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〈Research Paper〉

Storage Stability and Color Reproducibility of Yellow and Red Dyes Extracted from *Carthamus tinctorius* L.

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Abstract: The stability of yellow and red dyes prepared from safflower (*Carthamus tinctorius* L.) in aqueous solution and in solid state was investigated. External factors such as light irradiation and temperature on the stability were examined during storage. Changes in absorbance of dye solutions and the color changes of fabrics dyed after long time storage were measured. Also, color reproducibility during storage was investigated by dyeing test on various fabrics. Red colorant in aqueous solution was very unstable to light, resulting that about 40% of absorbance were lost in 12hrs. The absorbance of yellow dye solutions was not decreased within 84hrs. In aqueous medium, yellow dye was much more stable than carthamin. Both dyes are relatively stable for long storage when they are stored in solid state compared to when in aqueous solution. Color changes are marginal in both dyes.

Keywords: *yellow dye, carthamin, stability, degradation, color reproducibility, color difference*

1. Introduction

Currently, there is an upsurge interest in the revival of natural dyes for textile because they are advantageous in terms of sustainability, green technology, and no health hazards. However, the industrial application of natural dyes is not activated and limited by the following reasons: secure supply of sufficient amount of plant dye material; colorant extraction and storage; standardization of dyeing process on modern equipment; acceptable fastness properties[1)].

For introducing natural dyeing into modern dye plants, natural dyes are required as powder form like synthetic dyes rather than liquid extracts[2)].

It is necessary to make easy and convenient to use and store colorants for dyeing at all seasons[3)].

Safflower, the dried flower petals of *Carthamus tinctorius* L., has long been known for a dye plant used for cosmetics and textiles in Korea, Japan and China. It has also been used in oriental medicine for the treatment of menstrual irregularity, dysmenorrhoea, amenorrhoea, injuries from falls, coronary heart disease, thrombosis, epidemic hepatitis, etc.[4)].

Safflower contains yellow and red colorants. The main constituents of the water extract of safflower are safflower yellow colorant. The yellow colorant, water soluble C-glucosyl quinochalcones, has numerous components such as safflomin A, hydroxyl safflower yellow A and safflower yellow B being the main ones[4,5)]. The yellow safflower colorant has been used as a natural food colorant for a long time, mainly in colored juice, jelly and candy because of its water solubility[6)]. On the other hand, red safflower colorant was originally used for a cosmetic and textile dyeing and printing, and is also currently used as a food colorant[7)].

The main component of the red colorant is called carthamin and due to its low solubility in water, the red colorant is mainly used in colored chocolate in Japan. The stability of natural colorants in food has long been an important factor in particular when the food materials are pigmented through complicated manufacturing processes. There have been several reports on the stability of safflower pigments mainly focused on the point of food processing[6-11)].

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For textile use, the stability of natural colorants in aqueous medium as well as in solid state is an important factor because the textile materials are colored through dyeing process in aqueous solution and also the dyes are stored in solid state until they are being used after a certain period of time.

We investigated the storage stability of yellow and red dyes extracted from safflower in aqueous solution and in solid state. Effects of light irradiation and temperature were investigated to verify storage stability by recording changes in absorbance with storage time. Also, color reproducibility is evaluated by dyeing test on various fabrics.

2. Experimental

2.1 Materials

The fabrics used were shown in Table 1. Dried safflower petals were purchased in oriental medicine market. Chemicals used were reagent grade.

2.2 Preparation of yellow and red powder dyes

Safflower yellow colorant was extracted from dried safflower petals in a liquor ratio of 1:100 in distilled water at 40°C for 2 hrs two times using a constant temperature shaking bath. The first and second extracts were mixed together, filtrated, concentrated with a vacuum evaporator, and freeze-dried at -40°C to obtain safflower yellow dye in powder form. The yellow dye freeze-dried was used without further purification. Yield was about 34%.

From safflower after being extracted yellow colorants and rinsed with hot water twice, red colorant was extracted in a liquor ratio of 1:10 in 1% (owb) K_2CO_3 solution (pH 11) at 40°C for 2 hrs using a constant temperature shaking bath. Extraction was repeated twice at the same condition. First and second extracts were mixed together and adjusted to pH 5.5 with citric acid to precipitate red colorant, and then freeze-dried at -40°C to obtain safflower red dye in powder form. Yield was about 32%. The freeze-dried red dye was used without further purification.

2.3 Characterization

Absorbance and absorption spectra were measured with a UV-Visible Spectrophotometer (Agilent 8453, Agilent Technologies Mfg GmbH & Co.).

FT-IR(Fourier Transform Infrared Spectrometer, Nicolet 520, USA) analysis was done by KBr pellet method to characterize the yellow and red dyes prepared. Moisture contents of the dyes were calculated from weight difference before and after drying in a vacuum oven for 24 hrs.

2.4 Storage stability test of yellow and red dyes

A light box (Macbeth, Datacolor International, USA) was used for the irradiation of dye solutions with daylight. The solution samples of 20ml sealed with silicon film over the glass stopper and set in the light box at 30℃. The pH values of yellow and red dye solutions were 5.85 and 5.5, respectively.

The samples exposed to various irradiation conditions; light, dark (no light), light with yellow, red and green filters, respectively. Changes in absorbance were recorded with irradiation time. Powder dyes were kept in a freezer (-20℃) and at room temperature (25°C). Changes in absorbance were recorded with storage time.

Table 1. The profile of fabrics used

Fabric	Weave	Yarn count (w×f/5cm^2)	Weight (g/m^2)	Thickness (mm)
Cotton	plain	95×86	80	0.20
Ramie	plain	60×46	118	0.32
Rayon	plain	104×75	67	0.11
Silk	plain	160×98	42	0.11
Wool	plain	72×69	102	0.25
Nylon	plain	104×78	55	0.11

2.5 Dyeing

Dyeing was done in material to liquor ratio at 1:100, 0.6% (owb) dye concentration using an automatic laboratory dyeing machine (Ahiba Nuance, Datacolor International, USA). With yellow dye, dyeing was done in pH 3.5, at 90°C for wool and nylon, and at 30°C for silk for 40min. Dyeing of cotton, ramie and rayon with red dye was done in 0.6% (owb) dye solution (pH 5.85) at 40°C for 40min. The dyed fabrics were then washed, rinsed, and dried.

2.6 Color measurement

The dyed fabrics were evaluated in terms of K/S and CIE $L^*a^*b^*$ coordinates (Illuminant D_{65}/10° Observer) with a Macbeth Color-eye 3100 spectrophotometer at λ_{max}. H V/C values were obtained from L, a^*, b^* values using the CIE Munsell conversion program.

3. Results and Discussion

3.1 Characteristics of powder dyes

Maximum absorption peaks (λ_{max}) of yellow and red dyes were observed at 405 and 520 nm in the visible region, respectively (Figure 1). It has been reported the λ_{max} of yellow color in the range of 395 to 412 nm and red color (carthamin) at 520-521 nm in acidic conditions[6-9,11].

Table 2 shows the composition of yellow and red dyes prepared in this study. The non-polar part of powder dyes is a dissolved portion in chloroform, dried and weighed. Yellow dye composed of 95% of polar components including colorants, 4.6% of non-polar components, and 0.14% of moisture. Red dye composed of about 90% of polar component including red colorants, 10% of non-polar components, and 0.11% of moisture.

Table 2. Composition (%) of safflower yellow and red dyes in powder form

Dye	Moisture	Non-polar	Polar
Yellow	0.14	4.61	95.25
Red	0.11	10.00	89.89

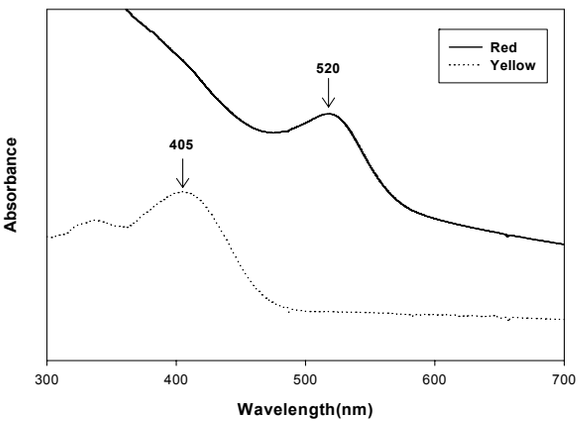

Figure 1. Absorption spectra of yellow and red dyes.

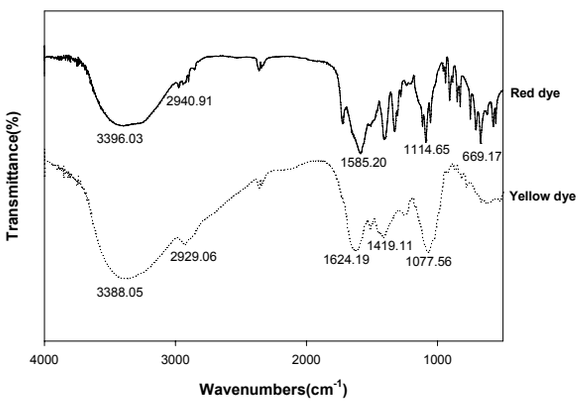

Figure 2. FT-IR spectra of yellow and red dyes.

FT-IR spectra of yellow and red dyes prepared are shown in Figure 2, respectively. Characteristic peaks corresponding to phenolic O-H stretching at 3300-3400 cm^{-1}, aliphatic C-H stretching at 2929 cm^{-1}, conjugated aromatic C=O stretching at 1624 cm^{-1}, C-H absorption at 1419 cm^{-1}, C-O stretching at 1000-1100 cm^{-1} were appeared in the spectrum of yellow dye. On the other hand, phenolic O-H stretching peak at 3300-3400 cm^{-1} decreased and aromatic C=O stretching peak at 1585 cm^{-1} increased in the spectrum of red dye[12]. Peak at 2929 cm^{-1} in the spectra of both dyes might be due to CH_2 or CH_3 stretching. A number of yellow colorants, water-soluble C-glucosyl quinochalcone family of flavonoids, have been identified in the safflower: safflor yellow A, safflor yellow B (safflomin B) being main component, safflomin C, hydroxysafflor yellow A, tintormin[4,6].

The red colorant, mostly carthamin, is a C-glucosyl quinochalcone. Several flavonol derivatives including

heterosides of 6-hydroxykaempferol and a glucoside of quercetin, and other phenolic compounds have also been identified[4]. Further analysis would be necessary for detail.

3.2 Color stability of dye solutions to light

Dye solutions were irradiated with daylight and their UV-Visible spectra were recorded to observe color degradation (Figure 3 and 4). Figure 3 shows the decomposition profile of yellow colorants. The absorbance of yellow dye solution at 405nm gradually decreased and about 93% of absorbance was retained after 200 hrs under daylight exposure. It is clear from the figure that the visible absorbance peak at 405 nm with yellow dye solution (pH 5.85) decreases marginally within 200 hrs. Figure 4 shows the decomposition profiles of carthamin in aqueous solution (pH 5.5) under daylight. Red dye in aqueous solution was very unstable to light, resulting that 40% of absorbance were lost in 12 hrs and then discolored completely to yield pale-yellow colored solution(λ_{max} = 395nm). This indicates that carthamin is much more unstable than yellow dye at acidic conditions. Carthamin in aqueous media is more readily decomposed to orange-yellow or yellow compounds[9,11]. On exposure to visible and ultraviolet light, the red color in aqueous solutions decreased with half -lives of approximately 1 hr and 40 min, respectively[9]. On the basis of the results, it was confirmed that red dye solution, with which dyeing is carried out in acidic condition for cellulose fibers, should not be stored for long time before use.

To improve light stability of red dye solution, we investigated the effect of irradiation light condition on the color stability behavior. We wrapped the container of dye solution with color films and foil, and absorbance at 520nm was plotted against time at different light irradiation conditions; light(control), dark(wrap with aluminum foil), and wrap with yellow, red and green color cellophane films (Figure 5), respectively.

The results are presented in Figure 6. Carthamin in liquid medium degraded continuously at all conditions. But less degradation occurred yellow and red color films as well as with aluminum foil, compared with control sample(light).

The least degradation of carthamin occurred when the container of dye solution was wrapped with red color film.

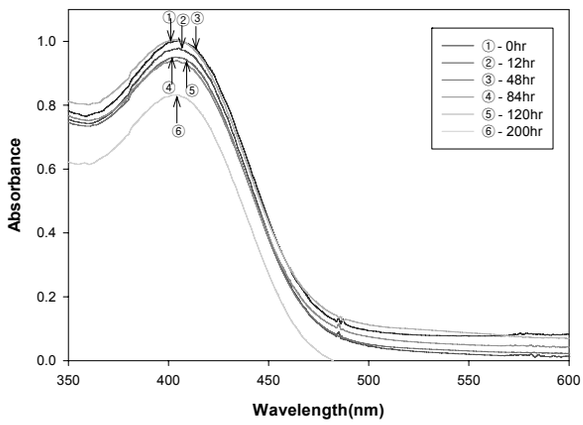

Figure 3. Absorption spectrum change of yellow dye solution depending on time.

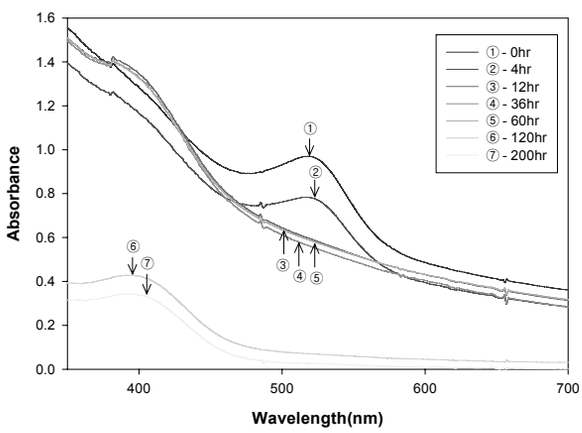

Figure 4. Absorption spectrum change of red dye solution depending on time.

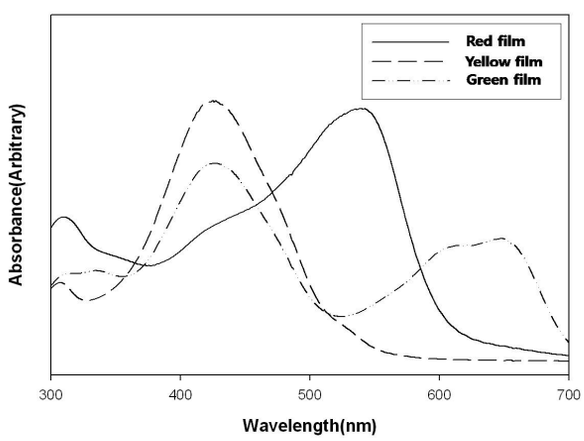

Figure 5. Spectrum profiles with red, yellow, green color films.

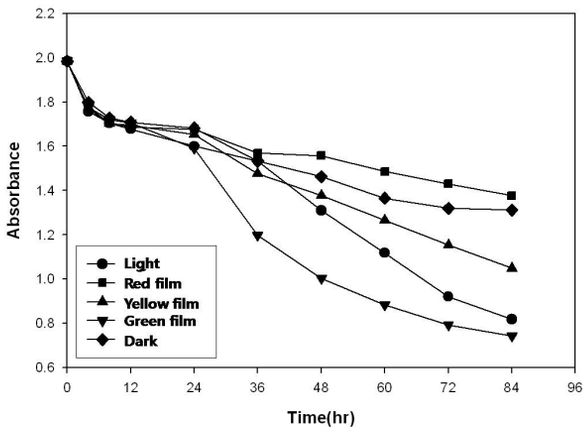

Figure 6. Absorbance change at 520nm of red dye solution under light exposure.

Carthamin is less stable than safflower yellow colorants, which is confirmed by its higher rate of discoloration. Therefore, it is preferable to wrap the container with red film, and to stock it in a dark place at low temperature level to lessen the discoloration of carthamin in aqueous solution.

3.3 Stability of powder dyes to storage temperature

In natural dyeing, water extract of colorants has been usually used so that it was difficult to control dye concentration and reproduce color comparing with synthetic dyes. In this study, safflower yellow and red dyes were prepared in powder form for improving color reproducibility. Natural dye in powder form would be also very convenient for use and storage as well as distribution in the commercial market.

In order to investigate the storage stability of powder dyes, the yellow and red powder dyes were kept at room temperature and in a freezer for 30 days. Changes in absorbance were measured every 5 days during 30 days storage(Table 3). The results show that both dyes in powder are relatively stable at 25℃ as well as -20℃. Yellow dye in powder state can be stored at room temperature. Red dye is slightly more stable at lower temperature, thus storing in a refrigerator is recommended. Safflower yellow B, a major component of yellow colorants in safflower, in aqueous solutions lost 21-46% of color on heating for given intervals at 121℃[8], indicating that temperature is a definitive factor in the stability of safflower yellow B in liquid media. Whereas, solid safflower yellow B resisted any serious discoloration by the heat treatment[8].

The red and yellow powder dyes prepared have been kept in a refrigerator for more than two years and used for dyeing fabrics to evaluate storage stability. Silk, wool and nylon fabrics which showed good affinity to yellow dye were used to evaluate the stability of yellow dye(Table 4). On the other hand, cotton, ramie and rayon fabrics which have good affinity to red dye were used to evaluate the stability of red dye(Table 5).

The color differences (ΔE^*) of dyed fabrics were 0.58-3.17 for yellow dye and 2.57-5.12 for red dye. Both dyes are relatively stable for long storage when they are stored in solid state compared to when in aqueous solution. Yellow dye powder was more stable than red dye powder in long term storage.

Table 3. Absorbance change of yellow and red powder dyes during storage

Storage time(day)	Storage temperature			
	25℃		-20℃	
	Yellow dye	Red dye	Yellow dye	Red dye
0	0.8395	0.8452	0.8395	0.8452
5	0.8338	0.8424	0.8251	0.8422
10	0.8202	0.8416	0.8199	0.8428
15	0.8182	0.8402	0.8183	0.8408
20	0.8167	0.8391	0.8152	0.8400
25	0.8142	0.8372	0.8144	0.8386
30	0.8138	0.8357	0.8138	0.8387

Table 4. Storage stability of yellow dye powder by dyeing tests

Fabric	Storage time (month)	K/S values (405 nm)	L^*	a^*	b^*	H V/C	ΔE^*
Silk	0	13.92	74.54	5.79	64.16	3.7Y 7.4/9.3	-
	27	12.87	74.36	6.28	63.89	3.6Y 7.4/9.3	0.58
Wool	0	26.60	50.18	13.75	54.30	1.0Y 5.0/8.5	-
	27	27.42	52.43	13.40	56.51	1.2Y 5.2/8.7	3.17
Nylon	0	14.14	54.55	12.88	46.46	0.3Y 5.4/7.3	-
	27	13.05	55.69	12.25	45.94	0.5Y 5.5/7.2	2.57

Table 5. Storage stability of red dye powder by dyeing tests

Fabric	Storage time (month)	K/S values (520 nm)	L^*	a^*	b^*	H V/C	ΔE^*
Cotton	0	0.83	69.96	24.23	-1.31	5.5RP 6.9/6.5	-
	27	1.35	71.43	28.34	-0.35	6.3RP 7.0/7.3	5.01
Ramie	0	2.97	60.86	28.52	5.92	0.2R 6.0/7.2	-
	27	3.80	64.76	31.46	7.46	0.9R 6.4/7.8	5.12
Rayon	0	0.93	69.36	25.99	1.52	7.6RP 6.8/6.7	-
	27	1.15	70.01	28.33	1.45	7.6RP 6.9/7.2	2.57

It is speculated that the consistent increase of K/S value with red dye(Table 5) after long time storage would be caused by the decrease of moisture content in dye powder.

3.4 Color reproducibility

Dyeing experiments were carried out for investigating color reproducibility of the prepared dye powders in different batch and during storage of two years. The results are presented in Tables 6 and 7.

Color difference was calculated on the basis of the sample dyed with batch No. 1 dye. Batch No. 1 dye was frozen in a refrigerator at -20ºC and then freeze-dried at -40ºC. Batch No.2 and 3 dyes were quick frozen at -60ºC and subsequently freeze-dried at -40ºC.

Color difference (ΔE^*) between two dyeing shows within range of 1.11-2.01 for silk, 0.53-1.75 for wool, and 0.59-1.98 for nylon. From technical point of dyeing with synthetic dyes a color difference of 1-1.2 is accepted as tolerable color difference between two dyeing[1].

For natural dyeing a somewhat more color difference could be argued because the use of natural resources makes possibly wider variations due to non-synthetic raw material[1].

It was concluded that the preparation of yellow dyes was adequate for obtaining reproducible shade and dye powder was relatively stable for long term storage.

With red dyes prepared in different batches, dyeing was done in 0.6% (owb) dye solution at 40ºC for 40min in a material to bath ratio at 1:100. Color difference between different batches of dyed fabrics shows within range of 3.39-5.01 for cotton, 5.12-5.34 for ramie, and 2.57-2.94 for rayon. Rayon showed less color difference than cotton and ramie. The red dye produced more variation in color than yellow dye. We also found that ramie fabric showed different shade with different origin of production. For example, dyed ramie originated from China appeared R color(Ramie samples 1-3) while ramie originated from Korea appeared RP color(Ramie sample #3) even though red dye from same batch was used.

Red dye powder was less stable than yellow dye powder. It is necessary to find the process producing more consistent quality of dye.

Table 6. Reproducibility test dyeing with yellow dye powder

Fabric	Batch No.	K/S values (420nm)	L*	a*	b*	H V/C	ΔE*
Silk	1	13.95	73.52	5.97	63.76	3.7Y 7.3/9.2	-
	2	13.92	74.54	5.79	64.16	3.7Y 7.4/9.3	1.11
	3	13.71	73.94	6.11	65.81	3.8Y 7.4/9.5	2.01
Wool	1	26.33	50.64	13.61	54.10	1.0Y 5.0/8.4	-
	2	26.60	50.18	13.75	54.30	1.0Y 5.0/8.5	0.53
	3	26.82	51.66	13.38	55.49	1.2Y 5.1/8.6	1.75
Nylon	1	14.14	54.55	12.88	46.46	0.3Y 5.4/7.3	-
	2	14.00	54.21	12.73	46.00	0.3Y 5.4/7.2	0.59
	3	14.34	53.07	13.50	45.32	10.0Y 5.3/7.2	1.98

Table 7. Color reproducibility of prepared red dye powder

Fabric	Batch No.	K/S values (520 nm)	L*	a*	b*	H V/C	ΔE*
Cotton	1	0.83	69.96	24.23	-1.31	5.5RP 6.9/6.5	-
	2	0.88	71.43	28.34	-0.35	6.3RP 7.0/7.3	5.01
	3	0.80	70.32	23.75	-2.03	5.0RP 6.9/6.4	3.39
Ramie	1	1.75	60.86	28.52	5.92	0.2R 6.0/7.2	-
	2	1.59	64.76	31.46	7.46	0.9R 6.4/7.8	5.12
	3	1.67	64.37	32.02	7.90	1.1R 6.3/7.9	5.34
	#3	2.54	54.51	33.42	3.30	8.6RP5.3/8.3	-
Rayon	1	0.93	69.36	25.99	1.52	7.6RP 6.8/6.7	-
	2	0.98	70.01	28.33	1.45	7.6RP 6.9/7.2	2.57
	3	0.94	70.66	28.52	1.59	7.6RP 7.0/7.2	2.94

4. Conclusions

The absorbance of yellow dye solution at 405nm gradually decreased and about 93% of absorbance was retained after 200 hrs under daylight exposure. Red colorant in aqueous solution was very unstable to light, resulting that 40% of absorbance were lost within 12 hrs and then discolored completely to yield pale-yellow colored solution. Carthamin is much more unstable than yellow colorants in aqueous media at acidic conditions. Both dyes are relatively stable for long time storage when they are stored in solid state compared to when stored in aqueous solution. After storing for long time, both dyes produced relatively consistent color.

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References

1. T. Bechtold, A. Mahmud-Ali and R. Mussak, Natural Dyes for Textile Dyeing: A Comparison of Methods to Assess the Quality of Canadian Golden Rod Plant Material, *Dyes and Pigments*, **75**(2), 287(2007).
2. K. W. Lee, J. H. Lee, S. J. Eum, E. M. Bae, T. Y. Kim, and S. H. Yoon, Natural Dyeing of Sangju Silk with Mulberry Extract Solution, *Textile Coloration and Finishing(J. Korean Soc. Dyers & Finishers),* **22**(3), 207(2010).
3. S. W. Nam and K. T. Kim, Preparation and Screen Printing of Natural Dye Powders, *Textile Coloration*

and Finishing(J. Korean Soc. Dyers & Finishers), **22**(4), 314(2010).
4. D. Cardon, "Natural Dyes", Archetype Publications Ltd., London, pp.53-59, 2007.
5. J. Zhang, K. Yu, H. M. Liu and X. Yang, Fingerprint Analysis of *Flos carthami* and Safflower Yellow Pigments by High-Performance Liquid Chromatography, *Analytical Letters*, **38**(6), 981(2005).
6. J. M. Yoon, M. H. Cho, J. E. Park, T. R. Hahn, and Y. S. Paik, Thermal Stability of the Pigments Hydroxysafflor Yellow A, Safflor Yellow B, and Precarthamin from Safflower(*Carthamus tinctorius*), *Journal Food Science*, **68**(3), 839(2003).
7. K. Kanehira and K. Saito, Stability of Carthamin and Safflor Yellow B on Silk Powders under Continuous Irradiation of Fluorescent or UV-C Light, *Lebensmittel-Wissenschaft Und-Technologie*, **34**(2), 55(2001).
8. K. Saito and T. Murata, The Influence of Thermal Treatments on the Stability of Safflower Yellow B, *Food Chemistry*, **51**(3), 307(1994).
9. T. Kanehira, A. Naruse, A. Fukushima, and K. Saito, Decomposition of Carthamin in Aqueous Solutions, *Lebensmittel-Wissenschaft Und-Technologie*, **190**, 299 (1990).
10. T. Watanabe and S. Terabe, Analysis of Natural Food Pigments by Capillary Electrophoresis, *Journal of Chromatography A*, **880**(1-2), 311(2000).
11. J. B. Kim and Y. S. Paik, Stability of Carthamin from *Carthamus tinctorius* in Aqueous Solution: pH and Temperature Effects, *Archives of Parmacal Research*, **20**(6), 643(1997).
12. Y. Shin, K. Son and D. I. Yoo, Optimization of Wool Dyeing with Yellow Dye from *Carthamus tinctorius* L., *Journal Korean Socicety of Clothing and Textiles*, **33**(12), 1971(2009).