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Dyeing and Fastness Properties of Vat Dyes on *meta*-Aramid Woven Fabric

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Abstract: *meta*-Aramid fibers have an excellent heat-resistant property and are widely used for protective clothings such as fire-fighter suit and racing suit. They can also be used as military uniforms such as flight suit or army uniform. Vat dyes are specially used for military uniforms owing to outstanding fastness properties, earth tone shade, and near infrared (NIR) camouflage. In this study, 100 % *meta*-aramid woven fabric was dyed with three vat dyes using an exhaustion method and their dyeing and fastness properties were investigated. Color yields of the vat dyes on the *meta*-aramid fabric were found to be dependent upon dyeing temperature, liquor ratio, amount of reducing agent, and amount of salt. Dyeing behavior of the vat dye on the *meta*-aramid fiber was very similar to that on cellulose fibers. It was found that the *meta*-aramid fabric dyed with 1% owf of C.I. Vat Green 1 satisfied the tolerance of the reflectance spectrum of forest green color in the Korean military standard. Thermal stability and mechanical property of the *meta*-aramid fabric did not significantly affected by the vat dyeing process. Wash and perspiration fastness was generally good but rubbing and light fastness was unsatisfied.

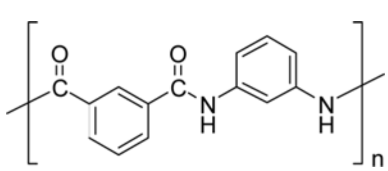
Keywords: *meta*-Aramid fibers, Vat dyes, Military uniform, NIR camouflage, Leuco form

Introduction

meta-Aramid fibers have an excellent heat-resistant property and are widely used for protective clothing such as fire-fighter suit and racing suit. They can also be used as military uniforms such as flight suit or army uniform. It is known to be difficult to dye meta-aramid fiber owing to its high glass transition temperature (T_g) and crystallinity [1]. There is no universal method of dyeing meta-aramid fibers except for dope dyeing. However, dope dyeing method has disadvantages such as limited color and incompatibility of pigments with fiber causing a problem in spinning. Several studies of dyeing methods for meta-aramid fibers have been reported [2-5]. However, dyeing mechanism or optimum dyeing system for the meta-aramid fibers is not fully established. Commercially, this fiber is dyed with cationic dyes with the use of carrier [6]. Although cationic dyeing method enables to dye meta-aramid fiber with a wide range of colors, light fastness of the dyeing is very low and many kinds of the carriers are very toxic.

Vat dyes are used to dye cellulosic fibers in relatively dull shades requiring good fastness. They are originally insoluble but can be reduced with the aid of alkali and reducing agent (sodium hydrosulfite). The reduced or leuco vat dye is soluble in water and has substantivity to cellulosic fiber. After the soluble leuco form penetrates into the fibers, the insoluble quinone structure is restored upon subsequent oxidation (Scheme 2) and the dye is retained within the fibers [7,8]. They are specially used for military uniforms owing to several advantages such as outstanding color fastness, earth tone shade and near infrared (NIR) camouflage. NIR camouflage uniforms can conceal the human body both in the visible and NIR ranges against NIR detection devices by mimic natural or artificial backgrounds. Several vat dyes are known to absorb infrared radiation sufficiently well and can be used for NIR camouflage textiles [9-11].

As the usage of meta-aramid fibers for military uniform increases recently, it is necessary to apply vat dyes with good color fastness as well as NIR camouflage property on the fiber. Except an US patent [12] by Burkinshaw *et al.*, vat dyeing properties of meta-aramid fiber have not been systematically studied yet. In this study, 100 % meta-aramid woven fabric was dyed with three vat dyes using an exhaustion method and their dyeing and fastness properties



Scheme 1. Molecular structure of meta-aramid fiber.

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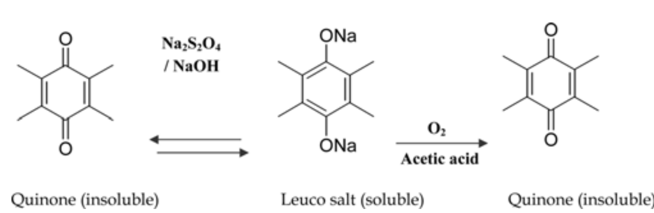


Structure	Quinone	Leuco salt	Quinone
Solubility	Insoluble	Soluble	Insoluble
Substantivity to meta-aramid	Low	High	Low

Scheme 2. The chemistry of a vat dye.

were investigated. The effect of dyeing conditions such as dyeing temperature, liquor ratio and dye concentration on the color yield was investigated. NIR camouflage property of the vat dyed meta-aramid fabric was investigated and LOI or tensile strength of the meta-aramid fabric before and after dyeing was compared. Finally, wash, light, rubbing and perspiration fastness of the dyed fabrics were also evaluated.

Experimental

Materials

100 % meta-aramid (twill, density 90×60 tpi, weight 240.6 g/m^2) was used. Three vat dyes employed were obtained from DyStar Co. and their structures and molecular weight are shown in Table 1. Protepone RSA, used as a soaping agent, was supplied by Protex Korea Co. Sodium hydrosulfite ($Na_2S_2O_4$) used as a reducing agent, sodium sulfate (Na_2SO_4) as a salt, and sodium hydroxide (NaOH) were purchased from Sigma Aldrich Chemicals Co. All the other chemicals used were of laboratory grade.

Vat Dyeing

The meta-aramid fabric was dyed in an IR dyeing machine (DTC-6000, DaeLim Co., Korea) using dyeing profile shown in Figure 1. The dyebaths were prepared with vat dye (0.5-5.0 % owf), NaOH (40^o Be', 25 m*l*/*l*), $Na_2S_2O_4$ (4-16 g/*l*), and salt (Na_2SO_4, 0-30 g/*l*). Liquor-to-goods ratio was varied from 10:1 to 50:1. Dyeing was commenced at 40 ^{o}C. The dyebath temperature was raised at a rate of 1 ^{o}C/min to 60 ^{o}C, maintained for 15 min, and then raised again at a rate of 2 ^{o}C/min to 70, 80, 90, 100, 110, 120, and 130 ^{o}C, maintained at each temperature for 45 min and cooled. The dyed fabrics were then removed and rinsed thoroughly in cold water. Oxidation involved a 3 g/*l* hydrogen peroxide solution (30 % w/v) at 65 ^{o}C for 25 min. Finally, the dyeings were soaped at 65 ^{o}C for 10 min with 1 g/*l* soaping agent.

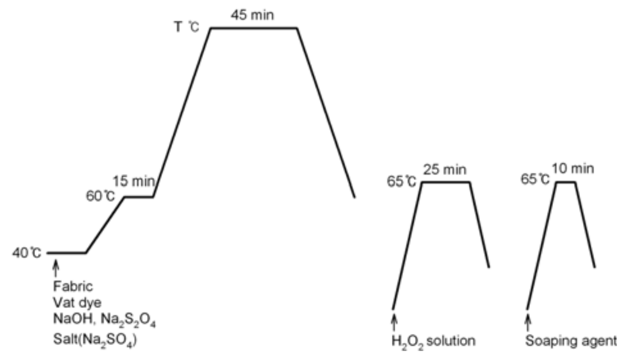
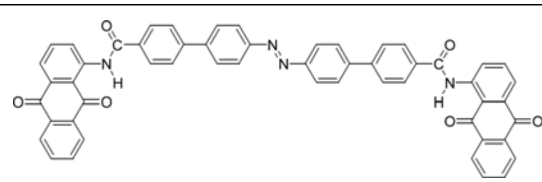
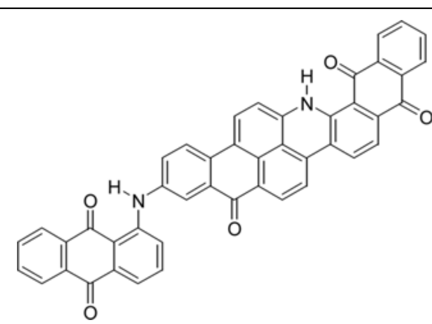
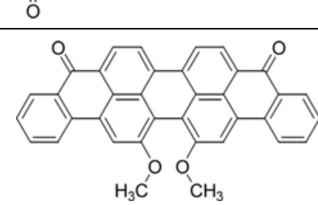


Figure 1. Dyeing profile of meta-aramid fabric with vat dyes.

Measurement of Color Yield, NIR Reflectance and Fastness

The color yield of the dyed fabric was determined from the *K/S* values by measuring the reflectance with the interval of 20 nm at the wavelength of visible range with a Macbeth Coloreye 3100 spectrophotometer, under illuminant D65

Table 1. Vat dyes used in this study

C.I. Generic name (Commercial name)	Structure	Molecular weight
C.I. Vat Yellow 33 (Indanthren Yellow F3GC)		832.23
C.I. Vat Black 25 (Mikethren Olive T)		686.18
C.I. Vat Green 1 (Indanthren Green FFB)		516.54

using 10 ^{o} standard observer. Then total *K/S* value was calculated by summation of the obtained *K/S* values from 400 to 700 nm. Reflectance of the dyed fabric in the Near Infrared (NIR) range was measured using a Datacolor Microflash MF 45 IR spectrophotometer.

The dyed fabrics were heat-set at 180 ^{o}C for 60 s and tested for fastness to washing (ISO 105-C10), light (ISO 105-B02), rubbing (ISO 105-X12), and perspiration (ISO 105-E04). The shade change, together with the staining of adjacent fabrics, was rated according to the appropriate ISO grey scale except light fastness which was rated using ISO blue scale.

LOI and Tensile Strength Measurement

LOI of the meta-aramid fabric before and after vat dyeing was measured according to ASTM Standard Method D2863-87. An average LOI value of each sample was obtained from 3 tests. The tensile strength of the meta-aramid fabric was evaluated using a Hounsfield H100 KS tensile testing machine according to ISO Standard 13934-1. Initial length of the test samples between clamps was 200 mm. Extension was carried out to the breaking point with an extension rate being 100 mm/min. Tensile strength was calculated using equation (1) and an average value of each sample was obtained from 5 tests.

$$\text{Tensile strength } (\sigma) = \frac{F_{max}}{A_0} \tag{1}$$

Where F_{max}: maximum tensile load (N)
A_0: area (thickness×width, mm^2)

Results and Discussion

Dyeing Properties

As mentioned earlier, vat dyes are reduced in an alkaline medium and converted to the soluble leuco form, which penetrates into the fibers. During the dyeing procedure in this study, dyebath containing vat dye, NaOH and reducing agent was heated to 60 ^{o}C and maintained at this temperature for 15 min in order for reducing reaction of the vat dye to occur. Then the dyebath was heated again to a certain dyeing temperature and dyed for 45 min at each temperature. During this dyeing process, the leuco vat dye seems to be exhausted on and diffused into the meta-aramid fiber. After dyeing, oxidation and soaping were carried out for restoration into the original insoluble vat dye and removing the unfixed dyes, respectively. In order to investigate the feasibility of vat dyeing on the meta-aramid fabric, the dyeing properties of vat dyes according to various dyeing conditions such as dyeing temperature, liquor ratio, and amount of reducing agent or salt were evaluated.

Figure 2 shows the *K/S* values in the visible range of meta-aramid fabric dyed with three vat dyes. C.I. Vat Yellow 33 exhibited a maximum *K/S* value at 400 nm which corresponds to the maximum absorption of the dye. However, double absorption maxima (400 and 620 nm) was obtained for C.I Vat Green 1 and C.I. Vat Black 25 showed a range of *K/S* values from 1.1 to 2.2 throughout the visible range instead of showing a maximum value at a certain wavelength. In order to evaluate the color yield of meta-aramid fabric in this study, sum of the *K/S* values (total *K/S* value) was calculated instead of *K/S* value at the absorption maximum.

Figure 3 shows the effect of dyeing temperature on the color yield of three vat dyes on meta-aramid fabric. The color yield of C.I. Vat Green 1 increased with increasing dyeing temperature, reaching a maximum value at 90 ^{o}C and decreased above 100 ^{o}C. This dyeing behavior is very typical for vat dyes and thus similar to that of a vat dyeing on cellulose fiber [13,14]. At the low dyeing temperature, the reduction of vat dye and formation of the leuco form which has

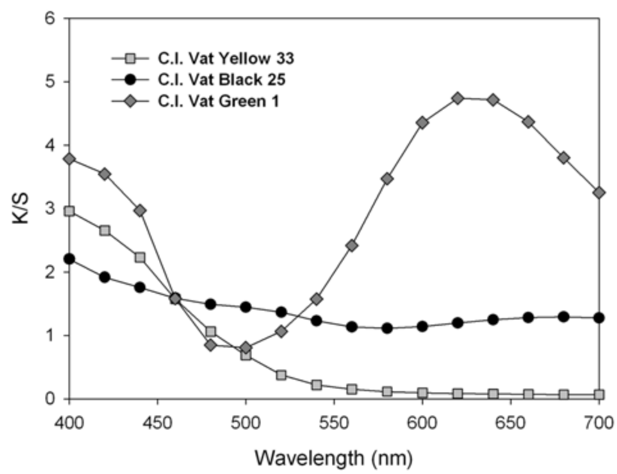


Figure 2. *K/S* values in the visible range of meta-aramid fabric dyed with three vat dyes (3 % owf, dyeing temperature 90 ^{o}C, reducing agent 4 g/*l*, salt 10 g/*l*).

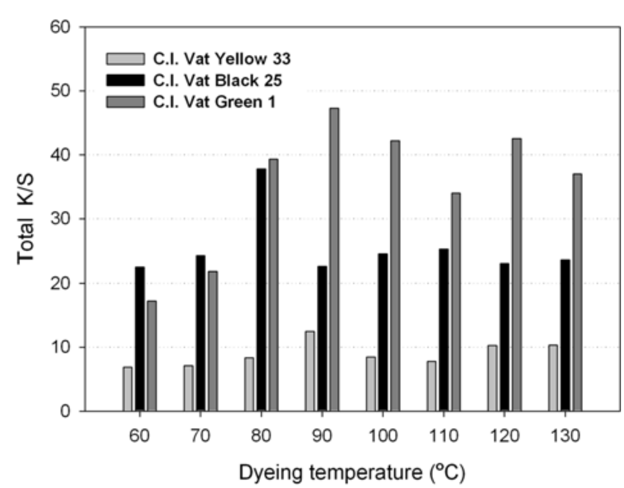


Figure 3. Effect of dyeing temperature on color yield (total *K/S*) of the vat dyes (3 % owf) on meta-aramid fabric (liquor ratio 20:1, reducing agent 4 g/*l*, salt 10 g/*l*).

substantivity to cellulose or meta-aramid fiber, would not be enough for satisfactory dye uptake. Diffusion rate of vat dye into the fiber increases with increasing dyeing temperature, resulting in an increase of color yield. However, when the dyeing temperature is too high, over-reduction or hydrolysis of vat dye might take place and the substantivity of the leuco vat dye to the fiber also diminishes, which causes the decrease of color yield [15]. Therefore, it can be said that optimum temperature exists in application of vat dye to meta-aramid fiber. As shown in Figure 3, the temperature in order to obtain a maximum color yield was 90 ^{o}C for C.I. Vat Yellow 33 and Green 1 and 80 ^{o}C for C.I. Vat Black 25. The optimum temperature was used in the subsequent experiment of dyeing.

Figure 4 shows the effect of liquor ratio on the color yields of vat dyes on meta-aramid fabric. The color yield of C.I. Vat Green 1 was highly dependent upon liquor ratio and it decreased with increasing liquor ratio. It is well known that higher liquor ratios lead to reduced dye uptake on the fibers because the probability of meeting of anionic leuco vat dye with meta-aramid fiber would be low at a high liquor ratio and vice versa [13]. The color yield of C.I. Vat Yellow 33 or Black 25 on the meta-aramid fiber was lower than that of C.I. Vat Green 1. This might be attributed to the large molecular weight of those vat dyes (832.23 for Yellow 33 and 686.18 for Black 25) compared to C.I. Vat Green 1 which has lower molecular weight (516.54). meta-Aramid fiber is well-known for its high degree of crystallinity and it would be difficult for big size of the dye molecule to diffuse into the fiber. It might also be this reason why the color yield of the two vat dyes increased just marginally as liquor ratio decreased.

The effect of the amount of reducing agent (sodium hydrosulfite, $Na_2S_2O_4$) on the color yield of C.I. Vat Black 25 on meta-aramid fabric is shown in Figure 5. The color yield was increased with increasing amount of reducing agent, showing maximum value when 10 g/*l* was used, and then decreased over 14 g/*l*. Reducing agent is essential for sufficient conversion of the vat dye into the soluble leuco form which can be exhausted to the fiber. Thus, when the small amount of reducing agent is added, the conversion into the leuco form would not be enough for exhaustion resulting in low color yield. Therefore, the color yield would increase until the sufficient amount of reducing agent would be added. However, when the amount of reducing agent is too high, over-reduction or hydrolysis of vat dye might take place which causes the decrease of color yield [16,17]. Similar behavior was obtained for C.I. Vat Yellow 33 and Green 1 although the optimum amount of the reducing agent was different from one another.

Figure 6 shows the color yield of C.I. Vat Yellow 33 on meta-aramid fabric in the presence of various amount of salt

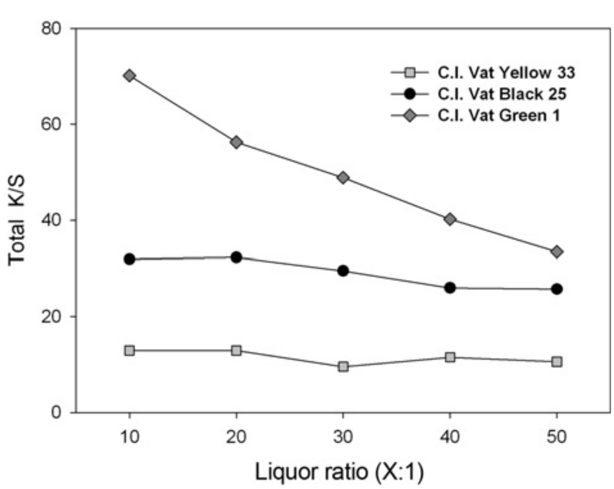


Figure 4. Effect of liquor ratio on color yield (total *K/S*) of the vat dyes (3 % owf) on meta-aramid fabric (dyeing temperature 90 ^{o}C for C.I. Vat Yellow 33 and Green 1 and 80 ^{o}C for C.I. Vat Black 25, reducing agent 4 g/*l*, salt 10 g/*l*).

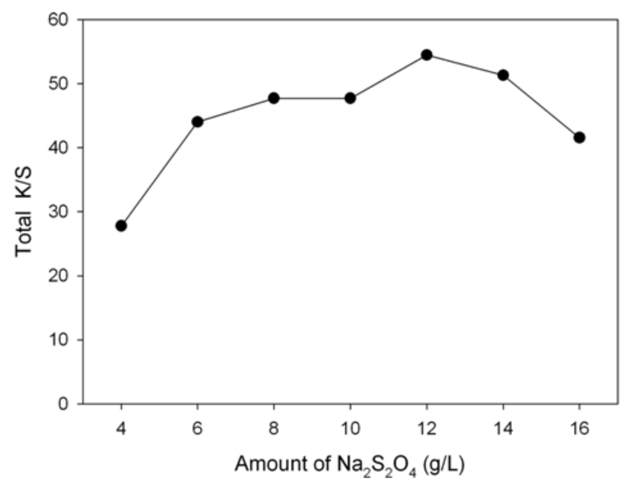


Figure 5. Effect of the amount of reducing agent ($Na_2S_2O_4$) on color yield (total *K/S*) of C.I. Vat Black 25 (3 % owf) on meta-aramid fabric (dyeing temperature 80 ^{o}C, liquor ratio 20:1, salt 10 g/*l*).

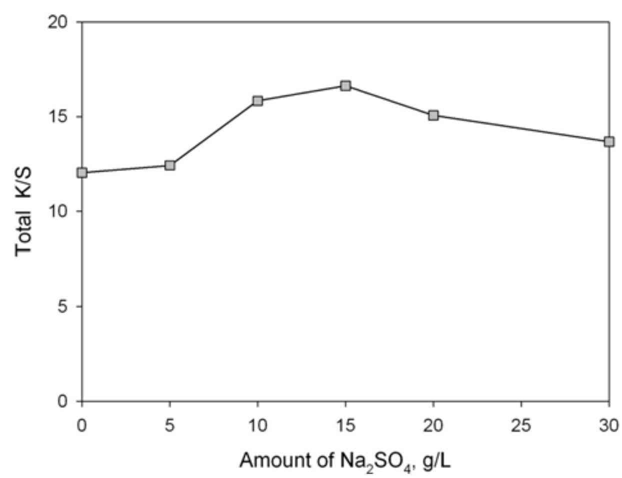


Figure 6. Effect of the amount of salt (Na_2SO_4) on color yield (total *K/S*) of C.I. Vat Yellow 33 (3 % owf) on meta-aramid fabric (dyeing temperature 90 ^{o}C, liquor ratio 20:1, reducing agent 4 g/*l*).

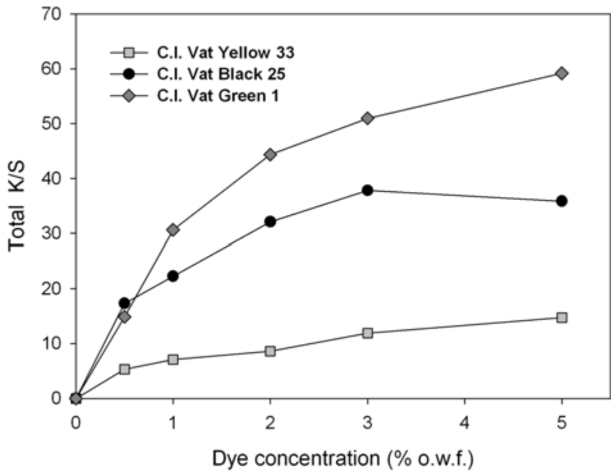


Figure 7. Color build-up of the vat dyes on meta-aramid fabric (dyeing temperature 90 °C for C.I. Vat Yellow 33 and Green 1 and 80 °C for C.I. Vat Black 25, liquor ratio 20:1, reducing agent 4 g/*l*, salt 10 g/*l*).

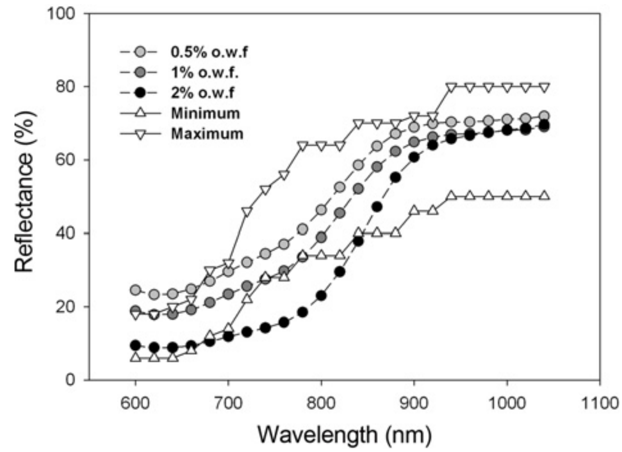


Figure 8. Minimum and maximum reflectance spectrum of forest green color in the military standard of South Korea and NIR reflectance spectra of meta-aramid fabric dyed with C.I. Vat Green 1 with various concentrations.

(sodium sulfate, Na_2SO_4). As the amount of salt increased, the color yield also increased and then decreased over 20 g/*l*. Generally, the pH level of the dyebath solution in vat dyeing process is very high by the presence of NaOH that there should be an electrostatic repulsion force between anionic leuco vat dye and the meta-aramid fiber which would show negative charge in the surface of the fiber or from the terminal carboxylic acid anion (COO^-) in strong alkaline solution. By adding a salt such as sodium sulfate to the dyebath, the electrostatic barrier between fiber surface and dye can be suppressed and facilitate dye-fiber contact leading to increased color yield [14]. However, when too large amount of salt is added, the dyebath would be more saturated with cation and anion from NaOH, $Na_2S_2O_4$, and salt, which might reduce the solubility of the leuco vat dye and cause decrease of color yield.

Figure 7 shows the build-up of three vat dyes on meta-aramid fabric. The color yield increased with increasing dye concentration. The build-up behavior of C.I. Vat Green 1 was better than those of C.I. Vat Yellow 33 and Black 25 which may be again explained by the large molecular weight of the dyes. It seems that C.I. Vat Yellow 33 and Black 25 would be adsorbed more in the surface area of the meta-aramid fiber rather than inside of fiber because of the big size of dye molecule as well as high degree of crystallinity of the fiber. Color strength of C.I. Black 25 at heavy depth might be increased when used more amount of reducing agent, as discussed in Figure 5.

NIR Camouflage

Visible and NIR spectra of meta-aramid fabric dyed with C.I. Vat Green 1 at the concentration of 0.5 to 2 % owf are shown in Figure 8. It was found that reflectance values at 600 to 1040 nm of the vat dyed meta-aramid fabric decreased as dye concentration increased. It is well known that the fabric, in which more dye is exhausted, can absorb more light in the visible and NIR range and will show lower reflectance values. Figure 8 also shows the tolerance of reflectance spectrum of forest green color in the military standard of the Korean combat uniform which has minimum and maximum values from 600 to 1040 nm. Five standard colors for Korean combat uniform are land, dark olive green, forest green, dark wood, and charcoal. Each color has specific minimum and maximum reflectance values in the visible and NIR range and camouflage textiles should satisfy the reflectance specifications covering both the visible and NIR regions. Thus, every sample of military uniform needs to show reflectance values between the specific minimum and maximum ones for corresponding 5 colors in the range from 600 to 1040 nm with the interval of 20 nm and less than 4 points in the range should be over the limit. As shown in Figure 8, the reflectance values of the vat dyed sample with 1 % dye concentration lies between the minimum and maximum ones in almost all the range of the standard for forest green color. This result suggests that meta-aramid fabric, with the appropriate color matching or careful control of dye concentration using vat dyes, can be applied to the military uniform with NIR camouflage property.

LOI and Tensile Property

Vat dyeing processes are usually performed in a strong

Table 2. LOI value and tensile strength of meta-aramid fabric before and after dyeing with C.I. Vat Green 1

	LOI (%)	Tensile strength (MPa)
Before dyeing	30.6±0.3	43.1±1.1
After dyeing	29.5±0.3	41.4±1.4

Table 3. Wash fastness of the vat dyes (3 % owf) on meta-aramid fabric

Dye	Wash fastness						
	Change	Staining					
		Acetate	Cotton	Nylon	PET	Acrylic	Wool
C.I. Vat Yellow 33	4-5	4-5	4-5	4-5	4-5	4-5	4-5
C.I. Vat Black 25	4-5	4-5	4-5	4	4-5	4-5	4-5
C.I. Vat Green 1	4-5	4-5	4-5	4-5	4-5	4-5	4-5

alkaline condition as well as with reducing agent, which might cause the degradation of the fiber or reduce the physico-chemical property especially in the case that the fiber is weak. In order to evaluate the effect of vat dyeing condition on the thermal stability or mechanical property of the meta-aramid fiber, LOI and tensile strength of the fabric was measured before and after dyeing with C.I. Vat Green 1 as shown in Table 2. After dyeing, LOI value and tensile strength of the meta-aramid fabric slightly decreased but it was marginal. Therefore, it can be said that vat dyeing does not change the properties of the meta-aramid fiber perceptibly.

Fastness Properties

Table 3 shows the results of testing wash fastness test for three vat dyes on meta-aramid fabric. On the whole, the three vat dyes showed very good (rating 4-5) wash fastness on meta-aramid fabric with an exception of C.I Vat Black 25 on nylon staining (rating 4). Table 4 gives the light and rubbing fastness results. C.I. Vat Black 25 and Green 1 exhibited poor light fastness (rating 2) and C.I. Yellow 33 showed very poor light fastness (rating 1). Vat dyes are well known for their excellent light fastness on cotton. It is thought to be ascribed to the lack of strongly polar substituents such as donor and acceptor groups found in other dye classes [18]. Planar structure of the vat dyes would be another reason for the excellent lightfastness because it is easy for the dyes to make aggregation. However, there are lots of variables such as fiber, existence of moisture or oxygen, dye-fiber bond, and dye itself which could affect the photofading of dyes. Thus dyes, showing good lightfastness on a certain fiber, might show poor lightfastness on another fiber. Unsatisfactory level of light fastness of the vat dyes in this study might be due to the inherent instability of meta-aramid fiber by photofading. Rubbing fastness of C.I. Yellow 33 was moderate to good (rating 3-4) while those of Black 25 and Green 1 were poor to moderate (rating 2-3). Table 5 shows the perspiration fastness results. All the dyes exhibited very good to excellent perspiration fastness on meta-aramid fabric.

Table 4. Light and rubbing fastness of the vat dyes (3 % owf) on meta-aramid fabric

	Light fastness	Rubbing fastness	
		Dry	Wet
C.I. Vat Yellow 33	1	3-4	3
C.I. Vat Black 25	2	2-3	2-3
C.I. Vat Green 1	2	2-3	2-3

Conclusion

Dyeing and fastness properties of meta-aramid fabric with vat dyes have been examined. The color yields of the vat dyes on the meta-aramid fabric were found to be dependent upon dyeing temperature, liquor ratio, amount of reducing agent, and amount of salt. Dyeing behavior of vat dye on the meta-aramid fiber was very similar to that on cellulose fibers although color yield on the meta-aramid fiber was relatively low. Low color yield seems to be due to the high degree of crystallinity of the fiber, which might be improved by controlling the dyeing condition, careful selection of vat dye, and using auxiliaries such as a swelling agent.

Although military uniforms are dyed with vat dyes using a printing method, we used an exhaustion method, as a basic research, for dyeing meta-aramid fiber and investigated the

Table 5. Perspiration fastness of the vat dyes (3 % owf) on meta-aramid fabric

	Type	Staining					
		Acetate	Cotton	Nylon	PET	Acrylic	Wool
C.I. Vat Yellow 33	Acidic	5	5	5	5	5	5
	Alkaline	5	4-5	5	5	5	5
C.I. Vat Black 25	Acidic	5	5	5	5	5	5
	Alkaline	5	5	5	5	5	5
C.I. Vat Green 1	Acidic	5	5	5	5	5	5
	Alkaline	5	5	5	5	5	5

feasibility of NIR camouflage. It was found that the vat dyed meta-aramid fabric with 1 % dye concentration of C.I. Vat Green 1 satisfied the tolerance of reflectance spectrum of forest green color in the Korean military standard. From the result of the NIR spectra, it is highly expected that meta-aramid or its blend fabric, with appropriate color matching, could be printed with vat dyes for the military uniform with NIR camouflage property.

Thermal stability and mechanical property of the meta-aramid fabric did not significantly affected by the vat dyeing process. Wash and perspiration fastness was generally satisfied but rubbing and light fastness was unsatisfied which need to be improved for commercialization.

Acknowledgement

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References

1. E. A. Manyukov, S. F. Sadova, N. N. Baeva, and V. A. Platonov, *Fiber Chemistry*, **37**, 54 (2005).
2. A. Nechwatal and V. Rossbach, *Text. Res. J.*, **69**, 635 (1999).
3. A. P. Mikhailovskaya, N. V. Dashchenko, T. Y. Dyankova, and I. B. Dmitrieva, *Fiber Chemistry*, **33**, 271 (2001).
4. K. J. Yong, Y. H. Park, K. P. Yoo, H. J. Lee, and S. U. Nam, *J. Korean Fiber Soc.*, **40**, 463 (2003).
5. E. M. Kim, B. G. Min, and J. Jang, *Fiber. Polym.*, **12**, 580 (2011).
6. E. Kim and J. Choi, *Fiber. Polym.*, **12**, 484 (2011).
7. C. S. Hughey, *Text. Chem. Col.*, **12**, 38 (1980).
8. D. M. Nunn, "The Dyeing of Synthetic-Polymer and Acetate Fibres", p.113, Dyers Company Pub., London, 1979.
9. S. M. Burkinshaw, G. Hallas, and A. D. Towns, *Rev. Prog. Coloration*, **26**, 47 (1996).
10. V. Rubeziene, G. Minkuviene, J. Baltusnikaite, and I. Padleckiene, *Mat. Science*, **15**, 173 (2009).
11. X. Yin, Q. Chen, and N. Pan, *Appl. Thermal Eng.*, **36**, 32 (2012).
12. S. M. Birkinshaw, S. Chevli, M. Hunt, L. Jones, D. Lewis, and D. Marfell, *U.S. Patent*, 642706 B2 (2005).
13. W. S. Shim, J. J. Lee, J. P. Kim, S. W. Chun, S. Kwak, I. S. Kim, J. S. Ahn, J. Koh, and Y. K. Kwon, *Text. Res. J.*, **74**, 787 (2004).
14. J. J. Lee, W. S. Shim, I. S. Kim, and J. P. Kim, *Fiber. Polym.*, **6**, 244 (2005).
15. F. R. Latham in "Cellulosics Dyeing" (J. Shore Ed.), pp.255-256, The Society of Dyers and Colourists, Bradford, 1995.
16. E. K. Hwang, M. S. Kim, D. S. Lee, and S. Y. Choi, *Korean J. Seric. Sci.*, **38**, 168 (1996).
17. M. H. Lee, S. R. Jin, and S. D. Kim, *J. Korean Fiber Soc.*, **37**, 189 (2000).
18. P. F. Gordon and P. Gregory, "Organic Chemistry in Colour", pp.281-298, Springer-Verlag, New York, 1987.