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Investigation of the Discharge Printing of Cotton and Silk Fabrics Dyed with Reactive and Natural Dyes

Mai Abd El-Aty [a], Mona Mohamed [a], Alaa M. E. Hashad [a], Samira S. Moawaed [a], Ahmed G. Hassabo [b]*, Hanan A. Othman [a] and Eman Abd-Elaziz [a]

[a] *Benha University, Faculty of Applied Arts, Printing, Dyeing and Finishing Department, Benha, Egypt*

[b] *National Research Centre (Scopus affiliation ID 60014618), Textile Research and Technology Institute, Pretreatment and Finishing of Cellulose-based Textiles Department, 33 El-Behouth St. (former El-Tahrir str.), Dokki, P.O. 12622, Giza, Egypt*

Textile substrates are printed in a variety of styles, including direct, discharge, resist, and so on. The dye of a ground-dyed fabric is released from the desired design or pattern in the discharge style of printing. This discharge might result in either a white or colorful pattern. Because of its emphasis on patterns with diverse colors on a dark backdrop, discharge printing is becoming increasingly popular in both local and foreign markets. It was discovered that a design might be bleached off or discharged from an already-piece painted material using chemical techniques. Printers may create elaborate and precise patterns using this discharge method. The chemicals used to discharge the dyes are classified as either oxidative or reductive agents.

Keywords: Discharge Printing; Cotton; Silk; Reactive and Natural Dyes

Introduction

Printing is commonly understood as "localized dyeing." Dyes are added to specific portions of the cloth that comprise the pattern during printing. The necessary reactions in printing are comparable to dyeing. Color is utilized in solution form in dyeing, whereas color is applied as a thick paste of the dye in printing. combining a natural or synthetic thickener with a substrate (usual cloth) and adopting a technique for correctly applying the colors Several processes were used, and the available colors were doubled.

The many techniques used in the textile production business contribute significantly to pollution. Significant amounts of complicated effluents that fluctuate in both amount and feature regularly arise in the textile wet processing sector. The effluent from the textile sector is known to be brilliantly colored, with a high concentration of suspended particles, pH swings, high temperatures, and high demand for chemical oxygen. Color influences light transmission and interrupt biological processes, which can directly damage aquatic life in the receiving stream. Several attempts have been made to reduce pollution by utilizing natural dyes and auxiliaries. [1-14]

Extract printing is another name for discharge printing. [15] The dye of a ground-dyed cloth is released from the desired design or pattern in the discharge style of printing. Unless a nondischargeable colorant is employed in the discharge printing paste, this discharge can result in a white or colorful pattern. Chemical cleavage of the chromophore, a molecule responsible for the visual appearance of color, releases the dye. This chromophore chemical cleavage can occur by either a reduction or an oxidation process. The substances employed to discharge the dyes are classed as oxidative or reductive agents on this basis. [15]

Sodium formaldehyde sulphoxylate ($NaHSO_2$ $CH_2O.2H_2O$), thiourea dioxide [$(NH_2)(NH)CSO_2H$], and tin(II) chloride are the most often utilized

Corresponding author: Ahmed G. Hassabo, Email: aga.hassabo@hotmail.com, Tel., +20 110 22 555 13
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discharge agents ($SnCl_2$). The reductant used is determined by the dyes used, both the ground and illuminating colors, as well as the cloth being printed. Because reductants and dyes have varying discharge abilities, it is possible to mix reductants and dyes for different discharging scales. $SnCl_2$ is not suggested for hydrophobic materials except expressly for developing unique styles, since capillary migration of the liquid causes haloing flaws around the pattern, diminishing its definition.

A good thickener for discharge printing must fulfill not only the requirements of direct printing but also the additional requirements of discharge printing. The thickener used should be reductant stable. As a result, a non-ionic type is chosen. Furthermore, a thickener with a high-solid, low-viscosity feature is required to ensure that specific patterns are effectively obtained. [16]

Important of Discharge Printing in the industry

- It is feasible to have large swaths of the ground color.
- Delicate hues and elaborate patterns are achievable on a dark foundation color, with superb depth and clarity.
- A very interesting way for removing color from a garment.
- There is little to no sense of the pattern on the shirt.
- Colors that glow.
- The most effective method for printing on dark clothes using non-traditional inks.
- Something distinct from the "norms" of screen printing.
- Maintaining a high level of detail.
- We offer discharge printing at no extra cost. It is frequently less expensive than regular ink.
- Higher production costs but long-lasting, distinctive designs. [17, 18]

The inconvenience of Discharge Printing in the industry:

- Because background dyes must be reasonably easy to discharge, they are often azo-based hues. However, dyes with particular structural properties discharge more easily than others. Monoazo dispersion dyes based on azobenzene are the most readily discharged in general. [17, 18]
- It is a costly procedure.
- Dyeing or padding and discharge printing are two-stage applications.
- Limited color options for the ground and theme.
- Requires strict process care since any failure would result in damages. [19]
- Some sizes may discharge more effectively than others.
- Can be difficult to utilize for photographic or process printing.
- Not all shirts will discharge (royal blue never works well, for example).
- The process might be eccentric. [17, 18]

Discharge printing of natural fabrics (cotton and silk fabrics) using Thiourea dioxide (TDO)

Cotton fibers are nature's purest supply of cellulose, the most common polymer. Cotton is a linear cellulose polymer, and cellobiose is a repeating unit made up of two glucose units (Figure 1). Cotton is made up of around 65–70% crystalline area and approximately 35–30% amorphous region. Cotton has several advantageous characteristics. It is breathable, pleasant, and long-lasting, making it useful in the textile business. [1]

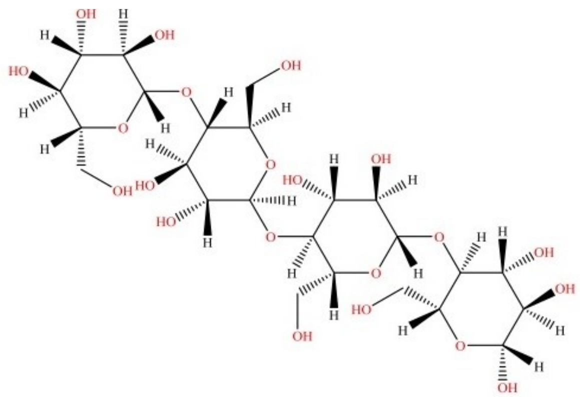

Figure 1: chemical structure of the cellulose

Silkworm-derived silk Bombyx mori is a natural protein composed primarily of sericin and fibroin proteins. Sericin accounts for 25–30% of silk protein and envelops the fibroin fiber with successive sticky layers that aid in cocoon formation. Sericin holds the cocoon together by bonding silk strands together. The majority of the sericin must be eliminated during the reeling mill and subsequent phases of silk processing. [20]

Designs are introduced into reactive print colored cotton and silk textiles using discharge methods. Patterns are transferred to reactive colored fabric using a chemical degradation procedure to the original-colored cloth. Discharging agents can include oxidizing or reducing agents, acids, alkalis, and various salts. However, the most adaptable and essential discharge techniques are based on formaldehyde sulphoxylates ($NaHSO_2.CH_2O.2H_2O$) and thiourea dioxide. The cloth is initially colored with reactive dye (Vinyl sulphone fiber reactive) that may be destroyed by specific discharging chemicals in the discharge style (sodium sulfoxylate formaldehyde). The discharge paste, which is an oxidizing and reducing chemical, destroys the color by oxidation and reduction to diminish and erase the chromophore color through printing After processing, the printed cloth has a white discharge.

Dyeing process of silk and cotton fabrics

Using exhaust dyeing methods, the cotton and silk materials were colored with reactive dyes and acid dyes, respectively. The dyeing procedure was carried out at a 1:30 liquor ratio. Table 1 and Figure 1 show the precise dyeing methods and associated parameters. [16]

Table 1: Dyeing parameters for cotton and silk fabrics**:**

Cotton fabrics		Silk fabrics	
Parameter	Value	Parameter	Value
Reactive dyes (owf)		Acid dyes (owf)	
Sodium sulfate, g l^{-1}	60	Sodium sulfate, g l^{-1}	4–10
Sodium carbonate, g l^{-1}	8–15	Glacial acetic acid, g l^{-1}	1–2
Liquor ratio	1:30	ALBEGAL SET, g l^{-1}	0.5–1
Time, min	60–80	ALBEGAL FFA-01, g l^{-1}	0.5
Temperature, °C	60–75	Liquor ratio	1:50
		Time, min	60
		Temperature, °C	90

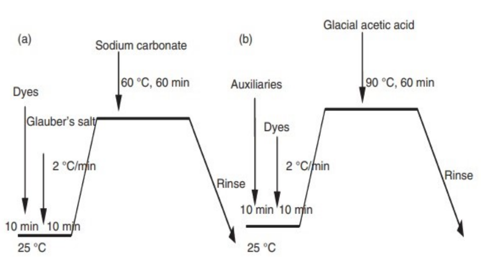

Figure (2): Dyeing conditions for (a) cotton and (b) silk fabrics

Thiourea dioxide (TDO), a reducing agent, is seen to be one of the most promising discharge agents for textile discharge printing due to its high reducing ability, minimal pollutant emission, and environmentally benign manufacture. TDO has received a lot of interest in recent years as an alternative to traditional discharging agents like formaldehyde sulfoxylate and related chemicals in textile discharge printing. TDO has little oxidability or reducibility at room temperature and is virtually inert to most chemical reagents. When heated, TDO eventually decomposes into carbamide and SO2-, the latter being a well-known anion radical with a high reducing capacity. [21]

A serious issue occurs as a result of its weak water stability and solubility. Temperature and alkali solubility concentrations When the concentration of TDO is slightly greater than the maximum solubility in screen printing recipes, a portion of the TDO will be suspended in the white discharge paste. Undissolved TDO particles will be left on the screen's surface, resulting in a significant loss of TDO. Furthermore, the suspended TDO particles quickly clog the printing screen's mesh. As a result, it is frequently used in alkaline media to demonstrate its reducing potential. TDO is readily degraded in an alkali solution, which has a detrimental influence on practical discharge printing applications. Based on the issues with TDO in water, it is required to increase its stability and solubility, particularly when employed as a discharge agent in the discharge printing process. Although the solubility of TDO powder in aqueous media is critical for practical use, it should be noted that oxygen and water molecules have negative effects on TDO reducibility; hence, it is better to find a non-aqueous medium to substitute water and stabilize the TDO. TDO ground by wet grinding in the presence of dispersants was utilized as a discharge agent, and D5 was used for the first time as a non-aqueous medium. We concentrated on TDO particles' high stability and dispersibility in a non-aqueous medium, and it demonstrated a strong and lasting discharging power on cotton and silk fabric in white discharge procedures. [22]

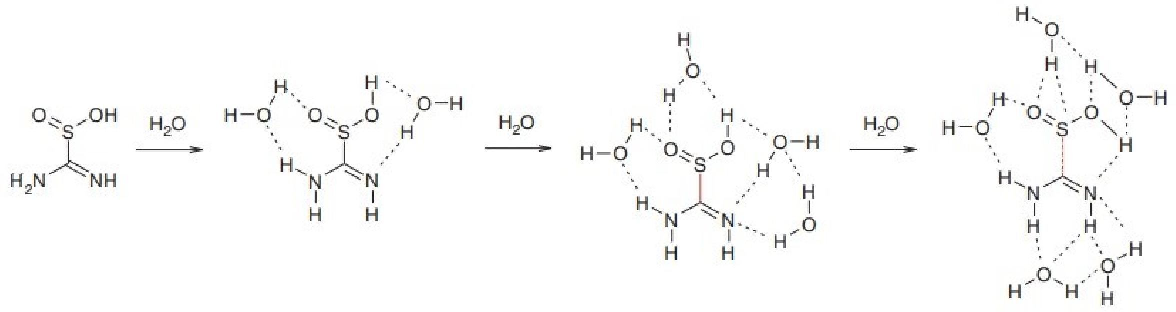

Figure 3: Reaction scheme of TDO-(H2O)n to C(NH2)2 and SO2

Discharge printing on turmeric-dyed cotton and silk fabrics

Natural dyes are those that are derived from plant, animal, or mineral resources. Carl Graebe and Carl Theodore Liebermann, both German chemists, discovered that colored organic molecules could be transformed into colorless compounds and that the original color could be restored by removing the hydrogen atoms by oxidation. Another German chemist, Otto Witt, offered the notion that color arises in organic compounds that include specific unsaturated groups, i.e. groups with multiple bonds. For example, the most basic organic chemical, glyoxal (O=HC-CH=O), is colored due to double bonds, but its reduction result is colorless. This is the fundamental operating concept of discharge printing. [23]

As a natural dye source, locally available Turmeric powder was used, which was then extracted by soaking in water for 15 minutes and boiling for 30 minutes with a dye concentration of 2% o.w.f. and MLR 1:40. The solution was then filtered through a fine cloth before being utilized in the dyeing process.

Myrobalan was extracted in water at 3 % o.w.f. using the same process as a dye; the filtrate was used for pretreating the cotton fabric at the boil and silk fabric at 60°C for 30 minutes, squeezing uniformly, dried, and entering the mordanting bath. (18)

Mordants include pomegranate rind powder (natural) and alum and copper sulfate (metallic). Pre-mordanting was chosen, with mordant concentrations set at 5% for pomegranate rind and copper sulfate, and 10% for alum o.w.f. Natural mordants were removed using the dye extraction technique, while metallic mordants were dissolved in water before application. Cotton samples were pre-mordanted for 30 minutes at boiling temperatures before being pressed uniformly, dried, and placed in the dye bath without any intermediate washing. (19)

For the standardization of the discharge printed, two discharge agents were chosen from each oxidizer and reduction group. The two oxidizing agents were hydrogen peroxide (35% concentration) and potassium permanganate, whereas the two reducing agents were safolite (Sodium Sulphoxylate Formaldehyde) and safolin (Zinc Sulphoxylate Formaldehyde). Many turmeric dye combinations show how the color of the turmeric dye and myrobalans alter separately and with different mordant combinations on cotton and silk fabric. The samples show that alum causes color darkening. Because turmeric dye produces a yellow hue at acidic pH, the color was more yellow in the shadow when Alum Mordant was used. Copper sulfate, on the other hand, gave turmeric its red color.

Oxidizing chemicals were discovered to be effective at removing all-natural color mixtures. Myrobalan and natural mordant pomegranate rind could not be released by reducing agents. Hydrogen peroxide provided the best whiteness index, tensile strength, and low effluent emission. Discharging natural silk coloring is simple, but it results in a significant loss of strength, whereas cotton is the opposite. Low quantities of natural colors may be used efficiently to decrease waste emission while preserving material strength. [10]

Discharge printing of natural fabrics (cotton fabrics) using Horseradish peroxidase:

Horseradish peroxidase is a protein with a molecular weight of approximately 40,000 Da and one protoporphyrin IX homegroup. This enzyme uses hydrogen peroxide to catalyze the oxidation of a range of substrates. To generate a discharge style on cotton and silk fabric treated with vinyl sulphone reactive dyes, the horseradish peroxidase enzyme was used instead of a hazardous reduction agent. Horseradish peroxidase enzymes are members of the plant peroxidase superfamily's class III (the 'traditional' secretory plant peroxidases), which contains peroxidases of bacterial, fungal, and plant origin. The other two classes are yeast cytochrome c peroxidase, gene-duplicated bacterial peroxidases and ascorbate peroxidases (class I), and fungal peroxidases (class I).

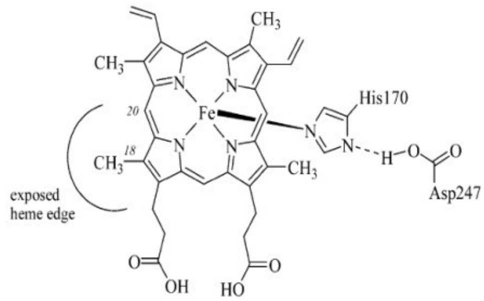

Figure 4: Structural features of the active site of the horseradish peroxidase enzyme

Extraction of horseradish

Horseradish plants produced at home were collected and refrigerated until the extraction. Roots were washed in cold water using a brush to remove dirt and other contaminants. 400 g horseradish root was mashed using a centrifugal juicer (Moulinex) that allows the extract to flow through a strainer basket while retaining the majority of the pulp. The crude extract was ultracentrifuged (Sorvall Discovery 90SE) at 32,000 rpm for 50 minutes after grinding to separate 65 ml supernatant from the sediment, which included the pulp particles. The crude extract supernatant was collected and stored in a freezer at 20°C for future use. [24]

Mechanism of horseradish peroxidase with hydrogen peroxide

In a series of two processes, hydrogen peroxide combines with ferrous horseradish peroxidase to form oxyperoxidase. The first process occurs when ferrous peroxidase reacts with H2O2 to generate Compound II, and the second occurs when Compound II reacts with H2O2 to form oxyperoxidase.

$$H_2O_2 + 2AH_2 \xrightarrow{HRP\ C} 2H_2O + 2AH^{\bullet}$$

Dyeing process of cotton fabrics

Using the process, the cloth was colored using a reactive dye. The exhaust dyeing was done at a liquor ratio of 1:30. Fabric dyeing was done at 60°C for 60 minutes. Fixation was carried out for 20 minutes with 6 to 8 g/l Na_2CO_3 and 0.01 to 0.5 g/l caustic lye.

The cotton textiles were printed using the following recipe:

Printing Recipe:

Peroxidase from Horseradish	80 g per kilogram
sodium alginate	20 g
hydrogen peroxide	20 mL
Water	Yg
Total weight:	1000g

The printed cotton samples were allowed to dry at room temperature before being placed in an oven for 30 minutes at various temperatures. Washing The printed materials were rinsed with cold water before being washed at 60°C for 30 minutes in the presence of sodium perborate. After washing, the incubated textiles were washed again at 60°C for 30 minutes with ECE detergent (4 g/L). Finally, the samples were placed in an air-drying chamber.

Enzymatic discharge printing was used using a phenol oxidizing enzyme system to selectively discharge reactive color from cotton fabric in specific regions, resulting in a printed surface. The effects of enzyme concentration, printing paste pH, treatment time, and enzymatic treatment temperature were investigated. The best parameters for enzymatic discharge printing were determined to be pH 8.5 at 70°C, a dye concentration of 80 g/L, and a treatment period of 60 minutes. Instead of the hazardous reducing agent formaldehyde sulphoxylate, the horseradish peroxidase enzyme was utilized. The peroxidase enzyme has its highest oxidizing activity at pH 8.5. [25]

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التحقيق في الطباعة بالازالة لأقمشة القطن والحرير المصبوغة بصبغات نشطة وطبيعية

مي عبد العاطي[١]، منى محمد [١]، آلاء محمد الهادي حشاد [١]، سميرة سيد معوض [١]، أحمد جمعه حسبو[٢]*، حنان علي عثمان[١]، ايمان عبد العزيز[١]

[1] جامعة بنها - كلية الفنون التطبيقية - قسم طباعة المنسوجات والصباغة والتجهيز - بنها - مصر

[٢] المركز القومي للبحوث (Scopus ID ٦٠٠١٤٦١٨) ، معهد بحوث وتكنولوجيا النسيج ، قسم التحضيرات والتجهيزات للألياف السليلوزية - الجيزة - مصر

*المؤلف المراسل: البريد الإلكتروني: aga.hassabo@hotmail.com

تُطبع ركائز النسيج في مجموعة متنوعة من الأنماط ، بما في ذلك الأنماط المباشرة ، الازالة ، والمقاومة ، وما إلى ذلك. يتم تحرير صبغة القماش المصبوغ بالاصل من التصميم أو النمط المطلوب في أسلوب الطباعة بالازالة. قد ينتج عن هذه الازالة إما نمط أبيض أو ملون. نظرًا لتركيزها على الأنماط ذات الألوان المتنوعة على خلفية داكنة ، أصبحت الطباعة بالازالة شائعة بشكل متزايد في كل من الأسواق المحلية والأجنبية. تم اكتشاف أن التصميم قد يتم تبييضه أو تفريغه من مادة مطلية بالقطعة بالفعل باستخدام التقنيات الكيميائية. قد تنشئ الطابعات أنماطًا متقنة ودقيقة باستخدام طريقة الازالة. يتم تصنيف المواد الكيميائية المستخدمة في الطباعة بالازالة إما كعوامل مؤكسدة أو مختزلة.

الكلمات الدالة: الطباعة بالازالة ، القطن ، الحرير ، الصباغات النشطة والطبيعية.