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The Effect of Anti-UV Agents on UV Shielding and Photolytic Aging of Paper

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ABSTRACT

The behaviors of deterioration in the mechanical and optical properties of paper during sunlight exposure are mainly attributed to UV irradiation. The effect of different additives (anti-UV agents) on paper properties during exposure was studied.
The results showed negligible changes in the mechanical properties of samples prepared with two different ways, whereas the shielding ability was increased when the additives were applied to the surface of handsheets. Also, the paper which is treated with anti UV agents can keep freshness more effectively of agricultural products from UV irradiation.

Keywords : *sunlight, packaging paper, anti-UV agent, destruction, photolytic aging, UV-tolerance.*

1. Introduction

The light sensitivity of paper has been recognized for more than a century. After Witz showed that the photodegradation of cellulose is chemical in nature (1), many researchers have been conducted to obtain information about the effect of ultraviolet light on cellulose (2). Free radicals are believed to be important intermediates involved in photodegradation. Understanding the free radical species generated can provide important clues about the entire degradation mechanisms. The rate of photodegradation for cellulose and hemicelluloses depend on the intensity and energy distribution of the light. Pure cellulose is not influenced by the irradiation of light without air. However, in the presence of air, cellulose degradation may take place at a slower rate when exposed to light of wavelengths longer than 340 nm(3-5).

Also, sunlight significantly degrades groundwood paper. The greatest changes in paper occur after approximately 30 days of irradiating (6) and the irradiation of groundwood paper by modified sunlight has a

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considerably high degradation effect which is manifested by yellowing, increased acidity and loss of mechanical qualities (7). Because the UV-beam in sunlight is increasing with destruction of O_3 zone in this century, the deterioration of paper with UV-irradiations is becoming more important aspect in paper industry.

Otherwise, the human life was effected with UV-beam at many aspect, directly in dermatological health and indirectly destruction of plastic and paper as well as the food and agricultural product industry. Especially, the nutritive substance such as vitamin C and chlorophyll et al in vegetable and/or fruit could be destructed by UV B (290~320 nm). Chlorophyll and their degradation products that are contained in vegetables and fruits act as the photosensitizers (8). Also, the fatty substance oxidized easily with UV irradiation (9). If the UV was cut off efficiently from the sun light, the paper and agricultural products might keep from severe and fast UV deterioration.

The anti-UV agent was used widely in plastic industry, especially, films for green housing and also in cosmetic industry. 2,4-Dihydroxybenzophenone(DBH) is known to be a reasonably efficient UV screen for preventing the color reversion of papers made from high pulps. DBH protect the paper from UV destruction by increasing its compatibility with cellulose and by the introduction of cationic groups (10). Some kind of UV stabilizer were used for paper as lamination and /or coating type (11,12).

The purpose of this study is to create a new valued paper with UV-tolerance for keep paper properties with sunlightand to evaluate a hardness and sweetness profiles of fruits wrapped with a commercial paper treated HS-770 anti-UV agent.

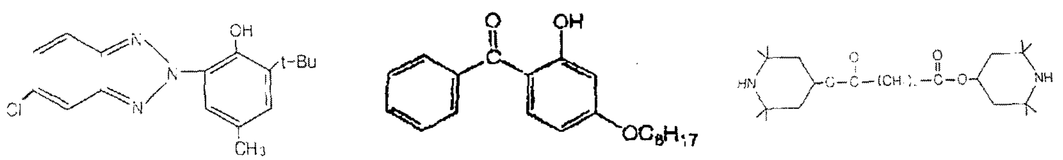
2. Materials and Methods

2.1 Anti-UV agents and papers

The anti-UV agents used in this study were HS-326, KL-UV40 and HS-770(Woo Sung chemicals Co., Daegu) and their chemical structures were shown in Fig. 1. Handsheets of 60 g/m^2 basis weight were made according to KS M 7030 and commercial papers having a grammage of 40 g/m^2 were used to evaluate the shielding effect by additives. The commercial papers had red, blue, yellow and white colors.

2.2 Handsheet preparation and mechanical properties

According to KS M 7030, laboratory-made handsheet having 30 g/m^2 basis weight was prepared by additions of dispersed additives



HS-326 KL-uv40 HS-770

Fig. 1. The chemical structures of some anti-UV agents.

into furnish. Addition levels for additives were 0.5% and 1.0% /g pulp. The commercial papers having 40 g/m^2 were applied 0.1, 0.5 and 1.0% additives by a laboratory coater. The samples were subjected to expose extensively different light sources. To evaluate the mechanical properties of each sample, the tensile and burst strengths of each sample were measured according to KS M 7014 and KS M 7017.

2.3 Optical properties

The % transmittances of wavelength range from 200 nm to 400 nm were measured using a UV-VIS-NIR Spectrophotometer (CARY 5G, Varian Co., Australia) to evaluate the shielding ability of additives. The samples were subjected to leave them in the indoors, outdoors and in the UV-irradiation room and measured theirs L*, a*, b* values using a brightmeter MICRO S-5 (Technidyne Co., USA) to evaluate the color change of samples.

2.4 Freshness of fruit

To evaluateits hardness and sweetness, apples were wrapped in the laboratory-made handsheets and commercial paper treated additives, and stored in the sunlight and UV-irradiation room for 4 weeks. The hardness was determined with hardness analyzer.

3. Results and Discussion

3.1 Mechanical properties of Laboratory-made handsheets

Fig. 2 showed the effect of breaking length of laboratory-made handsheets with different anti-UV agents. With HS-326, its breaking length was minimal, whereas the strengths of handsheets added with KL-UV 40 and HS-770 were increased by 20%. Moreover, there was

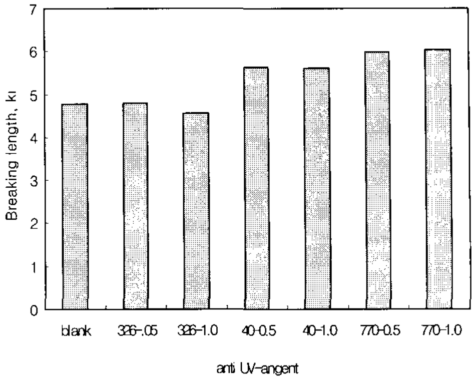


Fig. 2. Tensile strength of laboratory-made handsheets.

no significant decrease in breaking length by 1% of additives. When comparing the control test, it appeared that the increasein breaking length by the additions of KL-UV 40 and HS-770 was occurred. It indicated anti-UV agents was acting as adhesives and contributing to improve the hydrogen bonding during drying processing, while HS-326 anti-UV agents did not attributeto increase strength since it did not have ketone group but hydroxyl group. This pattern was also observed in burst strength results.

Fig. 3 showed the profiles of burst strength of laboratory-made handsheets irradiated with sunlight and UV rays. The results showed the anti-UV additives was more effective to shield

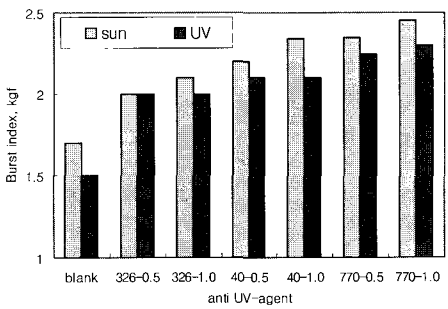


Fig. 3. Burst strength of laboratory-made handsheets after exposures for 4 weeks.

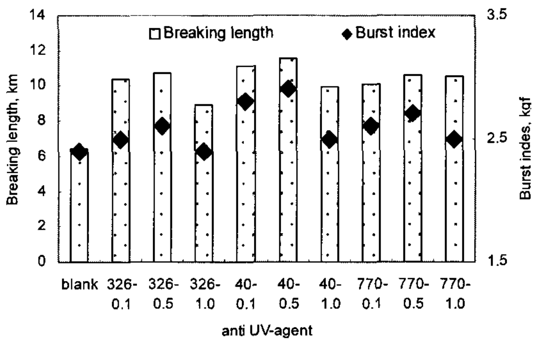


Fig. 4. Breaking length and burst strength of anti-UV agents coated paper.

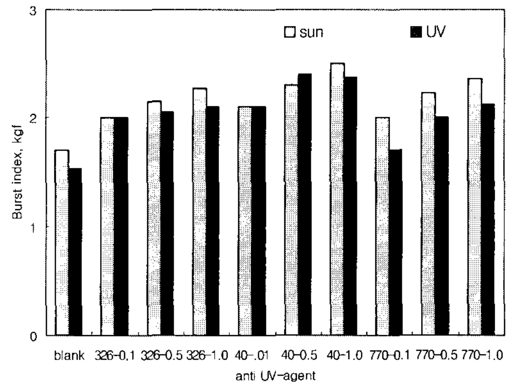


Fig. 5. Burst strength of anti-UV agents after exposure for 4 weeks.

UV rays compared to sunlight and the UV rays was detrimental to the mechanical properties of paper. There was no significant difference in the anti-UV agents, but the decrease in mechanical properties was reduced as the addition level of additives was increased.

3.2 Mechanical properties of commercial papers with surface treatments

Fig. 4 showed the results of mechanical properties with anti-UV agents coated papers. Although there was an increase of mechanical properties with the coated paper, it might be attributed to the anchoring agent having starch. When the addition levels of anti-UV agents were high, the ratio of increase in mechanical properties was reduced due to low addition level of the anchoring agent.

Fig. 5 showed the burst strengths of anti-UV coated papers after 4 week-exposures. As the loading levels of anti-UV agent solutions onto sample surface were increased, strength properties was increased. It might have been correlated to the increased dosage of an anchoringagent. Compared to the results from laboratory-made handsheets, the surface treatment of paper with anti-UV agents was more effective to shield the UV arrays.

3.3 Shielding ability

3.3.1 Shielding ability of Laboratory-made handsheets

Table 1. L*, a*, b* system of laboratory-made handsheets

	Blank			sun			UV		
	L	a	b	L	a	b	L	a	b
326-0.5	83.35	-3.53	9.89	81.73	-2.88	10.77	81.08	1-3.08	2.78
326-1.0	82.00	-3.16	11.88	81.03	-2.86	11.82	81.24	-3.23	12.47
40-0.5	81.80	-3.22	11.10	80.75	-3.14	11.30	82.43	-3.53	10.96
40-1.0	80.33	-3.02	13.43	80.01	-3.54	10.29	81.15	-3.52	12.82
770-0.5	80.44	-2.71	12.71	81.60	-2.90	10.67	79.94	-2.78	12.66
770-1.0	82.19	-3.05	10.65	81.52	-2.83	10.48	80.72	-3.02	12.05

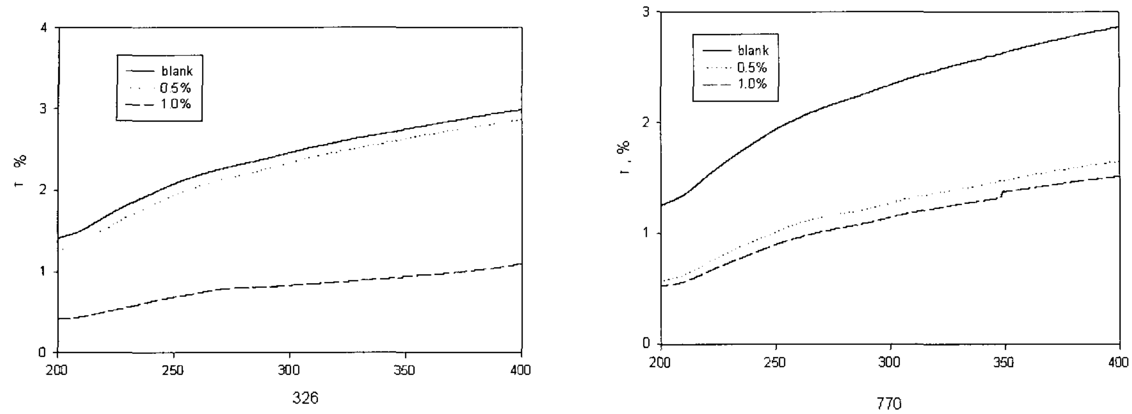
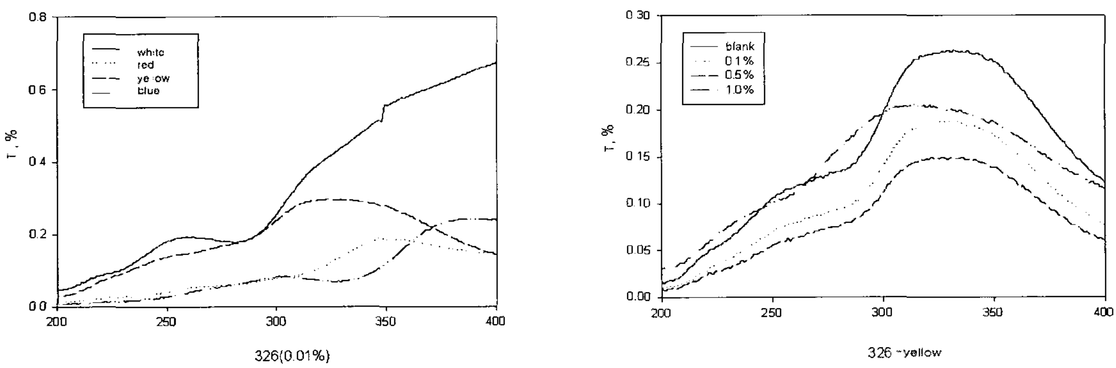


Fig. 6. Transmittance of UV through laboratory-made handsheets.

Fig. 6 showed the % transmittance of laboratory-made handsheets. For the handsheets added 0.5% HS-326, the transmittance was as high as the control, while the % transmittance of handsheets having HS-770 did not changed when the addition levels was 0.5% and 1.0%. This trend was also observed with KL-UV40. It might have been expected that the difference of shielding ability between anti-UV agents were caused by the deterioration behaviors of HS-326 during exposure. The result was in good agreement with date shown in Fig. 3.

3.3.2 Shielding ability of commercial papers with surface treatments

Although the UV reflectance of commercial papers was depended on their own color, the blue and red colored wrapping papers had lower % transmittances compared to results from the yellow wrapping paper shown in Fig. 7(a). Even though the white colored had similar transmittance profiles to the laboratory-made handsheet, the surface treatments was more effective than the addition method since the shielding power of surface treatment with 0.01% anti-UV agent was almost same compared to the 1% addition level of the



a. Different color papers b. Yellow wrapping paper

Fig. 7. Transmittance of UV through anti-UV coated papers.

Table 2. Color changes of a commercial white wrapping paper

	Blank			sun			UV		
	L	a	b	L	a	b	L	a	b
326-0.1	82.76	-3.71	12.07	84.11	-3.78	-3.78	81.78	-3.46	13.25
326-0.5	82.72	-3.86	11.51	83.69	-3.71	-3.71	82.42	-3.67	12.40
326-1.0	82.84	-3.84	11.78	82.34	-3.60	-3.60	82.68	-4.06	12.80
40-0.1	82.43	-3.03	11.01	83.42	-3.55	-3.55	82.18	-3.55	12.43
40-0.5	81.83	-3.35	11.49	82.15	-3.55	-3.55	81.56	-3.74	12.99
40-1.0	81.69	-3.07	11.83	82.09	-3.24	-3.24	82.60	-3.57	12.06
770-0.1	83.04	-3.66	11.71	83.14	-3.57	-3.57	81.74	-3.43	12.77
770-0.5	82.11	-2.87	12.40	83.65	-3.47	-3.47	81.66	-3.47	12.82
770-1.0	81.30	-3.33	13.02	83.27	-3.53	-3.53	81.61	-3.28	13.75

laboratory-made handsheet.

In the surface treatment with anti-UV agents, the shielding ability of samples was increased to the 0.5% loading level, whereas the ability was decreased with further loading of anti-UV agents (Fig. 7(b)).

3.4 Color profiles

3.4.1 Color profiles with laboratory-made handsheets

According to L*, a*, b* color space, the results of color differences in laboratory-made handsheets was shown in Table 1. After exposing the handsheets to the light, the values of L* had a tendency to decrease, thereby the difference of shades in handsheets were augmented. For KL-UV40 treated samples, the trends seemed to be higher under the UV-arrays, but the difference was negligible. However, the values of a* and b* were different with light sources; the value of a* hadhigher difference in the case of sunlight and b* was higher in the case of UV-arrays. For color changes during exposure, the sunlight made the reddish samples (+a) into greenish paper (+a) and the UV treatment converted the bluish paper into yellowish samples.

3.4.2 Color profiles with commercial papers with surface treatments

The de-coloration behaviors of a white commercial paper were not noticeable by UV

Table 3. Color changes of a commercial blue wrapping paper

	Blank			sun			UV		
	L	a	B	L	a	b	L	a	b
326-0.1	36.51	-3.08	-24.00	42.21	-3.66	-17.10	44.26	-3.11	-15.30
326-0.5	40.60	-3.10	-21.30	37.00	-3.78	-18.70	41.93	-2.60	-16.80
326-1.0	41.68	-3.97	-20.60	39.45	-3.60	-17.10	45.15	-3.53	-14.70
40-0.1	34.67	-2.61	-25.80	36.76	-3.73	-18.60	42.95	-2.50	-15.60
40-0.5	35.10	-2.17	-26.20	38.41	-4.29	-18.00	42.75	-3.20	-15.20
40-1.0	36.57	-3.18	-25.00	36.93	-3.52	-18.60	43.00	-2.78	-16.00
770-0.1	39.33	-3.42	-25.00	38.43	-4.19	-17.50	42.53	-2.54	-15.60
770-0.5	34.33	-1.30	-25.80	37.11	-2.51	-18.10	41.27	-1.76	-16.90
770-1.0	39.53	-4.00	-25.40	40.46	-3.65	-15.90	41.69	-1.77	-16.90

irradiations, but the values of b* were significantly affected by sunlight treatments. For the control, the + values of b* was changed into values after exposure to the sunlight and consequently the white color was changed into yellowish white color. This result indicated the colors of fiber itself were de-colorized by the visible rays from sunlights. Otherwise, the blue commercialsamples were de-colorized by sunlight and then increased the values of L*, which resulted to turn the sample brighter one. The change of values of a* was not noticeable, but the values of b* was decreased and then turn the sample yellowish. This trend of changed values of L*, a*, b* was more significant when the samples were treated under UV irradiation condition compared to the sunlight. In addition, the UV irradiation was detrimental to the color of anti-UV agents.

3.5 Hardness and sweetness

Table 4 showed the results of hardness and sweetness profiles in apples wrapped with a commercial paper treated HS-770 anti-UV agent for 4 weeks. With exposure to the sunlight and UV irradiation, their hardness and sweetness of apples were decreased. After 10 days to exposure to UV, their hardness of apples wrapped with a commercial paper having HS-770 were kept about 0.54 and 0.57, but the controls were diminished about 0.50 and 0.36. For the sweetness test, the commercial paper having HS-770 was higher values of sweetness than did the control. The results from the KL-UV40 were also similar, but the values of hardness and sweetness treated paper having HS-326 were the lowest. With the psychological experiment to its taste, the apples were virtually removed theirsours. However, further studies are needed to investigate the relationship between acidic compound and UV irradiation.

Table 4. Hardness and sweetness of apples

			blank	5days	10 days
Hardness Kg/∮5m	Sun	blank	0.62	0.56	0.50
		770		0.57	0.54
	UV	blank		0.49	0.36
		770		0.60	0.57
Sweetness Brix	Sun	blank	12.4	11.7	11.0
		770		12.0	11.6
	UV	blank		10.6	9.2
		770		11.8	11.4

4. Conclusions

The treatment of anti-UV agents on paper was suitable for shielding the deteriorations by UV irradiation. The surface treatments were more effective compared to the addition of anti-UV agents into furnish. With this treatment, we could prevent the de-coloration, decreasing mechanical properties of paper and keep freshness of agricultural products from UV irradiation.

Literature Cited

1. Witz, G., Bull. Rowen., Sur certaines alteration due cotton et applications, 11, 169 (1883).
2. Baugh, P.J., Photodegradation and photoxidation of cellulose, Developments in Polymer Degradation-2 ed, Applied Science Publishers, England, Chap. 5 (1985).
3. Hon, N.-S., Formation of free radicals in photo-irradiated cellulose, J. Polym. Chem.. ed., 14, 2497 (1976).
4. Hon, N.-S., Fundamental degradation processes relevant to solar irradiation of cellulose, J. Macromol. Sci. Chem., 10, 1175 (1976).
5. Kleinert, T.N., Free radical reactios in UV irradiation of cellulose, Holzforsch., 18, 24 (1964).
6. Bukovsky, V., The natural ageing of paper after ex-

posure to daylight, Restaurator, 21(4): 229-237 (2000).
7. Bukovsky, V., The influence of light on aging of newsprint paper, Restaurator, 21(2): 55-76 (2000).
8. Chan, H. W.-S., Photosensitized Oxidation of Food, J. Chem. Soc. Chem. Commun. 756 (1978).
9. Terao, J. and Matsushita, S., Light Oxidation of Fatty acid in Food, J. Am. Oil Chem.,54, 234 (1989).
10. Alain, C., Carole, N., R. Stephen, D., Attempts to photostabilize paper made from high yield pulp by application of UV screens containing groups to aid their compatibility with cellulose and lignin, J. of photochemistry and photobiology A: chemistry: 84(3): 311-316 (1994).
11. Stefan, S. Horst, B., Robert, H., Application EP 2002-28521, UV stabilizers for overay paper, Eur. Pat. Appl (2003).
12. Uchida, H., Application JP 98-295314, Paper mulch sheets having biodegradable moisture impermeable layers with good ground temperature rasing property and weather resistance, JPN. Kokai Tokkyo Koho (2000).