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Dyeing and Fastness Properties of Vat Dyes on a Novel Regenerated Cellulosic Fiber

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Abstract: enVix is a novel regenerated cellulosic fiber, which is prepared from cellulose diacetate fiber using environmentally friendly manufacturing process. Vat dyeing properties of the enVix were investigated and compared with those of regular viscose rayon. The enVix exhibited better dyeability than viscose rayon. The colour yields of vat dyes on the enVix were found to be dependent on dyeing temperature as well as the amount of levelling agent and salt. Good build-up and good to excellent fastness properties were obtained on the enVix fabric.

Keywords: Regenerated cellulosic fiber, Viscose rayon, Vat dye, Supramolecular structure

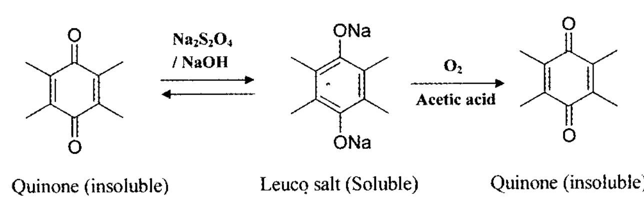
Introduction

The manufacturing process of viscose rayon was discovered by C. F. Cross and E. J. Bevan. Rayon fibers are made from chemical cellulose (dissolved wood pulp), sodium hydroxide, carbon disulfide (CS_2) and sometimes modifiers, which are usually based on ethoxylated natural fatty acid amines. Most rayon is made by the viscose process; however, some special rayon is made by the cuprammonium process in Italy, former USSR and Japan or by the solvent-spun process in United States, United Kingdom and Austria. In the manufacture of the various viscose (wet-spun) rayon fibers, the same basic process is used. However, a number of important variables in the viscose process can be manipulated to obtain fibers of substantially different characteristics. Broadly speaking, the main fiber categories include regular rayon, modified high-tenacity rayon, high wet modulus rayon and polynosic. The manufacturing process of all the rayons is not environmentally friendly [1-3].

Recently, SK Chemicals Co., Ltd. introduced a novel regenerated cellulosic fiber, with the commercial name of enVix. The enVix is made from the hydrolysis of cellulose diacetate fiber (Scheme 1). Therefore, the manufacturing process of the enVix is more environmentally friendly than that of conventional viscose rayon, which employs poisonous carbon disulfide [4].

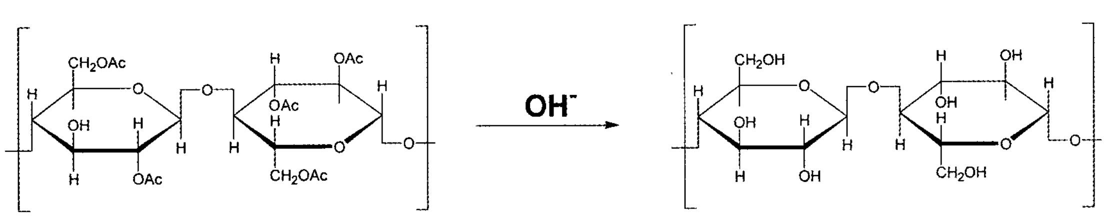
Vat dyes are used to dye cellulosic fibers in relatively dull shades requiring good fastness. The vat dyes are originally insoluble but can be reduced with the aid of alkali and reducing agent (sodium hydrosulfite). The reduced or leuco vat dye is soluble in water and has substantivity to cellulosic 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 [5,6].

In the previous studies, we reported the dyeing properties of enVix and viscose rayon using various types of dyes such



Structure	Quinone	Leuco salt	Quinone
Solubility	Insoluble	Soluble	Insoluble
Substantivity to cellulose	Low	High	Low

Scheme 2. The chemistry of a vat dye.



Scheme 1. Preparation of enVix by alkali hydrolysis of secondary cellulose acetate fibre.

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as direct [7], reactive [8] and vat dye [9] and discussed the correlation between supramolecular structures and dyeing properties of the fibers. In this study, three vat dyes were applied to the enVix and regular viscose rayon fiber and their dyeing properties were investigated and compared. The effect of vat dyeing conditions such as temperature, the amount of levelling agent and salt on the colour yield was investigated. Wash, light, rubbing and perspiration fastness of the dyed fabrics were also evaluated.

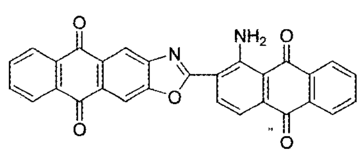
Experimental

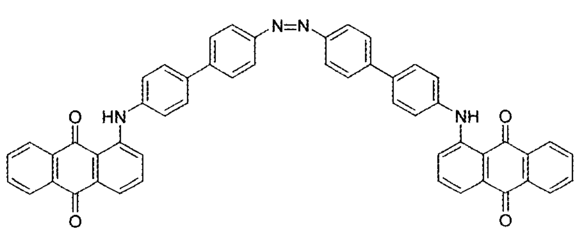
Materials

The scoured, woven fabrics of enVix and viscose rayon were provided by SK Chemicals Co., Ltd., Korea. The specifications of fibers are listed in Table 1. The three vat dyes employed were Cibanone Red 2B (C.I. Vat Red 10, Ciba Specialty Chemicals Co.), Indanthren Yellow F3GC (C.I. Vat Yellow 33, BASF) and Cibanone Yellow 3R (C.I. Vat Orange 11, Ciba Specialty Chemicals Co.) and their structures are shown in Figure 1. Peregal P, used as a levelling agent, was supplied by BASF. Setamol WS, a dispersing agent, and Dekol SN, a soaping agent, were supplied by Dae-Yang TexChem Co. Sodium hydrosulphite ($Na_2S_2O_4$) used as a reducing agent and sodium hydroxide (NaOH) were purchased from Sigma Aldrich Chemicals Co. All the other chemicals used were of laboratory grade.

Table 1. Specifications of the enVix and viscose rayon

Fiber	Fiber density (denier/filament)	Fabric density (threads per inch, tpi)	
		Warp	Weft
enVix	86/33	168	87
Viscose rayon	120/50	80	60


C.I. Vat Red 10


C.I. Vat Yellow 33

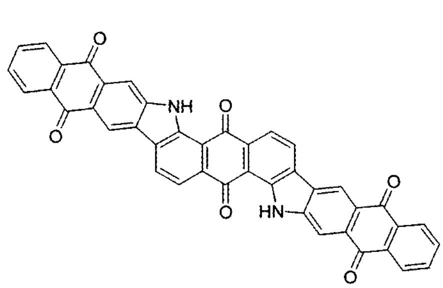

C.I. Vat Orange 11

Figure 1. Structures of the vat dyes used in this study.

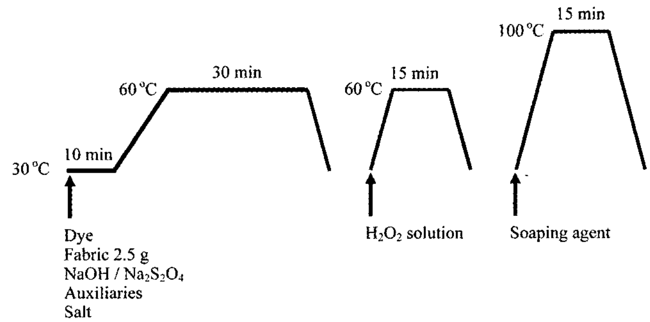


Figure 2. Dyeing profile of enVix and viscose rayon with vat dyes.

Vat Dyeing

The enVix and viscose rayon fabrics were dyed in an IR dyeing machine (DL6000A, Dae-Lim Co., Ltd., Korea) using dyeing profile shown in Figure 2. The dyebath was prepared with vat dye (1% owf), NaOH (5 g/*l*), $Na_2S_2O_4$ (5 g/*l*), dispersing agent (0.5 g/*l*), levelling agent (0-2 m*l*/*l*) and salt (Na_2SO_4, 0-50 g/*l*). The liquor ratio was 30:1. Dyeing was commenced at 30 °C and the temperature was raised by 1 °C/min to 60 °C, maintained at the temperature for 30 min and rapidly cooled to room temperature. At the end of dyeing, the dyed fabrics were removed, rinsed thoroughly in cold water. Oxidation was carried out with 2 m*l*/*l* hydrogen peroxide solution (30% w/v) at 60 °C for 15 min. Finally, the dyeings were soaped at boiling temperature for 15 min with 1.5 g/*l* soaping agent. The colour yield (K/S) value of dyed fabric was measured using a Macbeth Coloreye 3000 spectrophotometer (illuminant D_{65}, 10° observer).

Measurement of Exhaustion

After dye solution was prepared, the initial concentration of the reduced vat dye (leuco form) was determined by measuring absorbance at the wavelength of maximum absorption (λ_{max}) of the reduced dye using a HP8452 UV/Visible spectrophotometer. Then dyeing was carried out without hesitation in order to prevent possible oxidation of the dye. At the end of dyeing, the absorbance of the dye solution was measured as soon as possible for the same reason (preventing oxidation). From preliminary test, it was found that oxidation or degradation of a vat dye did not occur or occurred to a negligible extent under the dyeing condition studied. The percentage exhaustion of the leuco vat dye on enVix and viscose rayon was calculated using equation (1).

$$\text{Exhaustion (\%)} = \left(1 - \frac{A_1}{A_0}\right) \times 100 \quad (1)$$

Where A_0: absorbance of initial dyebath
A_1: absorbance of residual dyebath

Fastness Tests

The enVix and viscose rayon were dyed to give 1/1 standard depth (1/1 SD). The dyed fabrics were heat-set at 170 °C for 60s and tested for fastness to washing (ISO 105 C06:1994), light (AATCC test method 16-1998), rubbing (ISO 105 X12:2001) and perspiration (ISO 105 E04:1994). The shade change, together with the staining of adjacent fabrics, was rated using the ISO grey scales for staining and change in colour.

Results and Discussion

Effect of Dyeing Temperature

Figure 3 shows the colour yield of C.I. Vat Red 10 on enVix and viscose rayon at various dyeing temperature. The colour yield of the dye on enVix is higher than that on viscose rayon in all cases. This can be explained by the supramolecular structure of the fibre. According to the results of X-ray analysis in the previous study [7], although the crystalline structures of both fibres were similar each other, the value of crystallinity of the enVix was lower than that of viscose rayon. The birefringence of enVix was also lower indicating that the fibre molecules of the enVix are less oriented in the direction of the fibre axis than those of viscose rayon. Therefore, dye molecule of leuco form could diffuse into the less crystalline and less oriented enVix fibre more easily than viscose rayon, which results in the higher K/S value of enVix. The colour yield of C.I. Vat Red 10 on enVix increased as the dyeing temperature increased to 60 °C and then decreased above 70 °C, thus showing maximum value at 60 °C. At the low dyeing temperature (40 or 50 °C), the reduction of vat dye and formation of leuco form which has substantivity to cellulose fibre, would not be enough for satisfactory dye uptake. Diffusion rate of vat dye into cellulosic fibre increases with increasing dyeing temperature, resulting in an increase of colour 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 cellulose fibre also diminishes, which causes the decrease of colour yield [10]. Thus, it can be said that optimum temperature exists in application of vat dye to cellulose fibre. Vat dyes in this study also exhibited this tendency on enVix fibre as shown in Figure 4 and the temperature in order to obtain a maximum colour yield was 60 °C for C.I. Vat Yellow 33 and Red 10 and 70 °C for C.I. Vat Orange 11.

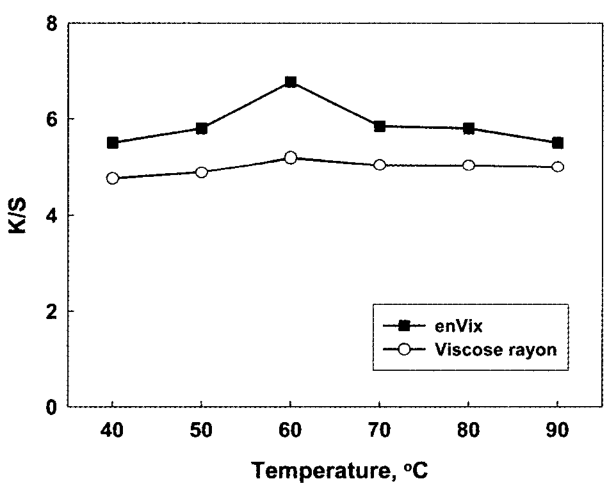


Figure 3. Effect of dyeing temperature on colour yield (K/S) of C.I. Vat Red 10 (1 % owf) on enVix and viscose rayon (levelling agent 0.5 m*l*/*l*, salt 15 g/*l*).

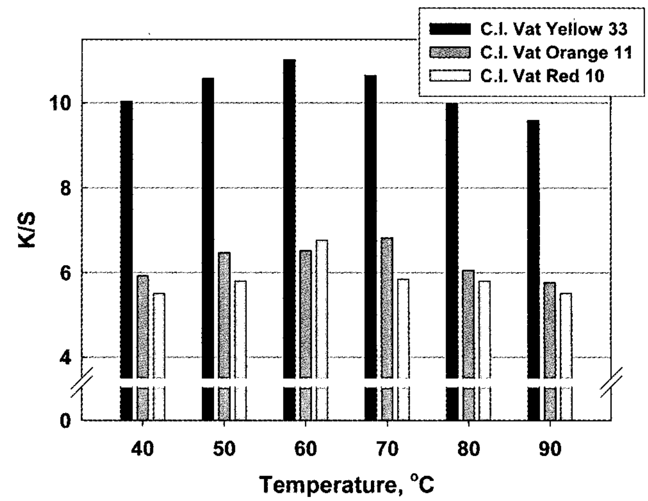


Figure 4. Effect of dyeing temperature on colour yield (K/S) of the vat dyes (1 % owf) on enVix (levelling agent 0.5 m*l*/*l*, salt 15 g/*l*).

Effect of Leveling Agent

In general, it is more difficult to produce level dyeing in practice with vat dyes than with other dyes. Without the careful control of the dyeing condition, initial dyeing rate of leuco vat dye to cellulose would be too fast, which might cause "ring dyeing" with an uncolored center core of the fibre. The levelling agent is used to decrease the initial dyeing rate in the vat dyeing process to ensure level dyeing. The effect of the amount of levelling agent on the colour yield of C.I. Vat Red 10 on enVix and viscose rayon is given in Figure 5. The colour yields on both fibre decreased with an increased amount of levelling agent. It is attributed to the interaction between the vat dye and the levelling agent. Peregal P, the levelling agent used in this study is cationic surfactant and shows high affinity to vat dyes. It can interact with anionic leuco vat dye and make a temporary complex with the dye

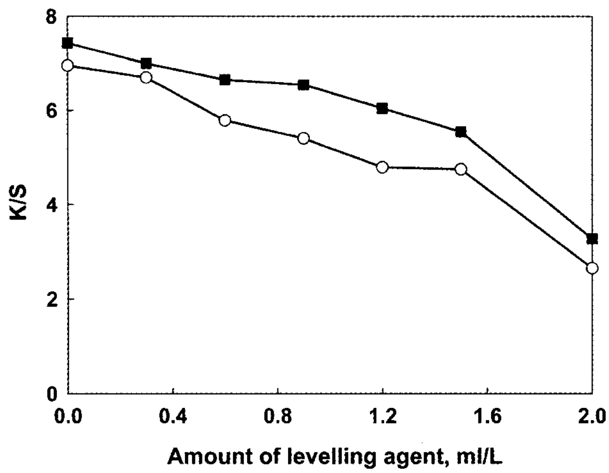


Figure 5. Effect of amount of levelling agent (Peregal P) on colour yield (K/S) of C.I. Vat Red 10 (1 % owf) on enVix and viscose rayon (dyeing temp. 60 °C, salt 15 g/*l*); for key see Figure 3.

during the dyeing process, thus lowering the dyeing rate on cellulose fibre. The colour yield was very low when the large amount of levelling agent was added. It seems that the attraction force of the levelling agent with vat dye was so strong that it was difficult for the dye molecule to be separated from the levelling agent and migrate into fibre in case of high concentration of levelling agent. Therefore, the minimum amount of levelling agent should be used for good colour yield as long as level dyeing can be obtained. The colour yield of the dye on enVix was higher than that on viscose rayon in all case indicating that it was easier for vat dye to migrate into less compact enVix fibre than viscose rayon. Similar behavior was obtained for C.I. Vat Yellow 33 and Orange 11.

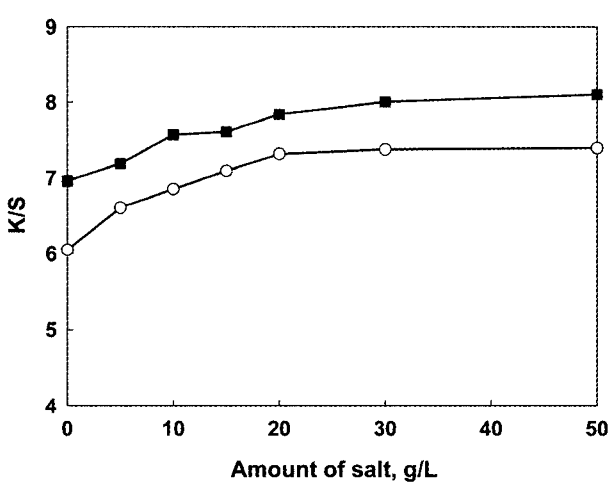


Figure 6. Effect of amount of salt (Na_2SO_4) on colour yield (K/S) of C.I. Vat Orange 11 (1 % owf) on enVix and viscose rayon (dyeing temp. 60 °C, levelling agent 0.5 m*l*/*l*); for key see Figure 3.

Effect of Salt

Figure 6 shows the colour yield of C.I. Vat Orange 11 on enVix and viscose rayon in the presence of various amount of salt (Na_2SO_4, sodium sulphate). As the amount of salt increased, the colour yield also increased. Generally, the pH level of the dyebath solution in vat dyeing process is very high that there should be an electrostatic repulsion force between anionic leuco vat dye and the cellulose fiber which would turn into the cellulosate anion in strong alkaline solution. By adding a salt such as sodium sulphate to the dyebath, the electrostatic barrier between fibre surface and dye, known as the Donnan potential, can be suppressed and facilitate dye/fiber contact hence improving substantivity. Also the diffusion rate of the dye is a function of both dye and salt concentration. The result in Figure 6 shows a good agreement with this statement. The colour yield reached saturation with the 20 g/*l* of salt concentration and did not increased much. The color yield on enVix was higher than that on viscose rayon in all cases. Similar result was obtained for C.I. Vat Red 10 and Yellow 33 and optimum amount of salt was 15-20 g/*l*.

Exhaustion and Build-up

The enVix fabric was dyed with three vat dyes with 1 % owf dye concentration and optimum dyebath condition obtained and then exhaustion of each dye was measured. The percentage exhaustion values of C.I. Vat Red 10, Yellow 33 and Orange 11 were 96.0, 96.8 and 94.9 % respectively. Figure 7 shows the build-up of three vat dyes on enVix fabric. All the dyes exhibited good build-up and the colour yield increased with increasing dye concentration. The build-up behaviors of C.I. Vat Red 10 and Orange 11 were similar each other. C.I. Vat Yellow 33 showed great initial build-up but the colour strength in heavy depth was lower than those of the other two dyes. This may be explained by the heavy molecular weight of the

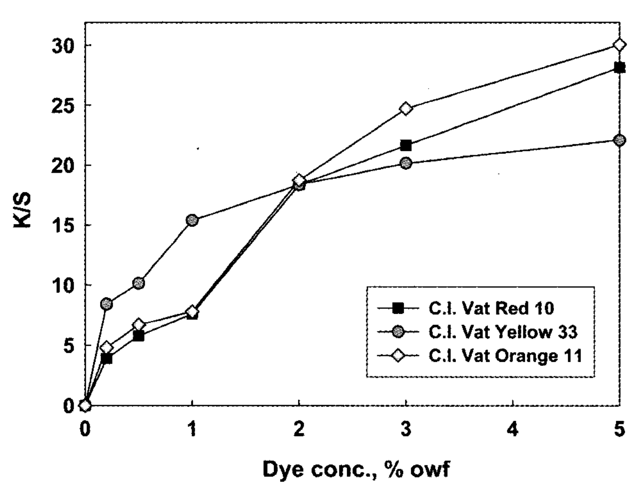


Figure 7. Colour build-up of the vat dyes on enVix (dyeing temp. 60 °C).

Table 2. The wash fastness of the vat dyes (1/1 SD) on enVix and viscose rayon

Dye	Fiber	Change	Staining					
			Acetate	Cotton	Nylon	Polyester	Acrylic	Wool
C.I. Vat Red 10	enVix	4/5	4/5	5	4/5	5	5	5
	Viscose	4/5	4	5	5	5	5	5
C.I. Vat Yellow 33	enVix	4/5	4	5	3/4	5	5	5
	Viscose	4/5	5	5	3	5	5	5
C.I. Vat Orange 11	enVix	4/5	4/5	5	4/5	5	5	5
	Viscose	4/5	4/5	5	4/5	5	5	5

Table 3. The light and rubbing fastness of the vat dyes (1/1 SD) on enVix and viscose rayon

Dye	Fiber	Light	Rubbing	
			Dry	Wet
C.I. Vat Red 10	enVix	7	4	4/5
	Viscose	7	4	4
C.I. Vat Yellow 33	enVix	7	4/5	4
	Viscose	7	4	3/4
C.I. Vat Orange 11	enVix	7	4/5	4
	Viscose	7	4	3/4

C.I. Vat Yellow 33 and thus greater substantivity to enVix. It seems that this dye would be adsorbed more in the surface area of the fibre than core owing to the large size of dye molecule, which might result in reaching saturation of colour yield earlier than the other dyes.

Fastness Properties

Table 2 shows the results of testing wash fastness test for three vat dyes on enVix and viscose rayon. C.I. Vat Red 10 and Orange 11 showed good to excellent wash fastness on enVix fabric while C.I. Vat Yellow 33 showed some staining on acetate and nylon. The fastness results for viscose rayon were similar to those for enVix. Table 3 gives the light and rubbing fastness results. All the dyes exhibited very good light fastness ratings for both fibers. The rubbing fastness results for enVix were good to very good but those for viscose rayon were moderate to good. Medium level of rubbing fastness on enVix and viscose rayon is possibly due to the physical properties of rayon fibers such as low tenacity and poor abrasion resistance. Table 4 shows the perspiration fastness results. The enVix exhibited very good to excellent perspiration fastness with some exception (Acid perspiration with C.I. Vat Red 10) and viscose rayon suffered from some staining in the case of C.I. Vat Red 10 and Orange 11.

Conclusions

The vat dyeing properties of the enVix, a novel regenerated cellulosic fiber have been examined and compared with those of regular viscose rayon. The colour yield of the enVix was higher than that of viscose rayon. The low crystallinity and orientation level of enVix seems to make the vat dye molecule diffuse into the enVix fibre more easily than

Table 4. The acid and alkali perspiration fastness of the vat dyes (1/1 SD) on enVix and viscose rayon

Dye	Fiber	Type	Staining					
			Acetate	Cotton	Nylon	Polyester	Acrylic	Wool
C.I. Vat Red 10	enVix	Acid	5	5	3	3	5	5
		Alkali	5	5	5	5	5	5
	Viscose	Acid	3/4	4/5	5	5	5	5
		Alkali	4/5	5	4	4	5	5
C.I. Vat Yellow 33	enVix	Acid	5	5	5	5	5	5
		Alkali	5	5	5	5	5	5
	Viscose	Acid	5	5	5	5	5	5
		Alkali	4/5	5	4/5	5	5	5
C.I. Vat Orange 11	enVix	Acid	5	5	5	5	5	5
		Alkali	5	5	5	5	5	5
	Viscose	Acid	4	5	5	5	4	5
		Alkali	3/4	5	5	5	5	5

viscose rayon. The colour yields of the vat dyes on the enVix were affected by the dyeing temperature and optimum temperature was assessed. The levelling agent should be added to prevent an unwanted ring dyeing but when used in excess, colour yield might be reduced. Addition of salt was found to have a beneficial effect on dyeing property. The vat dyes used in this study exhibited good build-up on the enVix and overall fastness was good to excellent. The enVix has a lot of advantages over the regular viscose rayon such as good dyeing and physical properties and environmentally friendly manufacturing process. We expect that the demand for this novel regenerated cellulosic fibre will increase in the near future.

Acknowledgements

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