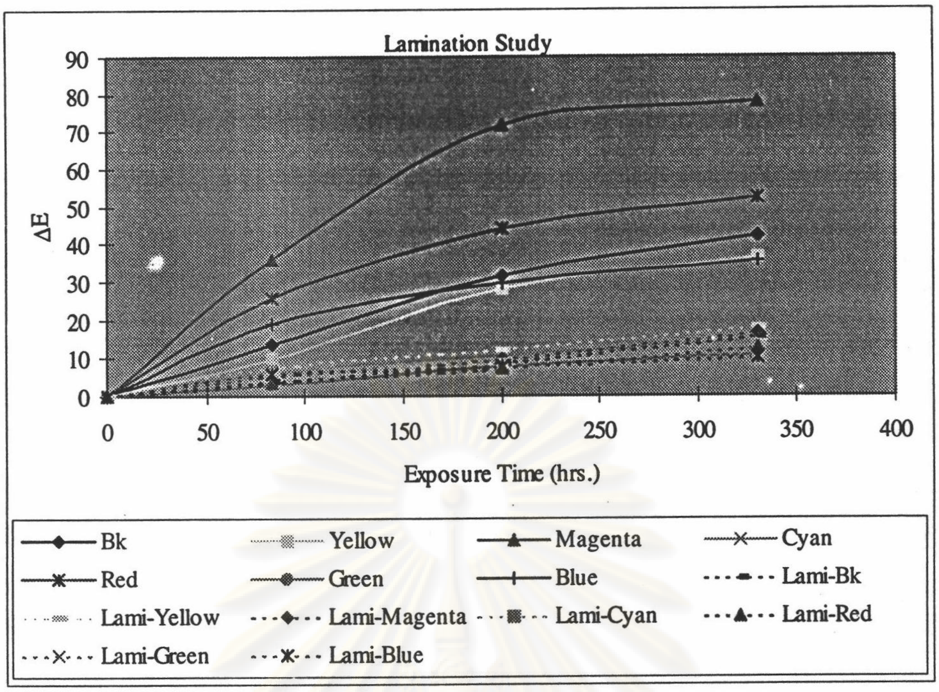


Figure 4-22 Comparison of the ΔEs of colors on the laminated sheet and non-laminated sheet

Based on the above results, the ink-receiving layer was modified to be similar to the structure of laminated sheet. The microporous inkjet film was first coated with 2 % w w^{-1} of HALS. After drying, it was then coated with 1% w w^{-1} of BP containing UV absorber and BTZ containing UV absorber. Table 4-3 shows ΔEs of the dye-based inkjet ink printed on the double-layered coated sheets after 100-hour exposure in the weather-o-meter (Xenon arc lamp). It was found that the light fastness of magenta and yellow colors on the two double-layered coated sheet was slightly changed, only the light fastness of black and blue colors was significantly improved. The ΔEs of cyan, red, green and background colors on the two double-layered coated sheets were higher than the ΔEs of these colors on the non-coated sheet. This may be concluded that the double-layered coated sheets were not effective to improve the total light fastness of dye-based inkjet ink.

Table 4-3 ΔE of the dye-based inkjet inks on the double-layered coated sheets after 100-hour exposure of weatherometer (Xenon arc lamp)

Substrate	ΔE of color after 100-hour exposure							
	Cyan	Magenta	Yellow	Black	Blue	Red	Green	Base
Non-coated	7	89	17	42	81	73	13	1
2 % HALS + 1% BP	18	87	15	31	60	76	31	3
2 % HALS + 1% BTZ	20	87	13	32	61	76	22	6

However, when the double-layered coated sheet was tested for the fading under the indoor condition similarly as these mentioned above in Section 4-3. The ozone exposure results shown in Figure 4-23 exhibit the same trend as the results of the HALS coated sheets in Section 4-3. There was a significant improvement on ozone fastness of black, cyan and its secondary colors.

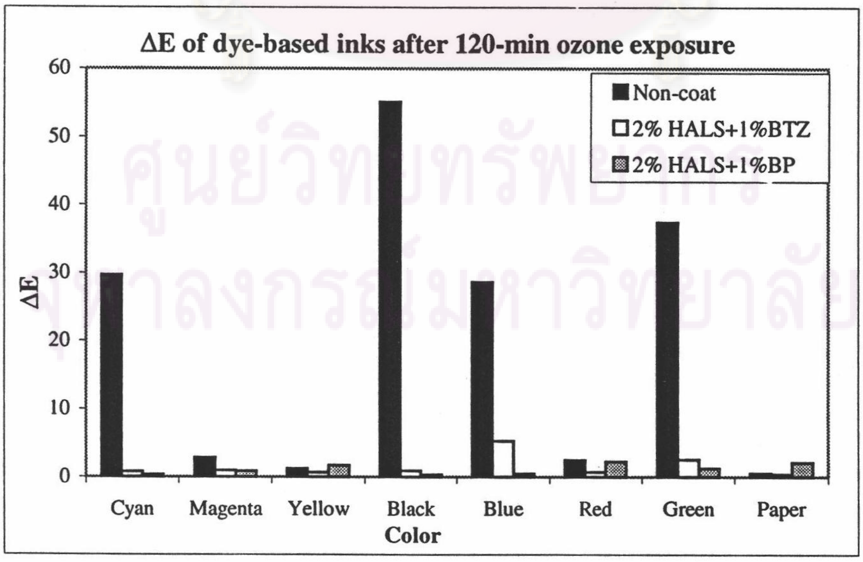


Figure 4-23 ΔEs of the color patches printed on double-layered coated sheets after 120-min ozone exposure

4.5 Effect of double-layered coated film on light fastness of pigmented inkjet ink

Apart from the dye-based inkjet ink, a pigmented inkjet ink is also used especially in outdoors application. It is well known that light fastness of a pigment is generally higher than that light fastness of a dye. However, the extent of light fastness of pigments is also numerous. In this section, the effect of double-layered coated sheets was investigated with two different sets of pigment.

The ΔEs of inkjet ink printed on the non-coated sheets and two double-layered coated sheets after 200-hour exposure in Xenon weather-o-meter were shown in Table 4-4.

Table 4-4 ΔEs of pigmented inkjet inks printed on the coated sheets after 200-hour exposure

Substrate	ΔE of colors after 200-hour exposure							
	Cyan	Magenta	Yellow	Black	Blue	Red	Green	Base
P-Hi inkset								
Non-coated	3	6	8	1	10	5	2	3
H-BP	12	8	26	10	15	21	27	6
H-BTZ	19	24	35	18	21	36	29	4
P-Lo inkset								
Non-coated	3	86	76	3	24	58	14	4
H-BP	13	49	30	7	31	37	24	6
H-BTZ	13	52	28	7	36	38	27	1

In case of P-Hi ink set, the results indicates that almost all the ink color printed on the non-coated sheet showed a good lightfast property. Only the light fastness of magenta color was moderately low. The ΔE of magenta color was higher than 10, while the ΔEs of the other colors were in the range of 1-10. When the P-Hi ink set was printed on the double-layered coated sheet, it was found that the ΔEs of the colors tended to be larger than the ΔEs of the colors on the non-coated sheet. Comparison between the two types of double-layered coated sheet, H-BP and H-BTZ, the ΔEs of the colors on the H-BTZ was higher than the ΔEs of the colors on the another one. It might be assumed that the double-layered coated sheet could not prevent the fading of these pigments.

However, when the curves plotted between the ΔE and exposure time as shown in Figure 4-24 was considered, a remarkable result was observed. The ΔE of color such as magenta color on the non-coated sheet slowly increases after exposure, but the ΔEs of magenta colors on the double-layered coated sheets rapidly increase when the exposure time is in the range of 50 hours. After that, the trends of the ΔEs of magenta color on the double-layered coated sheet are similar to that of the color on the non-coated sheet. There are no significant differences of ΔE of the magenta color after 200-hour exposure and 50 hour-exposures.

These results might be explained by the shielding effect of outer bound molecules of pigment particles and the surfactant desorption effect. As shown in Figure 4-25, only the outer bound molecules were attacked by the radiation. These molecules act as a barrier to prevent the direct light absorption of the inner molecules.

Therefore, the decomposition of outer bound pigment molecules occurs rapidly, but the decomposition of inner pigment took place rather slowly because of the shielding effect. In case of pigmented inkjet ink in this thesis, the small particle size of pigment particles was stabilized with the surfactant. When this ink was printed and dried on the non-coated sheet, the formation of surfactant layer around the pigment particles acts as a gas barrier to prevent the direct attack of the singlet oxygen. On the contrary, the top surface of the double-layered coated sheets was a water-soluble binder. When the pigmented inkjet ink was printed on these double-layered coated sheets, the surfactants were absorbed into the coated layer. The desorption of surfactant causes uncovered pigment particles. The singlet oxygen then can easily access the outer bound molecules of pigment particles. Therefore, the fading pigment on the double-layered coated sheet occurs faster than that on the non-coated sheet.

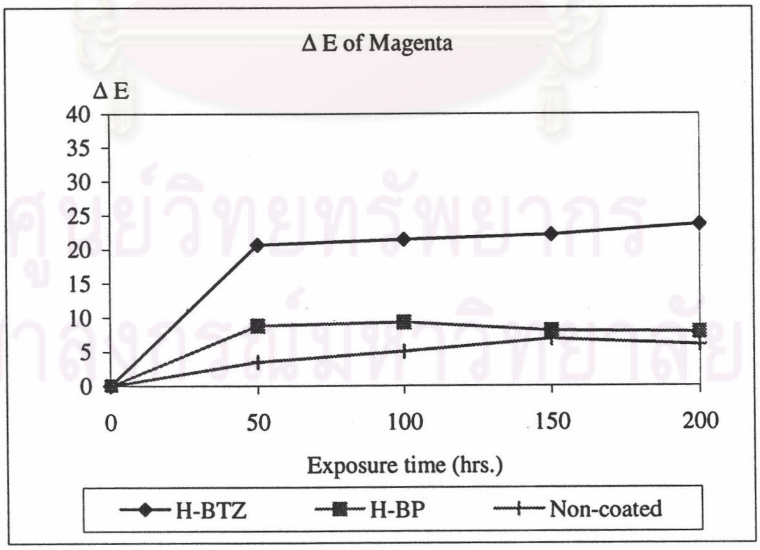


Figure 4-24 ΔE of magenta printed on the double-layered coated sheet

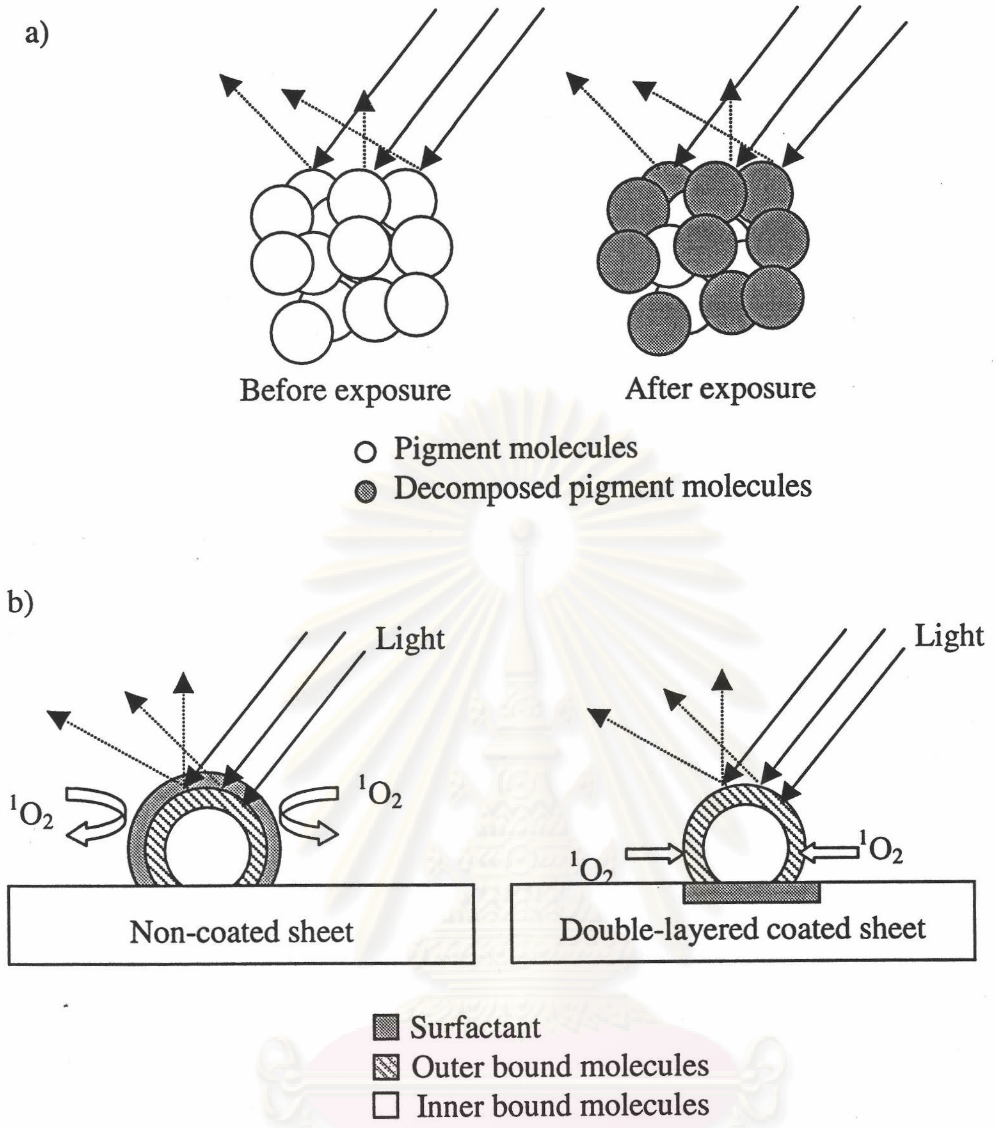


Figure 4-25 The model of pigment particle after exposure a) shielding effect b) surfactant desorption

In case of P-Lo ink set, magenta and yellow pigment used were C.I. Pigment Red 184 (magenta) and C.I. Pigment Yellow 17 (Yellow), respectively. The light fastness of prints, which were composed of these two pigments was relatively lower than the light fastness of the colors printed using other pigments, such as those in the P-Hi ink set. The chemical structures of pigments used are shown in Figure 3-3. The chromophores of Pigment Red 184 and C.I. Pigment Yellow 17 are the azo group, while the C.I. Pigment Red 122 and C.I. Pigment Yellow 138 contain the quinacridone and quinophthalone structure, respectively. As described in Section 4.1, the azo group is rapidly decomposed via either a photooxidation or photoreduction mechanism under the strong light intensity. When these two low lightfast pigments were printed on the double-layered coated sheet, their light fastness was significantly improved. The ΔEs of magenta, yellow and red on both double-layered coated sheets were lower than the ΔEs of these colors on the non-coated sheet. These can be explained that the double-layered coated sheets effectively retard the decomposition of the azo pigment.

A further experiment of a variation of the UV absorber layer's thickness on the light fastness of these two azo pigments was set up. The results in Table 4-5 exhibit that when the thickness of the UV absorber layer increased, the ΔEs of the colors tended to increase too. These can possibly be explained that when the thickness of coated layer increased, the lower ink penetration is observed. Therefore, the major part of pigmented ink was retained on the top surface of coated sheet, which cannot be protected by the UV absorber coated layer.

In order to prove this assumption, the new experiment was carried out by changing a step of coating UV absorber layer. Unlike the former experiment, the pigmented inkjet ink was printed on the only HALS coated layer. After drying, the printed sheets were then coated again with the UV absorber coated solution. This technique was named "overcoating". The results compared were shown in Table 4-6. It is clearly seen that there was the significantly different ΔE values between the light fastness of the colors on two techniques. Any colors composed of magenta and yellow pigment printed on overcoating sheet show the lower ΔE values than the colors on double-layered coated sheets. This could be explained that the pigment particles on overcoating sheets were covered with the UV absorber layer. Therefore, the photodegradation of the pigments was retarded by UV active agent in the layer, which removes some part of the harmful energy. However, the thickness of the second layer was unnecessary to be thick, because it can not effectively affect the color fading and the ΔE values.

Table 4-5 ΔE of P-Lo ink set printed on the double-layered coated sheets after 200-hour exposure

Substrate	(No. of wire bar coater)*	ΔE of color after 200-hour exposure							
		Cyan	Magenta	Yellow	Black	Blue	Red	Green	Base
Non-coated	-	2	78	74	4	24	59	14	1
H-BP	6	13	49	30	7	31	37	24	6
	24	34	67	45	18	46	44	36	11
	50	32	66	47	20	45	44	40	12
H-BTZ	6	13	52	28	7	36	38	27	1
	24	33	61	39	25	47	44	34	1
	50	31	61	35	18	43	38	28	1

* Used for the second layer coating

To conclude, it is not necessary to make a double-layered coating to improve the light fastness of the high lightfast pigment. Nonetheless, it shows a potential way to decrease the light-induced fading of the low lightfast pigment. It is much better off to coat the UV absorber layer after printing the pigmented inkjet ink on the HALS coated sheet rather than using a double-layered coated sheet. By the way, this method will not be friendly with the end-user, but it can be useful in the printing industry.

Table 4-6 Comparison of ΔE of pigmented inkjet ink on various substrates

Substrate	(No. of wire bar coater)*	ΔE of color after 200 hour exposure															
		Cyan		Magenta		Yellow		Black		Blue		Red		Green		Base	
		D	O	D	O	D	O	D	O	D	O	D	O	D	O	D	O
<u>P-Hi ink set</u>																	
Non-coated	-	3		6		8		1		10		5		2		3	
H-BP	6	12	17	8	10	26	5	10	8	15	27	21	12	27	19	6	4
H-BTZ	6	19	10	24	10	35	8	18	9	21	18	36	15	29	15	4	3
<u>P-Lo ink set</u>																	
Non-coated	-	3		83		76		3		24		58		14		4	
H-BP	6	13	5	49	23	30	10	7	11	31	20	37	18	24	14	6	6
	24	34	10	67	20	45	9	18	14	46	21	44	21	36	18	11	10
	50	32	9	66	14	47	10	20	14	45	15	44	20	40	21	12	9

* Used for second layer coating; D = Double-layered coating; O = Overcoating

Table 4-6 (continued) Comparison of ΔE of pigmented inkjet ink on various substrates

Substrate	(No. of wire bar coater)*	ΔE of color after 200 hour exposure															
		Cyan		Magenta		Yellow		Black		Blue		Red		Green		Base	
		D	O	D	O	D	O	D	O	D	O	D	O	D	O	D	O
H-BP	6	13	11	52	19	28	8	7	10	36	36	38	19	27	15	1	2
	24	33	9	61	20	39	11	25	14	47	32	44	24	34	24	1	1
	50	31	9	61	19	35	11	18	13	43	33	38	24	28	22	1	2

* Used for second layer coating; D = Double-layered coating; O = Overcoating

4.6 Yellowing of the coated sheet

Yellowing of the coated sheets caused an unsatisfactory result on light fastness of inkjet inks. The yellowing occurred in many cases, but almost of them was related to the BP containing UV absorber. The BP containing UV absorber coated sheets were yellowish either before or after exposure. Figure 4-25 shows the reflection spectra of non-printed area of the non-coated sheet and BP1 coated sheet. It was found that there was not significantly different of the reflection spectra between before and after exposure. The background color was still clear white even though the exposure time reached 50 hours. On contrary, the yellowing of non-printed area was slightly noticeable after the BP containing UV absorber coated solution was coated on it. The yellowing strongly increased when the coated sheets were exposed in Xenon arc lamp weather-o-meter. This phenomenon occurs on both BP1 and BP2 UV absorber. In case of the BP2 UV absorber, the yellowing was stronger than the BP1 UV absorber. The BP1 coated sheet was noticeable yellowish when the UV absorber

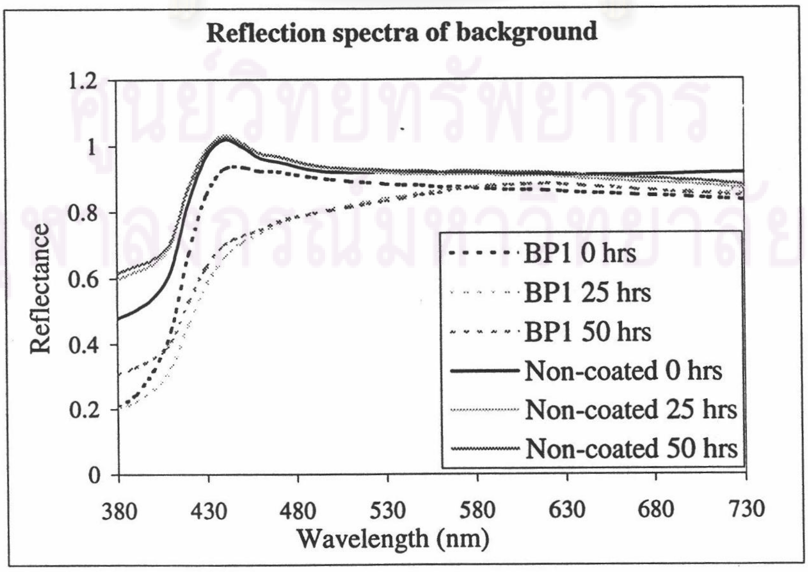


Figure 4-26 Reflection spectra of background

concentration is higher than 1 %. On the other hand, the BP2 coated sheet was yellowish even though the concentration is only 0.5 %.

From the above results, it can be said that the cause of yellowing is related to the characteristic of hydroxybenzophenone derivatives. There is some possible assumption of the cause of yellowing.

a) Hydrogen abstraction of hydroxybenzophenone[37]

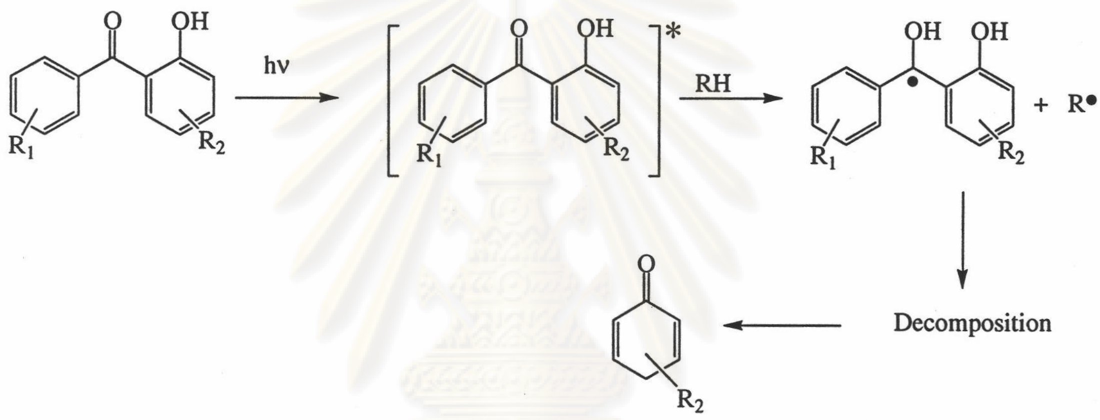


Figure 4-27 Break down reaction of hydroxybenzophenone

When the UV absorber was attacked by the photon the molecule will be excited to the high-energy rich state. The absorbed energy then will be transformed into harmless heat. The UV absorber will recover to the ground state. However, hydrogen abstraction of benzophenone with hydrogen donor can occur. This reaction may follow by the decomposition of UV absorber. As shown in Figure 4-26, the hydroxy group was changed to be the carbonyl group. This breakdown product which exhibited yellowish color is a major cause of the yellowing of coated sheet after exposure. In this thesis, there are many sources of hydrogen donor. For example, a solvent, which is used to dissolve the UV absorber was an alcohol-like, methanol. Poly(vinyl alcohol) also can be a hydrogen donor too.

b) Formation of exciplex[38]

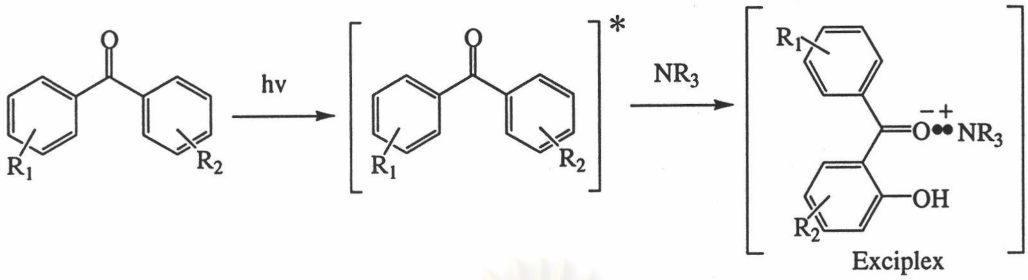
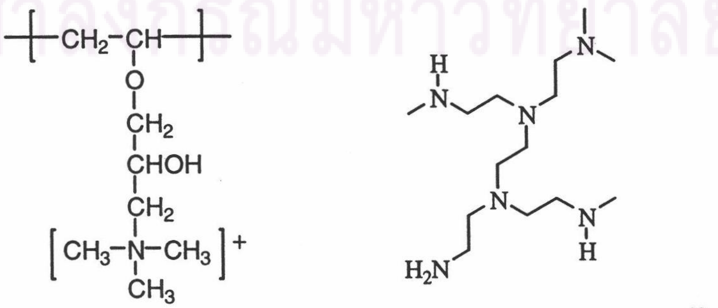


Figure 4-28 Formation of exciplex

In general, a hydrogen abstracting photoinitiator in conjunction with an amine coinitiators causes the greatest coloring problem.[38] This phenomenon is possibly related to the formation of excited state complex, which is called exciplex as shown in Figure 4-28. In this thesis, the ink-receiving layer of HG-201 composed of a cationic polymer [Figure 4-29 (a)] which contained nitrogen atoms. This ingredient then can react with the hydroxybenzophenone type UV absorber and form the yellowish intermediate. Moreover, in case of double-layered coated sheet, the yellowing occurs when the UV absorber was coated on the HALS coated layer. It can be explained that the formulation of HALS coated solution is also composed of poly (ethylene imine)[Figure 4-29 (b)]. This polymer also contains many nitrogen atoms, which is a source of amine too.



(a) Cationic polymer in HG-201[39] (b) Poly(ethylene imine)[40]

Figure 4-29 Chemical structure of N containing binder

4.7 Catalytic fading in inkjet

Catalytic fading is a phenomenon that happens in the area, which is printed with two or more dyes together. A dye which is printed in the presence of another dye is fading faster than that dye, which is printed alone. It is explained that that dye is catalytic degraded by the co-printed dye. In inkjet printing, many articles have reported the catalytic fading of magenta dye by cyan dye. It was found that the phthalocyanine dye can accelerate the fading of magenta dye. There are two possible assumptions on the mechanism of the catalytic fading.[34,41]

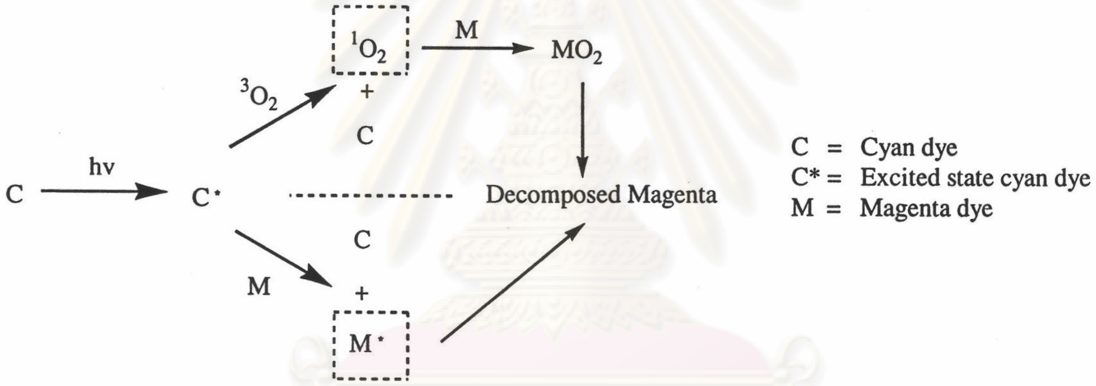


Figure 4-30 Mechanism of catalytic fading

a) Photosensitized oxidation by singlet oxygen.

As shown in Figure 4-30, A phthalocyanine dye is stimulated to the excited state after it absorbed a photon. At this state, the excited dye transfers its energy to an oxygen molecule. The cyan dye then returned to ground state and singlet oxygen is produced. This active singlet oxygen reacts with a magenta dye and causes a degradation of azo bond via a photooxidation mechanism as shown in Figure 4-3 (a).

b) Direct energy transfer to magenta.

This mechanism is similar to the first mechanism except oxgen is not included. After cyan dye was excited by a photon, the relaxation of cyan occurs by transferring its energy to a magenta dye. The magenta dye is then excited to the high energy level. This, therefore, leads to decomposition of azo dye via a photoreductive mechanism as shown in Figure 4-3 (b).

In this thesis, it is supposed that the catalytic fading occurred with magenta dye in the presence of cyan dye. As mentioned in Sections 4-3 and 4-4, the HALS coated sheet and double-layered coated sheets which are not effective to improve the light fastness of dye-based inkjet ink. However, there is an observation that the fading of blue color was lower when compared with the non-coated sheet. This might be related to the catalytic fading of magenta dye by cyan dye on the non-coated sheet. When the HALS was applied on the non-coated sheet, the catalytic fading, which is a major cause of fading of blue, is retarded. It can be explained that the HALS acts as a quencher in this system. Instead of the excess energy is transferred to oxygen or magenta dye, the HALS absorbs this energy and dissipates it in the form of harmless energy. This means the catalytic fading of magenta dye was partially inhibited.