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Resist and Discharge Printing Techniques on Different Textile Based Materials

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A substantial contribution to environmental contamination are the different procedures employed in the textile sector, so there are several initiatives to decrease pollution via using natural dyes or other natural auxiliaries in the textile wetting processes such as:- Discharge printing of polyester fabric using Thiourea Dioxide, Discharge printing of cotton and Silk fabrics dyed by turmeric natural dye, Discharge Printing of Denim Using Potassium Permanganate as Oxidative Agent, Application of Resist Printing using Flour of Wild Taro as a natural resist printing agent for Printing of Silk Fabric and resist printing of cotton fabrics using chitosan as a resist agent.

Keywords: Resist Printing, Discharge Printing, Textile material

Introduction

The most diverse and significant ways of introduction of colors and pattern to textile materials are the textile printing. It's a procedure of combining a design idea, one or more colors using natural or synthetic thickener with a substrate (typically fabrics), employing a method to accurately apply the colors. [1-5] Various techniques were employed and the available colors multiplied. A major percentage of pollution is achieved through different procedures employed in the textile processing sector. In the textile wet processing sector, substantial volumes of effluents frequently occur that are complex and vary in both amount and feature. The wastewater from the textile industry is known to be brightly colored with great quantities of suspended particles, pH widely fluctuations, high temperatures, and a significant requirement for chemical oxygen (COD) [6] Color also affects by light transmission and disrupts the biological processes, which can therefore directly destroy the aquatic lives of the receiving stream. There have been several attempts to minimize pollution by using natural dyes and auxiliaries. **[7-9]**

Discharge printing

Discharge printing is a process of printing fabrics, (extraction printing), which destroys specific parts of colored fabrics to generate delicate patterns in white or another color on a colorful background. [10] Sometimes the base color is removed, while another color is printed, although a white area is typically preferred to enhance the overall design, [11] The theory of discharge printing consists of the degradation of the chromophore system of the dyestuff applied in the fabrics by the chemical reagent. [12]

Discharge printing is often performed with discharge agents, including oxidizing and reducing agents. Specifically, reducing agents including sulfoxylate formaldehyde (Rongalite), zinc sulfoxylate formaldehyde, stannous chloride, and processed stannous chloride, is the most

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important discharging agents in textile printing today. However, during the discharge printing process, these discharge agents have numerous disadvantages. **[13, 14]** thus In the case of discharge printing, a dye quickly reduced in the discharge style, e.g., azo dye, is treated and a reducing agent, is printed and the fabric steamed, then the dye is destroyed with the discharge agents in the printed area. The last washing eliminates the dye molecules and giving a white printed appearance on a colored background. This style of printing is known as the white discharge. **[11, 15, 16]**

A colored discharge can be done by inserting a dye that is not discharged or reduced by the reducing agents into the discharge printing paste and printing the teated fabric followed by steaming, washing, and then we get colored discharge style. [11]

Discharge printing of polyester fabric using Thiourea Dioxide

The use of Thiourea Dioxide as a discharge agent in the discharge printing of polyester is unusual. ThioureaDiOxide has been employed as a discharging agent and has been successfully applied in discharge printing of silk and cotton fabric. [12] however hydrophobic polyester fibers do not have distinctive features such as hydrophilic fibers, The discharge printing of polyester textiles with TDO revealed various characteristics like those shown by hydrophilic materials, such as cotton or silk fabrics. [17]

Polyester fiber (polyethylene terephthalate) is manufactured via the exchange of esters of dimethyl terephthalate and ethylene glycol. Thus, nonionic disperse dyes are used with high-temperature dyeing or thermos dyeing procedures for the dyeing of polyester fibers. [18] The major parameters impacting the discharge printing of polyester materials by TDO have been investigated by evaluating the reduction of

discolored phenomena of disperse dyes handled with different techniques on different substrates and these techniques:- For instance, colors scattered and dissolved in water and dyes entered a polyester fabric into dyed polyester fibers.

The results offer considerable insight into the discharge printing of polyester products employing TDO as a discharge agent and enable the creation of a new, environmentally friendly discharge technique for polyester materials. **[10, 19]**

Evaluation of the Effect of TDO on the White Discharge of Dyed Polyester Fabrics with Disperse Dyes

In the exhaust dyeing process, the polyester textiles were treated with the specified dispersing colors, followed by a reductive washing bath. The dyed polyester was printed using a white discharge paste, dried, and then steamed in saturated vapor at 105°C for ten minutes. The samples were also washed in cold water after steaming and then air-dried. Finally, with a color measuring device, K/S values were measured three times, and then an average was taken. A 3D video microscope observes cross-sections of polyester fibers under various conditions. **Table 1** shows the dyeing conditions and content of the printing paste.

Effects of TDO on Disperse Dyes which Dispersed in an aqueous solution and Disperse Dyes Printed on the Surfaces of fabrics

The reactivity between TDO and dye dispersion in aqueous solution was assessed with the analysis of the change of solution containing TDO and disperse dyes before and after heating to show the possibility of discharge printing with TDO on dyed polyester materials. In particular, a digital camera measured the color changes in the solution and an ultra-violet visible spectrophotometer assessed the associated spectrum characteristics. *[11]* After heating, each solution is transparent and nearly colorless or light yellow and the absorption of each

Dyeing		Reduction cleaning		White discharge printing	
Parameter	Amount	Parameter	Amount	Chemical	Amount (wt %)
Disperse dyes	1 % .owf.	Sodium hydrosulfite	1.5 g/l	Discharge paste TM-2 (50 % TDO)	10
Liquor ratio	1:30	Sodium carbonate	1.5 g/l	Thickening agent PTRV	3
Time	40 min	Liquor ratio	1:50	Urea	8
Temperature	115 °C	Time	20 min	Discharge-aid auxiliary HS-312N	х
pН	4.5-5.0	Temperature	80 °C		

TABLE 1. Dyeing conditions and content of the printing paste

solution is considerably reduced corresponding to apparent color shifts. Because of this explanation, a substantial interaction of TDO and the chosen azo-dyes may be proven, directly leading to the destruction of the chromogenic coloration groups. In other words, TDO can be used for the discharge of polyester textiles dyed by the azo-dyes chosen. After heating, each sample had its original color lighter. Therefore, during the discharge printing process, TDO may destroy the chromogenic groups of certain azo dyes, which is beneficial for the discharge of polyester textiles. **[19] Fig. 1** shows the color changes attached with TDO and azo disperse dyes before and after steaming.

It was found that with increasing temperature the decomposition rate of the TDO was enhanced, TDO destroyed chromogenic groups of dyes put in aqueous solution on the surfaces of the textiles. The white discharge pastes with TDO have been added to the accelerant to loosen the structure of polyester fibers to create a good discharge effect. This might pave the way for TDO advancements and give valuable insight into polyester discharge printing. **[10]**

Discharge printing on turmeric dyed cotton and silk fabrics

Natural dyes refer to the colors derived from plants, animals, and minerals. Occasionally fashion requires large designs or Dark grounds to be added in colors or white with the delicate lines of decorative motifs. Technically, with direct printing, it is difficult to fulfill this criterion, so we resort to discharge printing. German chemists have found that colored organic compounds may be transformed to colorless and the original color recovered by destroying the hydrogen atom in the oxidation process. A theoretic is suggested by another German scientist; the color is generally shown in an organic molecule if it includes unsaturated groups, i.e. groups with multiple bonds. For example, the simplest organic glyoxal molecule (O=H, C-C, H=O) is colored because of double bonds, and its reduction compound

is colorless. This is the fundamental operating concept of organic discharge printing. [19]

Turmeric powder: selected locally as a natural dye source. Then it was extracted with water soaking at boiling. The solution was then filtered into fine textiles and then used for the dyeing process. [18] Myrobalan: The same dye technique employed to extract the color in water; after pretreatment of the cotton fabric in boiling and silk fabric at 60°C the filtration process was employed, properly squeezed, dried, and got into the mordant bath. Mordant: pomegranate rind (powder) was used for the research as a natural mordant and aluminum and copper sulfate as a metallic one. Premordanting was used in concentration 5% for pomegranate rind and copper sulfate and 10% for aluminum. The procedure used to extract dye was used to extract natural mordant. Before application, metallic mordants were dissolved in water. the samples were pre-mordant for 30 minutes at boiling for cotton and 60°C for silk, squeezed uniformly, and then dried and inserted into the dye bath without intermediate cleaning. [12]

Two discharge agents were selected from each oxidizer and reduction category for the standardization of the discharge printed. Hydrogen peroxide 35% and Potassium Permanganate were the two oxidizing agents and Safolite (Sodium Sulphoxylate Formaldehyde) and Safolin (Zinc Sulphoxylate Formaldehyde) were the two reducing agents selected for discharge printing on naturally dyed samples. **[17]** many combinations of turmeric dye illustrate that the color of the turmeric dye and myrobalans have changed individually and with combinations of different mordants on cotton and silk fabric.

The samples indicate that alum brings darkness in color. Since turmeric dye creates yellow color in acidic pH, The color was more yellow in shadow, using Alum Mordant. on the contrary, Copper sulfate provided redness to turmeric. [6]



Fig. 1. Color changes attached with TDO and azo disperse dyes before and after steaming

It was found that Oxidizing agents may efficiently remove all-natural dye combinations. Reducing agents could not release myrobalan and natural mordant pomegranate rind. The best whiteness index, tensile strength with little effluent emission, was given by hydrogen peroxide. Discharging natural silk coloring is easy, but with a substantial loss of strength while cotton is the reverse. To limit the waste emission and preserve the strength of the material, low concentrations might be efficiently employed by simple combinations of natural colors. [6]

Discharge Printing of Denim Using Potassium Permanganate as Oxidative Agent

The present study was conducted to enhance the discharge printing process for modern Denim clothing. The response surface approach includes three main factors: potassium permanganate (KMnO₄) concentration, pH of the printing paste, and reaction time was successfully employed. This research aimed to design an economic technique producing denim textile with additional value, where tensile loss and tear forces should be minimized, whereas the discharge brightness impact should be enhanced.

That is well recognized. A chemical breakage releases the color of the chromophore, which is responsible for the visual impression of color, This chromophore chemical separation can be achieved by reduction or oxidation. The chemicals that are utilized to discharge the dyes are therefore classified as oxidative and reductive agents. Common oxidative agents are potassium permanganate (KMnO₄), hydrogen peroxide, sodium hypochlorite, sodium perborate, and sodium percarbonate. Common reductive agents are thiourea dioxide, tin chloride, sodium dithionite, and formaldehyde sulphoxylates. The discharge of various colors also involves the

employment of microorganisms and enzymes. In the textile industry, enzymes like laccase and glucose oxidase are significant. Enzymes are, nevertheless, often specialized in nature and purpose. Therefore in the selection of these enzymes, the nature and characteristics of the cloth and the dye play a significant role. [11]

The fabric of denim is typically manufactured using a structure of twill weave, dyed w*ar*p, and grey weft. The warp yarn is usually dyed with indigo, vat, and sulfur dyes. The largest proportion of denim jeans in the world is indigo-dyed denim as shown in **Fig. 2**.

Sulfonated dimethyl phenyl ammonium salt and sodium chlorate were generally employed as oxidative agents to discharge indigo-dyed denim in the discharge printing process. The commercial use of sodium formaldehyde sulfoxylate is a reduction in the discharge printing industry. Laccase acts among enzymes in an oxidative way to discharge indigo-farmed material. The discharge behavior of commonly available oxidant agents such as KMnO4 must still be studied and optimized. (Siddique et al. 2017)

The choice of releases for denim is based on their activity against indigo coloration. for our investigation, $KMnO_4$ was used as the oxidative release agent for denim discharge printing. Recipes and process conditions for discharge printing have been optimized using the reaction surface methodology. To optimize material concentration and conditions for maximal discharge and improved physical characteristics, the CCD experiment has been employed using denim discharge printing. The whitening, tensile and tear strength of the discharged denim fabric employing KMnO4 as the oxidative agent have been developed with models.



Fig.2. indigo-dyed denim

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The denim fabric has been desized in a solution comprising amylase and wetting substances for 45 minutes at 70°C, on the Jigger machine. The RSM statistical approach was employed to improve the whiteness and reduce fabric strength losses in the experimental design and optimization process. The RSM is a useful way to examine the effect of various factors, which simultaneously alter the responses and perform limited experiments.

When the paste was placed on the deep purple cloth, the paste became brown by the processing of KMnO₄ into manganese oxide (MnO₂). After printing The samples were maintained for varying time durations in environmental conditions. **[20]** Fig. 3 shows the discharge printing of denim fabric samples

Afterward, the textile samples were treated with sodium bisulfite solution at 70°C at pH 6.5–7 for 10 minutes, followed by washing with cold water and later drying. Sodium bicarbonate solution altered the pH of the sodium bisulfite bath. To achieve the effect of white discharge,

sodium bisulfite was employed to decrease MnO_2 in water-soluble to form Mn^{2+} . Bleaching ensures the whiteness of textiles including denim through (oxidation reaction), And while MnO_2 does not convey any type of whiteness, it might stain bleached cloth and cause less whiteness, if not removed correctly. The removal of MnO_2 can therefore be done using sodium bisulfite by converting MnO2 into a solubilized form (Mn²⁺). (Siddique et al. 2017)

It was investigated that the whitening of the reaction time is directly related. It indicates that time has an important whiteness influence. The improvement of the whiteness by increased reaction time allowing longer contact time for MnO_2 production means the degradation of the colored chromophore. The KMnO₄ oxidizes the color chromophore and transforms it into colorless MnO_2 . Indigo dye is transformed by oxidation with KMnO₄ to isatin and anthranilic acid. On the other hand, the concentration of KMnO₄ is a connection to whiteness. The whiteness of the cloth gradually increases by raising KMnO₄



Fig.3. discharge printing of denim fabric samples

concentration to a specific limit; A gradual decrease in whiteness occurs when $KMnO_4$ is increased above this limit of concentration. This tendency towards decreased whiteness by raising beyond a specific level the KMnO4 concentration might be perceived as deposition of a greater amount of MnO_2 in the fabric. The colloidal form of MnO_2 prevents the diffusion of oxygen from a paste to a material structure, which reduces the whiteness of the fabric. brightness Increased with the pH reduced in the acidic direction. KMnO4 oxidation potential has been found to depend on the pH value. **(Siddique et al. 2017)**

This is a cost-efficient and hygienic way of discharging fashionable denim textile. This process is used for textile design and the decoloration of waste dyes, waste materials, and wastes which include such dyes. However, with various denim specimens, the discharge findings using this approach would probably differ (based on the varying penetration of indigo into the warp yarns). Therefore, the results only apply to the sample, and experiments for different thicknesses and other construction characteristics of the fabric should be carried out.

Resist printing using Wild taro extract

The resist printing style, as its name indicates, comes from the material is printed with a substance that resists dyes afterward. [21] Only portions that are not covered with resistant paste will be affected by a dye and therefore generate a pattern on a colored background. [22, 23]

The style of the resistance is split into the physical one, (those which use wax to prevent the dyeing of the fiber). In contrast, chemical-resistant prints are conductive to (1) dye dissolution (oxidative or reductive), (2) dye insolubility (via the use of an anti-solution agent), and blockage dye sites of fiber. **[11, 24]**

Wild taro, is a plant-based root crop of the monocotyledonous family Araceae and is cultivated in virtually every tropical location in the globe. Application of Flour of Wild Taro in Resist Printing Paste on silk fabrics.

Wild Taro leaves are 60 cm long and 50 cm broad and have a form of an arrowhead, top dark green velvety surface, and water resistance. The oxalic acid (C2H2O4) in the wild taro tuber or corm is a crystal compound of soluble oxalic acid and insoluble oxalate ions. and the wild taro plant is shown in **Fig. 4**.

The white-resist printing with color-proof material from wild taro flour utilizing pigment as a coloring agent was studied. The characteristics of printing and fastness were examined. **[25]**

The wild taro corms have been dried for 1 month in the sunlight and then crushed using a blender and ground through 355 micro meshes. The powdered resistance of wild taro corms has been made by adding wild taro corm powder to distilled water, with the presence of vegetable oil. At room temperature, the dispersal mixture was strongly stirred and then streamed to reduce oxalate salt. After that, The solution $(Ca(OH)_2)$ and (NaCl) have been then added and stirred by the mixer. [22]

The flat-screen technology was used for resistance printing. At room temperature, the samples were dried and proceeded by pigment printing. Samples were subsequently dried by hot air, then Samples were washed with cold water, then hot water, and then use an anionic detergent after that they rinsed well, then cool down and airdry at room temperature.[11, 25]

It was found that natural dyes or other auxiliaries give good results in various wetting processes like discharge and resist printing for eg.



Fig. 4: wild taro plant

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TDO made the polyester fibers structure looser To get a good discharge effect. This might open the door for TDO growth and give a valuable insight into polyester discharge printing, Discharge printing as a new way to market eco-friendly, naturally colored discharge products may be used efficiently. To minimize waste emissions and preserve fabric strength, lower dissipating agent concentrations can be efficiently utilized with basic combinations of natural dye.it was also investigated that Wild taro corms flour can be resistant to dyestuffs, and wild taro corms can be removed as easily. The pattern of sharpness and whiteness demonstrates a resistant printing area for textiles. With the addition of chitosan to the resistant printing paste, the resistant printing effect is typically higher. With an increased chitosan content from 0.4 to 1.6 percent, the resistance printing impact rises. These data show that chitosan causes resistance to physical impressions.

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تساهم الإجراءات المختلفة المتبعة في قطاع النسيج مساهمة كبيرة في التلوث البيئي ، لذلك هناك العديد من المبادر ات لتقليل التلوث عن طريق استخدام الأصباغ الطبيعية أو غير ها من المواد المساعدة الطبيعية في عمليات ترطيب النسيج مثل: - تفريغ طباعة أقمشة البوليستر باستخدام ثيوريا ثاني أكسيد ، طباعة التفريغ للأقمشة القطنية والحرير المصبوغة بصبغة الكركم الطبيعية ، طباعة التفريغ من الدنيم باستخدام برمنجنات البوتاسيوم كعامل مؤكسد ، تطبيق الطباعة المقاومة باستخدام المتوار الموا ما ما ما ما ما من المواد المساعدة القريغ للأقمشة القطنية الحرير ومقاومة طباعة القامشة القطنية باستخدام الشبتوزان كعامل معاومة.

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