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Research on the Dyeing Process of Chinese Traditional Plant Indigo Based on Tianmen BlueCalico

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Blue calico is an important component of Chinese traditional arts and crafts, which originated from the Ch'in-Han Dynasty, began in the Song Dynasty, and flourished in the Ming and Qing Dynasties. Tianmen's blue calico has a style of simplicity but elegance, and because of its relatively simple process, durable texture and meaningful patterns, it was once widespread in the Jianghan Plain and listed as the third batch of intangible cultural heritage in Hubei Province. This article focuses on the indigo dyeing process of Tianmen's blue calico, and the conclusion: the optimized parameters of reduction process – the dosage ratio of indigo, caustic soda and sodium hydrosulfite is 2:3:9; reduction temperature is 45°C; and the time is 20min. Compared withsynthetic indigo, the dosage of sodium hydrosulfite with plant indigoincreasesby about 50%. The optimized dyeing process ofplant indigo: the mass concentration of NaCl is 60g/L, padding time is 20s, oxidizing time is 2min, and the number of padding is 12~14 times.The dyeing process of synthetic indigo: padding time is 20s, oxidizing time is 3 min, and the number of padding is 12~14 times.The color fastness to soaping of dyed yarns with plant indigo and synthetic indigo is similar.

1. Introduction

Blue calico is a wonderful work in Chinese traditional printing and dyeing process. Its stencils making originated from the Valerian folder craft in the Ch'in-Han Dynasty, and the stencils which are engraved from e tung oil paper cover on fabric, then a layer of dye-resisting paste made of soybean and lime powder is scraped to form the pattern. After drying them in the air, put them into the tank of plant indigo to dip dyeing repeatedly, and then scrape off the dye-resisting paste after drying out, finally the bright pattern of blue-ground will appear (Zhou, 2010). At present, the most famous existing blue calico of starching dye-resist in China is Nantong's blue calico, and in June 2006 it was selected as the first batch of national intangible cultural heritage (Wu, 2014). So currently, most academic studies are about Nantong's blue calico, rarely involving Tianmen's blue calico, till June 2011 Tianmen's blue calico was listed as the third batch of intangible cultural heritage of Hubei Province. After hundreds of years of inheritance, Tianmen's blue calico contains a very profound artistic content, and it has become an essential part of Chinese traditional culture. (Fig.1)

Figure 1: The pattern of Tianmen's blue calico

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The earliest dye of Tianmen's blue calico is the plant indigo. At the same time, the plant indigo is also the earliest vat dye, and has a long history in Chinese textile dyeing. Not only does the plant indigo itself have superior ecological performance, but also its products have natural color and unique color tone. At present a series of studies on the dip dyeing of plant indigo have been conducted, and certain achievements have been gained (Zhang and Zhao, 2011).

2. Introduction of plant indigo dye

2.1 The origin of indigo dye

Indigo is a natural blue dye with a long history, which exists in the leaves and stems of bluegrass. Its chemical formula is $C_{16}H_{10}N_2$, whose structural formula is as Fig.2 shows.

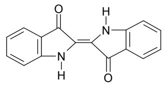


Figure 2: The structural formula of indigo

The application of indigo dye has already been five thousand years, which is believed to be the oldest dyeing history. In the west, clothes of ancient Egyptian mummies, with a history of 5000 years, and those of Tutankhamen, had adopted the indigo dye. During the period of Crusade, the indigo plant as a valuable "flavor" was shipped back to Europe. At the beginning of the 20th Century, due to the development of synthetic technology and enzyme technology, the market of natural plant indigo products almost died (Wu, 2001). The preparation of Chinese indigo dye started in the Xia Dynasty 3600 years ago, and at that time people had already started planting bluegrass and is used it to dye (Pei and Bing, 2003). The large-scale area of indigo production appeared in the Han Dynasty. Bluegrass itself does not contain indigo, so indigo exists in the bluegrass with the form of glycosides, namely indigo (Guan, 2006).

2.2 The preparation of indigo

2.2.1 The method of production

Put bluegrass into the fermenting vat, soaking and fermenting in the water .Fish out the residue after several months, then add quick lime to stir fully. At last, after precipitation, indigo come into being.

2.2.2 Technical principle

When maceration and fermentation, microorgan is largely propagates and secretes saccharifying enzyme, which fractures glycoside keys of blue glycoside in bluegrass (shown in Fig.3). The glucose of hydrolysis can be further decomposed into lactic acid, so that the enzyme activity is enhanced (Shen, 2005). At the same time, dilute acid could catalyze ester bond and glycoside keys, accelerating in doxylicdissociation. The indoxyl of hydrolysis is soluble in alkaline solution, occurring tautomerism of keto form (shown in Fig. 4):

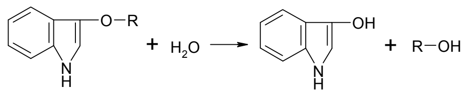


Figure 3: Break of the glycoside keys

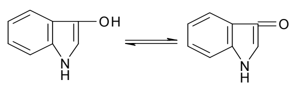


Figure 4: Tautomerismof keto formof indoxyl

Under conditions of alkaline, two molecules of indolone generate condensation reaction, the noxidate to indigo, in the state of suspended solids that insoluble in water, slowly sinking (shown as in Fig. 5):

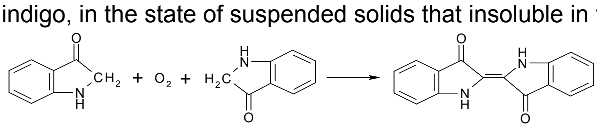


Figure 5: Indolone generate into indigo

In addition to provide the basic alkaline condition, adding lime has the other effect: the carbon dioxide gas produced during fermentation works with lime and produces calcium carbonate, which can absorb suspended indigo, and accelerate sedimentation rate.

2.3 Dyeing of indigo

2.3.1 Dyeing method

(1) The preparation of dye liquor

Put clean water into the dye vat, and then crush indigo with hands, dissolving itin water. Then add the alkali, wine, cusia leaves and sugarcane leaves. If there is thick and sticky foam coming out of the vat, and the color of the liquid is yolk yellow, then the dye liquor was made.

(2) Dyeing

Rinse fabrics that will be dyed, put them into the pot after wringing out, to cook for an hour together with gray thorn branches or red branches, and then take them to steep in the vat for about 12 hours, and then remove and ventilate for 2 hours before steeping again, then remove and ventilate again. Repeatedly like this, until 48 hours of steeping time, remove the fabrics and wash outthe residue, and then dry out fabrics.

(3) Lamination

In order to increase the strength of fabrics and improve the color fastness, the fabrics should be laminated after dyeing. Put the cowhide without fat and meat into the pot with water, and stew the cowhide with gentle heat to make it completely become glue. Put the glue and fabrics into a special vessel, and then use the wooden hammer to beat them to make the glue go into the fibers of fabrics.

(4) Steaming

Dry out the fabric after laminating, and then roll it and put it into the pot to steam for about 20 minutes. Throw it while hot into the vat of indigo after removing it from the pot and then twenty minutes later remove and ventilate it for half an hour. After repeating the process for several times, wash and dry out the fabric. Then roll the fabric on the flagstone and beat it for more than 10 minutes. Then repeated the process of steaming, dyeing, washing, drying, and beating several times, the dyeing process is over on the whole.

2.3.2 Technical principle

The principle of dyeing indigo is to restore the insoluble indigo to soluble leuco indigo white in the alkaline solution, and then ventilate and oxidize the fabric, finally turn it into the insoluble indigo and fixon the fabric. So the fabric of indigo has a good washing fastness. The reducing agent of the reduction process is mainly hydrogen produced by fermentation. The nutrients needed for fermentation are mainly monosaccharide and polysaccharide hydrolyzed by the sugarcane leaves, while cusia leaves are used as yeast (shown in Fig. 6).

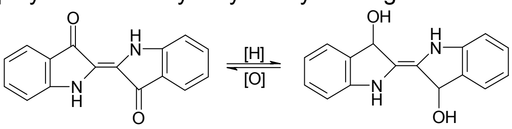


Figure 6: The oxidation and reduction reaction of indigo

3. Testing

3.1 Testing Materials

Materials: pure cotton bleaching yarns used for making blue calico (56 Tex)

Dyestuffs: plant indigo dyes (purified from dried indigo and the force is about 30%), synthetic indigo dyes, sodium hydrosulfite, sodium hydroxide, and urea.

3.2 Testing Instruments and Equipments

The electronic balance of JA5003, the thermostatic water bathHH-6, the absorbance tester V-5000, the measuring and matching color systemX-Rite, the color fastness to washing tester SW-10A, pneumatic electric staining small mangle SD-400.

3.3 Dyeing Method

3.3.1 The reduction process of plant indigo dye

The reduction method of vatting/(g·L-1)

The plant indigo 2 Urea 6

Sodium hydroxide 3 Sodium hydrosulfite 39

Temperature / °C 45 Reduction time /min 20

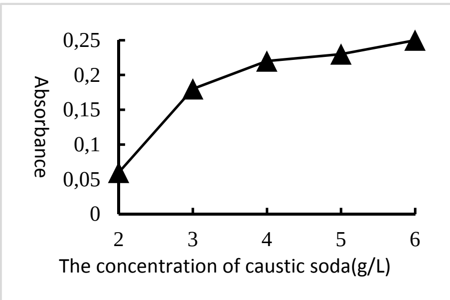
Bath ratio 1: 50

3.3.2 The dyeing process of indigo
Sodium chloride/(g·L－1) 0~150 Padding time/s 10~30
Oxidizing time/min 1~3.5 Number of padding/ times 6~16
Dyeing temperature room temperature

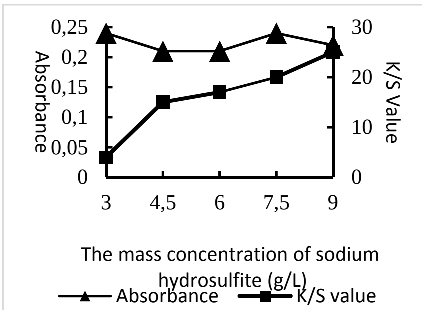
3.4 Testing Methods
(1) Absorbance
Measure the absorbance of reduction solution of indigo with the absorbance tester of V-5000.
(2) K/S values
Use the measuring and matching color system of X-Rite to measure the K/S value of each sample for 4 times, and take the average value.
(3) Color fastness to soaping
Test according to GB /T 3921-2008 Textile Color Fastness Test-Color Fastness to Soaping: the method of experiment 2.

4. Results and discussions

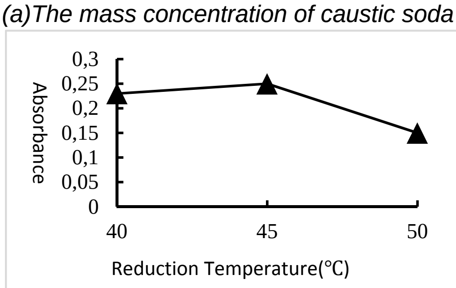
4.1 Confirmation of the plant indigo reduction process
Factors that influence the reduction process of plant indigo dye include the amount of caustic soda, the amount of sodium hydrosulfite, reduction temperature and time etc., the degree of dyes' reduction and dissolution is characterized by the absorbance of dye liquor. As shown in Fig.7(a), when the mass concentration of caustic soda is 2~3g/L, the degree of absorbance increases rapidly; when it is 4~6g/L, the rise tends to be gentle. Taking into account that alkalinity may be too strong to be reduced to alkali sodium, so the mass concentration of caustic soda is better to be 3~4g/L. Fig.7(b) shows that when the amount of sodium hydrosulfite is about 7.5g/L, the absorbance is the highest, and the dye is completely reduced and dissolved. In order to ensure that the reduced and the sodium hydrosulfite won't be oxidized during dyeing process, the amount of sodium hydrosulfite is better to be 8~9g/L. As shown in Fig.7(c), when the reduction temperature is 45°C, the absorbance is the highest, so the reduction temperature is selected as 45°C. Fig.7(d) shows that with the extension of the reduction time, the degree of absorbance is rising. From the foregoing, in the reduction process of plant indigo, the dosage ration of indigo: causticsoda: sodium hydrosulfite is 2:3:9, the reduction temperature is 45°C, and the time is 20 min (Li, 2002). In the reduction process of plant indigo, the dosage of sodium hydrosulfite increases by about 50%.



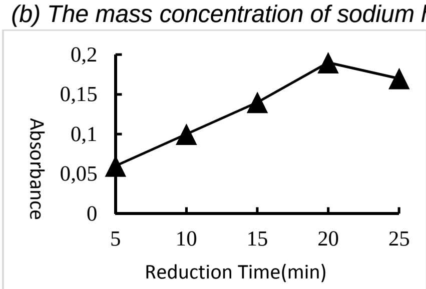
(a)The mass concentration of caustic soda



(b) The mass concentration of sodium hydrosulfite



(c)Temperature

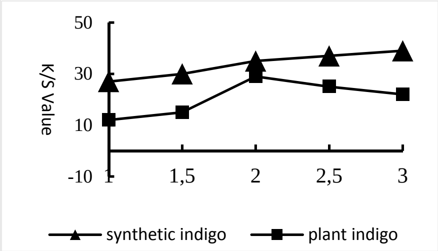


(d) Reduction time

Figure 7: Effect of reduction condition on plant indigo solution

4.2 Determination of the dyeing process
Through the single-factor experiment, investigate influences of each technical parameter on the dyeing effects of the plant indigo and synthetic indigo.

4.2.1The mass concentration of indigo
The effect of the mass concentration of indigo on K/S value is shown in Fig. 8.



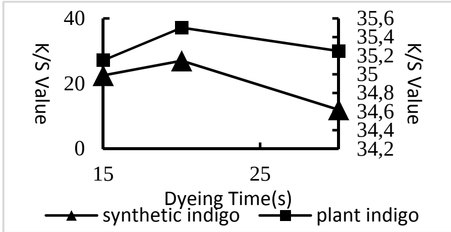
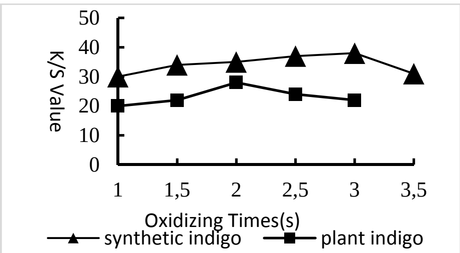


Figure 8: Effect of the mass concentration of indigo on K/S value

Figure 9: Effect of dyeing time on K/S value

4.2.2 Dyeing time
The effect of dyeing time of yarns on the K/S value in solution is shown in Fig. 9.
As we can see from Fig.9, no matter it is plant indigo or synthetic indigo, the K/S value is the highest when dyeing time is 20s, if continue to extend the dyeing time, the K/S value is significantly reduced. At this time, because the rate of leuco body sodium salt absorbed on the fiber is much larger than that of the dye desorbed to the dye solution from the fiber. When the dyeing time is more than 20s, the rate of desorption is greater than that of adsorption, resulting in decline of the rate of dye up-take. So the the suitable dyeing time is 20s.

4.2.3 Oxidizing time
The effect of oxidizing time of dyeing yarns on the K/S value is shown in Fig.10.
As shown in Fig.10, with the extension of oxidizing time, the dyeing K/S value of plant indigo and synthetic indigo increases, but when oxidizing time is up to 2 min, the K/S value of plant indigo will begin to decline, while synthetic indigo continues to increase until the time reaches 3 min, and then it shows a downward trend. In view of this, the oxidizing time of plant indigo should be 2 min, and the oxidizing time of synthetic indigo should be 3 min.



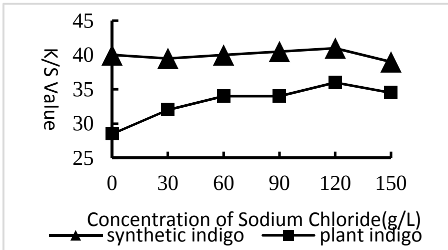


Figure 10: Effect of oxidizing time on K /S value of the dyeings

Figure 11: Effect of the mass concentration of sodium chloride on K /S value

4.2.4 The mass concentration of sodium chloride
From Fig.11, we can see that no matter plant indigo or synthetic indigo, with the increasing of sodium chloride, the K/S value will also increase. Compared with on the synthetic indigo, the accelerating effect of sodium chloride in dyeing is greater on the plant indigo. In order to improve the dye up-take rate of the plant indigo more effectively, add 60~120 g/L sodium chloride during dyeing. While whether adding sodium chloride or not in the synthetic indigo depends on the actual situation.

5. Color fastnesses of plant indigo and synthetic indigo

From table 1, we can see that in the similar condition of color yield, the color fastness to soaping of plant indigo and synthetic indigo are similar, too.

Table 1: Color fastness to soaping of the dyeings

	K/Svalue	Staining/level	Fading/level	K/Svalue	Staining/level	Fading/level
Plant indigo	31	4~5	4~5	38	4	3~4
Synthetic indigo	31	4	4~5	38	4	4

6. Conclusions

The plant indigo dye is the earliest dye used in China, while synthetic indigo replaces the plant indigo to a large extent in today's society (AbbiwD, 1990). At the same time, the plant indigo dye can be widely used in producing Tianmen’s blue calico, making the endangered intangible cultural heritage be inherited. Through the experiment, we can draw the conclusion: (1) in the reduction process of plant indigo dye, the dosage ratio of indigo, caustic soda and sodium hydrosulfite is 2:3:9; reduction temperature is 45°C; and the time is 20 min. Compared with synthetic indigo, the dosage of sodium hydrosulfite with plant indigo increases by about 50%. (2) The optimized dyeing process of plant indigo: themass concentration of NaCl is 60g/L, padding time is 20s, oxidizing time is 2min, and the number of padding is 12~14times.The optimized dyeing process of synthetic indigo: padding time is 20s, oxidizing time is 3min, and the number of padding is 12~14 times. (3) In the condition of similar color yield, the color fastness to soaping of dyed yarns with plant indigo and synthetic indigo is nearly the same.

Acknowledgments

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