

# Photochromic and Thermochromic Colorants in Textile Applications

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## ABSTRACT

Commercial photochromic and thermochromic colorants that change rapidly and reversibly from colorless to colored state when activated by stimuli like ultraviolet irradiation, temperature or pH are well established class of colorants for manufacturing of niche products. Use of photochromic and thermochromic systems in applications like medical thermography, plastic strip thermometers, photochromic lenses, food packaging and non-destructive testing of engineered articles and electronic circuitry is well documented. However, in the last few years, the research on application of these systems on textiles has picked up significantly which has the potential to unlock commercially significant nascent high-tech applications. This review paper presents a summary of the chemistry, mechanism, application on textiles and evaluation procedure of performance, other technical features, current and potential application areas as well as challenges encountered in wider acceptance of photochromic and thermochromic colorants on textiles.

**Keywords:** Photochromism, Thermochromism, Spiropyrans, Spirooxazines, Naphthopyrans, liquid crystal, microencapsulation

## INTRODUCTION

At the intersection of science, technology, materials and fashion, new multi-disciplinary partnerships are emerging as the basis for novel research on smart textiles. Use of chromic colorants has the potential to create many responsive or adaptive products. Chromic colorants are those colorants that change, radiate or erase color due to its induction by external stimuli. "Chromic" as suffix means reversible change of color and by extension, a reversible change of other physical properties. This external stimuli can be light (photochromic), heat (thermochromic), electricity (electrochromic) pressure (piezochromic) liquid (solvatechromic) or an electron beam (carsolchromic) [1-2]. There is considerable potential for application

of photochromism and thermochromism in the field of 'smart' fabrics and clothing, which are engineered to sense and respond to external environmental conditions and stimuli. Color-changing textile would allow people to dynamically change the aesthetics of their clothing to suit their mood, their style, etc. allowing them to be creative and expressive in many ways. 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. Thus, color changing technology offers unique and challenging design opportunities to the designer. Both Photochromism and thermochromism have important commercial applications in ophthalmics, including the familiar spectacles which become sunglasses when activated by sunlight, information recording materials, dye lasers, security printing, camouflage and others [3].

In last few decades a lot of research papers and patents have been published regarding, chemistry and mechanisms and application of photochromic and thermochromic colorants but relatively little work have been done that approaches these colorants from textile application point of view. Since in textile parlance, the term dye is used for those colorants which have affinity or substantivity for a textile substrate, the term colorant would be used for describing photochromic and thermochromic colors henceforth in this article.

## Difference between Thermochromic and Photochromic Systems

One of the major differences is the stimulus. While in case of thermochromic systems it is the temperature, it is sunlight or specifically UV radiation which causes transition from colorless to colored state or vice versa. In case of thermochromic systems, the stimulus or heat energy causes the color to fade, however in case of photochromic systems, the stimulant or light energy causes the color to develop. Hence the mode of

color change is opposite in the two cases.

### Photochromism

The phenomenon of photochromism may be defined as a reversible change in color induced in a compound driven in one or both directions by the action of electromagnetic radiation [4]. Many photochromic materials change color upon irradiation with ultraviolet (UV) or visible light and then revert back to their original color following removal of the illumination. This is known as T-type photochromism when the back reaction is driven thermally. If the photochromic material only returns to its original state through irradiation with light of another range of wavelengths, i.e. the change is photochemically driven, then it is said to exhibit P-type photochromism. Most of the colorants used in industry show thermally driven back reaction i.e. T-type thermochromism [5].

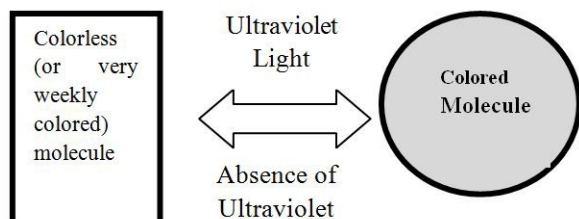


FIGURE 1. Behavior of commercially important photochromic colorants [5].

For most photochromic colorants, the absorption of light causes a rearrangement of the bonding between the atoms within a colorless or weakly colored molecule (photoisomerisation), creating a structure that is intensely colored (*Figure 1*). The wavelengths of light that affects this reversible conversion depend on colorants, but normally for commercial photochromic colorants it is within the UV region. For example, certain naphthopyrans respond best to UV-A radiation of wavelengths 350–380 nm, while some spirooxazines can be activated readily by blue light in the region of 410 nm. Thus pronounced photochromism can be produced by sunlight with such colorants as it has a significant UV component. Conversely, artificial light sources such as tungsten filament bulbs, which emit relatively little light at these wavelengths, are not very effective.

Photochromism is the reversible change of chemical species between two forms having different absorption spectra. This can be illustrated as a reversible change of color upon exposure to light (*Figure 2*).

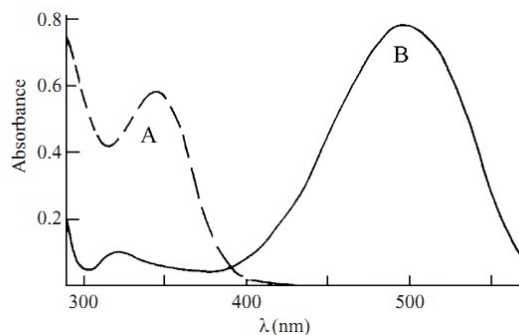


FIGURE 2. UV-vis-spectra of a photochromic compound before (a) and after (b) irradiation with UV light [6].

### T-Type Photochromic Colorants

Over the past 50 years, thousands of organic photochromic molecules have been synthesized, but only few of them have been commercialized due to complex technical and commercial challenges faced in developing a marketable product. Not only the candidate molecule should be practical and economical to manufacture, but also various aspects of its photochromism have to be satisfactory. Though specific requirements vary according to the application, general properties required in photochromic colorants can be laid down as:

- The photochromic effect should be ‘on demand’ i.e. they should activate rapidly from colorless to colored forms upon irradiation by UV light,
- The ‘half-life’ should be minimum (taken for absorbance to halve following removal of the activating light) for the desired application,
- Change from colorless to colored forms should be efficient, so that only a relatively low concentration of colorant produces a pronounced color change effect. There should be a balance between attaining sufficient depth of shade and acceptably quick bleaching,
- They should possess low residual color when not activated, but ‘color up’ to the desired hue when irradiated,
- Effect of variation in temperature in photochromic response should be relatively low.
- They should resist the tendency to ‘fatigue’, whereby, a fraction of the colorant gradually becomes weakened in color upon repeated activation by converting into non-photochromic molecules during activation [6].

### Classes of Commercial T-Type Photochromic Colorants

The following classes of photochromic colorants are of the greatest commercial importance:

- Spiropyrans
- Spirooxazines
- Naphthopyrans (also known as chromenes)

#### Spiropyrans

Photochromic spiropyrans have been receiving considerable interest in recent years, because they can be readily synthesized and photo chromed to deep colors that bleach at useful rates.

Colorless form of the spiropyran has the ability undergo a molecular rearrangement in which the pyran ring opens and generate a colored photomerocyanine colorant, thus they show photo chromatic properties (*Figure 3*). The color intensity of the system is dictated by a dynamic equilibrium

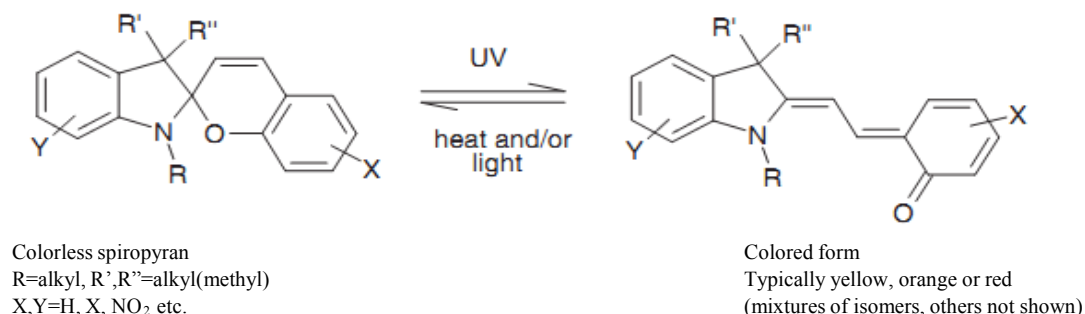


FIGURE 3. Photocromism of spiropyrans [5].

#### Spirooxazines

Spirooxazine colorants are similar to spiropyrans in terms of their molecular structure and the mechanism behind their photochromism but exhibit lower orders of magnitude of fatigues [7]. Like Spiroanthopyrans, spirooxazines changes from colorless or pale yellow to red, purple or blue when exposed to UV radiation (*Figure 4*). Photocolorability of all compounds are assured due to their large molar absorption coefficients, high reaction yields and relatively slow bleaching kinetics [8]. The application of spirooxazines as disperse dyes on nylon, polyester and acrylics has been studied by S M R Billah et al. [9]. They found that the intensity of the photochromic effect produced can be increased after subjecting the dyeing to a mild washing treatment. This may be due to the fact that aqueous alkaline surfactant treatment results in enhanced dye migration, colorant fiber

interactions and disaggregation of the colorant within the fabric which provides more favorable conditions for conversion to the merocyanine form. In another approach, they dyed the textile substrates like polyester, nylon and acrylic with spirooxazine disperse dyes and found that the photochromic textile substrates show much higher photochromic response when wet with selected organic solvents than dried fabric [10]. Another study done by Anna F Little et al. [11] described that ultraviolet reflecting properties of cotton give a higher level of photo coloration than polyester and degree of photo coloration is influenced by colorant concentration and the UV irradiation wavelength profile. In the colorants studied they found that spirooxazines showed slightly faster color development and fade much more rapidly than the naphthopyrans, and the latter show a residual color after fading (*Figure 5*).

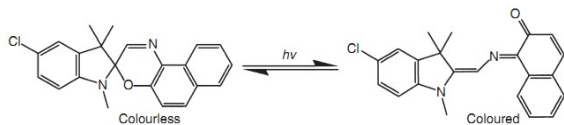


FIGURE 4. Photochromism of spirooxazines [7].

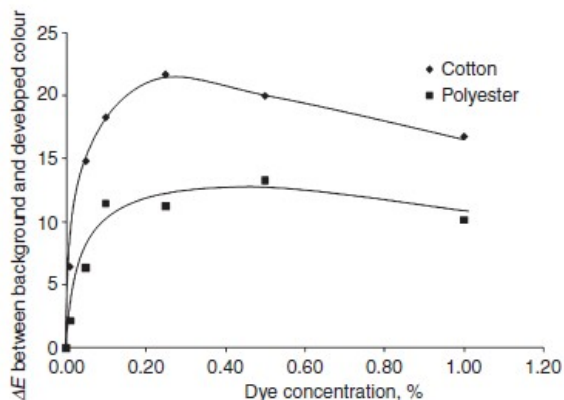


FIGURE 5. Effect of colorant concentration on the developed color strength of spirooxazine on cotton and polyester [11].

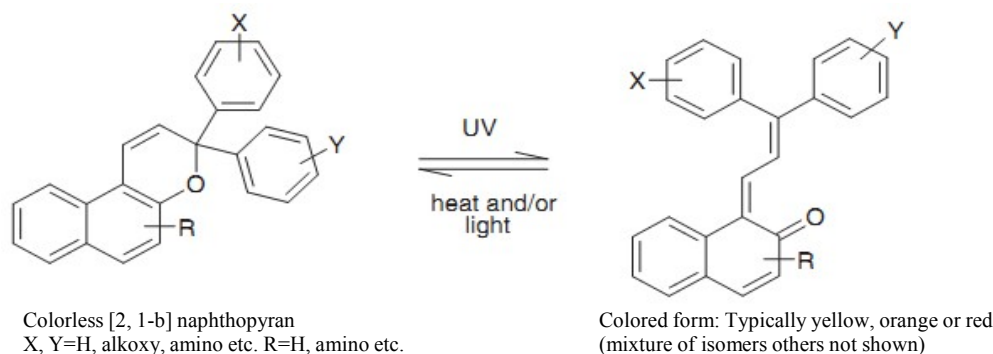


FIGURE 6. Light ring opening of naphthopyrans.

### **P-Type Photochromic Dyes**

As mentioned earlier, P-type photochromic colorants have received increasing attention over the past decade as a consequence of industry and academia seeking to make new applications based on photochromism a commercial reality. These technologies rely on controlled light-driven switching between molecular states [12], which is a mode of action that, by definition, is not possible with T-types. Consequently, there is great interest in finding optical equivalents to electronic components, such as switches and logic gates, based on P-type colorants [13].

### **Naphthopyrans**

Commercially Naphthopyrans are the most important class of photochromic molecule. Similar to spiropyrans and spirooxazines groups, their photochromism depends on light-induced ring opening (Figure 6). However, due to their flexible colorant chemistry, many different types of functional groups can be introduced cost-effectively, which facilitates a more extensive color gamut that spans across the visible spectrum from yellows through to oranges, reds, purples and blues. Like other known classes of photochromic colorants, commercial naphthopyrans generally have good stability properties and their photochromism is less sensitive to temperature than spirooxazines. [1].

Optically-switchable molecules have also formed part of the drive to develop next-generation memory technologies because they can in theory offer much greater data storage densities than existing systems [14]. For instance, numerous novel materials of interest in information technology have been created by covalently linking P-type colorants to non-photochromic systems so that the properties of the latter, such as fluorescence, can be photo-regulated [15-16]. P-type photochromic colorants are mainly used in textile application.

## **Methods of Application of Photochromic Colorants**

### **Direct Coloration**

Billah et al. [11] optimized the procedure for direct coloration of textile using photochromic colorants. According to the procedure, amount of colorants and auxiliaries were taken on the basis of fabric weight (2-3% owf). First the aqueous dispersion of the colorant was prepared by milling the colorants with a dispersing agent and ceramic balls (250 g) in rotating honey jars for 18 h. 1% aqueous acetic acid was used to adjust the pH to 5.5. The dyeing was started at 40°C temperature, increased to 60°C at 2°C/min gradient and continued for 10 min at this temperature (Figure 7). Temperature was further raised to 90°C at 1°C/min and the material run for one hour. Exhausted bath was drained after reducing the temperature to 40°C and the sample washed with cold water [10].

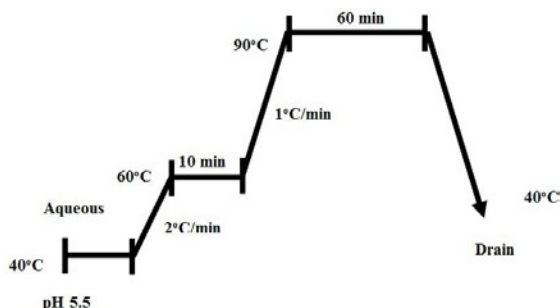


FIGURE 7. Schematic diagram of direct coloration method.

### **Exhaust Method**

Aldib et al. [17] described the application of commercial photochromic colorants as disperse dyes to dye polyester by exhaust dyeing. According to this method, appropriate amount (owf) of photochromic colorant is dissolved in a minimum volume of acetone and then this solution is added to the aqueous dye bath solution containing dispersing agent (1% owf). Acetic acid is added to adjust the pH to 4.5. Weakly acidic condition is normally used in traditional disperse dyeing of polyester, to minimize degradation of colorants by hydrolysis or reduction [18]. Then mixture is boiled for 5–10 min to evaporate the acetone from the dye bath before inserting the fabric. The fabric is introduced in the dye bath and dye bath volume adjusted to give a liquor ratio of 50:1. Dyeing is carried out by raising the temperature to 120°C and maintaining for 45 min. Dyed fabric is given a cold water rinse, followed by reduction clearing at 70°C for 20 min using sodium hydroxide (2 g/l), sodium dithionite (2 g/l) and a nonionic surfactant (1 g/l), at a liquor ratio of 30:1. Then the sample is rinsed with water,

washed with a queous solution of a nonionic surfactant (1 g/l) for a few minutes, rinsed again and then air-dried [17].

### **Continuous Method**

For continuous application of photochromic colorants on cotton fabric, first a small amount of dye is dissolved in acetone and stirred vigorously. The solution is then added drop wise to a binder formulation and mixed again vigorously. The dye solution is applied to the fabric using a padder under appropriate pressure. The fabric is dried at 80°C for 2 minutes in hot air, followed by curing at 140°C for 3 minutes again in a hot air oven or stenter [19].

### **Screen Printing of Photochromic Colorants**

#### **As a Pigment**

Photochromic colorants can also be applied by screen printing as a pigment. Anna et. al. [19] has described the screen printing of photochromic colorants on textile fabric. To use photochromic colorants as a pigment, it is dissolved in acetone and solution is added drop wise into a binder and thickener formulation. This formulation is referred to as printing paste of 0.05% w/w, representing the concentration of the colorant in the print paste. Then using a plain mesh print screen, printing is carried out, printed sample dried and cured at 140°C for 5 min in a hot air oven.

#### **As Disperse Dyes**

To use photochromic colorants as a disperse dye, first a colorant dispersion is prepared by mixing a photochromic colorant, an oil-based low foam wetting agent, a dispersing agent based on the disodium salt of a naphthalene sulphonic acid/formaldehyde condensate and water and milling for 30 min on a roller mill by using ceramic balls in a glass jar. A thickener solution is formulated using sodium alginate and water. The colorant dispersion is then mixed with the thickener solution to give a required colorant concentration in the printing paste. The fabric is printed, dried and cured at 140°C for five min. After fixation, reduction clearing is carried out, printed sample rinsed, washed with non-ionic detergent solution (1 g /l) for five min, rinsed again and dried in an oven at 60°C [11].

### **Surface Coating with Photochromic Colorants**

Surface coating of textiles with Photochromic colorants is also possible. Various fabrics like polyamide, polyester etc. can be coated with different coating systems like polyurethane (PU), polyacrylate (PA) and a Sol-Gel system. As photochromic colorants are not soluble in water, they must be solved in a first step in small



amounts of a solvent like acetone or methyl alcohol. The solved colorant is then mixed in the coating system and coating formulation applied to the fabric. The color effects depend on the fabric, the coating material and the amount of the photochromic colorant (*Figure 8*).

Good color effects can be obtained by small amount of photochromic colorant (<1%). The minimal amount depends on the dyestuff [18].

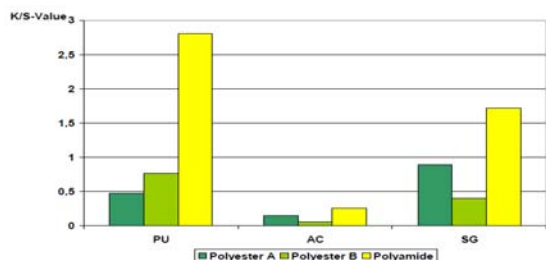


FIGURE 8. Photochromic activities (k/s-values) of three coatings (polyurethane, polyacrylate, sol-gel) on three fabrics (polyester a and b, polyamide).

### Color Measurement of Photochromic Textiles Using Spectrophotometer

Due to the dynamic color changing properties of photochromic colorants, it presents significant challenges for assessment using traditional color measurement instrumentation. For the measurement of color yield of photochromic textile materials, it is necessary to carefully control several experimental factors, including temperature (because of its effect on the thermal reversion of the photochromic reaction) and the time interval between UV irradiation of the sample and measurement. A F Little et al. [19] developed methodologies to assess photochromic textile samples using independent UV irradiation in combination with a traditional color measurement system. They used traditional spectrophotometer along with a UV source with an emission maximum at 365 nm for sample irradiation. Samples were mounted at a distance of 4.5 cm below the horizontal UV source, which was contained in a cabinet and controlled temperature in the laboratory was maintained by localized air heating system. They optimized color measurement method, using the small aperture, specular included and UV excluded a sample temperature of 24°C and a time of 3s between irradiation and measurement. As can be seen in *Figure 9*, the color gradually fades with time.

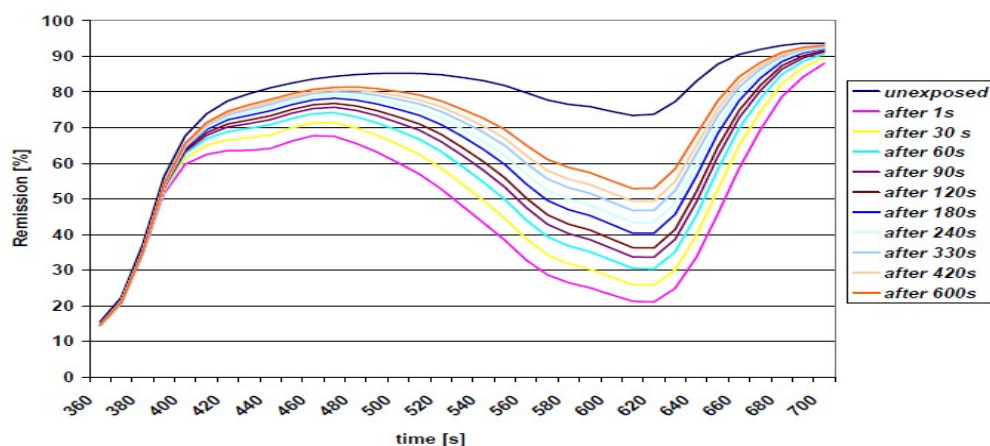


FIGURE 9. Bleaching of a photochromic fabric (polyamide with polyurethane coating, niso) (color measurement in 30 s steps).

### Intensity Measurement

Intensity of the light emitted from a fabric coated with a photochromic colorants can be measured by Illuminometer (expressed as 'lux'). Illuminometer contains a photon detector which is connected to a selenium chip. The specimen is kept on a photon detector, which absorb the photon emitted by the specimen. A current starts flowing due to the absorption of photon since selenium is a

semiconductor. The instrument is calibrated in such a way that this current value is converted to 'lux' value, which is shown on electric display [20].

### Wash Fastness Test of Photochromic Colorants

Wash fastness tests can be carried out according to any standard mild laundering method (BS1006:1990 CO6) [21] using a wash wheel. Due

to the dynamic color change properties of photochromic colorants, traditional assessment methods using grey-scale standards are not appropriate for determination of wash fastness ratings. Hence, wash fastness behavior of a test sample is measured by a comparative study of the photochromic color build-up before and after the wash fastness tests. This can be expressed as the color difference ( $\Delta E$ ) between the background (before UV irradiation) and developed colors after 1 min exposure to UVA irradiation [22].

The level of photo coloration developed by UV irradiation varies with colorant classes. In one study [22], three Naphthooxazine type of photochromic colorants [Green(1), Purple(2), Red(3)] type and two naphthopyran [Red(4), Yellow(5)] were applied on cotton and polyester fabrics by screen printing and repeated wash fastness tests were carried out. It was found that, in the case of the selected spirooxazine colorants, the degree of photo coloration increased with initial washing and then decreased with subsequent washings (Figure 10). In the case of the naphthopyrans, the degree of photo coloration decreased progressively with washing. It was proposed that the polymeric binder matrix loosens around the colorant molecules with initial washing, facilitating conversion between colorless and colored forms of the spirooxazines, which are more rigid in structure than the naphthopyrans. The wash fastness properties of the photochromic prints are associated with the binder rather than the colorants. This appears to be reasonable for applications that do not require frequent aggressive washing.

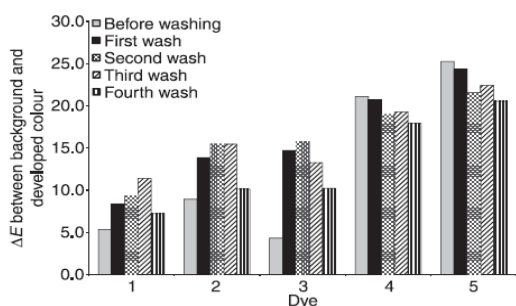


FIGURE 10. The effect of repeated washings on the degree of photo coloration of colorants 1–5 printed on cotton [22].

### Photostability of Photochromic Colorants

The photostability of colorants in application, usually referred to as light fastness in the case of traditional dyes, is generally assessed by exposing the sample to an accelerated fading instrument, such as the Xenotest fadometer. In the case of normal dyes, there is a well-known standard procedure for measurement of light fastness and the

degree of fading is generally assessed against the Blue Wool standards. This procedure is evidently inappropriate for photochromic samples due to their dynamic color change properties. That's why the degree of photo coloration is expressed as the color difference ( $\Delta E$ ) between the background (before UV irradiation) and developed colors after 1 min exposure to UVA irradiation. But in order to provide a meaningful comparison of different photochromic colorants, normalized values need to be calculated. This normalization process involves converting the degree of photo coloration after a particular time of exposure on the Xenotest instrument to a fraction of the initial degree of photo coloration, i.e.  $\Delta E / \Delta E_0$ , where  $\Delta E_0$  is the original color difference between the background and developed color for a particular colorant before exposure on the Xenotest [22]. Figure 11 shows the photostability of the above five colorants and it is clear that all five show poor photostability. Almost 90 % color is lost in less than 10 hours of exposure.

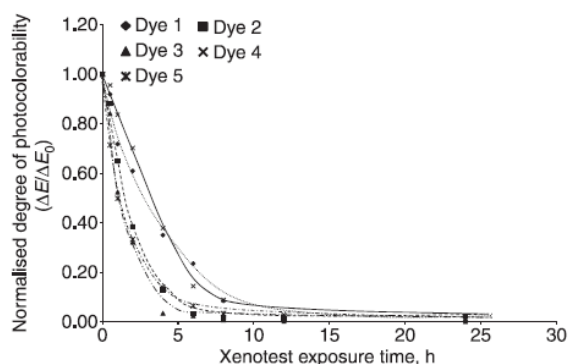


FIGURE 11. Normalized photostability curves for photochromic colorants (1–5) printed on cotton.

The photochromic colorants, when applied alone to the fabric show limited photostability and in some cases, incorporation of UV absorbers improves the photostability of the colorants. But the effect is specific to particular UV absorber/colorant combinations. Because of competition for the UV light between the colorant and the UV absorber, their use leads to a consistent reduction in the degree of photo coloration of the colorant. However, the incorporation of hindered amine light stabilizers (HALS), which are free radical scavengers, consistently and significantly enhanced the photostability of the colorants [22].

### Half-Life of Photochromic Colorants

Response time to fading of photochromic colorants is usually determined by using half-life ( $T_{1/2}$ ). Half-life time is the time in which the color effect is halved. The rate at which Photochromic colorants

fade back to their original state is determined by its half-life ( $T_{1/2}$ ). The half-life time is often short (< 90 seconds). So in order to measure the half-life the color measurement is repeated after 10 second intervals or the minimum time required for repeat measurement [18].

#### **Application Areas for Photochromic Colorants**

Photochromic colorants have been developed for use in both textiles and non-textile applications. On textiles they are basically used to produce novel coloration effects in many applications like T-shirts, handbags and caps. For example, there is this nightwear, which remains white at night but acquires colors like purple, blue, green etc. in daylight [1]. A California-based company named Solar Active International has started manufacturing a variety of photochromic products. It produces photo-colorable textured yarns for knitting, weaving and embroidery [23]. Embroidery threads of polypropylene are made by mass pigmentation method using different photochromic compounds in the molten state. In the absence of UV radiation/indoors, the thread/fabric appears white but in rainy or sunny conditions outdoors, the UV radiation penetrates the thread, which activates the photochromic compounds and causes the thread to be photo colored to specific colors. Within about one and a half minutes the threads returns to original colorless state when UV- source is removed. Since the photochromic material is incorporated in the polypropylene by mass pigmentation, it becomes a part of the fiber leading to a durable photochromic property [24].

Photochromic colorants are now used in the development of camouflage patterns for military protective clothing. This pattern can change from one color to another upon absorption of sunlight to mimic surrounding environment [25-27].

UV-light sensitive curtain has been developed by the Swedish Interactive Institute using photochromic colorants sensitive to UV-radiation. Various parts of the curtain are dynamically illuminated by a computer-controlled UV lamp, creating a dynamic textile pattern which is driven by a computer controlled digitized pattern [28].

A Taiwan based company named Super textile Corp, markets special types of photochromatic fabric. A special microencapsulated colorant technology is used to incorporate photochromic colorants in these high-tech photochromic fabrics which change colors upon exposure to sunlight or UV radiation. Due to the non-hazardous nature of these colors, they can

be used in general applications like knapsacks, dolls etc. [29].

Photochromism has also attracted considerable interest in non-textile applications including ophthalmics like spectacles which become sunglasses when activated by sunlight, information recording materials, surface coating application, dye lasers and other applications [3-4].

#### **The Effect of Temperature on Photochromism**

Temperature plays a role depending upon the type of reversibility (T or P systems) of photochromic colorants; temperature has a significant effect on the photochromic behavior of these colorants. Fausto Ortica reviewed a series of thermo-reversible photochromic molecules belonging to the classes of spirooxazines, arylethenes and chromenes and found that the rate of the thermal bleaching reaction increases with the increase in temperature, thus decreasing light-stimulated coloration. For some nitro-substituted chromenes, it was observed that temperature variations influenced the colorability by substituting the molecular structure. Temperature also significantly influences the quantum yields of photobleaching. Generally, the quantum yield for discoloration decreases with decreasing temperature, due to a barrier (of the order of a few kJ/mol) to the ring opening reaction [30].

#### **Problems Associated with Application of Photochromic Colorants on Textiles**

Though photochromatic colorants have opened a whole new world of opportunities for producing novel effects in apparels, they haven't achieved commercial success. The major technical reasons for this state of affairs are the difficulties encountered when applying industrial photochromic colorants by traditional textile coloration techniques. Often, such colorants are supplied in the form of slurry of microencapsulated pigments in a liquid which is difficult to dilute with water or even common organic solvents. This makes their application on textiles difficult with conventional exhaust or pad-dry-cure techniques. Also they have poor performance in terms of wash and light fastness.

Due to the dynamic color changing properties of photochromatic colorants, their assessment using traditional color measurement instrumentation is challenging. They require to be simultaneously irradiated with UV light during color measurement which requires specialized instrumentation.



In exhaustion dyeing of hydrophobic polymers such as polyester and nylon, several problems may arise with the use of conventional T-type colorants as these colorants are relatively delicate molecules that do not respond well to exhaust dyeing conditions. When compared with conventional disperse dyes, the relative bulk of the colorants does not diffuse into the fiber.

Several other factors also affect the properties of photochromic colorants on textiles. Degree of photochromism reduces with increasing temperatures as a result of thermal reverse reaction. Aggressive washing may cause loosen the pigment particles from polymeric binder. Their high cost is also a hindrance.

However, for wider application and commercial viability, it appears that, tailoring of colorant molecule structure and/or coloration process design will be necessary to give cost efficient, durable effects of acceptable intensities and kinetics with coloration by conventional dyeing techniques.

### Thermochromism

Thermochromism can be defined as the reversible change in the color of a compound with temperature [31]. This thermochromic color change is quite noticeable, often dramatic and occurs over a small temperature interval. Thermochromism is described below in *Figure 12*.

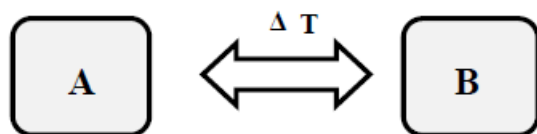


FIGURE 12. Reversible change in color from species A to species B.

Where A is a colored or colorless species and B is another colorless or colored species. From the beginning of 1970, the mechanisms of thermochromism have been investigated and today it is well established. Different mechanisms are applicable depending upon the type of thermochromic material. The following four types of materials have been found to exhibit thermochromism [32]:

1. Organic compounds
2. Inorganic compounds
3. Polymers
4. Sol-gels.

### Organic Thermochromic Systems

Organic thermochromic systems are 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, keto-enol, lactim-lactam, stereoisomers or between different crystal structures. The mechanism can be divided into three major categories:

1. Change in crystal structure
2. Stereoisomerism
3. Molecular rearrangement

In case of organic compounds, the occurrence of thermochromic color change is sharp and it is easy to control the temperature. The liquid crystal and the molecular rearrangement are the two types of thermochromic systems that have been successfully applied on textiles [1].

### Liquid Crystals

Certain organic materials when passing from crystalline solid to isotropic liquid state can form stable intermediate phases (mesophases). Transitions between phases can be brought either about by the influence of temperature (thermotropic mesomorphism) or solvent (lyotropic mesomorphism) respectively [33]. The cholesteric (chiral nematic) are the most important types of liquid crystals (*Figure 13*) for thermochromic systems, where adjacent molecules are so arranged that they form helices.

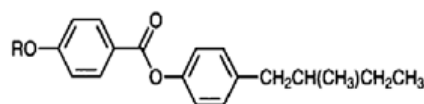


FIGURE 13. Chiral molecules that form cholesteric mesophases.

Temperature can influence the reflection of light by liquid crystals by reflecting the structure of helices. The refractive index of the liquid crystal and the pitch of the helical arrangement of the molecules govern the wavelength of the reflected light (*Figure 14*). When temperature varies, pitch length also varies. As a result wavelength of the reflected light is altered causing progressive change in color spectrum [34]. The liquid crystal material has to be microencapsulated, 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. Although subtle and highly

sensitive color effects can be achieved by this method, liquid crystals have limited textile end-uses due to their high cost and low color density [32].

### **Stereoisomerism**

Thermochromism arising from variations in stereoisomers is known as stereoisomerism, which is mostly associated with ethylenes. As the temperature is increased, the molecules of these compounds 'switch' between different stereoisomers. As a 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. Consequently, they are unsuitable as thermochromic colorants for textiles [32].

### **Molecular Rearrangement**

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 (i.e., color change). Such type of molecular rearrangement can be affected by variation in temperature or by a change in polarity of the solvent and/or the pH of the system [35]. The temperature-dependence of the acid-base equilibrium means that pH sensitivity can result in thermochromic behavior. The molecular rearrangement of spiro lactone dyes can be illustrated using crystal violet lactone as an example (*Figure 14*).

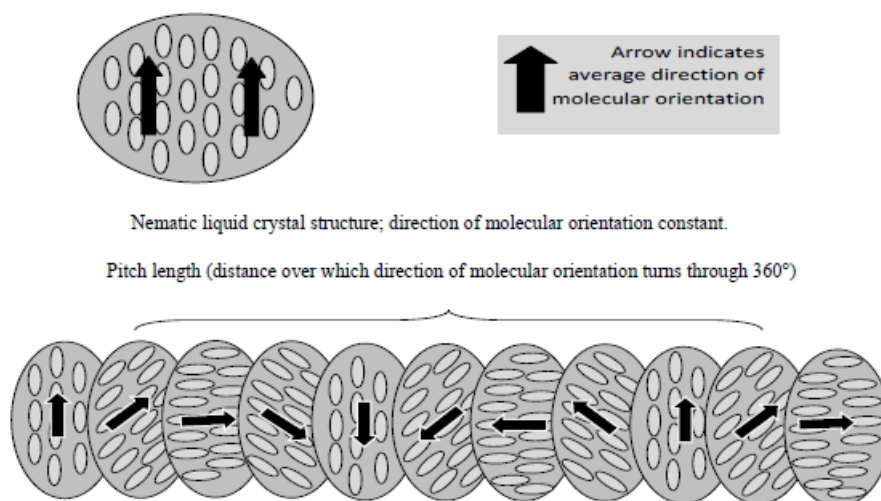


FIGURE 14. Cholesteric (chiral nematic) liquid crystal structure; direction of molecular orientation gradually changes between layers [36].

The equilibrium of Crystal violet lactone is pH rather than temperature-dependent. As a result it does not exhibit thermochromism. At pH values above 4, crystal violet lactone (A) itself is colorless and acts as a dye precursor. Below this pH level, it is rearranges itself to produce compound (B), which is violet. If the pH is then raised above 4 again, the lactone is formed again and the violet color disappears (*Figure 15*).

### **Inorganic Thermochromic Systems**

Thermochromic behavior is exhibited in solids or in solution by many metals and inorganic compounds also [37-40]. It has been suggested [41] that such thermochromic behavior of this kind arises from one of the following mechanisms:

- Phase transitions;
- Changes in ligand geometry;
- Equilibria between different molecular structures;
- Changes in the number of solvent molecules in the co-ordination sphere (e.g. dehydration)

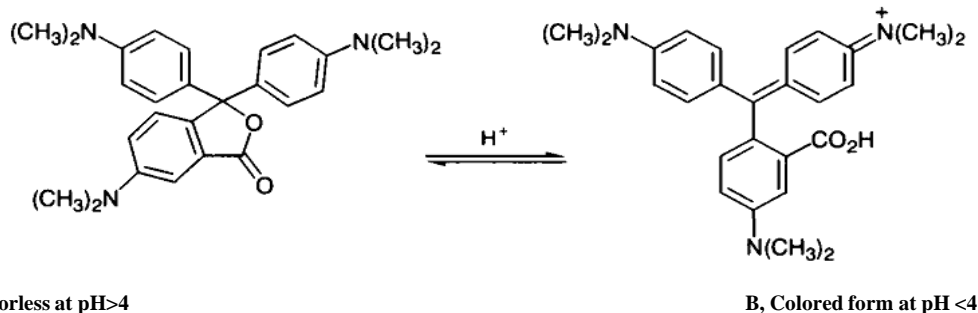


FIGURE 15. Dependency of molecular arrangement of crystal violet lactone on pH.

In textiles, inorganic thermochromic systems have not been used much as the change in color occurs at high temperature or in solution. Also the change in color is irreversible. For these to be applicable on textiles, they should be reversible, solid (or encapsulated) system that is suitable for dyeing and printing application. Also it should exhibit noticeable color change over a small temperature range, typically from low ambient temperatures to body temperature for apparel [32]. In organic systems find their application in crayons that provide a warning of the development of heat spots, in heat-indicating paints and and/or a permanent record of the thermal history of an object [32].

### Mechanism of Color Development

In reversible thermochromic systems a colorless dye precursor and a color developer are both dissolved in a hydrophobic, non-volatile organic solvent and the solution is then encapsulated so that all three components are held within a single closed system. On heating, the organic solvent melts, which leads either to color development or color loss. On cooling, the solvent solidifies and the system reverts to its original color [42].

### The Microencapsulation of Thermochromic Systems

Both thermochromic liquid crystals and thermochromic organic colorant mixtures cannot be used directly for coloration as they don't have any affinity for the substrates. Both require microencapsulation. Microcapsules have been defined as (spherical) particles, composed of an excipient polymer matrix (or wall/coating), referred to as shell and an incipient active component, known as core material and typical particle sizes are in the range 50 nm to approximately 2 μm.

Microencapsulation has some additional advantage; it protects these sensitive coloring agents from the external environment as well as it allows several

thermochromic colorants to be combined together, resulting in several narrow color ranges [43]. Among different processes for microencapsulation, physiochemical and chemical processes such as coacervation and interfacial polymerisation have been used for microencapsulation of photochromic and thermochromic colorants. Coacervation is the process of molecular aggregation (or phase separation) that occurs due to the partial desolvation of fully solvated macromolecules. Complex coacervation occurs in aqueous medium and is used to encapsulate water immiscible liquid or solids. In the coacervation of gelatin with gum arabic, the water insoluble core materials (the thermochromic mixture) is dispersed at required size in warm gelatin and then gum arabic and water is added and pH adjusted (<9). These two oppositely charged (gelatin & gum arabic) colloids form colloid-rich phase, which condenses around these droplets and encapsulates them [32].

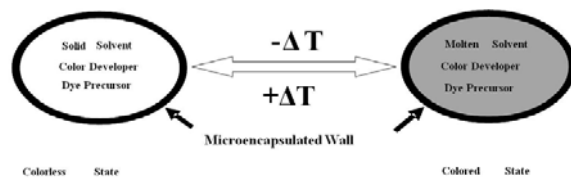


FIGURE 16. Thermochromism by microencapsulation.

The final choice for microencapsulation depends on the application and factors such as particle size, wall thickness, impermeability, thermal stability and compatibility with and adhesion to the surrounding chemicals and the end use [44].

As previously discussed, the color development is exhibited by tri-component, organic hydrophobic solvent, dye precursor, color developers (Figure 16). The organic hydrophobic solvents that have been employed fall into one of the following general types: alcohols, hydrocarbons, esters, ethers, ketones,

fatty acids, amides, thiols, sulphides and disulphides and alcohol-acrylonitrile mixtures.

The types of colorants that have been used in thermochromic compositions are relatively few. They include N-acyl leuco-methylene blue derivatives [BO], fluoran dyes, diarylphthalide compounds, diphenylmethane compounds and spiropyran compounds (Figure 17). Crystal violet lactone analogues (diarylphthalide compounds) and fluoran dyes are the dye types most commonly quoted in patent literature [32]. A wide range of compounds have been employed as color developers in these published compositions (Figure 18). In patents these substances or 'catalysts' are often referred to as 'electron acceptors', although how they function in such a respect is far from clear. It is preferable to consider them in most cases as 'proton donors', as they generally possess an acidic proton that is capable of direct transfer to the dye precursor or of strong Hydrogen bonding to the colored form of the dye.

A large number of patents discuss the use of phenol derivatives, specifically bisphenol A and bisphenol B. However, more recent work describes the use of 1,2,3-triazoles, such as 1,2,3-benzotriazole, dibenzotriazole, thioureas, saccharin and derivatives, halohydrins boric acid and derivatives, guanidme derivatives (for example, phenyl diguanide), as well as 4-hydroxy coumarin derivatives. These compounds have been employed in an attempt to improve the light fastness of thermochromic systems, as phenolic compounds are known to discolor rapidly on exposure to light [45-47].

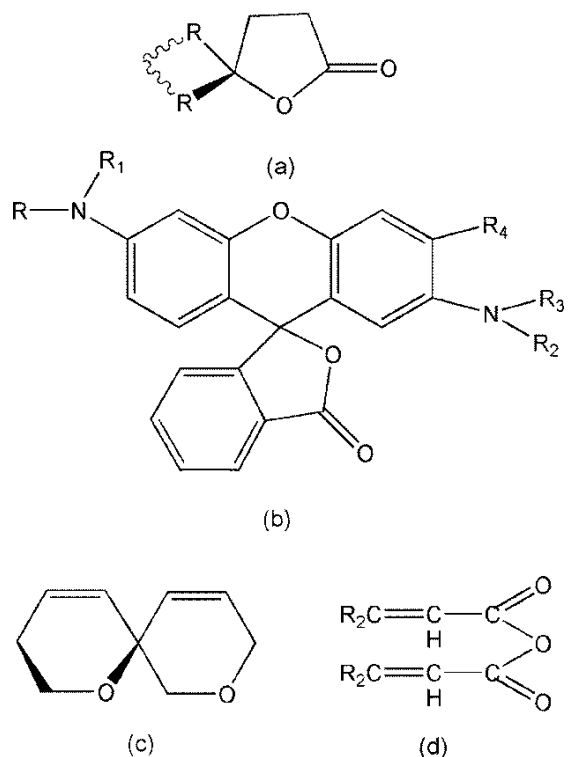


FIGURE 17. Typical leuco dyes include (a) spirolactones, (b) fluorans, (c) spiropyran, and (d) fulgides.

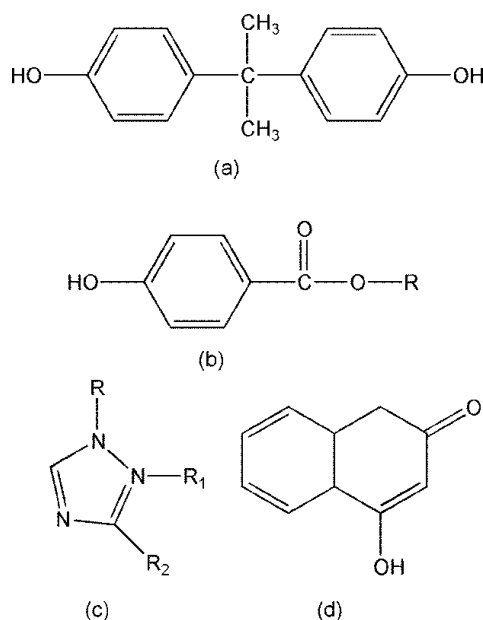


FIGURE 18. Color developers include weak acids such as (a) bisphenols (b) alkoxy-p-hydroxybenzoates, (c) 1,2,3-triazoles, and (d) 4-hydroxycoumarin.

## Exhaust Methods

### **Recipe**

Cationic Agent: 6-8% (owf)  
Thermochromic Pigment: 8-15% (owf)  
Non-ionic dispersing levelling agent: 10-15% (owf)  
Acrylic soft binder: 10-15% (owf)  
M:L ratio: 1:30  
Temperature: 70°C Time: 30 min

### **Procedure**

- Bleached fabric is taken. Water is taken to maintain a liquor ratio of 1:20.
- 6-8% owg of cationic agent is added to give the fiber a very strong cationic charge.
- Temperature is raised to 70°C maintained for 15 min at this temperature.
- Then bath is drained & fabric rinsed well with cold water. If needed, rinsing may be repeated.
- Bath is drained again and fresh water added in a ratio of 1:20 and temperature raised to 70°C.
- 8-15% owg thermochromic pigments are added to the dye bath & temperature maintained at 70°C for 10 minutes.
- 10-15% owg of Anionic or Non-Ionic dispersing levelling agent is added to the dye bath. The bath is maintained at 70°C for 5 minutes.
- 10-15% owg of Acrylic Binder is added to the dyeing bath and temperature maintained at 70°C for 10 minutes.
- Finally bath is drained and the fabric dried (Figure 19) [13].

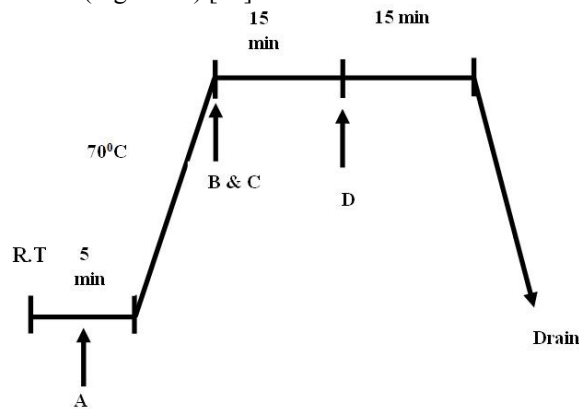


FIGURE 19. Schematic diagram of exhaust dyeing process (with thermochromic pigment).

(A=Cationic agent, B=Thermochromic Pigment, C=Anionic /Non- Ionic dispersing levelling agent, D=Acrylic Binder)

The melting temperature of the solvent controls the temperature at which decolorization/colorization of thermochromic colorant occur. In the literature, several definitions are used to describe this temperature, such as activation temperature [42], switching [33], or decolorization [48]. Theoretically, by varying the solvent and the color developer, both the onset temperature and the direction of change in color can be predetermined [42].

### Continuous Method

**Recipe (For 100 ml solution)** Cationic Agent: 10-15ml Thermochromic Pigment: 50 ml  
Non-ionic dispersing levelling agent: 10-15%  
Acrylic soft binder: 20%  
Temperature: Room Temp.

### **Procedure**

- Pad at room Temperature
- Dry at 80°C for 3min.
- Cure at 140°C for 2-3 min

## Printing with Thermochromic Colorants

### **Recipe**

Thermochromic colorants: 20 parts  
Emulsion thickener: 76 parts  
Acrylic binder: 4 parts

### **Mass Coloration**

In the context of their application to polymers, the thermochromic microcapsules can be added to a polymeric system during polymerization, as exemplified by the polymerization of polyurethane foams and plastics [49], or during the spinning of fibers [50]. One patent even discusses the formation of a thermochromic core-sheath composite fiber [51] in which the core fiber consists of a thermoplastic resin that contains the thermochromic microcapsules. In systems such as these the microcapsules act only as diluents, although the manufacture of polymeric thermochromic compounds has been described [32].

## Color Measurement of Thermochromic Colorant by Using Spectrophotometer

R M Christie et al. developed an instrumental set up for the measurement of color yield of thermochromic textiles using traditional spectrophotometer [51]. It consisted of a hot-stage and a temperature controller, held against the aperture of a reflectance spectrophotometer. The calibration of the hot-stage was carried out using a K15 liquid crystal with a clearing point of  $35.3 \pm 0.1^\circ\text{C}$ . The instrument was set using small aperture, specular reflectance and UV included options. After temperature stabilization, color measurement was



carried out for illuminant D65 and 10° observer. L\*, a\* and b\* values were computed using average of two measurements. Figure 20 illustrates the absorption spectral changes in spiroxazine 7 with increasing temperature [53].

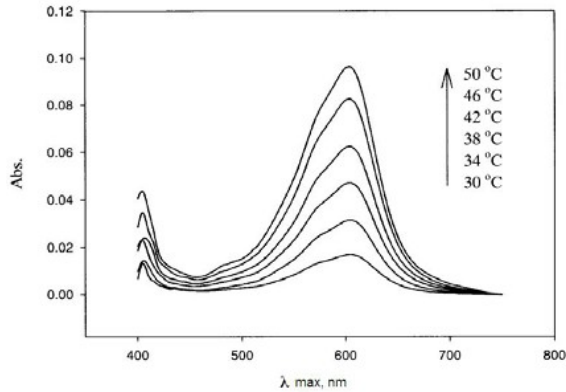


FIGURE 20. Variation in optical absorbance of spiroxazine 7 solution in chloroform with increasing temperature [53].

Figure 21 shows the reflectance spectra of TCP 1001 (a thermochromic ink) applied on black polyester and recorded over the temperature range 26–47°C [54]. The gradual shifting of reflectance maxima (characterizing the color) with temperature is clearly seen.

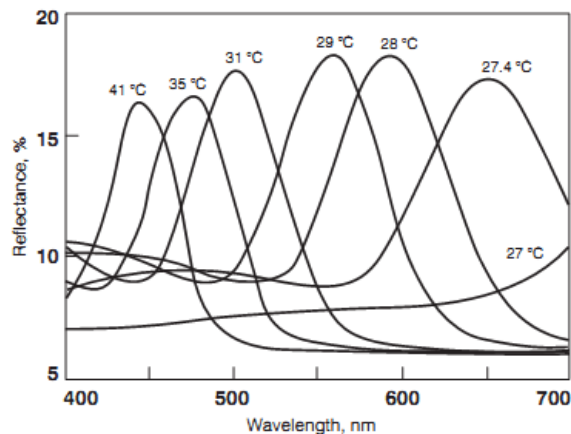


FIGURE 21. Reflectance of tcp 1001 on black polyester at selected temperatures [54].

The figure shows reflected wavelength bands typical of a chiral nematic liquid crystal which are centered about wavelength  $\lambda_o$  as follows:

$$\Delta\lambda_o = np \quad (1)$$

Where p is the helical pitch length and n the average refractive index. The bandwidth is given by:

$$\Delta\lambda = p\Delta n \quad (2)$$

where  $\Delta n$  is the difference between the refractive indices parallel to the liquid crystal direction and at right angles to it [55].

#### **Wash Fastness Test of Thermochromic Colorants**

Wash fastness tests can be carried out according to any standard mild laundering (BS1006:1990 CO6) [21] method using a Roaches Washtec P. Like photochromic colorants, wash fastness assessment using grey-scale standard is not appropriate in case of photochromic colorants. Hence, wash fastness behavior of a test sample is measured by a comparative study of the thermochromic color build-up before and after the wash fastness test [22].

#### **Application of Thermochromic Colorants**

Researchers from both colorant manufacturers and academic organizations have been working on dyes and pigments to develop fast coloring materials that are physically unresponsive and chemically inert when applied to a substrate [56]. Thermochromic organic colorants are successfully applied in both textile and non-textile application for producing novel coloration effects. Like photochromic colorant, thermochromic colorants are applied to textile material like in T-shirts and caps for producing aesthetic and functional design, which are known as “smart materials”. A change in surrounding temperature or heat from direct sunlight can readily cause reversible change in color [57].

Thermochromic colorants are now also used in the manufacture of camouflage patterns for military protective clothing. This pattern can change from colorless to color form with the influence of environmental heat to mimic with surrounding environment [25, 58-59].

The range of non-textile applications incorporating thermochromic materials are diverse and include thermometers and temperature indicators which are used for special purposes like non-destructive testing and security printing. These devices can indicate the suitable temperature for different application, e.g., proper temperature for storage or serving [1]. Due to some limitations, thermochromic materials used in textile sector are not properly exploited and lag

behinds other sectors. The main drawback is that the activation temperature of the majority of these materials lies typically in the range of 10°–20°C which is well above the room temperature for cold countries and below the room temperature for hot countries, so thermochromic effects on textiles is not produced properly.

But, by using thermochromic materials of liquid crystalline type, it is possible to change the appearance of the color over narrow temperature ranges of 5–15°C and detect any variation in temperature, < 1°C [56]. One Japanese company named Pilot Ink Co. is a leading company working on thermochromic materials for many years and has filed a significant number of patents. It has developed especially thermo responsive materials for different objects like toys etc. By using the three primary colors, virtually any hue from white to black can be produced. The thermo sensitivity remains functional at wide temperature range, from –10°C to 60°C, covering almost all situations [57].

#### **Thermochromic Cellulose Fibers**

Marcin Rubacha et al. developed a method to obtain thermochromic cellulose fiber [60]. They incorporated thermochromic pigments in cellulose using Lyocell process. In this method fibers are spun from a concentrated solution of cellulose in N-methylmorpholine N-oxide (NMMO) by using dry-jet-wet spinning method. The features of the fibers thus obtained were evaluated for possible practical use. 1-10 wt% Chromicolor AQ-INK, Magenta type 27 pigmentation was used as a thermochromic modifier in this study.

Quite interestingly, a patent reveals a method to change the color of a textile at will using electricity [61]. It describes manufacture of woven or embroidered textiles by using conductive/resistive and non-conductive fibers. These textiles are printed using thermochromic colorants. When electrical power is supplied, thermochromic heating causes the resistive fibers to heat up and raise the temperature of the textile. When the temperature of the textile increases beyond the activation temperature of the thermochromic colorant, the color change takes place. Thus an electronically controllable, visually dynamic textile material is created.

#### **Problems Associated with Application of Thermochromic Colorants on Textiles**

The fundamental problem encountered in the application of thermochromic microcapsules to both synthetic and natural fibers is that the encapsulated

thermochromic system must be impermeable to and insoluble in water. Printing techniques have been developed in which the microcapsules are used as conventional pigments and are thus applied in a standard acrylic printing paste [62]. Thermochromic materials are not capable of directly dyeing the fiber because of their lack of affinity with the fiber [63]. Several patents have also been published that describe the coating of synthetic fibers with polymeric binders that contain thermochromic microcapsules [64-65] however, both techniques lead to low color strength and often have an adverse effect on the handle of the fabric. An alternative method has been developed, involving pre-treating cotton with a cationic agent to increase the substantivity of the microcapsules for the fiber and thus secure greater uptake [66-67] even without the use of a binder.

The color strength of thermochromic compositions is generally very low, because only a small amount of colorant is present in the final system. A typical formulation contains only 2% colorant, by mass, prior to encapsulation, and only about 1% in the final product. The problem is accentuated when the capsules are applied onto a fabric in a printing paste, where a concentration of 15-30% of the micro-encapsulated material is recommended [43, 62], leading to a further dilution in color. Consequently, the use of thermochromic encapsulated systems in apparel has been limited to pastel shades.

Another problem associated with textile application is that many commercial formulations exhibit poor fastness properties. It is found in the literature that many color-forming colorants, specifically crystal violet lactone [68-71] and phenol-derived color developers readily undergo photochemical fading, resulting in poor light fastness. Often, these compositions also exhibit poor wash and rub fastness properties, owing to the encapsulated system having a low affinity for the fiber and being poorly adhered to its surface via a printing paste or cationic pre-treatment [32].

It has been also reported that some solid inorganic systems such as mercury iodide double salt exhibit color changes from yellow to orange at 51°C and from red to black at 70°C, respectively [72]. Transition metal systems have also been examined in relation to thermochromic and electrochromic 'smart window-coatings', whose infrared reflectance varies with temperature or with the application of a low voltage electric pulse [38].

## CONCLUSION

An exciting new era is opening in the field of textile materials due to development of innovative yarns, fabrics, functional finishes and coloration systems. These open a whole new world of opportunities and challenges to the user. Thermochromic and photochromic materials occupy a unique place as they are exciting materials, not yet fully explored on textiles and come with associated problems regarding application on textile substrates.

Photochromic/thermochromic colorants occupy a niche position within the coloration industry, the majority of applications in the textile sector limited to fashion, leisure and sports garments. Efforts are on by various stakeholders to widen the application spectrum for these colorants, to improve properties (e.g., light fastness) and simplify application procedures. Japan and USA have developed wide range of thermochromic and photochromic materials but still many innovations are waiting for commercial applications. Considerable volume of scientific study needs to be carried out in different application areas of before large-scale production can become a reality. At present, only two types of thermochromic system, liquid crystal type and the molecular rearrangement type have been commercially successfully applied to textiles and both are based on microencapsulation. Though the color-change phenomena are well understood, the factors influencing the equilibrium between the colored and colorless forms of the colorant as the solvent melts are still a matter of conjecture, and there is a need for further research in this area.

Presently, only a small number of commercial organizations are engaged in the development of improved compositions. Clearly, more study needs to be carried out with respect to the formulation, encapsulation and application of thermochromic and photochromic systems on textiles. This should help to resolve a number of the problems which are inherent in current systems and at present restrict their commercial use. Also the price, availability and temperature range need to improve to make it popular to the end user.

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