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Preparation of a Cationic Environment-Friendly Fixing Agent

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Abstract
Initially waste feather protein was used to prepare a reactive cationic crosslinking modified agent, WLS, as a starting material which was used to prepare a quaternary ammonium type cationic environment-friendly fixing agent (named WLSPR) for dyeing cotton fabric with reactive dyes after solid colour processing. In this paper, the degree of staining on white cloth from colored cloth after a soaping process was assessed (by determination of the K/S value) as well as the washing fastness etc. as the evaluation indices. The optimum synthetic conditions of fixing agent WLSPR were determined, and the structure and properties of the additives characterised. The results show that the maximum absorption wavelength of the cationic protein fixing agent WLSPR is 195nm. Synthesis of the environment-friendly fixing agent WLSPR using optimum conditions can reduce white staining during soap washing, effectively improving the cotton fabric in terms of colour fastness to washing and rubbing fastness. Based on infrared spectral characterisation, it was confirmed that the protein-based cationic auxiliary additives were synthesised.

Key words: *preparation, environment-friendly fixing agent, K/S value, fastness.*

Introduction

The reactive dye application class features a complete set of colours, bright colour properties, good levelness, and low cost. It has become the preferred dye class for cellulosic fibre fabric [1-3]. At present, the annual production of reactive dyes is 200 thousand tons, accounting for about 20% of the annual output of global dye [4-7]. Although water-soluble reactive dyes can form covalent bonds with cotton fibre, at the same time, a reactive dye reacts by a hydrolysis reaction with water. Hydrolysed dye is not easy to remove and can have a certain affinity for fibre [8-10]. Therefore there is a need for strongly fixed colour after dyeing, in order to improve the colour fastness [11-14].

With the increasing demand for the enhanced colour fastness and reduced formaldehyde content of textiles in the domestic and foreign markets, researchers from all over the world are actively developing eco friendly dyeing and fixing agents [15-17]. In the late 1980s, our country began to strengthen the development and application of formaldehyde-free fixing agents which can improve colour fastness performance, in order to replace the traditional formaldehyde-containing dye fixative agents [18-19]. Judging from the current situation, the use of formaldehyde-free fastness improvers are mostly based on amines (mainly dimethylamine and diethylene triamine) and polycationic fixing agents which are made from epoxy chloropropane [20-21]. This study uses waste protein as a raw material. The keratin agent was extracted, and then a quaternary ammonium type cationic crosslinking modification agent, WLS, was prepared from studies within our research group, leading to modified protein additives. Protein derivative cationic additives were made and put to use in the dyeing of cotton fabrics, after solid color processing. Based on the characteristics of the additive structure, its chemical composition contains the polypeptide chain, with the structure also containing many amino (-NH_2), carboxyl (-COOH), hydroxyl (-OH), sulfhydryl (-SH), epoxy ethane and cationic groups. Dyed fabric which is treated by the additives is likely to increase the interaction between the dye and fabric as well as reduce the dye water solubility, so as to enhance the colour fastness to washing of fabrics. In addition, the auxiliary processed fabric will also improve moisture absorption, comfort and health performance. The emphasis of the research in the study was to develop additive synthesis conditions leading to an ecological environmental protection type of fixing agent, and achieve effective use of waste resources, turning waste into value, and to achieve the aim of environmental protection and clean production.

Experimental

Main materials and instruments

Materials: Reactive Dark Blue CD-2BG, Reactive Orange CD-2BR, Reactive Black DS-DH (industrial products, provided by the Shanghai KELONG dye Co., Ltd., China), cationic modification agent WLS (self-made), feather protein powder (self-made), sodium hydroxide, urea, sodium bisulfite, sodium carbonate, epoxy chloropropane (ECH), triethanolamine (TEA), etc.

Instruments: HHS-24 type electric thermostatic water bath (Shanghai East Star Building Materials Laboratory Equipment Co., Ltd., China), SF300 electronic balance (Shanghai Liang Ping instrument and Meter Co., Ltd., China), SF-300 computer colour measuring instrument (Shenyang Thinking Technology Co., Ltd., China), etc.

Feather protein powder preparation process

Pretreatment of feather → dissolve → preparation of protein powder → put into use.

Pretreatment of feather: collect and wash the feathers, and soak with 0.5 % glacial acetic acid solution for 10 minutes. Wash with water, dry and stand-by.

Feather dissolving procedure:

The first step in the pretreatment process:

sodium bisulfite, g/l	6
temperature, °C	90
time, min	15
solid-liquid ratio, ratio of feather quality and treatment liquid	1:20

The second step in the solution process:

urea, g/l	6
sodium hydroxide, g/l	8
temperature, °C	90
time, min	120-180
solid-liquid ratio, ratio of feather quantity to treatment liquid	1:20

After completion of the feather protein dissolution, the mixture was cooled, filtered with gauze 3 times, and the pH value of the filtrate was adjusted to 4.0-5.0. If there was a precipitate, it was separated and dried. In this way, feather protein powder was obtained. ***Figure 1*** is the feather protein degradation reaction.

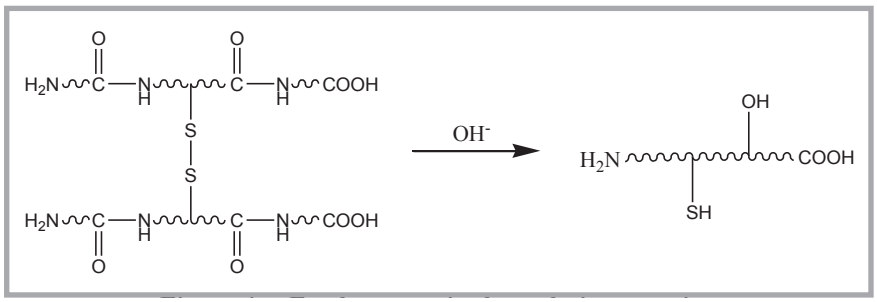

Figure 1. *Feather protein degradation reaction.*

Preparation process and structural characteristics of cationic modification agent WLS

Cationic modification agent (WLS) preparation process

1. Reaction principle
   Monomer triethanolamine and epichlorohydrin are selected to react in alkaline conditions and cationic agent containing a quaternary ammonium salt structure, and multiple epoxy groups are generated, the equation for which is shown in ***Figure 2***.

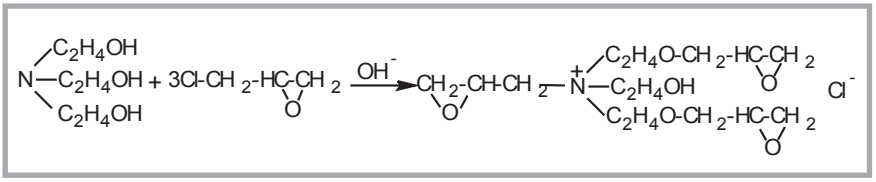

Figure 2. *Preparation process of cationic modification agent (WLS).*

2. Preparation process of the cationic modification agent (WLS)
   Add n (triethanolamine): n (epoxy chloropropane) = 1:1~1:3 into a three-necked flask, stir for 10 minutes under a temperature of 50-70 °C, then stir and add a certain amount of sodium hydroxide solution (mass fraction of 40%) drop-wise at the same time. After the drops, leave it to react for 6~18 hours under constant temperature, then remove the resultant salt particles, and under vacuum distillation a pale yellow liquid-like honey is generated, named WLS.

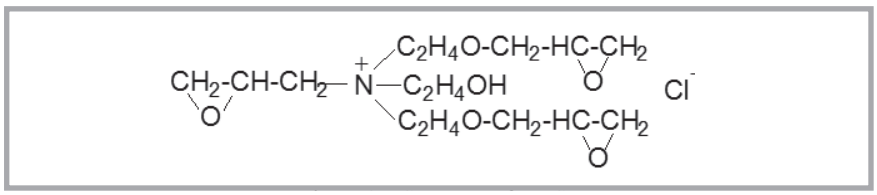

Figure 3. *Structure of WLS.*

Structural characteristics of cationic modification agent (WLS)

WLS is a cationic quaternary ammonium salt type crosslinking modification agent, which was prepared by our research group, containing a plurality of epoxy ethane groups. It is a light yellow viscous liquid, and the main feature of its chemical structure is the presence of highly reactive epoxy ethane groups. These can react with the amino (-NH_2), carboxyl (-COOH), hydroxyl (-OH), sulfhydryl (-SH) and other polar groups. Therefore it can be used as a crosslinking modification agent, reacting with protein additives which are modified to become cationic. ***Figure 3*** is the structure of WLS.

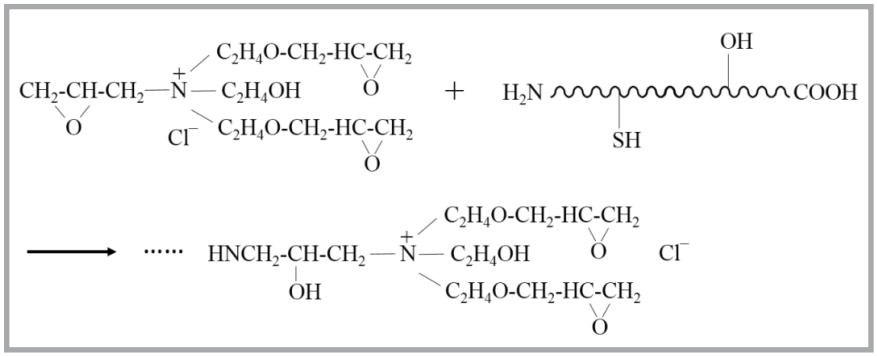

Figure 4. *WLSPR synthetic reaction.*

Preparation of fixing agent WLSPR

Reaction principle

Waste protein powder is dissolved in sodium hydroxide solution, and then by precipitation is prepared, which is odourless and non-toxic. Its chemical composition consists of a polypeptide chain which contains many amino (-NH_2), carboxyl (-COOH), hydroxyl (-OH), sulfhydryl (-SH) and other polar groups. These groups can react with the additive, which contains ethylene oxide and other reactive groups. ***Figure 4*** is the WLSPR synthetic reaction.

Preparation technology

In the temperature range 45-75 °C, a certain amount of WLS was placed in a three neck flask and stirred at a certain speed for a certain period of time. Then feather protein powder was added and dissolved by the aqueous sodium hydroxide solution. It was stirred at 45 °C to 75 °C for 1-6 h, after which the cationic protein fixing agent, named WLSPR, was obtained.

Dyeing process

The formulation of the reactive dyes is as follows:

Dye	3 %, o.w.f.
Sodium chloride	50 g/l
Sodium carbonate	20 g/l
liquor ratio	25:1

Figure 5 is the temperature profile of the reactive dyeing process.

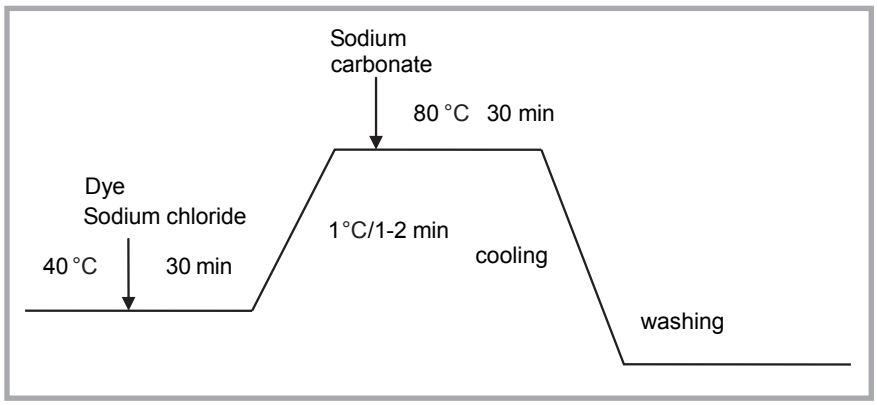

Figure 5. *Temperature profile of the reactive dyeing process.*

Post treatment process of dyed cotton fabric

a. Dyed cotton fabric – cold water wash – fixation – cold water wash – soaping – cold water wash – drying
b. Dyed cotton fabric – cold water wash – hot water water (no fixation) – cold water wash – soaping – cold water wash – drying

Fixing process: protein post treatment agent 20% (owf), 60 °C constant temperature processing for 30 min, liquor ratio 30:1.

Hot water washing process: water, 60 °C constant temperature processing for 30 min, liquor ratio 30:1.

Soaping process: soap powder 2 g/l, 90 °C constant temperature processing for 20 min, liquor ratio 50:1.

Test indices

Determination of dyeing depth

The depth of dyeing is expressed by K/S values determined using a X-Rite Colori 7 spectrophotometer, with a 10 degree observer and D 65 illuminant. The specimen was folded into 3 layers, the measurement obtained 10 times, and the average value taken. The °C K/S value is the difference between the K/S values of the fabric before soaping and after soaping.

Determination of colour fastness to washing

According to GB/T3921.3-2008 Textile, color fastness to washing of the fabric is tested. Then according to GB/T 251-2008, the fastness to colour fading rating with a grey card, which changes in colour, was assessed. According to GB/T 250-2008, the staining scale rating was assessed with a staining grey card.

Determination of color fastness to rubbing

According to GB/T 3920-1997 Textile, color fastness to rubbing of the fabric was tested. Then the GB/T 250-1995 Gray scale for assessing staining was used to assess the rating.

Production of calibration curve

The absorbance value of different concentrations of the auxiliary agent at the maximum absorption wavelength (λ_{max}) was measured. The concentration determined is taken as the abscissa, and the absorbance value as the ordinate, and thus the calibration curve is obtained.

Infrared spectrum

The infrared spectrum of WLSPR was determined by an FTIR-5700 type Fu Liye frequency conversion infrared spectrophotometer.

Table 1. *Effect of mass ratio of feather protein to WLS on Reactive Orange CD-2BR dyed cotton fabric in terms of colour fastness to washing and white staining.*

Mass ratio of feather protein to WLS	K/S value of white stained fabric after soaping	Washing fastness, level	
		Discoloration	Colour fastness on cotton
1:8	0.089	3-4	3-4
1:12	0.088	3-4	3-4
1:16	0.079	3-4	4
1:20	0.083	3-4	3-4

Table 2. *Effect of mass ratio of feather protein to WLS on Active Dark Blue CD-2BR dyed cotton fabric in terms of colour fastness to washing and white staining*

Mass ratio of feather protein and WLS	K/S value of white stained fabric after soaping	Washing fastness, level	
		Discoloration	Colour fastness on cotton
1:8	0.096	3-4	4
1:12	0.094	3-4	3-4
1:16	0.087	4	4
1:20	0.089	3-4	4

Table 3. *Effect of mass ratio of feather protein to WLS on Active Black DS-DH dyed cotton fabric in terms of colour fastness to washing and white staining.*

Mass ratio of feather protein and WLS	K/S value of white stained fabric after soaping	Washing fastness, level	
		Discoloration	Colour fastness on cotton
1:8	0.067	4	4
1:12	0.068	4	4
1:16	0.063	4	4
1:20	0.077	4	3-4

Results and discussion

Fixing agent (WLSPR) synthesis process conditions optimisation

Optimisation of feather protein to WLS mass ratio

According to the process described in Preparation of the fixing agent WLSPR chapter, cationic protein fixing agent WLSPR was prepared. The quantity ratio of feather protein powder to WLS was varied, with a quantity of sodium hydroxide of 1% (relative to the WLS mass percentage), with stirring at 65 °C for 6h. Also the cotton fabric was dyed according to the process of reactive dyeing described in Dyeing process chapter. Then according to the fixing process described in Post treatment process of dyed cotton fabric chapter, the synthesis of WLSPR additives as a fixing agent was undertaken in the dyeing of cotton fabric. The experimental results are shown in ***Tables 1-3***.

From ***Tables 1-3***, it can be seen that when m (protein): m (WLS) = 1:16 (mass ratio), for the cotton fabric dyed with three reactive dyes, after soaping, the white cloth shows least resistance, and color fastness to washing – the best. This is because the feather protein powder contains more polar groups, which contain active hydrogen atoms such as -OH, $-NH_2$, -SH, and the WLS agent is a cationic crosslinking modifier which contains reactive ethylene oxide groups. In alkaline conditions, WLS can react with polar groups, which contain active hydrogens in the protein molecules, and generate cationic protein derivatives. The additives contain both cationic groups and polar nucleophilic groups in their protein structure. The agent can react with dyes and fibres. Initially WLSPR produces electrostatic interactions between the cationic agent and dye anions, which reduces the water solubility of the dyes. The dyes and agents are also attracted by van der Waal and hydrogen bonding forces. The additives can react directly with the fibre, making the fibre cationic, and hence it is attracted to the anionic dye,, thus increasing the force between the dye and fibre. The WLSPR agent can also react with the dye and fibre, fibre being linked firmly by the WLSPR as a bridge, thereby increasing the interaction between the dye and fibre, reducing the water solubility of the dye, and improving the colour fastness to washing. In order to obtain a high degree of cationic character in the feather protein derivative additives, it would be expected that the WLS agent dosage be increased. However, the experimental results show that, in terms of WLS agent dosage, more is not always better, and the optimum experimental quantity of protein to WLS agent ratio is 1:16. Taking into account that the WLS itself is a cationic modification agent, it can also act as a cationic fixing agent, thus improving the dyeing fastness. Therefore the experiment leading to the synthesis of WLSPR additives does not remove the excess WLS additive.

Optimum dosage of sodium hydroxide

According to the process described in Preparation of the fixing agent WLSPR chapter, cationic protein fixing agent WLSPR was prepared. The quantity of sodium hydroxide was varied, with a quantity ratio of feather protein powder and WLS of 1:16, and stirring at 65 °C for 6 h. Also cotton fabric was dyed according to the process of reactive dyeing described in Dyeing process chapter. Then according to the fixing process described in Post

Table 4. *Effect of sodium hydroxide dosage on Reactive Orange CD-2BR dyed cotton fabric in terms of colour fastness to washing and white staining.*

Dosage of sodium hydroxide %, relative to the mass percentage of WLS	K/S value of white stained fabric after soaping	Washing fastness, level	
		Discoloration	Colour fastness on cotton
1	0.079	3-4	4
2	0.066	4	4
3	0.054	4-5	4-5
4	0.060	4	4

Table 5. *Effect of sodium hydroxide dosage on Active Dark Blue CD-2BR dyed cotton fabric in terms of colour fastness to washing and white staining.*

Dosage of sodium hydroxide %, relative to the mass percent of WLS)	K/S value of white stained fabric after soaping	Washing fastness, level	
		Discoloration	Colour fastness on cotton
1	0.081	4	4
2	0.078	4	4
3	0.069	4	4-5
4	0.070	4	4

Table 6. *Effect of sodium hydroxide dosage on Active Dark Black DS-DH dyed cotton fabric in terms of colour fastness to washing and white staining.*

Dosage of sodium hydroxide %, relative to the mass percent of WLS	K/S value of white stained fabric after soaping	Washing fastness, level	
		Discoloration	Colour fastness on cotton
1	0.066	4	4
2	0.067	4	4
3	0.062	4	4-5
4	0.062	4	4

Table 7. *Effect of synthesis temperature on Reactive Orange CD-2BR dyed cotton fabric in terms of colour fastness to washing and white staining.*

Synthesis temperature, °C	K/S value of white stained fabric after soaping	Washing fastness, level	
		Discoloration	Colour fastness on cotton
45	0.065	4	4
55	0.059	4-5	4
65	0.056	4-5	4-5
75	0.058	4-5	4

Table 8. *Effect of synthesis temperature on Reactive Dark Blue CD-2BR dyed cotton fabric in terms of colour fastness to washing and white staining.*

Synthesis temperature, °C	K/S value of white stained fabric after soaping	Washing fastness, level	
		Discoloration	Colour fastness on cotton
45	0.081	3-4	3-4
55	0.069	4	4
65	0.066	4	4
75	0.074	4	4

Table 9. *Effect of synthesis temperature on Reactive Dark Black DS-DH dyed cotton fabric in terms of colour fastness to washing and white staining.*

Synthesis temperature, °C	K/S value of white stained fabric after soaping	Washing fastness, level	
		Discoloration	Colour fastness on cotton
45	0.086	3-4	3-4
55	0.074	4	4
65	0.064	4	4-5
75	0.065	4	4

Table 10. *Effect of reaction time on Reactive Orange CD-2BR dyed cotton fabric in terms of colour fastness to washing and white staining.*

Time, h	K/S value of white stained fabric after soaping	Washing fastness, level	
		Discoloration	Colour fastness on cotton
1	0.070	4	4
2	0.068	4	4-5
3	0.060	4-5	4-5
4	0.056	5	4-5
5	0.058	4-5	4-5
6	0.056	4-5	4-5

Table 11. *Effect of reaction time on Reactive Dark Blue CD-2BR dyed cotton fabric in terms of colour fastness to washing and white staining.*

Time, h	K/S value of white stained fabric after soaping	Washing fastness, level	
		Discoloration	Colour fastness on cotton
1	0.076	4	3-4
2	0.069	4	4
3	0.069	4	4
4	0.064	4-5	4
5	0.067	4-5	4
6	0.066	4-5	4

Table 12. *Effect of reaction time on Reactive Dark Black DS-DH dyed cotton fabric in terms of color fastness to washing and white staining.*

Time, h	K/S value of white stained fabric after soaping	Washing fastness, level	
		Discoloration	Colour fastness on cotton
1	0.069	4	4
2	0.067	4	4
3	0.067	4	4
4	0.063	4	4-5
5	0.065	4	4-5
6	0.064	4	4-5

Table 13. *Linear relationship between absorbance and concentration at different wavelengths.*

Wavelength, nm	Linear relationship	R^2
193	Y=4.4246x+0.0707	0.9950
195	Y=5.0027x+0.0588	0.9972
198	Y=4.7294x+0.0446	0.9959
200	Y=4.2627x+0.0392	0.9957
210	Y=2.3183x+0.0242	0.9931

Table 14. *Effects of WLSPR additives on the post treatment of cotton fabric dyed with different reactive dyes.* ***Note:*** *#1 Reactive Orange CD-2BR fabric K/S staining value 9.037; #2 Reactive Deep Blue CD-2BG fabric K/S staining value 16.920; #3 for Reactive Black DS-DH fabric K/S staining value 14.667; #4 Reactive Brilliant Red K-2BP, dyed cotton fabric K/S value 2.679.*

Dye	Technology	K/S value of coloured cloth	K/S value of white cloth	Rubbing fastness, level		Washing fastness, level	
				Dry friction	Wet rubbing	Discoloration	Colour fastness on cotton
#1	Fixation	6.758	0.145	4-5	3-4	4-5	4-5
	No fixation	5.968	0.572	4-5	3	4	4
#2	Fixation	15.287	0.095	4-5	3-4	4	4
	No fixation	13.773	0.576	4-5	3	3-4	3-4
#3	Fixation	13.668	0.179	4-5	3	4-5	4-5
	No fixation	13.106	0.309	4	2-3	4	4
#4	Fixation	2.421	0.109	5	4	4-5	5
	No fixation	2.271	0.114	5	3-4	4	4-5

treatment process of dyed cotton fabric chapter, the synthesis of WLSPR additives as a fixing agent was performed in the dyeing of cotton fabric. The experimental results are shown in ***Tables 4-6***.

From ***Tables 4-6***, it can be seen that with an increase in the dosage of sodium hydroxide, the colour fastness to washing increases first and then decreases. When the sodium hydroxide quantity is 3% (relative to the mass percentage of WLS), the colour fastness to washing of the three reactive dyeing of cotton fabric is at its best, and white cloth stains with the least colour. This is due to the alkali added being conductive to dissolved protein. However, the amount of alkali added should be appropriate, As too much alkali will lead to the hydrolysis of WLS additives, resulting in a reduction in the amount of cationic protein additives formed. The optimum dosage of sodium hydroxide is 3% of the WLS quantity, as from the experimental results.

Optimisation of synthesis temperature

According to the process described in Preparation of the fixing agent WLSPR chapter, cationic protein fixing agent WLSPR was prepared. The reaction temperature was varied, with a quantity of sodium hydroxide of 3% (relative to the WLS mass percentage) and stirring for 6 h. Also cotton fabric was dyed according to the process of reactive dyeing described in Dyeing process chapter. Then according to the fixing process described in Post treatment process of dyed cotton fabric chapter, the synthesis of WLSPR additives as a fixing agent was performed in the dyeing of cotton fabric. The experimental results are shown in ***Tables 7-9***.

From ***Tables 7-9***, it can be seen that with an increase in the reaction temperature, the colour fastness to washing shows an increasing trend. When the reaction temperature is 65 °C, for the three reactive dyeings of cotton fabric, the colour fastness to washing is at its best, and white cloth staining is least. Thus, in a certain range, a temperature rise is conducive to the reaction of protein and WLS additives, improving the degree of cationic protein modification of the cationic agent. When the temperature is higher than 65 °C, colour fastness to washing decreases, which is due to the fact that the additives and protein are easily hydrolysed at high temperature, reducing the molecular weight of the cationic ad-

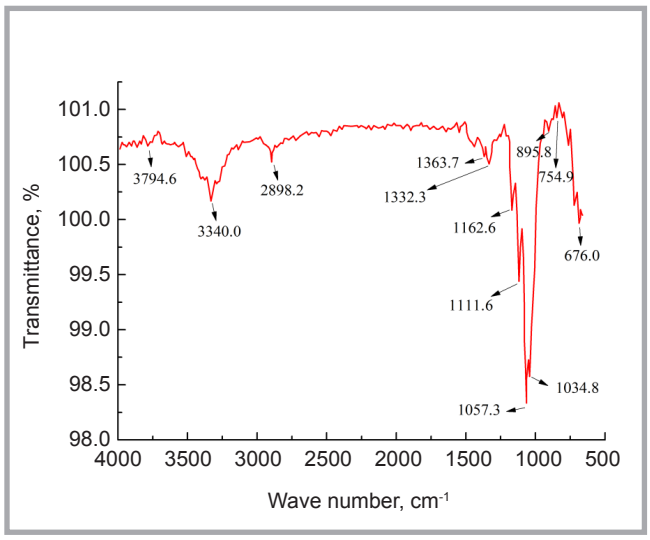

Figure 6. Infrared spectrum of WLSPR.

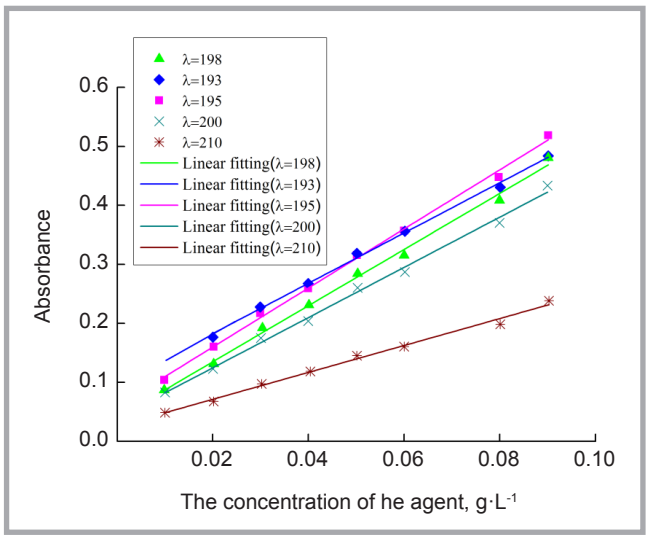

Figure 7. Standard calibration curve of WLSPR at different concentrations.

ditives and assistants, and hence the force between the fibre of the additives and dyes is reduced, resulting in lower resistance to washing. Thus the optimum reaction temperature is determined to be 65 °C.

Optimisation of synthesis time

According to the process described in Preparation of the fixing agent WLSPR chapter, cationic protein fixing agent WLSPR was prepared. The reaction time was varied, with a quantity of sodium hydroxide of 3% (relative to the WLS mass percentage) and stirring at 65 °C . Also the cotton fabric was dyed according to the process of reactive dyeing described in Dyeing process chapter. Then according to the fixing process described in Post treatment process of dyed cotton fabric chapter, the synthesis of WLSPR additives as a fixing agent was performed in the dyeing of cotton fabric. The experimental results are shown in ***Tables 10-12***.

From ***Tables 10-12***, it can be seen that with an extension of the reaction time, the colour fastness slightly improves, but when the time is over 4 h, obviously it does not change. When the reaction time is 4 h, the colour fastness to washing of the three reactive dyeing of cotton fabric is at its best, and white staining is the least. Therefore the optimum reaction time is determined as 4 h.

In summary for the WLSPR fixing agent, the optimum synthesis conditions are identified as follows: quantity ratio of feather protein to WLS – 1:16, quantity of sodium hydroxide 3% (relative to the WLS mass percentage), and stirring at 65 °C for 4 h.

Infrared spectral analysis of WLSPR additives

As can be seen from the spectrum in ***Figure 6***, the WLSPR characteristic absorption peaks are at 3340 cm^{-1}, 2898.2 cm^{-1}, 1363.7 cm^{-1}, 1332.3 cm^{-1}, 1162.6 cm^{-1}, 1111.6 cm^{-1}, 1057.3 cm^{-1}, 1034.8 cm^{-1}, 895.8 cm^{-1}, 754.9 cm^{-1} and 676.0 cm^{-1}. The characteristic peaks due to the epoxy ethane group is at 895.8 cm^{-1}; close to 920cm^{-1} there are weak absorption peaks due to quaternary ammonium salt. For C-N stretching vibration the primary hydroxyl is at 1034.8 cm^{-1}, 1057.3 cm^{-1} with two absorption peaks for primary hydroxyl C-O stretching vibrations; 1111.6 cm^{-1} is the stretching vibration peak for CH-OH C-O; the peaks at 1332.3 cm^{-1} and 1363.7 cm^{-1} are due to – CONH – CN vibration absorption (amide III), and close to 3340 cm^{-1} are the -OH and -NH stretching vibration absorption peaks. This spectral interpretation is consistent with the WLSPR promoter as a quaternary ammonium salt derivative protein promoter, which contains the epoxy ethane reactive group and amino group.

Standard calibration curve for protein agent WLSPR solution

The absorbance value of different concentrations of the auxiliary agent at the maximum absorption wavelength (λ_{max}) was measured. The concentration is taken as the abscissa, and the absorbance value as the ordinate to obtain the standard calibration curve. Curve fitting was applied to provide R^2 values, as shown in ***Figure 7*** and ***Table 13***.

From ***Figure 7*** and ***Table 13***, it can be seen that at around the maximum wavelength, different wavelengths were tested for fit, and finally it was found for the additive that at wavelength 195 nm, linear fitting was the best. The linear relationship between the concentration of WLSPR agent and the absorbance was the best, which is consistent with the Longbow Bill absorption law. Thus to determine the amount of residual WLSPR additives and the amount of additives on the fabric on a theoretical basis, determination of the residual liquid absorbance wavelength was selected as 195 nm.

Fixing agent (WLSPR) fixation effect evaluation

According to optimum conditions of the synthesis process, the agent (WLSPR) was prepared. According to the process described in Dyeing process chapter, cotton fabrics were dyed with four different reactive dyes. According to the solid colour process described in Post treatment process of dyed cotton fabric chapter, the dyed cotton fabrics were treated with WLSPR, the experimental results of which are shown in ***Table 14***.

From ***Table 14*** it can be seen that after the dyeing of cotton fabric with four reactive dyes with fixative WLSPR and soaping, not only does the cloth colour fade less, but also the white staining is lower, and the dyed fabric rubbing fastness and washing colour fastness increase by a grade of 0.5. The reason is that cationic protein additive WLSPR contains not only structural protein, but also cationic groups. These can produce electrostatic forces, hydrogen bonding, van der Waal

forces and a hydrophobic effect with dye ions and other molecules, thus improving the interaction between dye and fibre. At the same time, the additives containing reactive groups can react with the hydrolysed dyes and fibre, and then through the cationic protein cross-linking effect, the hydrolysed dye undergoes fibre crosslinking fixation, thus reducing the amount of surface dyeing. Also the cationic protein additives and washing liquid dye forces are greater than the interaction between the dye and fibre, with loose dye forming a stable dispersion in the solution to prevent dye from staining the fabric. This can effectively remove residual loose colour, thereby reducing the consumption of water in washing as well as dye staining on white fabric and on printing fabric of white bottom colour, and effectively preventing wash off from dyed fabric.

Conslusions

1. The optimal process conditions for the synthesis of WLSPR are as follows: m (protein): m (WLS) = 1:16, sodium hydroxide solution concentration 15 g/l, reaction temperature 65 °C, and time 4h. WLSPR agent is a cationic quaternary ammonium salt derivative protein additive which contains epoxy ethane, amino and hydroxyl groups. Its character is a brown tasteless viscous liquid and it has UV absorption properties, with a maximum absorption wavelength λ_{max} of 195 nm. At this wavelength, the concentration of the WLSPR agent and absorbance gives the best linear relationship.
2. The WLSPR agent can give the firm fixation of dye in fabric and achieve an effective solid colour, reduce the surface dyeing of fabric, and at the same time an additive can be added in the soaping process. The additive can combine with dye which detaches from the fabric to prevent loose dye from staining the fabric, thus reducing water consumption of the soap wash treatment process, decreasing the staining of white cloth from the dyed and printed fabric, and leading to an improved fabric of high colour fastness to rubbing and washing fastness of the dye. WLSPR agents are used for dyeing cotton fabric after solid colour processing, and in the soaping after treatment. The results show that soap washing can reduce cloth colour fading and white staining, and thus the dyed fabric washing colour fastness is improved. WLSPR additives use waste protein as raw material, which is conducive to the effective use of waste resources, waste to value, to achieve the aim of environmental protection and clean production. Therefore this product is in line with the concept of building a resource-saving and environment-friendly society, and is conducive to reducing environmental pollution, to achieve the aim of environmental protection and clean production.

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