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Improving the Wash Fastness of Direct Dyes on Cotton by Si/Ti Composite Nanosol

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Abstract
A series of Si/Ti composite nanosols were prepared to improve the wash fastness of six different coloured direct dyes. As a result Si/Ti composite sols with molar ratios of 14:1 are recommended as the most appropriate recipe. When dyed fabrics were treated with Si/Ti composite nanosol by the traditional pad-dry-cure process, the gel particles linked together in -Si-O-Ti-O-Si- bonds to form a compact inorganic-organic hybrid network, as observed in SEM pictures; the wash fastness of direct dyes on the cotton fabric had obviously improved. The strength and handle of the fabrics treated also showed no negative effects with the suitable recipe.

Key words: *composite nanosol, direct dyes, wash fastness, gel, cotton.*

Introduction

Direct dye is one of the most popular dyes used for cotton as it possesses remarkable advantages, such as wide colour ranges, excellent dye penetration, low cost, short dyeing time, and so on. However, its fastness to wet processing, especially wash fastness, is poor mainly because of its hydrophilic sulphonic groups in a molecule structure. To enhance the wash fastness of cotton dyed with direct dyes, cationic compounds, resin fixatives, metallic salts, and polyfunctional cross-linking agents, etc. are widely applied [1].

The sol-gel processes based on the hydrolysis and condensation of metal alkoxide compounds have various technical applications such as the preparation of special glass, ceramic and coatings [2 - 6]. The basic kinetics of the processes can be neatly described as two reactions [7]: hydrolysis and polycondensation (Equations 1, 2 and 3).

$$M(OR)_x + H_2O \rightarrow \rightarrow M(OR)_{x-1}OH \quad (1)$$

$$2M(OR)_{x-1}OH \rightarrow \rightarrow (OR)_{x-1}M - O - M(OR)_{x-1} + H_2O \quad (2)$$

$$M(OR)_{x-1}OH + ROH \rightarrow \rightarrow (OR)_{x-1}M - OR + H_2O \quad (3)$$

Where M is a metal species (Ti, Si, Al, Zr, etc.) and R is an alkyl group (methyl, butyl, ethyl, etc.). These reactions generate an oxide skeleton in the solution. Upon exposure to the atmosphere or when heated, the solution will gel and become rigid.

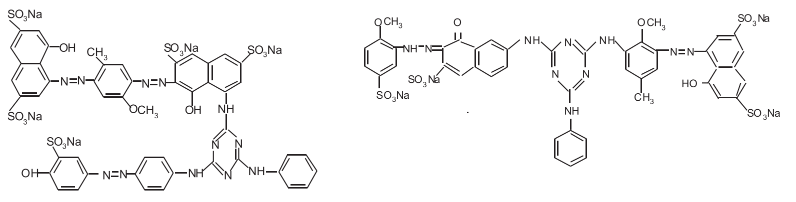
It has been reported that the sol-gel method can bring about improvements in the wash fastness of direct dyes with silica sol, but only for direct black dyes [8 - 9]. Therefore, the aim of this research was to improve the wash fastness of different coloured direct dyes by an appropriate process using Si/Ti composite sol.

Experimental

Materials

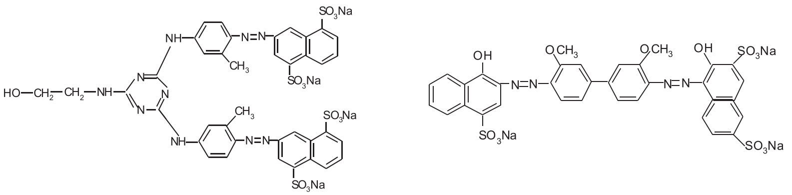
Scoured and bleached cotton woven (120 g/m^2) was obtained from Shanghai No.1 Dyeing Factory. The reagents were of analytical grade as follows: γ-glycidyloxypropyltrimethoxysilane (GPTS) (99%)(HuaRong Chemical New Materials Ltd.), tetrabutyl titanate (99%) (Shanghai Chemical reagent Co.), hydrochloric acid (37%) and acetic acid (99.5%) (Jin Du Reagent Plant). The direct dyes used were CI Direct Green 26, CI Direct Red 89, CI Direct Yellow 86, CI Direct Blue 9, CI Direct Black 22, and CI Direct Orange 39, respectively, all from the Dystar corporation limited company. The chemical structures of these direct dyes are illustrated in ***Figure 1***.

Cotton was dyed (dye concentration 2% omf; sodium chloride, 25 g/l; goods to liquor ratio, 1:25) in a jet Dyeing Machine (Mathis Lab Jumbo Jet JFO) according to the procedure shown in ***Figure 2***.



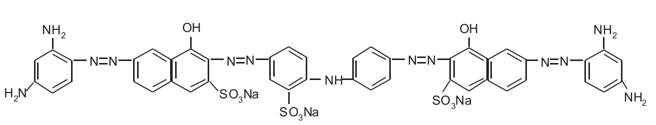
(1) CI Direct Green 26

(2) CI Direct Red 89

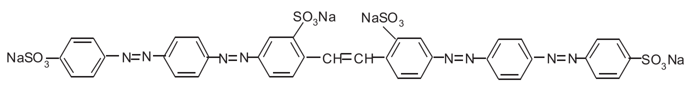


(3) CI Direct Yellow 86

(4) CI Direct Blue 9



(5) CI Direct Black 22



(6) CI Direct Orange 39

Figure 1. *Molecular structure of direct dyes.*

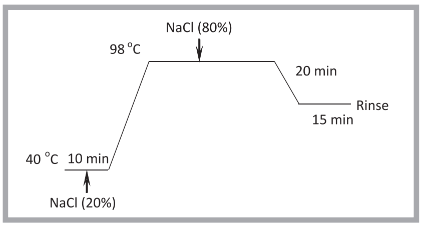


***Figure 2.** Dyeing profile.*

Preparation of the Si/Ti composite nanosol

Tetrabutyl titanate (TTB) was used as the precursor; acetic acid (AcOH) was used to retard the hydrolysis and condensation of the TTB, and hydrochloric acid (HCl) was used as a catalyst for TTB hydrolysis. The molar ratio of the TTB : AcOH : HCl : H_2O is 1 : 3.5 : 0.014 : 100. TTB was dissolved in the acetic acid, and the solution was agitated until it became homogeneous. The resulting solution was slowly added to the HCl-water mixture and stirred for 3 hr in a three-necked flask at ambient temperature. A 2% concentration of titanium hydrosol was thus obtained with pH ~ 2.

γ-glycidyloxypropyltrimethoxysilane (GPTS) was used as the precursor, and hydrochloric acid (HCl) was used as a catalyst for GPTS hydrolysis. The molar ratio of GPTS : HCl : H_2O is 1 : 0.00001 : 65. GPTS was slowly added to the HCl-water mixture and stirred for 2 hr in a three-necked flask at ambient temperature. A 2% concentration of silica hydrosol was thus obtained with pH ~ 5.

The 2% concentration of silica hydrosol and 2% concentration of titanium hydrosol were mixed at different ratios (shown in ***Table 1***) and stirred for one hour at ambient temperature. A Si/Ti composite nanosol was thus obtained with pH ~2 - 3.

Sol-gel treatment

The dyed cotton samples were dip-and-nipped twice in the composite hydrosol with a pick up of 60 - 70%. The samples treated were dried at 75 °C for 4 ~ 5 min, then rinsed with distilled water for 30 seconds to remove excessive hydrochloric acid and acetic acid, thus avoiding damage to the fabric when cured at higher temperature. Subsequently, the samples treated were dried and cured at 135 °C for 4 ~ 5 min.

Characterisation

The size of sol was measured by a Nanosizer made by Malvern Instruments Ltd. The morphological structure of the cotton surface was measured by JSM - 5600LV Scanning Electron Microscopy (SEM), operating at 10 kV.

Test methods

The samples were washed according to ISO 105-C10-2006. The colour difference (ΔE) was obtained with a Datacolor SF600+ spectrophotometer and colour quality control system from Datacolor, which was connected to a digital PC under D65 illumination using a 10° standard observer with ultraviolet (UV) and specula components included. The SF600+ light source was a pulsed Xenon flashlamp filtered to provide D65 illumination, including a UV component for whiteness measurements and specula. Each sample was measured three times, and the average value was calculated. The degree of colour change and colour staining were respectively evaluated according to Standards ISO 105-A05 and ISO 105-A04. The tensile strength was measured according to Standard ASTM D 5034-95. The tear strength was measured by the Elmendorf method (ASTM D1424-96). Finally, the handle of the samples was tested according to the ASTM D1388 test method.

***Table 1.** Results of the wash fastness-staining of accompanying cotton fabric for cotton samples treated with Si/Ti composite nanosols.*

Samples (2%)		Dye					
		Red	Orange	Yellow	Green	Blue	Black
Untreated	rating	1	1 ~ 2	1	2 ~ 3	2	1 ~ 2
	ΔE	30.131	27.939	29.801	13.745	19.372	21.347
Si/Ti = 1:0	rating	1 ~ 2	1 ~ 2	1	2 ~ 3	2	4
	ΔE	27.818	27.115	29.608	10.462	16.283	4.473
Si/Ti = 14:1	rating	2 ~ 3	3	3	4 ~ 5	3 ~ 4	4 ~ 5
	ΔE	10.832	7.834	7.366	1.928	5.948	3.154
Si/Ti = 7:1	rating	2 ~ 3	3	2 ~ 3	4 ~ 5	4	4
	ΔE	12.257	8.351	10.309	2.667	3.373	3.641
Si/Ti = 1:1	rating	2 ~ 3	2 ~ 3	2 ~ 3	4	3	3
	ΔE	13.562	10.254	14.313	3.994	7.838	9.724
Si/Ti = 1:7	rating	2	2	2	3 ~ 4	2 ~ 3	3
	ΔE	18.813	18.813	17.892	6.255	12.633	8.417
Si/Ti = 1:14	rating	2	2	2	3 ~ 4	2 ~ 3	3
	ΔE	18.285	17.762	15.316	7.151	12.979	9.414
Si/Ti = 0:1	rating	1 ~ 2	1 ~ 2	1 ~ 2	3	2	2 ~ 3
	ΔE	24.093	23.179	23.478	9.244	18.367	13.069

Results and discussion

Wash fastness

Results of the wash fastness/staining of the accompanying cotton fabric for both the treated and untreated samples are shown in ***Table 1***.

Compared with the untreated samples, it is clear that those dyed with Direct Black and treated with silica sol (Si/Ti = 1:0) show an obvious improvement in colour staining from grades 1 - 2 up to 4. However, the samples dyed with the other five dyes retained their original colour staining grades. It is presumed that the above-mentioned results may be related to the molecular structure of direct dyes, as shown in ***Figure 1***. It is known that Direct Black dye molecules contain more amino and hydroxyl groups than the other dyes, which is advantageous in forming hydrogen bonds and covalent bonds between the dyes and silica sol so that the dye molecules are tightly fixed into the gel network, displaying better wash fastness. It can also be observed that all six of the dyed samples treated with titanium sol (Si/Ti = 0:1) show no enhancement in colour staining, perhaps resulting from the poor affinity between organic dye molecules and inorganic gel particles. However, it is very interesting that the samples dyed with six direct dyes show an obvious improvement in colour staining, compared with the untreated ones after treatment with different molar ratios of Si/Ti composite sols, especially when the molar ratios were 14:1 and 7:1. A visible improvement in colour staining may result from the mechanical blockage of dye.

Results of the change in wash fastness/sample colour for both the treated and untreated samples are shown in ***Table 2***.

It can be seen from these results that, compared with the untreated samples,

Table 2. Results of the change in wash fastness/sample colour for cotton samples treated with different Si/Ti composite nanosols.

Samples (2%)		Dye					
		Red	Orange	Yellow	Green	Blue	Black
Untreated	rating	3 ~ 4	3	3	3	2 ~ 3	4
	ΔE	2.271	3.545	3.410	3.158	4.326	1.952
Si/Ti=1:0	rating	4 ~ 5	3	3	4 ~ 5	3	4 ~ 5
	ΔE	1.173	4.004	3.612	1.088	3.146	1.218
Si/Ti=14:1	rating	4 ~ 5	4	3 ~ 4	4	4 ~ 5	4
	ΔE	0.603	1.968	2.691	1.673	1.188	2.008
Si/Ti=7:1	rating	4	3 ~ 4	3	4 ~ 5	4	4
	ΔE	1.489	2.864	3.548	0.872	1.599	1.423
Si/Ti=1:1	rating	4	4	2 ~ 3	4	3 ~ 4	4
	ΔE	1.520	1.462	5.019	1.458	2.492	1.793
Si/Ti=1:7	rating	3	4	2 ~ 3	3 ~ 4	3 ~ 4	3
	ΔE	3.044	1.409	4.870	2.435	2.256	3.979
Si/Ti=1:14	rating	3	3 ~ 4	2 ~ 3	3	3 ~ 4	3
	ΔE	3.394	2.394	4.665	3.582	2.737	2.987
Si/Ti=0:1	rating	3	3	2 ~ 3	3	3	3
	ΔE	3.989	3.104	4.478	3.927	3.107	3.639

the samples treated with Si/Ti composite sols with molar ratios of 14:1 and 7:1 show an obvious improvement in colour change. However, the dyed samples treated with the other molar ratios of the composite sol retain their original colour staining grades, becoming even worse, which is inconsistent with the colour staining given in ***Table 1***. The reason for this being that titanium sol has a negative impact on colour change due to its light yellow colour, and that the colour change grade becomes lower as the molar ratios of titanium sol increases. Fortunately, it is negligent in the color change of the dyed samples treated with composite sols with molar ratios of 14:1 and 7:1. As titanium sol contains more acid, this will lead to the damage of fibers when cured at higher temperature. We can draw the conclusion that Si/Ti composite sol with a molar ratio of 14:1 is the most appropriate to improve the wash fastness of direct dyes on cotton.

Particle size analysis of nanosol

The dimension dispersion of Si/Ti composite nanosol (Si:Ti = 14:1) by a Nanosizer is shown in ***Figure 3***, where the x-axis is the diameter of the hydrosol tested in nm), and the y-axis is the corresponding percentage number in %.

From ***Figure 3*** it can be seen that the Si/Ti composite nanosol particles formed are very small after hydrolysis. The size of 99.60% of the sols tested is no more than 10.1 nm, and 92.0% of the sols tested are less than 5.6 nm, which shows that the hydrolysis of the precursors is thoroughly complete and uniform. It can be observed that the sol particles are smaller, which was helpful in forming a more even and thinner coating on the fiber, thus avoiding negative effects on the handle and strength.

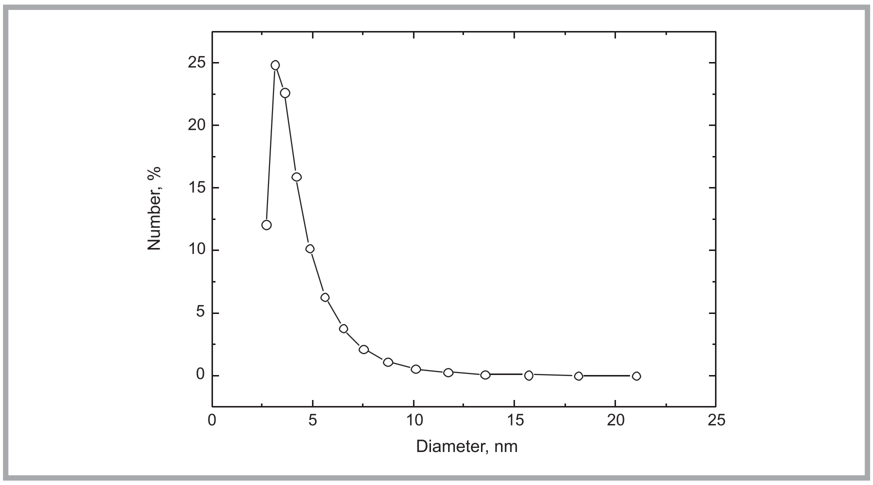


Figure 3. Size dispersion of the composite nanosol (Si:Ti = 14:1).

Morphology analysis of the cotton fibre by SEM

When the Si/Ti composite nanosol was coated on the cotton fabric, the morphology of the cotton fabric surface could be illustrated, as shown in ***Figure 4***.

It is evident that the grooves and fibrils of untreated cotton fibre (***Figure 4.a***) can be clearly observed, whereas the surface of the treated cotton fibre is coated with a continuous thin layer (***Figure 4.b***), which looks smoother in the SEM pictures. Furthermore, gel particles on the cotton fibre surface are tightly linked together with interconnected -Si-O-Ti-O-Si- bonds seemingly forming a complex and compact inorganic-organic hybrid network.

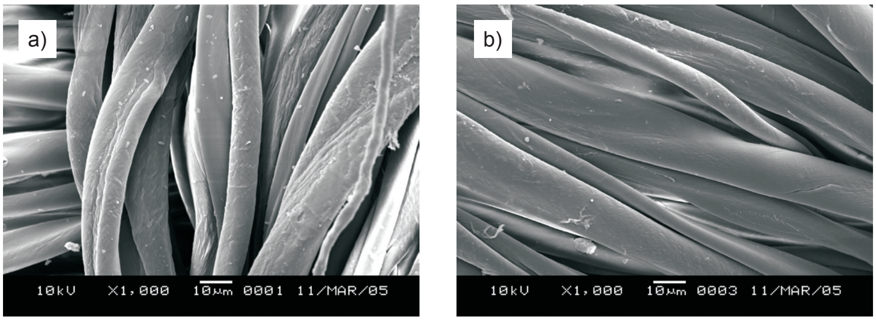


Figure 4. SEM images of the cotton fibre (Si:Ti = 14:1); a) untreated, b) treated.

Mechanical properties

For fabric application, the mechanical property is a basic requirement, hence the fabric treated with Si/Ti composite nanosol was also tested for tensile and tear strength, shown in ***Table 3***, where Si:Ti = 14:1.

From ***Table 3*** (see page 96) it can be seen that when treated with an appropriate composite sol with a molar ratio of 14:1, the tensile strength and tear strength of the treated fabric change a little, which shows that the sol-gel treatment did not have an obvious negative impact on the cotton fabric.

At the same time, the handle of the sample treated with an appropriate composite

Table 3. *Tensile strength and tear strength results of cotton fabric treated with an appropriate composite nanosol*

Samples	Tensile strength				Tear Strength	
	Warp		Weft		Warp	Weft
	Strength, N	Elongation, %	Strength, N	Elongation, %	Strength, N	Strength, N
Untreated	689.6	8.98	312.6	15.21	865.8	549.2
Treated	631.7	8.13	297.5	13.68	812.1	509.0
%Difference	-8.3	-9.46	-4.8	-10	-6.2	-7.3

Table 4. Handle of samples treated with an appropriate composite nanosol.

Sample	Bending length	
	Warp, cm	Weft, cm
Untreated	5.09	4.23
Treated	5.17	4.32

sol with a molar ratio of 14:1 was also tested in terms of the bending length, the results of which are listed in ***Table 4***. It is clear that the handle of fabrics does not deteriorate after the sol-gel process and is as soft as untreated ones.

Conclusions

Cotton fabric dyed with CI Direct Black 22 and treated with silica sol showed an improved wash fastness in both colour change and staining, while the samples dyed with the other five direct dyes and treated with silica sol showed no obvious improvement in wash fastness. The cotton samples dyed with six direct dyes and treated with titanium sol showed no obvious enhancement in both colour change and staining. However, the samples dyed with six different colour direct dyes and treated with Si/Ti composite sols with molar ratios of 14:1 and 7:1 all showed a sudden improvement in colour staining and change, which is the critical value. Considering the negative effects on the strength, Si/Ti composite sols with molar ratios of 14:1 are recommended as the most appropriate recipe. The strength and handle tests of the fabrics also showed no negative effects of the sol-gel treatment on fabrics treated with this recipe.

Si/Ti composite nanosol was prepared using tetrabutyl titanate and γ-glycidy loxypropyltrimethoxysilane as precursors, including hydrochloric acid, acetic acid and water. When the fabric is treated with Si/Ti composite nanosol using the traditional pad-dry-cure process, the gel particles will probably link together in interconnected -Si-O-Ti-O-Si- bonds to form a thin film with the dye and fibers, hence the wash fastness of direct dyes is obviously improved.

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