Clean and Green Textile Processes

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1. INTRODUCTION

Over a year ago four Thai textile companies were awarded the EU Ecolabel, consisting of Asia Fiber Co., Ltd. for nylon yarn, Greenville Trading Co., Ltd. for silk fabric (the first award receiver in Asia), Rama Textile Industry Co., Ltd. for cotton yarn, and Thong Thai Textile Co., Ltd. for cotton garments. The event has brought more attention to the Thai textile industry as it shows that the production of green textiles is not only safe to the environment but it can also open the Thai textile industry to the European market.

EcoDesign, also known as Green Design, was first introduced to the Thai industry in 1999. Since then several EcoDesign projects have been conducted by many Thai organizations including the Thai Textile Institute (THTI) and many Thai textile associations such as the Textile Dyeing, Printing, and Finishing Association. With an aim to be the ASEAN production center of green products by the year 2015, Thailand is currently boosting the promotion of EcoDesign and Life Cycle Thinking of product development among all stakeholders.

This article shows the research and development of green textile products and processes in Thailand in the areas of dyeing, printing, and finishing.

2. RESEARCH & DEVELOPMENT

<u>Natural Dyes Production</u>

Her Majesty Crown Princess Sirinthorn of Thailand established the Center of Plant Genetic Reservation in 1995 at Nakhonrachasima province in order to collect local rare plants, to produce natural dyes, and to dye silk. Since then, over 100 plant species have been collected and over 50 of them can be used to make natural dyes for silk dyeing. Various color shades of products are being made daily from various plant species, plant parts (e.g., leaves, barks, and roots), and mordants (e.g., alum, and soils) such as blue, red, yellow, green, brown, gray, black, pink, gold, and orange [1]. Several dyes show brilliant colors with good to very good colorfastness to washing (grey scale 4-5 of 5) and to light (blue wool scale 6 of 8). Natural dyes and natural dyed silk products are made there in small lots according to local demands. The Center has planned to expand its production capacity especially for the natural dye production. Examples of plants in this Center are shown in Figures 1-4.

Figure 1. Indigo for blue dyes [1].

Figure 2. Ma phut for brilliant yellow dyes [1].

Figure 3. Khontha for gray/tan dyes [1].

Figure 4. Cassod tree for yellow/brownish green dyes [1].

Natural Dyeing

Nakpathom and Likibanakorn [2] dyed cotton and silk fabrics with lac dye using pad-batch and pad-dry techniques. Three different compounds were used as mordants consisting of alum, ferrous sulfate, and copper sulfate. They found that in order to achieve good wash fastness of dyed cotton and silk fabrics, ferrous sulfate and copper sulfate must be used as mordants. For cotton dyeing, results indicated that it's necessary to treat dyed cotton fabric with chitosan after mordanting in order to achieve high color strength the dyed fabric while Kittinaovarat [3] found that pretreatment of undyed cotton fabric with chitosan helped enhancing the absorption of Mangosteen Rind dye onto cotton fabric as well as improved its wash and light fastness. Later on, Nakpathom and Likibanakorn also used tannic acid and tartaric acid as mordants for lac dyeing. Currently, they are working on printing natural dyes.

Kittinaovarat [4] successfully combined natural dyeing and durable press finishing in one step process. In this work, cotton fabric was dyed with Mangosteen Rind dye and finished with glyoxal in a single bath using exhaustion process and pad-dry-cure process. Aluminum sulfate was used as catalyst for cross-linking glyoxal onto the fabric and this would trap dye molecules on the fabric in order to improve colorfastness to washing. It was speculated that aluminum sulfate might work as mordants for Mangosteen Rind dyeing. Dyed and finished fabrics showed higher color strength, higher wrinkle recovery angle, and better light fastness than dyed fabrics (see Table 1).

Table 1. Properties of dyed and finished fabrics [4].

Catalyst (g/l)	Wrinkle recovery angles (°)	Color strength at 360 nm	Wash fastness	Light fastness
Dyeing+Finishing: exhaustion process				
0.5	153	2.558	4	3
1	155	2.229	3-4	3
2	160	2.896	3-4	3
Dyeing+Finishing: pad-dry-cure process				
0.5	167	1.587	4	3-4
1	171	1.627	4	3-4
2	176	1.588	4-5	3-4
Dyeing only				
0	153	1.016	4	2

Application of Chitosan in Finishing

Pitchayangkul and Sangwatanaroj [5] are currently preparing small molecular weight chitosan for textile finishing. The prepared chitosan has molecular weight in the range between 20,000-30,000 Dalton while typical chitosan is prepared at molecular weight of 300,000-500,000 Dalton.

In a preliminary work, chitosan was used in acid solution. The work has indicated that cotton fabric finished with the chitosan solution showed antibacterial and anti-soiling properties (see the expansion of oily stain in Figure 5). The finished fabric was soft and durable to washing. Scanning electron microscopic analysis of the fabric surface showed no chitosan film on the fiber (see Figure 6) which indicated a complete sorption and diffusion of chitosan solution into the fiber due to its low molecular weight. Further applications of the chitosan solution are being studied.

Figure 5. Staining of engine oil on chitosan treated fabric (left) and on untreated fabric (right) [5].

Figure 6. SEM of chitosan treated fabric [5].

Another research group of Srikulkit, Charuchinda and Ratanawalediroj [6] also used chitosan for textile finishing. One of their works concerned the flame retardant finishing of cotton fabric using chitosan and polyphosphoric and another was wrinkle resistant and antimicrobial finishing of cotton fabric using citric acid and chitosan. In addition, they also used chitosan for recovering and recycling dyes from waste dye solution.

Application of Silk Sericin/Fibroin in Finishing

Sonthisombut and his group [7,8] prepared two kinds of silk powders from silk sericin and silk fibroin, and used them for garment fishing. Sericin powder was prepared by first degumming raw silk with water, then evaporating water, complete drying the remaining portion until turning into powder, and finally grinding powder into nanoparticle using a special equipment. Fibroin powder was prepared by first dissolving degummed silk fiber in 2.5-5% (w/w) sodium hydroxide solution at 100°C for 10-15 minutes, then evaporating water, drying the remaining portion until turning into powder, drying, and finally grinding powder into nanoparticle.

Suspensions and solutions of silk nanopowders were then treated (spraying for suspensions and padding for solutions) on polyester and fixed with urethane fixing agent. Results indicated that sericin (solution) treated (padding) polyester obtained 10-12% moisture content while it was 0.4% in typical polyester. Unfortunately, suspended finishes were not durable to washing. In terms of sericin content per each shirt, it was estimated that 5 grams of sericin powder would be needed to treat one shirt.

Application of Degumming Waste in Silk Dyeing

Boonpavanitchakul [9,10] and Sangwatanaroj [9] studied a possibility of using the enzymatic degumming waste solution to modify triazine reactive dyes and using the dye solutions to dye silk in one bath.

In this work a local hand reeled silk fiber (Dok Bua, Thai-Japanese mixed species) was enzymatic degummed using protease enzyme (Aspergillus oryzae with activity of 14,000 U/g), then the degumming solution waste (containing amino acids, see Table 2) was used to modify triazine reactive dyes (Procion Red H-E7B, Procion Turquoise H-A, and Procion Blue H-EGN), and finally the dye solutions were used for dyeing silk fabric, all three processes (degumming/dye modifying/dyeing) in a single bath. For a comparison, triazine reactive dyes were also modified with a single amino acid (glutamic acid) and then the modified dyes were used for dyeing silk fabric. A proposed structure of modified triazine reactive dyes is shown in Figure 8.

Figure 7. Hand reeling of silk fiber.

Table 2. Amino acids content found in degumming solution waste using HPLC technique [10].

Amino acids (mg/100 ml, 4 g silk fiber degumming)			
Serine	0.85	Aspartic	0.17
Lysine	0.40	Valine	0.17
Arginine	0.36	Leucine	0.15
Alanine	0.25	Histidine	0.12
Theronine	0.24	Isoleucine	0.11
Glutamic	0.21	Phenylanine	0.06
Tyrosine	0.21	Proline	0.04
Glycine	0.18		

and very low content of Methionine, Tryptophane, and Cystine.

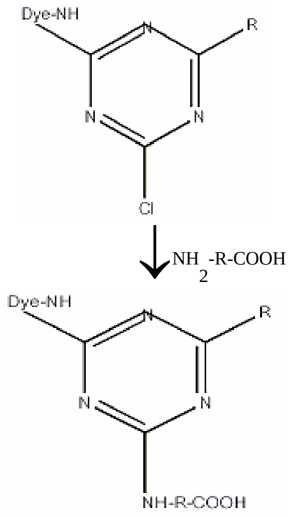

Figure 8. Proposed structure of modified triazine reactive dye [10].

Dyed fabrics were tested for various properties and suitable conditions for reactive dye modification and for silk dyeing were determined. FTIR analysis indicated the presence of modified dyes and the changes of dye structures for both modifications using glutamic acid and degumming solution waste (see Figure 9). All dyed fabrics were measured for color strength using a colorimeter and found that fabrics dyed with modified dyes had higher color strength (darker color, see Figures 10-11) than fabrics dyed with unmodified dyes with no shade difference (L*, a*, and b* of fabrics dyed with modified and unmodified dyes are about the same).

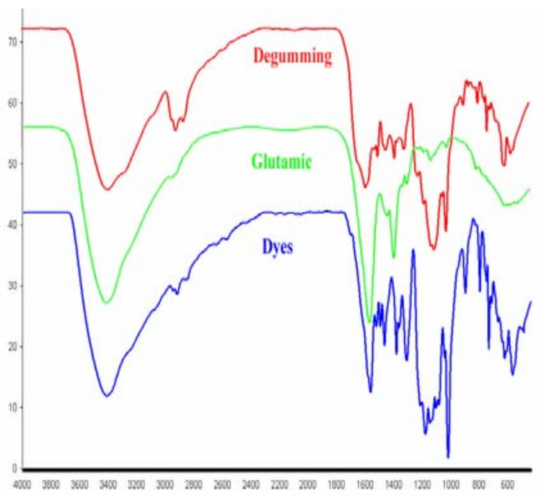

Figure 9. FTIR spectra of modified dyes (top = with degumming waste, middle = with glutamic acid) and unmodified dye (bottom) [10].

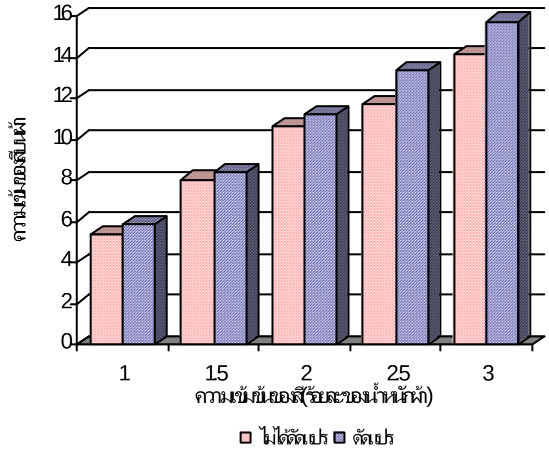

Figure 10. Color strength (K/S, Y axis) of fabrics dyed with modified (right bar) and unmodified (left bar) Procion Red H-E7B reactive dye at 1-3% dye (concentration, X axis) [10].

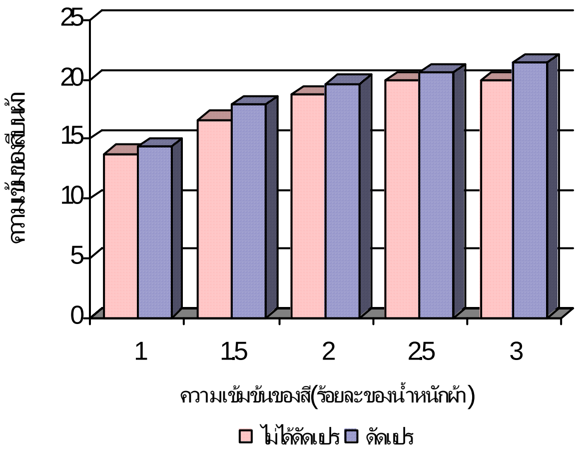

Figure 11. Color strength (K/S, Y axis) of fabrics dyed with modified (right bar) and unmodified (left bar) Procion Turquoise H-A reactive dye at 1-3% dye (concentration, X axis) [10].

Moreover, dyes modified with degumming solution waste (containing various amino acids) could dye silk to deeper color than those modified with glutamic acid. In terms of colorfastness, all dyed fabrics showed good colorfastness to washing (grey scale 4-5 of 5) and moderate colorfastness to crocking (grey scale 3-4 of 5).

This work has shown that the degumming waste solution could be used to modify triazine reactive dyes for dyeing silk successfully in the same single bath. In addition, this three-step (degumming/dye modifying/dyeing) single-bath process helps reducing the amount of wastes and reducing the water uses in textile wet processes.

<u>Application of By-Product (from Lactic Acid Production) in Cotton Printing</u>

Purac (Thailand) Co., Ltd. is the producer of lactic acid for food industry at a capacity of 250 tons per day. All raw materials used in the production are claimed to be safe for the environment. Upon this production capacity, the company also generates 60-70 tons of by-product daily. Generally, the company sells this by-product for animal feed industry and for fertilizer industry. According to by-product analysis, it was found that the by-product contained various metals as shown in Table 3). To make this by-product more valuable, the following research has used it in cotton printing process.

Table 3. Metals content found in by-product from lactic acid production using ICP technique according to the test method EPA 3052 [12].

Metal	By-product (powder), mg/kg	By-product (extracted aqueous solution), mg/kg
Arsenic	10.25	not found
Boron	not found	not found
Cadmium	not found	not found
Calcium	312,266.79	23.67
Chromium	53.15	not found
Copper	not found	not found
Iron	1806.73	0.11
Lead	not found	not found
Magnesium	28,023.83	3.13
Mercury	not found	not found
Molybdenum	not found	not found
Sodium	132.77	0.42
Zinc	28.53	not found

Note: ICP technique can not detect substances lower than 5 mg/kg. Therefore the word “not found” in this table could also mean that the content was less than 5 mg/kg.

Narumol [11,12] and Sangwatanaroj [11] studied a possibility of using by-product from lactic acid production to substitute urea in the reactive dye printing of cotton fabric. By-product was used in forms of powder and extracted aqueous solution (safer than the powder form due to no hazardous metal, see Table 3), and was used individually and in combination with urea as printing auxiliary. Print pastes of various formulations were prepared, consisting of water; wetting agent; alkali; antibacterial agent; oxidizing agent; thickener; chelating agent; reactive dye; and urea/by-product. Then each print paste was screen printed on cotton fabric and printed fabric was dried, steamed, washed, and finally dried again. Printed fabric was analyzed for its color (color strength or color depth or K/S, color difference or ΔE, and color shade change or L* a* b*), colorfastness to washing and crocking, and stiffness.

Results indicated that the application of by-product alone or in combination with urea for cotton printing could obviously help increasing the fabric’s color strength with no color shade change from the fabric conventionally printed using urea (see Table 4). According to by-product analysis, it was found that the by-product contained various cationic metals and it’s speculated that these metals were responsible for enhancing the fabric’s color strength by fixing more dye molecules (anionic) onto the fabric.

Table 4. Color values of fabrics printed with Procion Blue PX-3R reactive dye using by-product and urea as printing auxiliaries [12].

Auxiliary	K/S	ΔE	L*	a*	b*
Urea 15 g	5.12-6.68	0	43.83-47.13	0.90-2.29	-39.36 to -41.00
By-product powder 5 g	5.60-6.06	0.82-1.45	45.21-46.00	1.45-1.70	-40.12 to -40.67
By-product powder 5 g and urea 1 g	5.42-5.59	0.21-0.96	46.12-46.45	1.32-1.36	-40.09 to -40.10
By-product solution 20 g	5.79-6.39	0.81-2.22	44.10-45.68	1.69-2.09	-40.27 to -40.75
By-product solution 20 g and urea 1 g	5.66-6.96	0.73-1.37	43.16-45.99	1.37-2.59	-40.19 to -40.99

In terms of fabric colorfastness, test results showed that all printed fabrics had good to excellent colorfast to washing (grey scale 4-5 of 5) and crocking (grey scale 3-5 of 5). Printed fabrics showed acceptable stiffness and did not contain hazardous metals (only calcium, iron, magnesium, and sodium were found).

Commercial Textile Products

Material Connexion, the materials library located in Thailand Creative and Design Center (TCDC), is now showing over 100 materials from Thailand, in addition to thousands of materials from all over the world. Two examples of green textile products from Thailand (only finishing process) are described as follows [13].

Covenant Co., Ltd. introduced anti-mosquito fabric for hospital and household uses, sportswear, outwear, and bedding. In the fabric finishing process, small amounts of Thai herb with mosquito repellent property are micro-encapsulated and incorporated into fabrics. The process itself passed Thailand Ministry of Public Health Standards. On the first use of this finished fabric, it was found that the rate of mosquito bites was reduced by 90% while after passing 20 washes the bite-rate was still reduced by 50%.

People's Garment Public Co., Ltd. produced fabric containing natural extracts of Vitamin E, Aloe Vera, and Jojoba oil for the maintenance of healthy skin. In addition, the company has recently produced Super Cool fabric from fabric finishing with eucalyptus. Eucalyptus oil was micro-encapsulated and incorporated into fabric and the finished fabric was subjected to the standard test KES-F7 (Kawabata Evaluation System-Thermo Labo II): Touch feeling of warmth or coolness Q-max (W/cm^2) in order to measure the fabric's heat absorption. It was found that the finished fabric was able to absorb 0.118 W/cm^2 of heat or absorb heat 32% better than the unfinished fabric which absorbed 0.089 W/cm^2 [14].

In addition to the previous finished fabrics shown in the Material Connexion library, there are other textile products finished with various kinds of Thai herbs. Mostly, small amounts of natural herbs are micro-encapsulated and the capsules are incorporated into fabric using resin or polymer coating. One promising product is the antibacterial and anti-dust mite bed sheeting from the Echo Trend Inter Co., Ltd. The sheeting was prepared from tightly weaving and was finished with 4 Thai herbs containing anti-dust mite property. Upon dust mite counting, the test result showed that 90-100% death rate of dust mite was found on finished bed sheet [15].

3. REFERENCES

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