SCREEN PRINTING ON SILK FABRIC USING NATURAL INDIGO

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Abstract: *The purpose of this research was to study the printing silk fabric with natural indigo, using a modified starch produced from wild taro (Colocasia esculenta (L.) Schott) corm as thickening agent. The effects from the concentration of the natural indigo dye, added to the modified starch of wild taro corm, in recording the results of thiourea dioxide and sodium hydroxide were examined, after combining the printing paste. The colour values, colour strength, and the fastness properties of printed silk fabric were investigated and the results recorded in the following study. The optimal formula of printing silk fabric using natural indigo paste was prepared by mixing 50% natural indigo paste, 5% thickening agent from modified starch of wild taro corm, 6% thiourea dioxide, 0.4% sodium hydroxide and 38.6% water. The pattern design produced from these combinations in the printing areas on fabrics showed an excellent standard of printing quality and satisfactory colour fastness results were recorded at a level of good to very good.*

Keywords: *printing, natural indigo, silk, thickening agent, wild taro*

1 INTRODUCTION

Natural colourants are generally eco-friendly and have many advantages over synthetic dye [1]. Natural dyes have been an integral part and parcel of human lives since time immemorial [2]. Natural dyes are derived from naturally occurring sources such as animals, insects, bacteria, fungi, minerals and various parts of plants, including roots, bark, leaves, flowers, and fruit, etc. [3-5]. Natural dyes are currently undergoing a revival in craft, food, cosmetic, leather, dye sensitizer, medical plants and textile dyeing and printing [4-5]. In recent years, the ban on toxic azo and benzidine synthetic dyes with 24 carcinogenic aromatic amines set by many countries worldwide has increased the scope for the reintroduction of colourants from natural sources once again, with positive cause and effect to our environment [6-7]. Natural dyes produce very lustrous soft and soothing shades as compared to synthetic dyes [8]. Natural dyes have become quite popular amongst environmentally conscious consumers and are receiving more and more attention in the market of ethical conscious environmentally friendly sales [9]. Nowadays, the market for natural dyes in the textile industry is experiencing a positive resurgence, as Western consumers have become more concerned about the possible health and environmental impact of synthetic dyes [4, 10].

Silk is a natural fiber produced by the silk worm and has been used as a fiber material for over thousands of years [11]. Silk fiber contains an amount of amino (-NH_2) and carboxylic (-COOH) groups, at either ends of its chemical structure, this combination makes it possible to be able to dyed the silk with acid dyes, reactive dyes, metal complex dyes, etc. [11].

Natural indigo, known in different names in different parts of the world, has been in use since around 7000 BC for the dyeing of cotton in attractive and bright blue shades [12]. Plants belonging to the genus *Indigofera* species are most valuable for producing natural indigo. The leaves of these species are usually divided into smaller leaflets. The small rose, purple or white flowers are grown and developed naturally into spikes. The fruit is a type of pod, usually with a thin partition between the seeds [13]. The leaves, flowers and pod of the indigo plant are shown in Figure 1. The colouring matter in the plant leaves are present as a glucoside of indoxyl, known as indican, an organic compound, which is hydrolysed to the indoxyl, by enzymatic action, of which an indigo blue dye is then obtained by a subsequent oxidation process (Figure 2) [14]. In ancient times, reduction of indigo was carried out by a fermentation technique, which included use of ripe fruit and stale urine mixed together, then assisted by wood ash or lime as an alkaline, to produce the desired results.

The solution prepared in this way was left overnight for reduction and solubilization of the indigo dye produced from this process. The reduction of indigo dye into its leuco from is shown in Figure 3 [14].

Wild taro (*Colocasia esculenta* (L.) Schott) is a vegetative propagated root crop species of the monocotyledonous family *Araceae*. It is grown in almost all tropical regions of the world [15, 16]. Wild taro tubers or corms contain considerable amounts of starch (70-80 g/100 g dry taro) [17]. The corm of wild taro is shown in Figure 4. Wild taro tubers contain an oxalic acid crystal in the form of a soluble oxalic acid and insoluble oxalate salts, which cause a skin irritation and pungent odor in unwashed wild taro corms [16].

Figure 1 Indigo plant: (left) leaves and pod (right) flowers

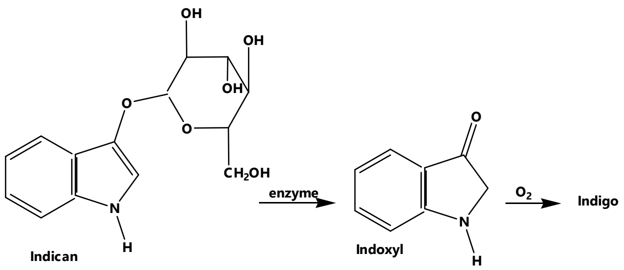

Figure 2 Natural synthetic route to indigo from indicant in *Indigofer tinctoria* [14]

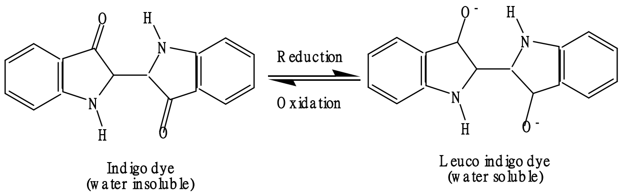

Figure 3 The reduction and oxidation of indigo dye [14]

Figure 4 Wild taro tubers or corm

The aim of this present work was to study the printing of silk fabric with the effects created from the use of natural indigo dye, using a new thickening agent from the modified starch of wild taro corm. The printing and fastness properties were investigated and recorded.

2 EXPERIMENTAL

2.1 Materials and chemicals

A commercially produced plain-weave silk fabric was purchased from market. Silk fabric was scoured with an aqueous nonionic surfactant solution at a temperature of 50°C for 30 mins, then thoroughly rinsed and air dried at room temperature. Fresh materials of *Indigofera tinctoria* Linn were collected from Nakhon Phanom province, Thailand. The following chemicals of laboratory grade were used in the experiment: thiourea dioxides ($(NH_2)_2CSO_2$), sodium hydroxide (NaOH) and hydrogen peroxide (H_2O_2), supplied by Star Tech Chemical Industrial Co., Ltd. A nonionic soaping agent was purchased from Boonthawee Chemephan Co, Ltd. (Thailand). Wild taro corms used in this experiment was collected from Chantaburi province, Thailand.

2.2 Extraction of indigo dye

Plant materials were cut to small pieces, fermented in water for one night and then added twice in volume of $Ca(OH)_2$ solution (pH~11), blew the air for 15 mins to precipitate indigo [18]. The precipitated indigo or indigo paste was used for printing as such without any further purification.

2.3 Preparation modified starch of wild taro corms

The wild taro corms were dried in sunlight for 1 month and then crumbled using a blender; the corms were then milled and ground through a 355 µm mesh sieve. The resulting powder produce from the wild taro corm was dispersed in alkaline aqueous methanol at 80%v/v. Then, monochloro-acetic acid (MCA) was added in solid form to the (above mentioned) solution and mixed for 10 min. The temperature was adjusted and raised to 70°C for a further 60 min. The mixture paste was cooled in room temperature and then filtered through a suck funnel, to resolve in water. An added amount at 50% of HCl was added drop by drop until it became neutral. The development reaction of this product through all of the above processes and methods was then precipitated and washed with ethanol to remove ionic salts. The carboxymethylated wild taro corm (or modified starch of wild taro) was removed by filtration and an added process of washing three times with methanol. The washed product was dried at 40°C for 4 h. The milling was size reduced to 355ve size. The powder was stored in a desiccator.

Table 1 Recipe of natural indigo printing paste

Parameters	Recipe [g/kg]				
	Indigo paste [g]	Modified starch [g]	Thiourea dioxide [g]	NaOH [g]	50°C water [ml]
Effect of indigo paste conc.	500-900	50	60	10	X
Effect of modified starch conc.	500	0-90	60	10	X
Effect of thiourea dioxide conc.	500	50	0-120	10	X
Effect of NaOH conc.	500	50	60	0-10	X

2.4 Preparation of printing paste

The printing paste was prepared using the following recipe as shown in Table 1. It was prepared by mixing concentrations of indigo, modified starch of wild taro, thiourea dioxides and sodium hydroxide in water, then continual stirring for 20 min to produce a homogenous paste until the reduction was completed. With indigo the colour of the leuco indigo solution is yellow green when reduced with thiourea dioxide.

2.5 Printing process

The printing process consisted of forcing a various print paste through the open areas of the screen with a flexible synthetic rubber squeegee. The rubber blade, which is contained in a wooden support, is drawn steadily across the screen at a constant angle and pressure. The pressures exerted must be as similar as possible [11]. The fixation was done by hot air at 60°C for 10 mins. Following these steps, the fabric was then immersed with 5 g/L of H_2O_2 for 15 min and finally the samples were washed in 1 g/L of a soaping agent at 60°C for 15 min and then air-dried at room temperature.

2.6 Measurement of the viscosity of the printing paste

The rheological properties of the printing pastes were measured at 25°C using a viscometer (BROOKFIELD DV-II+Pro). The apparent viscosity (η) of the printing pastes at various rates of shear was calculated from the shearing stress (τ) [dyne/cm^2] and rate of shear (D) as follows [19-20]:

$$\eta = \tau / D \tag{1}$$

2.7 Evaluation of colour value and colour strength

The colour value (*CIE L**, *a**, *b**) and color strength (*K/S*) of the printed samples were evaluated using a spectro-photometer (Hunter Lab Color Quest XE, USA). The *K/S* value and colour value (*CIE L*, a*, b**) of all printed fabrics were determined at 650 nm (λ_{max}) and measured for five different locations for each sample. The average of these values were reported and showed a standard deviation within the order of ±0.04 in all cases. The *L** value indicates perceived lightness in CIELAB colour space. The *L** scale ran from 0 (black) to 100 (white); the higher the *L** reading the lighter the colour. The *a** value indicates red (+*a**) and green (-*a**) while the *b** value indicates yellow (+*b**) and blue (-*b**) [21-22]. The colour strength in terms of *K/S* values were calculated using the Kubelka-Munk equation:

$$K/S = (1-R)^2/2R \tag{2}$$

where R is representative of reflectance, K is the sorption coefficient and S is the scattering coefficient [21-22].

2.8 Colour fastness evaluation

The color fastness to washing, light, rubbing, water, perspiration of the printed samples was determined according to ISO 105-C06 A1S: 2010, ISO 105-B02: 1994, ISO 105-X12: 2001, ISO 105-E01: 2010, and ISO 105-E04: 2008 respectively.

3 RESULTS AND DISCUSSION

3.1 Effect of dye concentration on colour value

Silk fabric samples printed with natural indigo at different natural indigo dye concentrations is shown in Table 2. It can be observed that the colour strength increased when the natural indigo concentration ranged from 500 to 800 g. The changes of *K/S* values are not obvious when the concentration of dye is above 800 g. The reason was that the penetration of natural indigo has reached in it saturated state when the concentration was more than 800 g. The *b** values varied from about -8 to -12 when the natural indigo dye concentration ranges from 500 to 900 g. From the results, it is promising that the silk fiber has various carboxylic (-COOH) groups in its structure. The carboxylic groups helped to interact very well to the amine (-NH) or carbonyl (C=O) groups of the natural indigo via hydrogen bonds resulted to easy printed with natural indigo [23]. The silk with these measurements when printed with natural indigo paste showed a blue shade.

Table 2 Colour values, colour strength, viscosity and colour obtained at varying dye concentrations

Dye conc. [g]	L*	a*	b*	K/S	Viscosity [cpi]	Colour obtained
50	50.10	-4.22	-8.84	3.04	18.476	
60	49.95	-4.37	-8.69	3.45	19.109	
70	48.30	-4.59	-12.86	4.19	20.823	
80	47.57	-4.70	-12.70	4.26	21.723	
90	46.06	-4.29	-12.37	4.29	22.874	

Table 3 Colour values, colour strength, viscosity and colour obtained at varying modified starch of wild taro concentrations

Modified starch conc. [g]	L*	a*	b*	K/S	Viscosity [cpi]	Colour obtained
0	52.23	-5.50	-8.22	2.63	9.598	
30	51.97	-4.88	-9.35	2.72	9.838	
50	50.10	-4.22	-9.84	3.04	18.476	
70	50.28	-5.47	-10.45	3.01	18.956	
90	49.19	-4.96	-9.94	3.09	19.036	

3.2 Effect of modified starch of wild taro concentration

The colour value, colour strength and viscosity of the effect from the modified starch of wild taro concentration results are obtained and presented in Table 3. Table 3 shows that increasing the modified starch of wild taro concentration from 0 to 50 g resulted in an improvement in the *K/S* values of the natural indigo print, which could be discussed in terms of higher paste viscosity and minimum undue penetration or flashing of the dye. A further increase in the concentration of the modified starch of wild taro has practically no effect on the depth of the obtained print and was accompanied with the negative impact on softness [20].

3.3 Effect of thiourea dioxide and sodium hydroxide concentration

The effect of thiourea dioxide concentration on silk fabric printed with the natural indigo in a print paste including thiourea dioxide and sodium hydroxide is shown in Table 4. At a constant concentration of 10 g sodium hydroxide, the *K/S* value increased with an increasing concentration of thiourea dioxide. This increase almost saturated over the concentration of 90 g thiourea dioxide. The effect of the sodium hydroxide concentration on silk fabrics printed with natural indigo is shown in Table 5. The total *K/S* value decreased with the added increasing concentration of sodium hydroxide over the range of 4 g. The effect and use of the amount of sodium hydroxide used in its concentrated form was not enough at 6 g sodium hydroxide. The effect of the thiourea dioxide and sodium hydroxide on the *K/S* value of the dye indicates clearly that the solubilization of the dye from the *Indigofer tinctoria* leaves is very similar to that found in vat dyes which ordinarily is initiated by the reduction of the insoluble dye species in the plant tissue into soluble leuco forms which are sparingly soluble [24].

3.4 Fastness properties of printed silk

The fastness properties of silk fabric printed with 500 g of natural indigo dye, 50 g of modified starch of wild taro corm, 60 g of thiourea dioxide and 10 g of sodium hydroxide are presented in Table 6. Table 6 indicates that the washing and water fastness rating of silk fabrics printed with the natural indigo were good to very good (4 to 4-5). The results indicated that the silk fibers much be reached to the indigo dye via strongly chemical bonds. The formed bond should be enhanced the stability of dye when exposed to wash and water. Colour fastness to light was fair (5). Colour fastness to perspiration of all printed silk fabrics showed good to very good (4 to 4-5). The results showed that indigo dye and silk fibers interacted very well via the hydrogen bonds which helped to sustain the colour of dye. Colour fastness to rubbing was found to be in the range of 4-5 (good to very good). This result can be also attributed to the insolubility of the indigo characteristics [25].

Table 4 Colour values, colour strength, viscosity and colour obtained at varying thiourea dioxide concentrations

Thiourea dioxide conc. [g]	L*	a*	b*	K/S	Viscosity [cpi]	Colour obtained
0	67.66	-3.67	0.09	0.74	8.548	
30	60.35	-3.20	-4.17	1.20	15.490	
60	50.10	-4.22	-8.14	3.04	18.476	
90	49.09	-4.16	-8.13	3.10	19.101	
120	48.98	-4.17	-8.25	3.13	19.116	

Table 5 Colour values, colour strength, viscosity and colour obtained at varying sodium hydroxide (NaOH) concentrations

NaOH conc. [g]	L*	a*	b*	K/S	Viscosity [cpi]	Colour obtained
0	48.78	-4.35	-8.33	2.01	18.670	
2	48.58	-4.66	-9.63	2.30	18.754	
4	48.14	-5.46	-10.12	3.34	18.695	
6	49.62	-5.02	-9.03	3.10	18.800	
10	50.10	-4.22	-8.84	3.04	18.476	

Table 6 Colour fastness to washing, water, perspiration and light

Colour fastness to	Colour change	Colour staining					
		Acetate	Cotton	Nylon	Polyester	Acrylic	Wool
washing	4	4-5	4-5	4-5	4-5	4-5	4-5
water	4-5	4-5	4-5	4-5	4-5	4-5	4-5
perspiration (acid)	4	4-5	4-5	4-5	4-5	4-5	4-5
perspiration (alkaline)	4	4-5	4-5	4-5	4-5	4-5	4-5
light	5	-	-	-	-	-	-

4 CONCLUSION

It is evident from the results that silk fabric can be successfully screen printed with natural indigo using modified starch of wild taro corms. The investigation shows that the recipe is suitable for printing. The modified starch of wild taro corms could be used as a thickening agent for natural indigo printing on silk fabric. Printed silk fabric exhibited good to very good colour fastness.

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