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Investigating the Relationship between Thermochromic Pigment Based knitted Fabrics Properties and Human Body Temperature

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Abstract: *Thermochromic based pigment considered as one of the most functional dyes that used to give new functions to the fabrics which have been printed by them. The aim of this research is to approve the benefits of applying of the thermochromic based pigment on the knitted interlock fabrics for detection of skin temperature indication of physical exhaustion of the human body, the samples made of cotton, wool and polyester fabrics have been printed by using screen printing technology. The color of the thermochromic pigment based interlock fabrics changed from color to non-color in the temperature window (36-41) ˚C. The heat transfers are increasing with the increasing of the samples' temperature, the most value of the conduction and convection heat transfer was in wool samples and the less was in cotton ones, and the most value of the radiation heat transfer was on polyester samples. The bursting strength of knitted cotton fabrics was 5% higher than that of the un-printed samples; the degree of staining was intermediate between excellent and very good.*
Keywords: *Thermochromic, bursting strength, knitted fabrics, heat transfers, degree of staining.*

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I. Introduction

Research centers and commercial organizations are engaged in developing the formulation, encapsulation and application of thermochromic and photochromic systems on textiles [1]. The scientist and technologists resolve a number of the problems which help in reduction of the price, and improving the availability and temperature range of chromic products to make the novel thermochromic technologies popular to the end users [2, 3]; and particularly in smart clothes industries [4].

Chromic phenomena involve processes causing visible color change, absorption and reflection of light, absorption of energy and emission of light, absorption of light and energy transfer or a conversion and manipulation of light (thermochromic) [5], The external stimuli can be light (photochromic), electricity (electrochromic), pressure (piezochromic), liquid (solvatechromic), or an electron beam (carsolchromic) [6, 7]. Photochromic colors generally belong to one among the following organic chemical groups such as triarylmethanes, stilbenes, azastilbenes, nitrones, fulgides, spiropyrans, naphthopyrans, spiro-oxazines and quinines [8].

From the beginning of 1970, the mechanisms of thermochromism have been investigated, the term thermochromism refers to a change in color as a function of temperature defined thermochromism as an easily noticeable reversible color change brought about by the boiling point of each liquid [9], this thermochromic color change is quite noticeable, often dramatic and occurs over a small temperature interval [10]. Different mechanisms are applicable depending upon the type of thermochromic material which are thermochromism, organic compounds, and inorganic compounds [9]. The reversible change in the color of a compound with temperature from a colored or colorless type to another colorless or colored type [11].

Due to the possibilities for developing new creative designs, color-changing smart materials are generating intense interest among the artists and designers due to their interaction, responsiveness and ultimate functionality [12]. Thermo chromic based pigments are widely used in toys, dolls, recording media and novelties such as seals on beverage mugs that change color when a hot or cold beverage is placed in the mug, they are used in camouflage nets for military equipments, and in umbrella that would exhibit different colors under shade and in sunlight [13]. Thermochromic pigments were applied as a visual tool for skin temperature indication of physical exhaustion; these microcapsules contain leuco dyes capable of changing chemical structure to alter the dye molecule absorbance. Thermochromic pigments were applied to Nylon/spandex fabric, a garment for physical exhaustion in athletes was created [14].

A new method to obtain thermochromic cellulose fiber has been developed using lyocell process, 1-10 wt% chromic-color AQ-ink, magenta type 27 pigmentation was used as a thermochromic modifier [15]. An electronically controllable, visually dynamic textile material is created; Woven or embroidered textiles could be manufactured by using conductive/resistive and non-conductive fibers, and reveals a method to change the color of a textile at will using electricity [16]. When the temperature of the textile increases beyond the activation temperature of the thermochromic colorant, the color change takes place.

The ultraviolet reflecting properties of cotton give a higher level of photo coloration than polyester, the degree of photo coloration is influenced by colorant concentration and the UV irradiation wavelength profile [17]. Spirooxazines showed slightly faster color development and fade much more rapidly than the naphthopyrans, and the latter show a residual color after fading, Figures 1 shows the effect of colorant concentration on the developed color strength of spirooxazine on cotton and polyester. The change in physical properties to the used clothe after the printing process by thermochromic dyes has been studied, a clear reduction (up to 70%) in the air permeability on printed region comparing with the unprinted region [17], Dye fitness can also be increased by using binders and thickeners and the reduction in dyes on the surface of cloth is reached (15%) after (100) washing cycle [18].

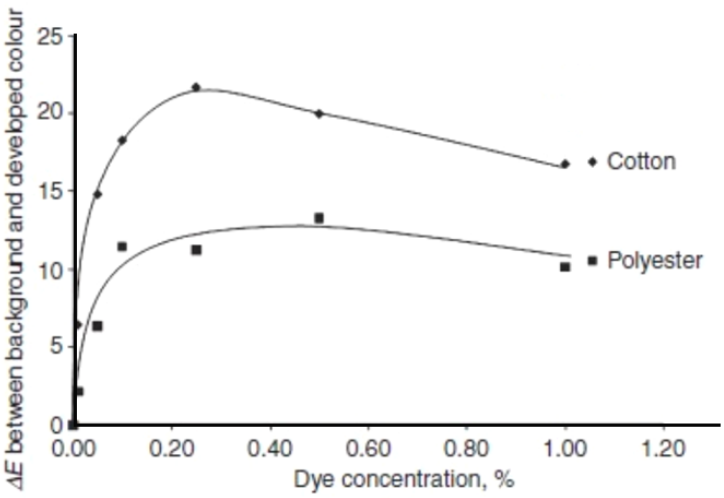

Figure 1. Effect of colorant concentration on cotton and polyester [17]

Interlock fabric is used for making undergarments, sportswear, children wear, and baby's outerwear. When the fabric density for each fabric design is taken into consideration, the heat loss due to air circulation becomes more important than the conductive heat loss due to fibers and air gaps. The effects of fabric density and fabric design on the thermal coefficient are statistically important [19]. The physico-mechanical properties of knitted fabric can be changed due to use of various count of yarn, type and quality of yarn, loop length, structural geometry, fibre composition of yarn, fabric thickness decreases with the increased loop length [20], thickness can also vary for high yarn diameter, low yarn twist, less lateral compression force.

In the screen printing of photochromic colorants on textile fabric, some formulation is referred as printing paste of 0.05% w/w, representing the concentration of the colorant in the print paste [19].

Although, extension is very effective parameter on the bursting strength property of the knitted fabrics [21], it is more appropriate for testing materials prone to necking, such as coated fabrics with knitted Substrates There is no determined relation between bursting strength and extension of the fabrics, the structures of the fabric are the effective parameters; Stronger yarns in the fabrics are less elastic and reach the elastic limit quickly and break [22]. Theoretically, the level of photo coloration developed by UV irradiation varies with colorant classes; in the case of the selected spirooxazine colorants, the degree of photo coloration increased with initial washing and then decreased with subsequent washings [23]. In the case of the naphthopyrans, the degree of photo coloration decreased progressively with washing; Pre-treating cotton with a cationic agent to increase the substantively of the microcapsules for the fiber and thus secure greater uptake even without the use of a binder [24]. Generally, the human body keeps its temperature constant at 37 ± 0.5 °C under different climatic conditions. The heat resistance increases by laying a knitted fabric layer or under real conditions when the body is dressed in lightweight knitwear by 25%, the differences within the observed relationships are higher than it was in the case of heat transfer resistance [25].

II. Theoretical Aspects

1) Organic thermochromic systems

Organic thermochromic systems could be used in many applications like fibers, optics, photo-storage instruments and optical sensors. Different thermochromic mechanisms may be applicable depending upon the molecular structure. It may occur as a result of equilibrium between molecular species like acid-base, ketoenol, lactim-lactam, stereoisomers or between different crystal structures. The mechanism could be divided into three major categories which are change in crystal structure, stereoisomerism, and molecular rearrangement. The liquid crystal and the molecular rearrangement both are the two types of thermochromic systems they have been successfully applied on textiles [6]. The cholesteric (chiral nematic) are the most important types of liquid crystals for thermochromic systems, where adjacent molecules are arranged that they form helices, figure 2. transitions between phases in liquid crystals could be brought either about by the influence of temperature (thermotropicmesomorphism) or solvent (lyo-tropic mesomorphism) [10]. When temperature varies, pitch length also varies, and wavelength of the reflected light is altered causing progressive change in color spectrum [26]. The liquid crystal material has to be micro-encapsulated in order to develop the thermochromic effects in a fabric and like pigments these microcapsules are applied on the fabric using a suitable resin binder.

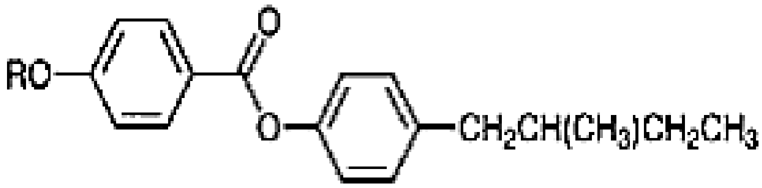

Figure 2. Chiral molecules that form cholesteric mesophases

As the temperature increased, the molecules of these compounds switched between different stereoisomers and the result of this switching color of the compounds varies. Majority of compound show stereoisomerism develop color above their melting point, commonly in excess of 150°C [10] . The molecular rearrangement of an organic compound can occur resulting in an increase in the conjugation of the molecule and the formation of a new chromophore; The temperature-dependence of the acid-base equilibrium means that PH sensitivity can result in thermochromic behavior, Figure 3 [27].

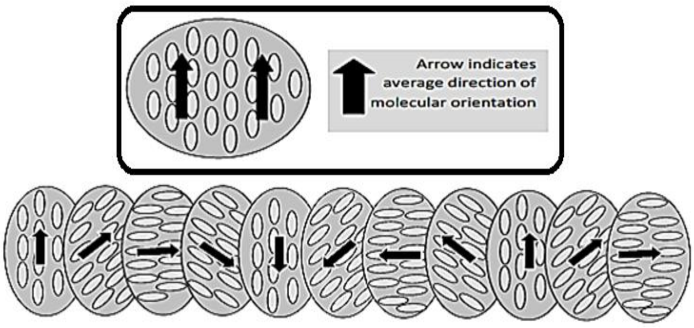

Figure 3 . Direction of molecular orientation gradually changes between layers

The equilibrium of crystal violet lactone is PH rather than temperature dependent, it does not exhibit thermochromism. If the PH is then raised above 4, the lactone is formed again and the violet color disappears, Figure 4 [27], At pH values above 4, crystal violet lactone (A) is colorless and acts as a dye precursor. Below this pH level, it is rearranges itself to produce compound (B), which is violet. Inorganic thermochromic systems are suitable for dyeing and printing application, they should exhibit noticeable color change over a small temperature range, typically from low ambient temperatures to body temperature for apparel [28].

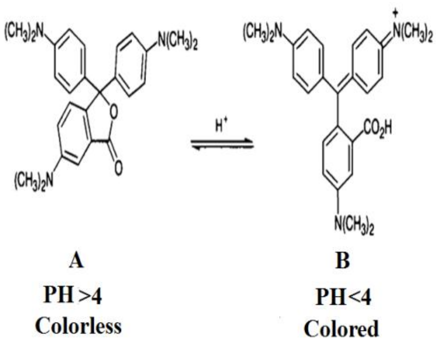

Figure 4. Dependency of molecular arrangement of crystal violet lactone on pH

2) **Heat Transfer**

Researches provide methods for measuring temperature changes at or near one or more areas of a human subject, where the apparatus comprises a thermochromic pigment based garment [29], methods involving monitoring changes in temperature of a human subject or a portion of the human subject that is in contact with the garment; Equation 1 show heat balance equation:

$$S = M - (\pm W) \pm K \pm C \pm R - E \quad (1)$$

Where, M is equal to metabolic heat production (resting metabolic rate=3.5 ml/kg/min or 50 kcal/hr/m^2; for every L of VO2, approximately 5.0 kcal are expended); W is equal to work; K, C, R, & E represent the mechanisms of heat transfer. The heat is lost from the surface of the body by three main types of heat transfer:

- Conduction Heat Transfer:
  Conduction is the transfer of heat from one part of a body at a higher temperature to another part of the same body at a lower temperature, or from one body at a higher temperature to another body in physical contact with this body which has a lower temperature. The conduction process takes place at the molecular level and involves the transfer of energy from the more energetic molecules to those with a lower energy level [30].
- Convection heat transfer:
  The convection heat transfer mode is comprised of two mechanisms, in addition to energy transfer due to the random molecular motion (diffusion); energy is also transferred by the bulk, or macroscopic, motion of the fluid [26]. Because the molecules in the aggregate retain their random motion, the total heat transfer is then due to a superposition of energy transport by the random motion of the molecules and by the bulk motion of the fluid [30].
- Radiation heat transfer:
  Thermal radiation is the energy which is emitted by the matter that is at a nonzero temperature. The emission may be attributed to changes in the electron configurations of the constituent atoms or molecules. On the macroscopic level, the calculation of thermal radiation is based on the Stefan-Boltzmann law [30]. Human thermal comfort depends on the metabolic rate, the heat losses from the body, and the climatic conditions.

III. Methodology And Experiments

1. SAMPLES

Knitted fabric samples made of cotton 100%, wool 100%, and 100% polyester have been used. The 1×1 Interlock fabrics were produced on knitting machine by formation and interlinking of loops (10 loop/cm^2) by the action of two knitting needles, samples color were bleached white. The thickness was measured according to standard ASTM D 1777-64 under pressure of 20 g/cm^2, with 0.01 mm accuracy. Samples were conditioned for 48 hours in the atmospheric conditions of temperature 20±2°C and relative humidity 65±2% RH, before the measurements were taken.

2. Thermochromic powder

The pigment which used for printing the samples was non-toxic thermochromic pigment (Turn Thurmo - USA), Orange color, it has a low UV tolerance without proper protection. Binders used for printing were bricoprint binder SF20E, prepared PU New, thermistor (textile bath dyeing binder); it is a white paste containing a cross-linking polyacrylate, with mineral oil in water. Pigment print paste contains thickener and other auxiliaries. The thickener is used in the formulation of pastes for printing chromazone slurries, it has a smooth and creamy consistency and it is an inverse copolymer emulsion of ethylenically unsaturated monomers in hydrocarbons. The thermochromic pigment had been mixed with binder to attach the ink onto fabric; binder has the ability of forming a three-dimensional film used to hold the pigment particles in place on the surface of a textile substrate.

3. Preparation of the printed samples

Screen printing of photochromic colorants were applied to print the samples at 30o by screen printing with plain mesh print screen (1-2 mm, 50 μ m) stretched over a frame, a three-dimensional film was formed to hold the pigment particles in place on the surface of a textile substrate, it could affect the air permeability on printed region of fabric. The printed area was 30% of total samples area, which is (10×20) cm^2. Representing the concentration of the colorant in the print paste, then using a plain mesh print screen, printing is carried out, printed sample dried at 80 ˚C for 3 minutes in hot air and cured at 140 ˚C for 3 minutes in a hot air oven.

IV. Results And Discussion

This research have analyzed the values of heat transfers that occur between the human body and the cloth which printed by the thermochromic pigment. Where the change of the body's temperature is transferring to the cloth which is in touch with the body; the temperature of the cloth is changing and changing the color of the thermochromic pigment.

1. Analyzing of Convection, Radiation sand Conduction Heat Transfer

To analyze the convection, radiation heat transfer and conduction heat flux, three samples had been selected:

- Cotton fabric, weight (180) g/m^2 and thickness (0.77 mm).
- Wool fabric, weight (210) g/m^2 and thickness (1.23 mm).
- Polyester fabric, weight (150) g/m^2 and thickness (0.52 mm).

The samples were printed using screen printing technology, the recipe for 100 ml solution were thermochromic pigment (4%) and acrylic binder (10%) and emulsion thickener (90%). The laboratory temperature was about (30˚C).The three thermochromic printed fabrics (polyester, cotton, and wool) put in a surrounding temperature, and the temperature of the samples had been raised by heaters, It was clear that the colors changed from strong to light with the temperature rising. The color of the dye was orange at 37 ± 0.5 °C (the natural heat of the human body), then the heat was raised to 41˚C, the color of the pigment begun to change to pink at temperature 38˚C, then to non-color at 41˚C.

Conduction is the transfer of heat from one part of a body at a higher temperature to another part of the same body at a lower temperature. The conduction process takes place at the molecular level and involves the transfer of energy from the more energetic molecules to those with a lower energy level. The heat transferred from the body to the cloth to the atmosphere, so the color began to change from Orange when the temperature at degree (36˚C) to non-color at degree (41˚C).

It's clear that the conduction heat transfer increases from Orange color to colorless value with the increase of the temperature degrees, but it's different at the same temperature with the different of the raw materials, conduction heat flux values, and the thickness of the samples.

Thermal conductivity of wool is the highest but the chart shows that conduction heat flux of the polyester is the highest at the same temperature, that's due to the sample thickness. From the experience, it's clear that the sample thickness is the main term of conduction heat transfer value despite of the thermal conductivity, Figure 5 shows the heat transfer over the body and infrared image of a man, woman and child not wearing clothes.

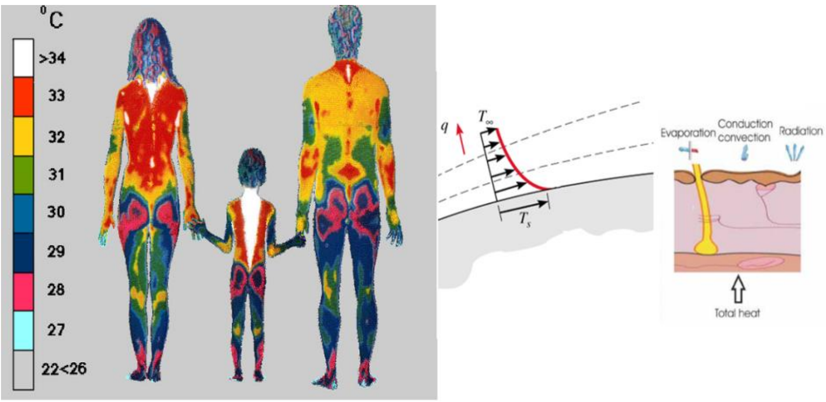

Figure 5. Infrared image of the human body and Heat transfer over the body

The convection heat fluxes for the three samples were as shown in Figure 6, the appropriate rate equation is of the form [30]:

$$q_2 = h\,(T_s - T_\infty) \qquad (2)$$

Where, q_2 the convective heat flux (W/m^2), Ts and T∞ is proportional to the difference between the surface and fluid temperatures respectively, and the parameter h is termed the convection heat transfer coefficient which depends on conditions in the boundary layer, the nature of the fluid motion, and an assortment of fluid thermodynamic and transport properties. In percent research h = 20 (w/m^2k) [30].

In conclusion, the radiation heat transfer has increased with the emissivity coefficient increased for studies samples; the radiation heat flux for polyester was the highest because the polyester has the highest emissivity coefficient compared with cotton and wool.

Temperature's human body considered as an important indicator for the health and safety of the body, the high temperature is an important factor for many illness [31]. The heat transfer in the children's cloth appears between the high temperature of child body and the cloth which has lower temperature degree than the body, and results obtained support that idea.

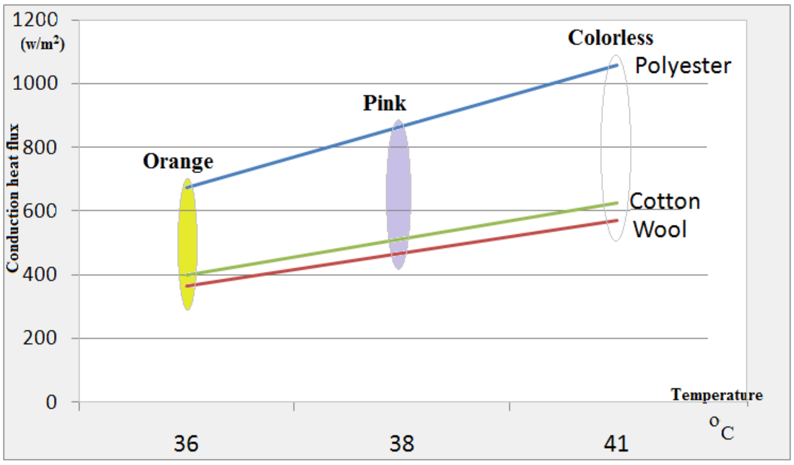

Figure 6. Conduction heat flux toward temperature and color changing

The different of the temperature degrees between the surface of each sample and the surrounding occurs radiation heat transfer from the heated surface, Figure 7. The radiation heat transfer values were calculated between two temperature degrees; when the color was disappeared and the completely colored statue between 36 ˚C and 41 ˚C by using the equation (3) for the three studied samples at the two cases, colored, and non-colored.

$$E = \varepsilon \sigma T_s^4 \qquad (3)$$

Where Ts is the absolute temperature (K) of the surface and σ is the Stefan-Boltzmann constant $\sigma = 5.67 \times 10^{-8}\, W/_{m^2.k^4}$, ε is a radiative property of the surface termed the emissivity, emissivity coefficient is 0.9 for wool and 0.77 for cotton and 0, 98 for polyester.

If the fabric density for each fabric design is taken into consideration, the heat loss due to air circulation becomes more important than the conductive heat loss due to fibers and air gaps, the effects of each level of fabric density and fabric design on the thermal coefficient are statistically important.

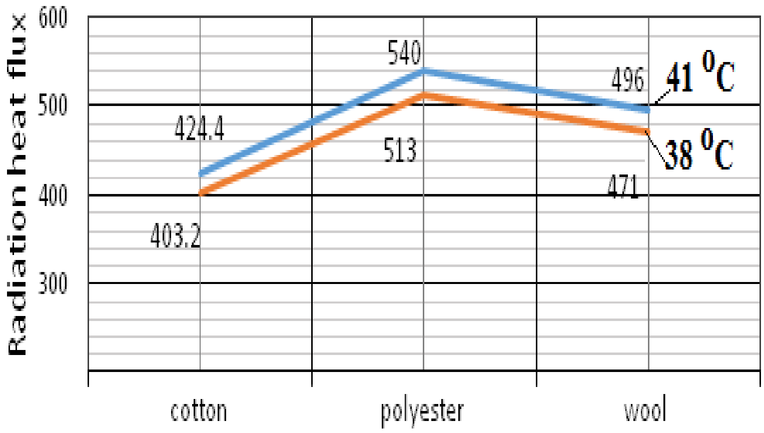

Figure 7. Radiation heat transfer due to raw materials

The convection heat transfer occurs between a surrounding air static in motion and a bounding surface when they are at different temperatures. When temperature rose from 36 oC to 41oC, the color of the thermochromic pigment was changed from orange to pink to colorless. In this research, it was considered that the convection heat transfer coefficient. The convection heat transfer for the all samples at the same temperature degree was the same, the convection heat transfer increases with the increases of the temperature in each sample. Figure 8 shows the relationship between the different convection heat transfer and temperature is linearly.

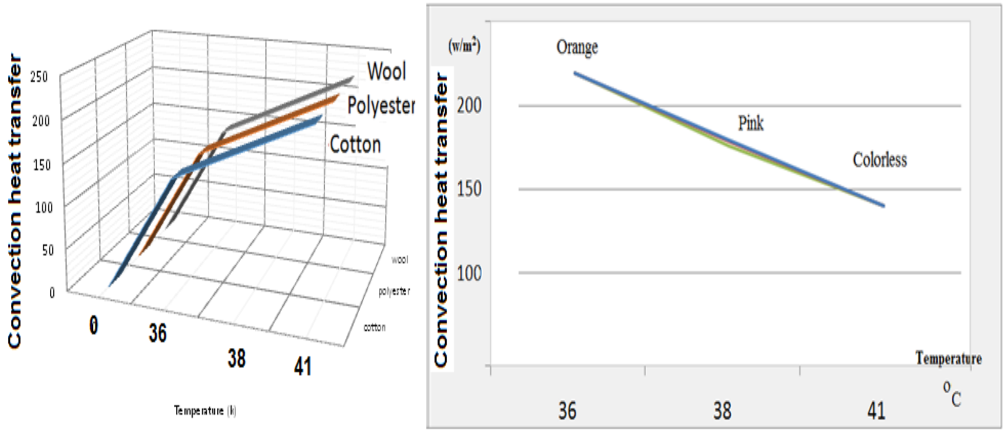

Figure 8. Convection heat transfer due to the temperature changing

When the three samples have been left in the surrounding to reach the temperature degree 36˚C, the radiation heat transfer decreased with the temperature of the samples decreased from 41 to 36˚C, and the color returned to appear. The most value of the radiation heat flux was in polyester, then in wool, and smallest in cotton, because of the different emissivity coefficient of cotton (0.77), wool (0.90), and polyester (0.98).

2. Investigation Cotton Fabric Samples

Conduction heat transfer related to the thickness of the fabrics in the same surrounding condition of temperature degree with different types of raw materials. After analyzed the previous result, 1×1 Interlock cotton fabrics was selected as a suitable material for human body. Bursting strength and the effect of repeated washings on the degree of photo coloration of colorants and assessment of staining had been analyzed, the weight of unprinted 1×1 Interlock cotton fabrics was (1.75) g/m^2, and thickness was 0.5 mm. The samples were printed using screen printing technology described previously; the recipe for 100 ml was thermochromic pigment (20%), and acrylic binder (5%), and emulsion thickener (75%).

- **Sample Weight Changing**

The weight of printed 1×1 Interlock cotton fabrics was (2) g, with 14.3% weight increasing, regarding to the pigment and the pinder and the thickness film located on the fabric surface, the thickness of the coating layer (a thin three-dimensional film) should not effect on the mechanical properties and the porosity of printed areas.

- **The color changing**

The color of the studied cotton fabrics was changed from orange at 34 ˚C, light orange at temperature of 37 ˚C, light pink at 38 ˚C, and then colorless at 41 ˚C. When the temperature of the samples decreased from 41 to 34˚C, the color returned to appear.

- **Bursting Strength**

Digital Bursting Strength Tester (Netra) is used to measure the resistance of fabric to rupture; it provides a hydraulic load under a rubber diaphragm of a specific area to test the burst strength of textile. Bursting strength is defined as the hydrostatic pressure required producing rupture of the fabric when the pressure is applied at a controlled increasing rate through a rubber diaphragm, test area was 10 cm^2.

The thermochromic pigment had been mixed with binder to attach onto the fabric; binder has the ability of forming a three-dimensional film used to hold the pigment particles in place on the surface of a textile substrate, that effect on the porosity of fabric; Moreover, increasing the three dimensional film thickness produced decreased air permeability.

The strength of sample knitted fabrics was measured by bursting strength test method; since the range of bursting strength value of printed samples was 8.5 to 9 bar. According to Figure 9, the bursting strength values of the samples were closer to each other. Cotton fabrics gave the best printing quality, a clear increasing up to 5% in the Bursting strength on printed region comparing with the unprinted region; the result is a desired result since in prediction of textile materials' properties it is a difficult task to estimate the material property with a low deviation.

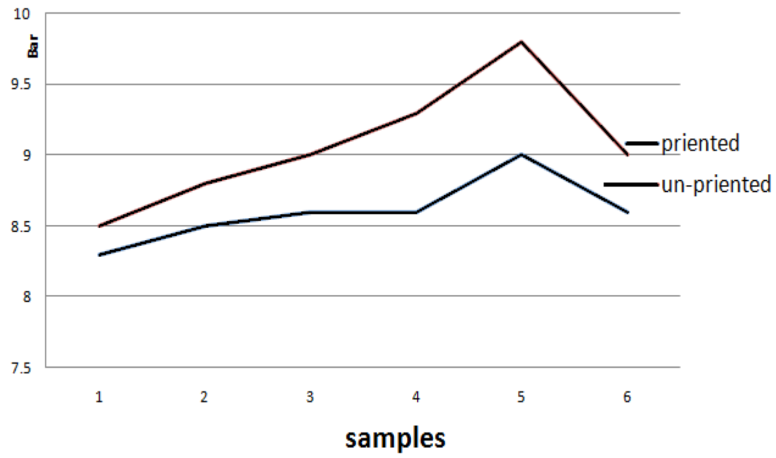

Figure 9. Bursting strength curve of the samples

- **Assessment Of Staining:**

The degree of staining of the adjacent samples during test is assessed using the Grey Scale for assessing staining, it consists of nine pairs of pieces of card numbered 5, 4-5, 4, 3-4, 3, 2-3, 2, 1-2, 1; where 5 is a pair of white and the others consist of a white and grey. Staining is assessed without reference to the depth of color of the specimen results, the wash fastness properties of the photochromic prints are associated with the binder rather than the colorants [23].

The sample was washed (15) washing cycle with the same liquor ratio of soap solution at a temperature of 40˚C for 30 min; followed by rinsing and drying for 15 times, the degree of staining was increased by using binders and thickeners

The change in the staining of the tested specimen was assessed with the appropriate grey scales. The fabrics were intermediate between excellent and very good (4-5) drops slightly, which is very good fastness characteristics in both change in color and staining test of the ISO3, they were (4-5), the results appears to be reasonable for applications that do not require frequent aggressive washing because the polymeric binder matrix could be loosed around the colorant molecules with initial washing.

V. Conclusions

The color change of the studied samples was clear by the naked eye, thermochromic pigments can have an activation temperature selected from the group consisting of 34°C, 35°C, 36°C, 37°C, 38°C, 39°C, 40°C, and 41°C. It's useful for medical application and physical exhaustion analyzing.

From the research results, the convection heat transfer changes by the changes of the temperature at the same convection heat transfer coefficient. The changing of the pigments colors were between (36- 41^{o}C) for samples used. For the cotton samples there was 14.3% weight increasing in sample weight after printing. The range of bursting strength value of printed samples was 8.5 to 9 bar with 5% higher than that of the un-printed samples, the degree of staining was between excellent and very good (4-5) drops slightly for condition applied. This illustrates the effect of the type of raw material and the thickness of the cloth on the heat transfer and therefore of dye color change.

Printing thermochromic pigments on the cloth can be considered a good alarm to change the temperature of the body regardless of the type of the fabrics raw material. The cloth have turned to sensitive to temperature change, that's makes it suitable for application on children's clothing, as the index of temperature change is very clear. In other embodiments, a suitable thermochromic pigment can have an activation color and an activation temperature corresponding to any combination of activation color and activation temperature.

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