Impact of Properties of Thermochromic Pigments on Knitted Fabrics

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Abstract⎯⎯Thermal dye is one of the important indicators when temperature is changed. It is used in medical, domestic and electronic applications. It indicates the change in chemical and thermal properties. In this work it is used to indicate the change in human body temperature where the change in temperature between (30 – 41 ^{o}C) is studied .The change in color begin to be clear at (30 ^{o}C). From this study it is clear that heat flux increased (81%) between printed and non-printed clothes which is due to the increase in heat transfer between body and the printed cloth. The temperature has been increased to the maximum level that the human body can reach and a gradual change in color is observed which allow the use of this dye on baby clothes to indicate the change in baby body temperature and monitoring his medical situation. An additional experiment has been made to explore the change in physical properties to the used clothe after the printing process such as air permeability which shows a clear reduction in this property on printed region comparing with the unprinted region, the reduction can reach (70%) in this property and in some type of printing the reduction can reach (100%) which give non permeable surface. 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.

Keywords⎯⎯Thermochromic Pigments, printing, heat flux, knitting fabrics, and colour changes.

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1 Introduction

Through out history the function and the original role of the textile changed very little. One could only think of only few generations of textiles that would bear significant differences when compared one to another. Textiles were to provide the necessary shielding against climatic conditions and only later on in history the shear design of it became more importance. Nowadays, textile engineers and technologists like to think there is a new generation of textiles emerging. This thinking is supported by new functionalities being added onto textiles in the last few several decades. For this to happen, it was necessary to combine state of the art electronics and newly synthesized organic molecules which would bring the functionality of the textile to another level. Scientists of various research branches working together, looking at issues and solving problems applying multisciplinary approaches was the right angle of looking at things. Results of this can be seen daily, as textiles are emerging into a new era in which "know how" and "state of the art" have to be combined to give products of highly added values.

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Producing "highly added value" products can give the leverage to companies of the western world in an ongoing "battle" against massively produced, low quality textiles of mainly eastern origin. Although, the way to commercialization of many of the ideas of how to upgrade the functionalities of the textile is long, the results may be far greater than the challenges encountered. Often, the answer on how to do it lies in using technologies and knowledge that have been around for centuries. Therefore, this paper will deal with the phenomenon of photochromics, which has first been noticed in 19th century and so far not exploited nearly enough within the realm of textiles [1]. It will cover the historical overview, division of photochromic systems and their synthesis, principals and triggering mechanisms, various fastness property issues and applicability to fibres of different origin [2]. Application methods and state of the art shall be described thoroughly, providing scientific and technological achievements from the relevant literature references [2]. Group of authors addresses the combination of photochromic phenomenon and textile in general as newly derived system, bearing all the qualities of a sensory material. Within it, molecule of photochromic dye may be observed as "smart", as it is triggered by a specific and quantifiable physical value. Properly applied, this "smart dye" and adequate textile fibre form a textile sensor capable of sensing and reacting to a particular impulse in a predictable manner [2].

1.1 Dyeing

Is the process of adding colour to textile products like fibers, yarns, and fabrics. Dyeing is normally done in a special solution containing dyes and particular chemical material. After dyeing, dye molecules have uncut chemical bond with fiber molecules. The temperature and time controlling are two key factors in dyeing. There are mainly two classes of dye, natural and man-made.

The primary source of dye, historically, has generally been nature, with the dyes being extracted from animals or plants. Since the mid-18th century, however, humans have produced artificial dyes to achieve a broader range of colours and to render the dyes more stable to resist washing and general use. Different classes of dyes are used for different types of fiber and at different stages of the textile production process, from loose fibers through yarn and cloth to completed garments [1].

Fig.1. Colors of dyes [1].

1.2 Classification of Dyes

Natural dyes: are dyes or colorant's derived from plants, invertebrates, or minerals. The majority of natural dyes are vegetable dyes from plant sources-roots, berries, bark, leaves, and wood ….etc. [3].

Acid Dyes: A class of dyes used on wool, other animal fibers, and some manufactured fibers. Acid dyes are seldom used on cotton or linen since this process requires a mordant [3,4].

Basic (Cationic) Dyes : Basic dyes are water-soluble and are mainly used to dye acrylic fibers. They are mostly used with a mordant. basic dyes are used for cotton, linen, acetate, nylon, polyesters [4].

Synthetic Dyes: Synthetic dyes are classified based upon their chemical composition and the method of their application in the dyeing process.

Direct (substantive) Dyes : Direct dyes colour cellulose fibers directly without the use of mordents. They are used for dyeing wool, silk, nylon, cotton, rayon etc. These dyes are not very bright and have poor fastness to washing although they are fairly fast to light [4].

Sulfur Dyes: Sulfur Dyes are insoluble and made soluble by the help of caustic soda and sodium sulfide. Dyeing is done at high temperature with large quantities of salt so that the colour penetrates into the fiber [4].

Pigment Dyes: Although pigments are not dyes in a true sense, they are extensively used for coloring fabrics like cotton, wool and other manmade fibers due to their excellent light fastness [4].

Vat Dyes: Vat dyes are insoluble in water and cannot dye fibers directly. Indigo is the original vat dye. These dyes are the fastest dyes for cotton, linen and rayon. They are used with mordents to dye other fabrics such as wool, nylon polyesters,…. etc.[4].

Reactive Dyes: Reactive dyes react with fiber molecules to form a chemical compound. they are either applied from alkaline solution or from neutral solutions which are then alkalized in a separate process. Sometimes heat treatment is also used for developing different shades. Reactive dyes were originally used for cellulose fibers only but now their various types are used for wool, silk, nylon, acrylics and their blends as well [4].

Others: Mordant Dyes - Macromolecular Dyes - Premetallized Dyes - Azo Dyes - Aniline Dyes - nthraquinone Dyes.

1.3 Stages in Dyeing

First stage: Diffusion of the dye from the dyebath to the fibre surface.

Second stage: Adsorption of the dye on the fibre surface.

Third stage: Diffusion of the dye to the fibre core.

Fourth stage: Fixation of the dye on the fibre [5].

1.4 Printing

Whereas dying conveys a uniform colour, printing allows a range of different colours to be applied. Usually between 5 and 10 pastes are required for a single pattern. Colour may be supplied by either pigments or dyes [6].

printing is the process by which a localized coloration is made on the textile fabric. The printing is normally done by using dyes showing affinity to the fibre . On the other hand, it can be performed superficially with pigments, which could be fixed using thermocurable resins [3].

1.4.1 printing methods

Direct printing: colour is applied directly to fabric in pattern & location desired in finished fabric.

Screen printing : incredibly versatile, simple process separate mesh screens used for each colour .

Digital printing.

Ink-jet printing.

Electrostatic printing : prepared screen covered with powdered dye; passes through electric field & pulled onto material.

Others [3].

1.4.2 Printing Process

Fabric preparation: The fabric should have uniform hydrophilicity and the surface should be free of fibres.

Deposition of colorant on a dry textile surface: Operating in a continues way to deposit the colorant on the fabric surface.

Fixation of printed colour: It is possible by 3 ways – physical, physico-chemical and chemical ways.

Elimination of thickener paste: Normally by means of washing [6].

1.5 Spectral Color

A spectral colour is a colour that is evoked by a single wavelength of light in the visible spectrum, or by a relatively narrow band of wavelengths, also known as monochromatic light. Every wavelength of visible light is perceived as a spectral colour, in a continuous spectrum; the colours of sufficiently close wavelengths are indistinguishable [7].

The spectrum is often divided up into named colours, though any division is somewhat arbitrary: the spectrum is continuous. Traditional colours include: red, orange, yellow, green, blue, and violet.
The division used by Isaac Newton, in his colour wheel, was: red, orange, yellow, green, blue, indigo and violet [7].

One needs at least trichromatic colour vision for there to be a distinction between spectral and non-spectral colours: trichromacy gives a possibility to perceive both hue and saturation in the chrome. In colour models capable to represent spectral colours [8], such as CIELUV, a spectral colour has the maximal saturation among all colours of the same hue In colour spaces which include all, or most spectral colours, they form a part of boundary of the set of all real colours. If luminance is counted, then spectral colours form a surface, otherwise their locus is a curve in a two-dimensional chromaticity space.

Theoretically, only RGB-implemented colours which might be really spectral are its primaries: red, green, and blue, whereas any other (mixed) colour is inherently non-spectral. But due to different chromaticity properties of different spectral segments, and also due to practical limitations of light sources, the actual distance between RGB pure colour wheel colours and spectral colours shows a complicated dependence on the hue. Due to location of R and G primaries near the almost "flat" spectral segment, RGB colour space is reasonably good with approximating spectral orange, yellow, and bright (yellowish) green, but is especially poor in reaching a visual appearance of spectral colours between green and blue, as well as extreme spectral colours. The SRGB standard has an additional problem with its "red" primary which is shifted to orange due to a trade-off between purity of red and its reasonable luminance, so that the red spectral became unreachable.

In the seventeenth century, Isaac Newton that the red purple at one end of the visible spectrum looked very similar to the purple at the other end. He therefore drew the two ends of the spectrum together, producing the first color wheel Fig. 2 [7].
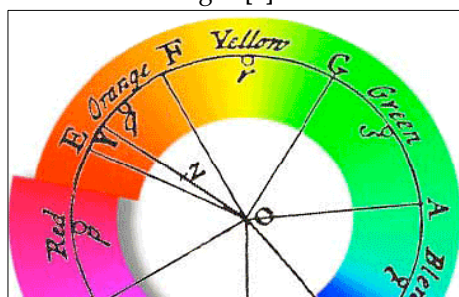
Color wheels are two dimensional models of color ships that deal only with hues–the names of colors. Hues opposite each other on a color wheel are said to be complementary; hues next to each other are called analogous. If complementary hues are juxtaposed, each appears brighter, if closely analogous hues are juxtaposed, they tend to blend visually, and it may be difficult to see the edge that separates them [7].

Even in simple color-wheel models, controversies have arisen over which few hues are the basic ones from which all other hues can be mixed Fig.3 There are at least five different possibilities that seem to be true, depending on the situation. In light mixtures, as in film, photography, computer graphics, and TV, where refracted light operates, all hues can be obtained from combinations of the rays that produce red, green, and blue-violet.
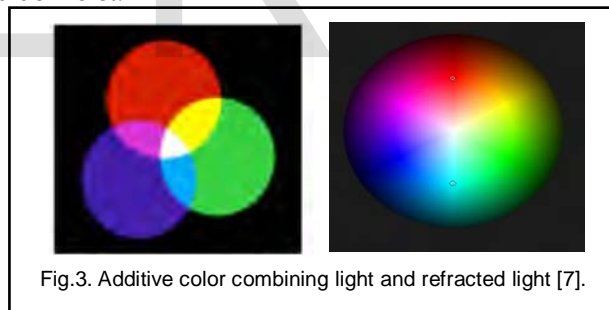

Fig.3. Additive color combining light and refracted light [7].

1.6 Color Theory

Color is defined a s the net response of an observer to visual physical phenomena involving visible radiant energy of varying intensities over the wavelength range 400. The net color seen by the observer is dependent on integration of three factors: the nature of the light source, the light absorption properties of the object observed, and the response of the eye to the 1ight reflected from the object. The relative intensities of the various wavelengths of visible 1ight observed by the eye are translated by the mind of the observer resulting in the perception of color. In color measurement, the human eye is replaced by a photocell which detects the light energy present at various visible wavelengths.

Visible 1ight is a narrow band of electromagnetic radiation from (400 to 700 nm) (1 nm equals 10-9 meters) detected by the human eye. Radiation falling

below (400 nm) is ultraviolet radiation, and that falling above (700 nm) is infrared radiation; both are unseen by the human eye. If pure light of a given wavelength is observed, it will have a color corresponding to that wavelength. Pure wavelengths of light are seen when white light is refracted by a prism into a "rainbow" spectrum of continuous color. Light sources such as sunlight, incandescent light, and fluorescent light are continuums of various wavelengths of light with the relative amounts of the various wavelengths of light being dependent on the overall intensity and type of light source. Sunlight at noon has very nearly the same intensity of each wavelength of 1ight throughout the visible spectrum, whereas at dusk sunlight is of lower intensity and has greater quantities of the longer, red wavelengths than of shorter, blue wavelengths. Fluorescent lights generally contain large amounts of shorter, blue wavelengths, while incandescent tungsten lights contain a large component of longer, red wavelengths compared to noon sunlight. Differences in intensity and wavelength distribution between light sources has a profound effect on the color observed for a dyed textile, since the textile can absorb and reflect only that 1ight available to it from the source. When a dyed fabric appears different in color or shade under two different light sources, the phenomenon is referred to as "flare" When two fabrics dyed with different dyes or dye combinations match under one light source but not under another, the effect is called "metamerism" [9].

1.7 Chromism

Chromism is the term used for a change in colour. Substances having the ability to exhibit the phenomenon of chromism are known as chromic materials. Normally, chromic phenomena involve processes causing eversible colour 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 [10]. These interactions may be categorized into following five groups:

- Reversible change in colour.
- Absorption and reflection of light.
- Absorption of energy followed by the emission of light.
- Absorption of light and energy transfer or transformation of energy.
- Use (manipulation) of light [11,12].

1.8 Thermochromism

The term thermochromism refers to a change in color as a function of temperature defined thermochromism as 'an easily noticeable reversible colour change brought about by the boiling point of each liquid, the boiling point of the solvent in the case of a solution or the melting point for solids[11].

According to the investigations thermochromism occurs base on different mechanisms in which either of the following materials are used: [13].

- Organic compounds.
- Inorganic compounds.
- Polymers.
- Sole gels.

In general , Thermochromic systems may belong to both chemical groups– inorganic and organic [13].

1.9 Thermochromic Pigments

Thermochromic pigments have reached widespread use through different industries including textile industry, military applications and plastic industry. In order to be functional. Thermochromic dyes are typically produced in two types:[12].

1.9.1 Liquid crystal type

Liquid crystal thermochromic inks show a spectrum of color changes because they selectively reflect specific wavelengths of light from their structure. This continuous color change occurs due to the change in molecular arrangement of the liquid crystal in contact with temperature. These thermochromic substances may consist of cholesteric liquid crystals or mixtures of cholesteric and nematic1 liquid crystals. Cholesteric liquid crystals normally have a helical structure accordingly they are chiral. Molecules in each layer of the helix do not have special order but the director in each layer twists with respect to the above or below layer.1 The distance in which the director rotates 360° and returns to the initial direction is called Pitch of the helix (Exhibited in the following picture Fig.4 Pitch is the most important characteristic of a cholesteric liquid crystal because it results in selective reflection of the light with wavelengths equal to the pitch length. The sensitivity of the pitch length to temperature results in chromic behavior of cholesteric liquid crystal. In the proper temperature they form a cholesteric liquid crystal; an intermediate phase between the crystalline phase and the liquid phase. Change in the temperature effectively results in thermal expansion of the liquid crystal structure. Consequently, the visual color change effect varies with the temperature owing to the changes in layer spacing and pitches of the liquid crystal. The main advantage of this group of dyes is their ability to exhibit a finely colored image. Whilst, according to many literatures their low color density and being expensive are the major drawbacks of this product [13].
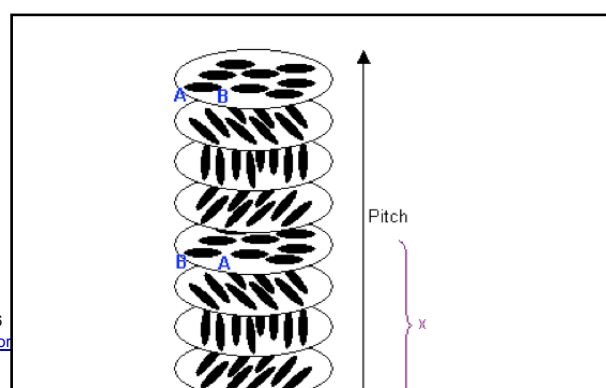
In chiral nematic liquid crystals, each layer of molecules experiences a gradual twist with respect to the director in adjacent layers. So the molecules twist gradually like a screw into a helical arrangement layer by layer until it reaches 360º against the original director. The thickness required for a turn of 360º is known as the pitch length of the helix .The distance in which the director rotates 360°and returns to the initial direction is called pitch of the helix. Pitch is the most important characteristic of a cholesteric liquid crystal because it results in selective reflection of the light with wavelengths equal to the pitch length. The sensitivity of the pitch length to temperature results in chromic behavior of cholesteric liquid crystal.

1.9.2 Leuco dyes

Leuco dyes; also known as molecular re-arrangement dyes, basically, show a single color change due to a molecular re-arrangement in their chemical structure. Their color change effect can be visualized as a reversible shift between two colors or a transition from colored state to a colorless state. Keto-enol tautomerism or ring opening are the two predominant mechanisms of molecular rearrangement. In general, tautomerism refers to the interconversion of two organic isomers in an equilibrium state. Normally, this reaction occurs based on the migration and relocation of hydrogen atoms (protons). One of the most common types of tautomeric reaction is the conversion of ketone structure and to its enol form. The following picture Fig.5 illustrates equilibrium of ketone-enol tautomers[11].
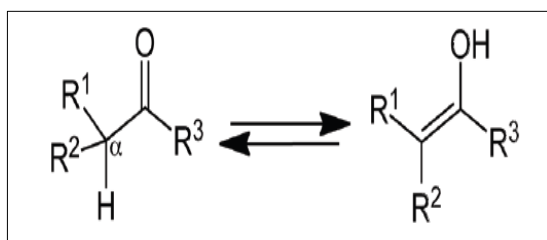

Fig.5 Mechanism of keto-enol tautomerism / Wikipedia pictures [11].

As ... actical the ... o-enol rearrangement; In this case, change in the temperature induces the tautomerism rearrangement, which leads to an increase in the conjugation and production of a new chromophore In general, leuco dyes are functionally made of a combination of chemicals. In most cases the leuco dye includes an electron donating color former, an electron accepting color developer and a color change controlling agent in other words, a Leuco dye is made from an organic dye, an acidic activator and a non-polar co-solvent medium. The solvent is a solid with low melting point like ester or alcohol. At low temperatures (lower than the melting point of the solvent) the color former and the developer are in contact and the distinct color is visible. Upon heating (above the melting point of the solvent) separation of the color former and color developer avoids any electron interaction and results in the colorless state [11].

1.9.3 Application of Thermochromic dyes

Thermochromic dyes have been widely used in textile applications, specifically, they have brought novelty into fashion industry. However, this is not the only field in which thermochromic pigments are being used. Variety of non-textile applications and product manufacturers are also consumers of thermochromic pigments. Thermometers, temperature indicators and body monitoring devices can be counted among the non-textile applications. During the recent years, smart textile section has opened new ways to functionalize thermochromism. Specially designed T-shirts capable of showing wearer's body temperature is an example of such innovations. Very slowly shimmering flower is a textile base non-emissive display made from conductive and insulating yarns woven together with Jacquard loom. Custom electronic components have been used to control sending power to different areas of the textile. Ultimately, the fabric is printed with thermochromic inks. Current of electricity through the conductive yarns provide the heat required to initiate dynamic visual effect [13].

1.10 Heat Transfer

From the study of thermodynamics, you have learned that energy can be transferred by interactions of a system with its surroundings. These interactions are called work and heat. However, thermodynamics deals with the end states of the process during which an interaction occurs and provides no information concerning the nature of the interaction or the time rate at which it occurs [14]. Heat transfer (or heat) is thermal energy in transit due to a spatial temperature difference. Whenever a temperature difference exists in a medium or between media, heat transfer must occur. As shown in Fig.6 we refer to different types of heat transfer processes as modes.

When a temperature gradient exists in a stationary medium, which may be a solid or a fluid, we use the term conduction to refer to the heat transfer that will occur across the medium. In contrast, the term convection refers to heat transfer that will occur between a surface and a moving fluid when they are at different temperatures. The third mode of heat transfer is termed

thermal radiation. All surfaces of finite temperature emit energy in the form of electromagnetic waves. Hence, in the absence of an intervening medium, there is net heat transfer by radiation between two surfaces at different temperatures [14].
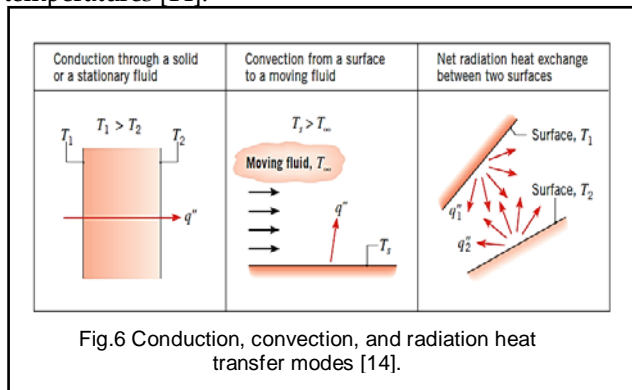

Fig.6 Conduction, convection, and radiation heat transfer modes [14].

In our research , we are especially interested in convection heat transfer, and radiation heat transfer .

1.10.1 Convection

The convection heat transfer mode is comprised of two mechanisms. In addition to energy transfer due to random molecular motion (diffusion), energy is also transferred by the bulk, or macroscopic, motion of the fluid. This fluid motion is associated with the fact that, at any instant, large numbers of molecules are moving collectively or as aggregates. Such motion, in the presence of a temperature gradient, contributes to heat transfer. 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. The term convection is customarily used when referring to this cumulative transport, and the term advection refers to transport due to bulk fluid motion.

We are especially interested in convection heat transfer, which occurs between a fluid in motion and a bounding surface when the two are at different temperatures. Consider fluid flow over the heated surface of Fig.7 a consequence of the fluid–surface interaction is the development of a region in the fluid through which the velocity varies from zero at the surface to a finite value u_ associated with the flow. This region of the fluid is known as the hydrodynamic, or velocity, boundary layer. Moreover, if the surface and flow temperatures differ, there will be a region of the fluid through which the temperature varies from (Ts at y = 0 to T_∞) in the outer flow. This region, called the thermal boundary layer, may be smaller, larger, or the same size as that through which the velocity varies. In any case, if ($T_s > T_\infty$) convection heat transfer will occur from the surface to the outer flow [14].

The convection heat transfer mode is sustained both by random molecular motion and by the bulk motion of the fluid within the boundary layer. The contribution due to random molecular motion (diffusion) dominates

near the surface where the fluid velocity is low. In fact, at the interface between the surface and the fluid (y = 0) , the fluid velocity is zero, and heat is transferred by this mechanism only. The contribution due to bulk fluid motion originates from the fact that the boundary layer grows as the flow progresses in the x-direction. In effect, the heat that is conducted into this layer is swept downstream and is eventually transferred to the fluid outside the boundary layer. Appreciation of boundary layer phenomena is essential to understanding convection heat transfer. For this reason, the discipline of fluid mechanics will play a vital role in our later analysis of convection.
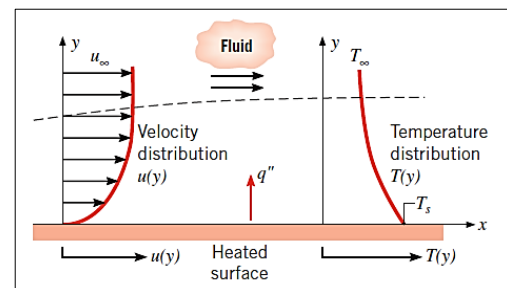

Fig.7 Boundary layer development in convection heat transfer [14].

Convection heat transfer may be classified according to the nature of the flow. We speak of forced convection when the flow is caused by external means, such as by a fan, a pump, or atmospheric winds. However, for some convection processes, there is, in addition, latent heat exchange. This latent heat exchange is generally associated with a phase change between the liquid and vapor states of the fluid. Regardless of the nature of the convection heat transfer process, the appropriate rate equation is of the form [14].

$$q'' = h\,(T_s - T_\infty) \qquad (1)$$

where, q″, the convective heat flux (W/m²) is proportional to the difference between the surface and fluid temperatures, Ts and T_∞ respectively.

This expression is known as Newton's law of cooling, and the parameter h (W/m².K) is termed the convection heat transfer coefficient. This coefficient depends on conditions in the boundary layer, which are influenced by surface geometry, the nature of the fluid motion, and an assortment of fluid thermodynamic and transport properties. The following Table.1 shows Thermal conductivity for common materials and products When the temperature (25 °C) [14].

TABLE 1

THERMAL CONDUCTIVITY (K) (W/M.K)

Material/Substance	Thermal Conductivity (k) W/(m. K)
Acetone	0.16
Acrylic	0.2
Air, atmosphere (gas)	0.024
Alcohol	0.17
Carbon	1.7
Cellulose, cotton, wood pulp and regenerated	0.23
Cellulose acetate, molded, sheet	0.17 - 0.33
Cellulose nitrate, celluloid	0.12 – 0.21
Cotton	0.04
Polyester	0.05
Polypropylene, PP	0.1 – 0.22

1.10.2 Radiation

Thermal radiation is energy emitted by matter that is at a nonzero temperature. Although we will focus on radiation from solid surfaces, emission may also occur from liquids and gases. Regardless of the form of matter, the emission may be attributed to changes in the electron configurations of the constituent atoms or molecules. The energy of the radiation field is transported by electromagnetic waves (or alternatively, photons). While the transfer of energy by conduction or convection requires the presence of a material medium, radiation does not. In fact, radiation transfer occurs most efficiently in a vacuum. Consider radiation transfer processes for the surface of Figure 1.6a. Radiation that is emitted by the surface originates from the thermal energy of matter bounded by the surface, and the rate at which energy is released per unit area (W/m²) is termed the surface emissive power, E. There is an upper limit to the emissive power, which is prescribed by the Stefan Boltzmann law [14].

$$E_b = \sigma T_s^4 \tag{2}$$

Where T_s is the absolute temperature (K) of the surface and _ is the Stefan. Boltzmann constant σ=5.67*10⁻⁸ (W/m². K⁴) Such a surface is called an ideal radiator or blackbody. heat flux emitted by a real surface is less than that of a blackbody at the same temperature and is given by :

$$E = \varepsilon \sigma T_s^4 \tag{3}$$

Where ε is a radiative property of the surface termed the emissivity. With values in the range $0 \leq \varepsilon \leq 1$, this property provides a measure of how efficiently a surface emits energy relative to a blackbody. It depends strongly on the surface material and finish, and representative values are provided in Appendix A. Radiation may also be incident on a surface from its surroundings.

The radiation may originate from a special source, such as the sun, or from other surfaces to which the surface of interest is exposed. Irrespective of the source(s), we designate the rate at which all such radiation is incident on a unit area of the surface as the irradiation G . Fig.8 A portion, or all, of the irradiation may be absorbed by the surface, thereby increasing the thermal energy of the material. The rate at which radiant energy is absorbed per unit surface area may be evaluated from knowledge of a surface radiative property termed the absorptivity α .That is [14].

$$G_{abs} = \alpha G \tag{4}$$

Where $0 \leq \alpha \leq 1$ and the surface is opaque, portions of the irradiation are reflected. If the surface is semitransparent, portions of the irradiation may also be transmitted. However, whereas absorbed and emitted radiation increase and reduce, respectively, the thermal energy of matter, reflected and transmitted radiation have no effect on this energy. Note that the value of α depends on the nature of the irradiation, as well as on the surface itself. For example, the absorptivity of a surface to solar radiation may differ from its absorptivity to radiation emitted by the walls of a furnace.
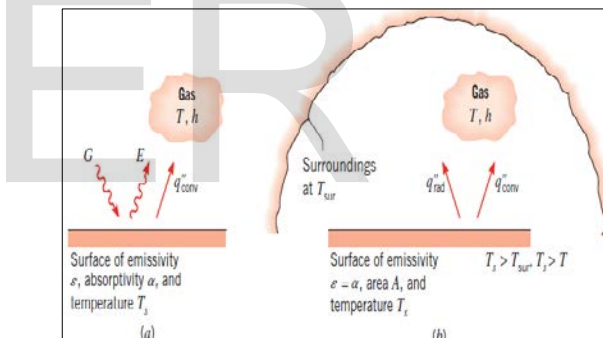

Fig.8. Radiation exchange: (a) at a surface and (b) between a surface and large surroundings [14].

In many engineering problems (a notable exception being problems involving solar radiation or radiation from other very high temperature sources), liquids can be considered opaque to radiation heat transfer, and gases can be considered transparent to it. Solids can be opaque (as is the case for metals) or semitransparent (as is the case for thin sheets of some polymers and some semiconducting materials). A special case that occurs frequently involves radiation exchange between a small surface at T_s and a much larger, isothermal surface that completely surrounds the smaller one Fig.8. The surroundings could, for example, be the walls of a room or a furnace whose temperature T_{sur} differs from that of an enclosed surface ($T_{sur} \neq T_s$) for such a condition, the irradiation may be approximated by emission from a blackbody at T_{sur} in which case $G = \sigma T_{sur}^4$ If the surface is assumed to be one for which $\alpha = \varepsilon$ (a gray surface), the

net rate of radiation heat transfer from the surface, expressed per unit area of the surface, is: [14].

$$q^{"}_{rad} = \frac{q}{A} = \varepsilon E_b(T_s) - \alpha G = \varepsilon \sigma (T_s^4 - T_{sur}^4) \qquad (5)$$

This expression provides the difference between thermal energy that is released due to radiation emission and that gained due to radiation absorption. For many applications, it is convenient to express the net radiation heat exchange in the form .

$$q_{rad} = h_r A(T_s - T_{sur}) \qquad (6)$$

where, from Equation [5] the radiation heat transfer coefficient hr is :

$$h_r = \varepsilon \sigma (T_s + T_{sur})(T_s^2 - T_{sur}^2) \qquad (7)$$

Here we have modeled the radiation mode in a manner similar to convection. In this sense we have linearized the radiation rate equation, making the heat rate proportional to a temperature difference rather than to the difference between two temperatures to the fourth power. Note, however, that hr depends strongly on temperature, whereas the temperature dependence of the convection heat transfer coefficient h is generally weak. For the conditions of the total rate of heat transfer from the :

$$q = q_{conv} + q_{rad} = hA(T_s - T_\infty) + \varepsilon A\sigma(T_s^4 - T_{sur}^4) \qquad (8)$$

2   Methodology and Experiments

2.1 Materials

2.1.1 Thermochromic Powder

We used Turn Thermo pigment orange colour of (30°C, 86F) thermochromic pigment, Turn Thermo's thermochromic (Heat Activated) pigment. As the pigment is heated, the pigment becomes colour-less.

2.1.2 Binders

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. It is a ready-for-use pigment print paste and contains thickener and other auxiliaries .

2.1.3 Thickener

Was used in the formulation of pastes for printing chromazone slurries. It has a smooth, creamy consistency and is an inverse copolymer emulsion of ethylenically unsaturated monomers in hydrocarbons.

2.1.4 Fabric

The fabric used for printing was (100%) Cotton, White, Interlock knitted, Cotton was selected for experimental purposes due to its common usage in textiles and its natural origin.

2.2 Preparation of Printed Samples

2.2.1 Screen printing

Is a printing technique whereby a mesh is used to transfer ink onto a substrate, except in areas made impermeable to the ink by a blocking stencil. A blade or squeegee is moved across the screen to fill the open mesh apertures with ink, and a reverse stroke then causes the screen to touch the substrate momentarily along a line of contact. This causes the ink to wet the substrate and be pulled out of the mesh apertures as the screen springs back after the blade has passed.

Screen printing is also a stencil method of print making in which a design is imposed on a screen of polyester or other fine mesh, with blank areas coated with an impermeable substance. Ink is forced into the mesh openings by the fill blade or squeegee and by wetting the substrate, transferred onto the printing surface during the squeegee stroke. As the screen rebounds away from the substrate the ink remains on the substrate. It is also known as silk-screen, screen, serigraphy, and serigraph printing. One color is printed at a time, so several screens can be used to produce a multicolored image or design.

There are various terms used for what is essentially the same technique. Traditionally the process was called screen printing or silkscreen printing because silk was used in the process prior to the invention of polyester mesh. Currently, synthetic threads are commonly used in the screen printing process. The most popular mesh in general use is made of polyester. There are special-use mesh materials of nylon and stainless steel available to the screen printer. There are also different types of mesh size which will determine the outcome and look of the finished design on the material.

Caviar beads: Is a glue that is printed in the shape of the design, to which small plastic beads are then applied – works well with solid block areas creating an interesting tactile surface.

Cracking ink: Effect is when the ink produces an intentional cracked surface after drying.

Discharge inks: Is used to print lighter colours onto dark background fabrics, they work by removing the dye of the garment – this means they leave a much softer texture. The cons with this process is that they are less graphic in nature than plastisol inks, and exact colours are difficult to control. One of the pros of using this process is they are especially good for distressed prints and under-basing on dark garments that are to be printed with additional layers of plastisol. It adds variety to the design or gives it that natural soft feel.

Expanding ink (puff): Expanding ink, or puff, is an additive to plastisol inks which raises the print off the garment, creating a 3D feel and look to the design. Mostly used when printing on apparel.

Flocking: Consists of a glue printed onto the fabric and then flock material is applied for a velvet touch.

Foil: Is much like flock, but instead of a velvet touch and look it has a reflective/mirror look to it. Although foil is finished with a heat press process it needs the screen printing process in order to add the adhesive glue onto the material for the desired logo or design.

Four-colour process or the CMYK colour model: Four-colour process is when the artwork is created and then separated into four colours (CMYK) which combine to create the full spectrum of colours needed for photographic prints. This means a large number of colours can be simulated using only 4 screens, reducing costs, time, and set-up. The inks are required to blend and are more translucent, meaning a compromise with vibrancy of colour.

Glitter/Shimmer: Glitter or Shimmer ink is when metallic flakes become an additive in the ink base to create this sparkle effect. Usually available in gold or silver but can be mixed to make most colours.

Gloss: Gloss ink is when a clear base laid over previously printed inks to create a shiny finish

Metallic: Metallic ink is similar to glitter, but smaller particles suspended in the ink. A glue is printed onto the fabric, then Nano-scale fibers applied on it. This is often purchased already made.

Mirrored silver: Mirrored silver is a highly reflective, solvent-based ink.

Nylobond: Nylobond is a special ink additive for printing onto technical or waterproof fabrics.

Plastisol: Plastisol is the most common ink used in commercial garment decoration. Good colour opacity onto dark garments and clear graphic detail with, as the name suggests, a more plasticized texture. This print can be made softer with special additives or heavier by adding extra layers of ink. Plastisol inks require heat (approx. 150 °C (300 °F) for many inks) to cure the print.

PVC and Phthalate Free: Is relatively new breed of ink and printing with the benefits of plastisol but without the two main toxic components. It also has a soft texture.

Suede Ink: Is a milky colored additive that is added to plastisol. With suede additive you can make any color of plastisol have a suede feel. It is actually a puff blowing agent that does not bubble as much as regular puff ink. The directions vary from manufacturer to manufacturer, but generally up to 50% suede can be added to normal plastisol.

Water-Based inks: these penetrate the fabric more than the plastisol inks and create a much softer feel. Ideal for printing darker inks onto lighter colored garments. Also useful for larger area prints where texture is important. Some inks require heat or an added catalyst to make the print permanent.

High Build: Is a process which uses a type of varnish against a lower mesh count with many coats of emulsion or a thicker grade of emulsion (e.g., Capillex). After the varnish passes through to the substrate, an embossed-appearing, 'raised' area of varnish is created. When cured

at the end of the process, the varnish yields a braille effect, hence the term 'high build'.
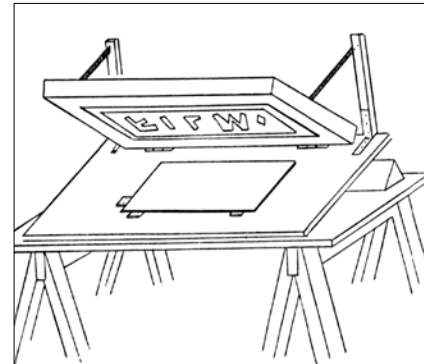

Fig.9 Silk screen machine.

Pigment Paste : We prepare the pigment paste by using this percentage.

TABLE 2

SHOWN PERCENTAGE OF MATERIALS.

| Materials	percentage (%)
Thermochromic Pigment	4
Acrylic binder	10
Emulsion thickener	90

2.2.2 Printing technique

A screen is made of a piece of mesh stretched over a frame. A stencil is formed by blocking off parts of the screen in the negative image of the design to be printed; that is, the open spaces are where the ink will appear on the substrate.

Before printing occurs, the frame and screen must undergo the pre-press process, in which an emulsion is 'scooped' across the mesh and the 'exposure unit' burns away the unnecessary emulsion leaving behind a clean area in the mesh with the identical shape as the desired image. The surface to be printed (commonly referred to as a pallet) is coated with a wide 'pallet tape'. This serves to protect the 'pallet' from any unwanted ink leaking through the screen and potentially staining the 'pallet' or transferring unwanted ink onto the next substrate. Next, the screen and frame are lined with a tape. The type of tape used in for this purpose often depends upon the ink that is to be printed onto the substrate. These aggressive tapes are generally used for UV and water-based inks due to the inks' lower viscosities. The last process in the 'pre-press' is blocking out any unwanted 'pin-holes' in the emulsion. If these holes are left in the emulsion, the ink will continue through and leave unwanted marks. To block out these holes, materials such as tapes, specialty emulsions and 'block-out pens' may be used effectively.

The screen is placed atop a substrate. Ink is placed on top of the screen, and a flood bar is used to push the ink through the holes in the mesh. The operator begins with the fill bar at the rear of the screen and behind a

reservoir of ink. The operator lifts the screen to prevent contact with the substrate and then using a slight amount of downward force pulls the fill bar to the front of the screen. This effectively fills the mesh openings with ink and moves the ink reservoir to the front of the screen. The operator then uses a squeegee (rubber blade) to move the mesh down to the substrate and pushes the squeegee to the rear of the screen. The ink that is in the mesh opening is pumped or squeezed by capillary action to the substrate in a controlled and prescribed amount, i.e. the wet ink deposit is proportional to the thickness of the mesh and or stencil. As the squeegee moves toward the rear of the screen the tension of the mesh pulls the mesh up away from the substrate (called snap-off) leaving the ink upon the substrate surface.

There are three common types of screen printing presses. The 'flat-bed', 'cylinder', and the most widely used type, the 'rotary' as shown in Fig.10.

Fig.10 A. Ink. B. Squeegee. C. Image. D. Photo-emulsion.
E. Screen. F. Printed image
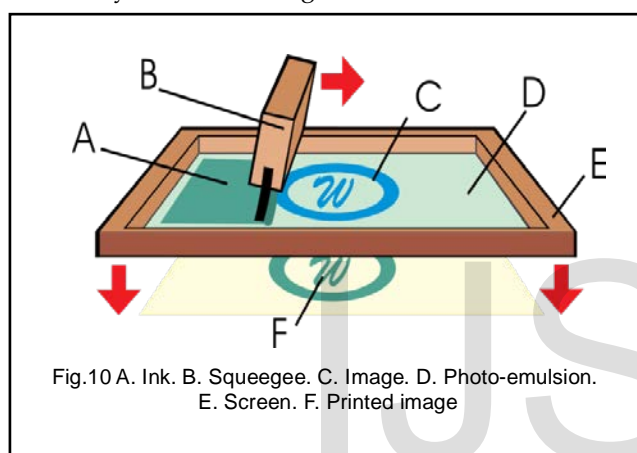
Textile items printed with multicolored designs often use a wet on wet technique, or colours dried while on the press, while graphic items are allowed to dry between colours that are then printed with another screen and often in a different colour after the product is re-aligned on the press.

2.3 Testing

2.3.1 Change Colour Measurement (Colour Stability towards Heat)

The colour measurement conditions have taken to change the temperature between (30 – 41 °C). During that we have surveillance dye colour changes. We were determined the severity of the spectrum colour changes at temperatures between the conditions we have set out. It was noted the visible spectrum change from color orange when the temperature of (30 °C) to colorless when the temperature (41 °C), and the heat flux have been calculated between this temperature. considering, that the laboratory temperature around (30 °C), we have seen that the colours changed from strong to light with high temperature.

TABLE 3

INTERESTING RESULTS AT $T = 30\,^{\circ}C$, $H = 0.04\,W/M^2$

Strong of the colour	Temperature ($^{\circ}C$)	Heat flux (W/m^2)
Orange	30	0
Light orange	32	0.08
Light pink	36	0.24
Colorless	41	0.44

2.3.2 Wash Fastness

The wash fastness of printed fabrics was testing by washing them with a soap. The standard ISO soap solution of (5g/L) was prepared in distilled water. The liquor ratio was kept at (50:1 ml/g). A washes P machine provided by roaches was used for this test. The test was conducted for (30 minutes) at (40 °C). The samples were have to be assessed by colour measurement. But we do not have colour measurement, so we had taken the GMS (gram per meter square) of the fabric and compared between the fabric weight after every wash cycle, to knew approximately how the weight decrease, and how the fastness of the pigment. shown that the weight of the printed fabric have been decrease after the washing cycles, but in a very little rate, due to the binder, and fastness enhancers that had been used during printing. Interesting results in the following Table 4.

TABLE 4

RESULTS OF THE WASH FASTNESS.

Printed fabric weight(g)	Washing cycles (num)	Fabric area (cm²)
1.20	-	50
1.20	3	50
1.19	10	50
1.18	15	50
1.16	25	50

2.3.3 Air permeability

Air permeability has been tested after printing and it is observed that a reduction in this property is observed after the printing. This is due to the adhesion dye particle on the cloth which make it non- permeable surface. Three samples are tested and the results are shown in Table 5.

TABLE 5

RESULTS OF AIR PERMEABILITY

Permeability L\m²\s	Samples
653.93	1
213.75	2
190.33	`3

3.   Results and Discussion
## 3.1 The Change in Color Due to Heat Flux

When temperature is changed from (30 to 41 ^{O}C) which is the usual temperature in human body, the color of the printed cloth is changed from Orange to non-colored gradually from light orange – light pink – non-colored, in other work the intensity of color is increased with the decrease in temperature which is clear shown in Fig. 11. This is due to that benzene ring opened and the color is began to be developed gradually due to the change of the thermally induced particles.

As the temperature increased, heat flux are increased too due to the   increase in the difference between clothes and human body surface temperature which is appeared as change in color. The increase in heat flux is reached (81 %) as obtained using Newton cooling law, see equation (1).

Fig.11 Related between changes of colours, temperature, and heat flux.
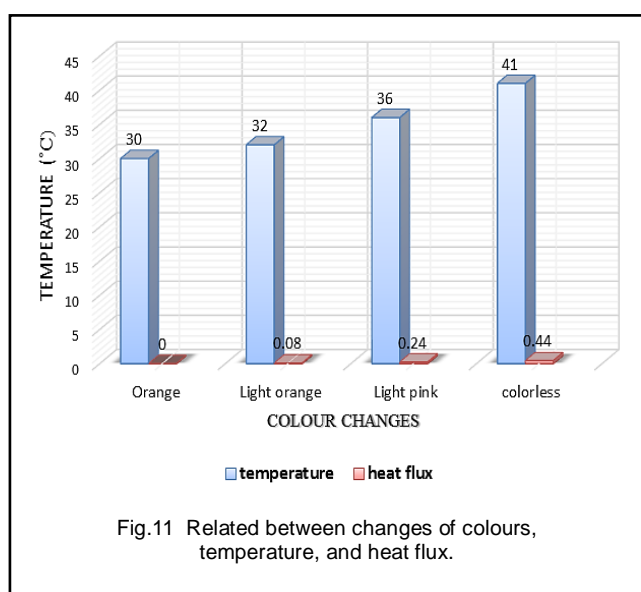
3.2 Dye Fitness

This type of dye is seemed to have low fitness when it is washed, this is due to its large particle which forbidden it from being permeable through cloth fiber where the particles are adhesive to the outer cloth surface which facilitate its removal through cyclic washing processes but by using the printing technique that depends on using thickeners and binders, the ability of fixing of cloth color is increased. The color strength is shown to be reduced after (12) washing cycles and the removed of color is observed after (25 – 30) washing cycles and above as shown in Fig.12 which indicate the relation between cloth weight and number of washing cycles where a decrease in weight is observed reaching (15 %) (i.e. the color is reduced (15 gram) after 100 washing cycle. From the previous observation one can conclude that by using binders and thickeners a contribute in increasing the adhesion between dye particle and cloth fibers, which increase color fitness on cloth so that color will stay on cloth for long time.

Fig.12 Related between the fabric weight and number of washing cycles
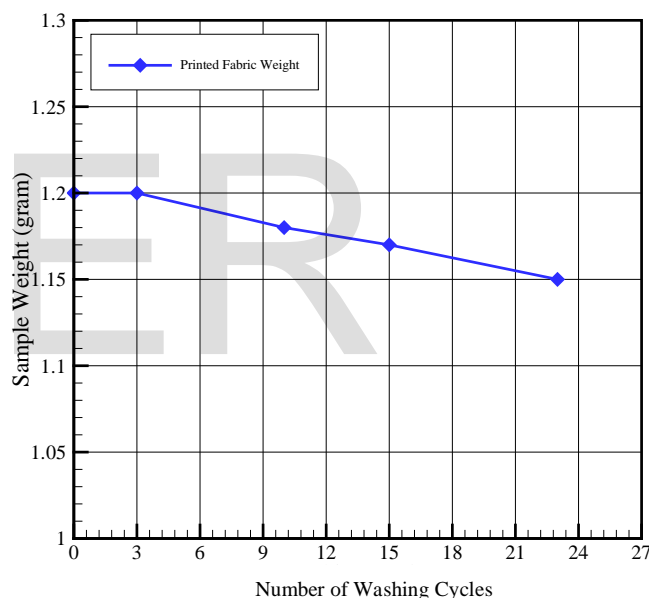
3.2 Air Permeability

It is one of the most important tests on printed cloth, where the process of adding color on the surface of cloth will reduce the ability of air to pass through colored cloth, this is due to closing in pores of cloth which is shown in   Fig. 13 that shows that the air permeability is reduced clearly in the printed region comparing with unprinted region. The percent of reduction is almost reaching (70 %). The reduction in air permeability in cloths depend on cloth nature, dye type, and thickness of the printed layer where the air permeability is vanished in clothes that has swell printing.
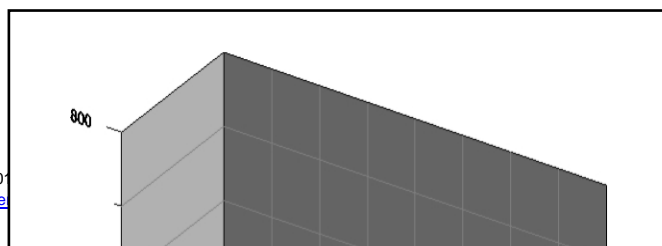
(0.8 w/m²) when the temperature (50 °C) the emergence of the orange color, because of the increased heat transfer between the fabric and the body when contact with him.

7. The characterized this dye consistently and show it can keep fixed up to (15) wash cycle, so with the use of installed materials.

8. Considered smart fabrics, suitable to monitor the health status of children, which give an indication of when the chromatic difference in body temperature.

NOMENCLATURE

A	Area, m²
E	Thermal plus mechanical energy, J
G	Irradiation, $W.m^{-12}$
h	Convection heat transfer coefficient, $W.m^{-2}.K^{-1}$
Q	heat transfer rate, W
q″	Heat flux, $W.m^{-2}$
q	Heat transfer rate, W
T	Temperature , °C
μ	Permeability, $L.m^{-2}.^{-1}s$
α	Thermal diffusivity, $m^2.s^{-1}$
ε	Emissivity, -
σ	Stefan–Boltzmann constant, $W.m^{-2}. K^{-1}$

4. CONCLUSIONS

1. Air permeability is reduced clearly in the printed region comparing with unprinted region, the percent of reduction is almost reaching (70 %).

2. Heat flux has been increased with the increased of the colour depth , due to the increased of the temperature through the time. Where the colour registered change.

3. Turn Thermo pigments is colored at normal temperatures , and show a change to colorless with high temperatures. As in this research the turn thermo pigment appeared depth at 30 °C and changed to clear at (41 °C) and above.

4. The reduction in air permeability in cloths depend on cloth nature, dye type, and thickness of the printed layer where the air permeability is vanished in clothes that has swell printing.

5. Decrease in cloth weight is observed reaching (15 %) (i.e. the color is reduced (15 gram) after 100 washing cycle.

6. Print this dyeing the cloth has earned him an increase in heat flux that reached a maximum

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