NC STATE
College of Textiles
JTATM
Journal of Textile and Apparel,
Technology and Management

Volume 9, Issue 2, Spring2015

Improving Photostability of Thermochromic Colorants with Ultraviolet Absorbers and Hindered Amine Light Stabilizers

Muksit Ahamed Chowdhury[1], B S Butola[2] and Mongala Joshi[3]
[1]Department of Textile Engineering, Ahsanullah University of Science & Technology
Bangladesh.
[2,3]Department of Textile Technology, Indian Institute of Technology, New Delhi
India
muksit.iitd@gmail.com

ABSTRACT

Light fastness of thermochromic colorants, which shows reversible changes in color with temperature, is of great importance for different textile and non-textile application. Light fastness of commercial thermochromic colorants was determined by measuring the color strength (K/S) of cotton fabric dyed with thermochromic colorants at regular intervals after exposure in Xenon Arc Light fastness tester and found to be poor for any application. An attempt to improve the light fastness of thermochromic colorant was made by using two ultraviolet absorbers (UVA) and two Hindered Amine Light Stabilizer (HALS) individually and in combination as additives in dye-bath formulation. UV absorbers showed better performance than HALS in terms of photostabilization. Significant improvement of photostability was observed when UV absorber and HALS were used in combination.

Keywords: Thermochromic colorants, Light fastness, UV absorber, HALS, Photostabilization

---

Introduction

Thermochromic colorants which show reversible color change with temperature, offer significant potential for aesthetic and functional textile design in the area of smart materials which are designed to sense and react to environmental conditions and stimuli. These colorants are microencapsulated, comprising a colorless dye precursor and a color developer, which are both dissolved in a hydrophobic, non-volatile organic solvent so that all three components are held within a single closed system (Figure 1). Microencapsulation helps to protect these sensitive chemicals from external environment. 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 [1-4].

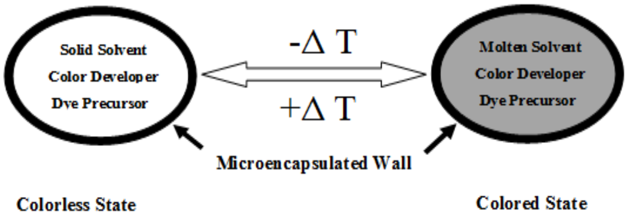

Figure 1. Reversible change in color with temperature,

Thermochromic textiles used in aesthetic or functional applications would require an appropriate lifetime in terms of exposure to light to an extent dependent on the demands of the particular envisaged end use of the material. The light fastness of these colorants is generally not adequate for any application. This paper describes the results of an assessment of photostability of thermochromic colorants. An evaluation of the potential of selected stabilizing additives to enhance photostability is also reported.

It is commonly observed that colors are faded or degraded by prolonged exposure to sunlight. Upon sunlight absorption, the ultraviolet light present in the sunlight excites the electrons in the chromosphere to a higher energy level so that they become more active. Thus, ultraviolet component in the sunlight initiates degradation reaction and these reactions are normally accelerated in moist condition [5]. The mechanism by which dyes undergo photo degradation are thought to be more complex. However, most of the studies suggest that normally three types of mechanisms are involved in degradation of colors in textiles, i.e., photo-oxidation through singlet oxygen, photo-oxidation through superoxide and photo-reduction through radical species [6]. In the first two processes, the light raises the colored molecule to an excited state, i.e., its triplet form as shown in Equation 1. In the first mechanism, the excited triplet form sensitises the oxygen, which further reacts with the colored molecule to degrade it as shown in Set of equations 2. In the second mechanism, an electron from the excited triplet form of the colored molecule transfers to the oxygen to form superoxide which further reacts to decompose the molecule as shown in Set of equations 3. There is less chance of oxidation if the excited triplet form remains for only a short period of time.

$$Dye + h\upsilon \rightarrow \; {}^{3}Dye^{*}$$

Equation 1

$$ {}^{3}Dye^{*} + O_2 \rightarrow Dye + \; {}^{1}O_2$$

$$ {}^{1}\mathrm{O}_2 + Dye \rightarrow Decomposition$$

Set of Equation 2

$$Dye^{*} + \mathrm{O}_2 \rightarrow \mathrm{Dye}^{*-} + \mathrm{O}_2^{-\bullet}$$
$$\mathrm{O}_2^{-\bullet} + Dye \rightarrow Decomposition$$

Set of Equation 3

In the third mechanism, the excited triplet form of the color reacts with a nearby substrate, impurity, etc. to abstract a hydrogen atom which leads to the decomposition of the dye as shown in Set of equations 4.

$$Dye^{*} + RH \rightarrow Hdye^{\bullet} + R^{\bullet}$$
$$\mathrm{Hdye}^{\bullet} + \mathrm{R}^{\bullet} \rightarrow Decomposition$$

Set of Equation 4

UV absorbers are additives used to prevent the photo degradation of polymeric materials by reducing the UV contents in the incident light. UV absorbers basically shield the colorants from UV light by converting the energy from the irradiation into heat and dissipate it through the substrate harmlessly. The major classes of commercial ultraviolet-radiation stabilizers include derivatives of 2 hydroxybenzophenone, 2-(2H-benzotriazol-2-yl)-phenols, phenyl esters, substituted cinnamic acids and nickel chelates.

The application of HALS (mainly 2,2,6,6-tetramethylpiperidine derivatives) as a photo stabilizer are well established and widely used in polymer stabilization. Unlike UV absorber, which basically protect the dye from UV degradation, HALS inhibit degradation by scavenging reactive free radical intermediates formed in the photodegradation process forming transformation products, such as nitroxyl radicals and hydroxylamino ethers. They operate in a cyclic mechanism in which the HALS is regenerated so that the effect is relatively last long [7-10]. By using such materials, the protection can be relatively long-lived [11-12]. Improvements in the light fastness of photochromic, reactive and natural colorants have been reported using these products [13-15]. But no literature was available regarding improvement in light fastness of thermochromic colorants for textile applications.

Materials and methods

Materials

Fabric Particulars

The fabric used in the study was scoured, bleached cotton plain woven fabric containing no fluorescent brightening agent of the following construction:

Ends/inch : 130
Picks/inch : 103
Warp count : 60Ne
Weft count : 50Ne
Areal Density : 106 g/m^2
Sample size : 15 inch X 15 inch
CIE Whiteness Index : 70.0
Absorbency :< 3s

Thermochromic Colorants:

A series of commercial thermochromic colorants as given in Table 1, were supplied by Americos Industries Inc., Gujarat, India.

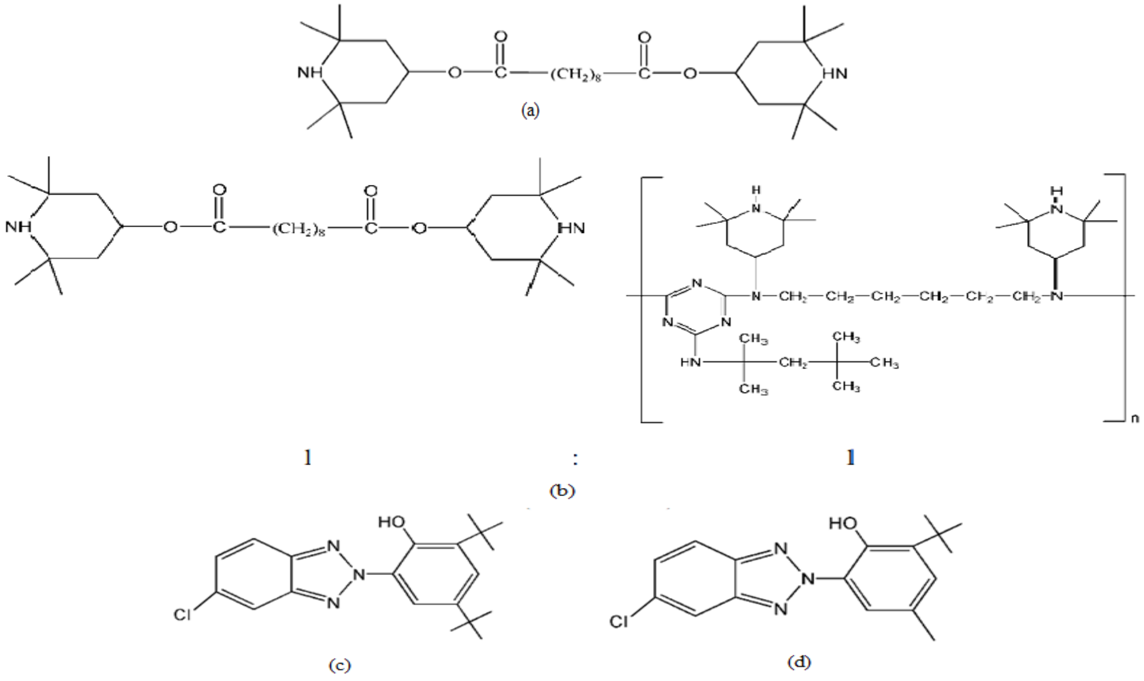

Figure 2. Different photostabilizers and UV absorbers (a) HALS 1 (TINUVIN 770), (b) HALS 5 (TINUVIN 791), (c) UVA 1 (TINUVIN 327), (d) UVA 2 (TINUVIN 326),

Table 1. Commercial Thermochromic Colorants[2]

Thermochromic Colorant	Activation Temperature (°C)
Americos Thermochromic Red	27
Americos Thermochromic Yellow	25
Americos Thermochromic Light Blue	27
Americos Thermochromic Green	26

UV Absorber & HALS:

UV absorbers and HALS were used for improving the photostability of a selected red colorant. The UV absorbers and HALS were supplied by High Grade Polymers, India.

Two commercially available organic UV absorbers and two HALS, as listed in table 2, with chemical structures given in Figure 2, were selected in order to assess the effect of different chemical classes with different UV absorbing characteristics on light fastness of thermochromic colorants under investigation. The additives were incorporated with the dyeing solution at three different levels: 1%, 3% and 6%.

Table 2. Commercial UV absorber and Hindered Amine Light Stabilizer (HALS)

HALS		**UV Absorber**	
HALS Name	**Commercial Name**	**UV Absorber Name**	**Commercial Name**
HALS 1	TINUVIN 770	UVA 1	TINUVIN 327
HALS 5	TINUVIN 791	UVA 2	TINUVIN 326

Methodology:

Surface Coloration:

The plain weave fabric samples were surface colorized using thermochromic colorants (red, blue, yellow & green) by continuous method (pad-dry-cure). For dyeing, first a homogenised colorant solution was prepared by mixing a cationic agent (Americos AC NRL 9000) 10 ml, thermochromic colorant 25 ml, non-ionic dispersing levelling agent (Dispersol DX) 15 ml, acrylic soft binder (Americos Acrylic Binder 16000) 20 ml, Water 30 ml (total 100 ml). The intensive mixing of the components was done using a high speed homogenizer. The fabric was then padded (wet pick-up 80%) in the solution at 2 bar pressure at room temperature, dried at 80^{o}C for 3 min, followed by curing at 140^{o}C for 3 min.

Application of UV absorbers and HALS:

Two UV absorbers (UVA-1 & UVA-2) of concentrations 1, 3 and 6 wt % and two HALS (TINUVIN 770 & TINUVIN 791) of concentrations 0.5, 1 and 2.5 wt % were applied in single and in combination to improve the light fastness of thermochromic colorants. The UV absorbers and HALS were incorporated with homogenized colorants solution and intensive mixing was done using a high speed homogenizer and applied on 100% cotton fabrics using pad-dry-cure process as described earlier.

Instrumental methods:

Color measurement of cotton fabric dyed with thermochromic colorants was carried out using a reflectance spectrophotometer (Grytag Mcbeth, Color Eye 700A). As the activation temperature of all the colorants was above 25^{o}C, the temperature of the room where measurements were taken was set at 20^{o}C to allow the dyed cotton fabric to develop color fully. Spectrophotometer was calibrated using the black and white reference tiles provided by the manufacturer. The instrument was used with the small aperture and specular reflectance and UV included. After temperature stabilization, the average of the two measurements was obtained and L*, a* and b* values computed for illuminant D65 and 10° observer.

Light fastness test:

The determination of photostability of the dyed samples was done by exposing them in an accelerated weathering instrument

(Xenotest Alpha, Atlas, Germany) according to AATCC test method 16-2004 (color fastness to light) [16]. The traditional assessment of light fastness using blue wool standards is not appropriate to provide light fastness rating for thermochromic materials due to their dynamic color change properties. Hence, a comparative study of the thermochromic color build up on the test sample before and after exposure over specific time intervals were used as a measure of light fastness behavior. The test conditions are given below in table 3.

Table 3. Experimental Condition for Light Fastness Measurement

Component	**Condition**
Light Source	Xenon
Black Panel Temperature	63±1ºC
Chamber Air Temperature	43±1ºC
Relative Humidity, %	30±5
Irradiance W/m^2(300-400 nm)	48±1

Result and Discussion

Light fastness of thermochromic colorants: The ability of dyed textiles to withstand prolonged sunlight exposure without fading or undergoing physical deterioration, usually referred to as light fastness in the case of traditional dyes, is largely determined by the photochemical characteristics of the absorbing dyestuff itself. The photostability of dyes in application is generally assessed following exposure to an accelerated fading instrument, such as the Xenotest Alpha used in this investigation.

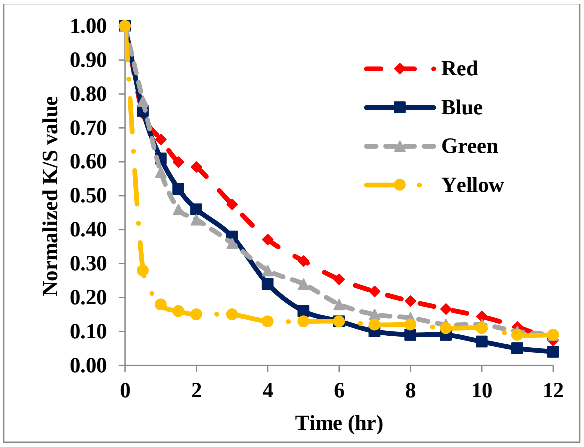

Figure 3. Normalized photostability curves for thermochromic red, blue, green & yellow colorants,

In this investigation, the degree of photostability of four investigated thermochromic dyed samples was measured by spectrophotometer after each 30 minutes exposure to UVA irradiation up to 12 hours. The strength (K/S) of the four thermochromic (Red, Blue, Yellow & Green) dyed samples are plotted against time is shown in figure 3. In order to provide a meaningful comparison of the photostabilities of the four thermochromic colorants, normalized values were calculated. This normalization process involved measuring the color strength (K/S) of the colorant after a particular time of exposure on the Xenotest instrument to a fraction of the initial color strength (K/S) of the colorant, i.e. $(K/S)/(K/S)_o$ where $(K/S)_o$ is the original color strength for a particular colorant before exposure on the Xenotest.

As illustrated in Figures 3, the color strength (K/S) of the colorants decreases fairly quickly on exposure on Xenotest. Red colorant has better photostability than blue, green and yellow colorants. The yellow colorant in particular has very poor light fastness compared to other colorants. The level of light fastness found for assessed colorants is not sufficient for many applications and thus an investigation into the use of stabilizing additives commonly used to improve light fastness was carried out with a view to enhance this particular feature. This investigation involved two UV absorbers and two HALS.

Improvement of light fastness using UV absorber & HALS:

Table 4. Effect of UV absorber on the time (min) for 50% photodegradation of red colorant after exposure in Xenotest

UV	Contro	1%	3%	6%
UVA-1	170	290	360	390
UVA-2	170	260	380	430

The results in Tables 4 show the effect of the UV absorbers on the photostability of red colorant, selected as representative example of thermochromic colorants, in terms of the time required for 50% photodegradation; i.e. the Xenotest exposure time required for the colorant to reach $(K/S) \,/(K/S)_o = 0.5$. The plots for individual UV absorbers are given in figure 4 and 5. The results show that the effect observed is dependent on the UV absorber's concentration. Up to 3% concentration of either UV Absorber, there is only a marginal improvement in light fastness. But at higher concentration (6%), the time for 50% photodegradation is significantly improved and UVA-2 performs slightly better than UVA-1. The enhanced protection provided by UVA-2 at higher concentration may be attributable to their absorption of lower wavelengths (higher energy) light, to which these colorants may be more sensitive. The effect of the presence of UV absorbers on the degree of photocoloration of red colorants is shown in figure 4.

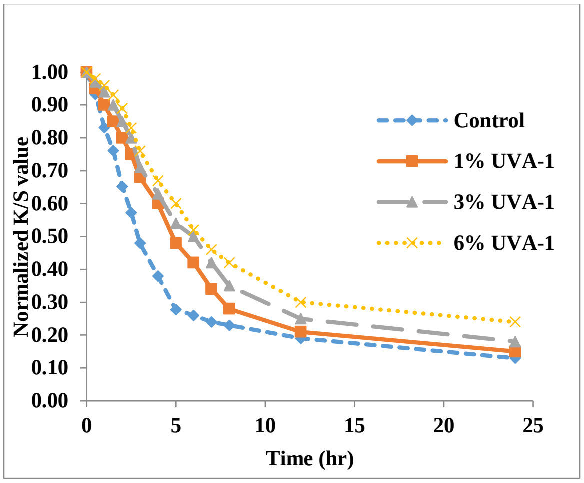

Figure 4. Effect of UVA-1 on photostability of red colorant,

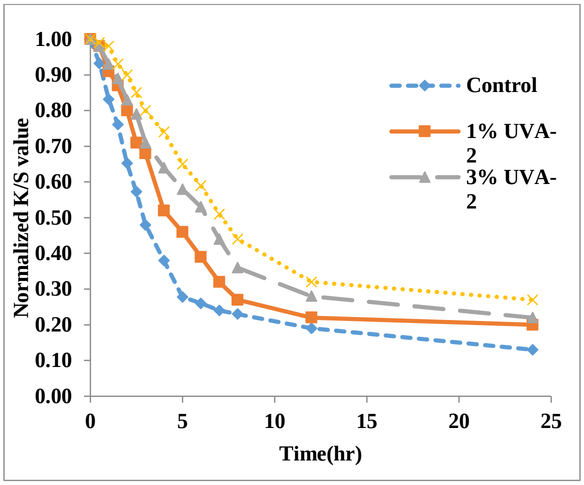

Figure 5. Effect of UVA-2 absorber on photostability of red colorant,

The application of HALS as a photo stabilizer is well known and they are widely used in polymer photo stabilization. The HALS selected for improvement of light fastness thermochromic colorants were Tinuvin 791 and Tinuvin 770 (Figure 2). The concentrations of the stabilizers were varied in the range 0.5, 1 & 2.5 wt % as they are quite effective even at such low levels. The effect of adding HALS-770 and 791 in dyeing bath on light fastness of thermochromic colorants is shown in figure 5 & 6 and table 4. It was found that improvement of light fastness of the colorant is very marginal at low concentration.

Moreover, at higher concentration, there is actually no improvement in the light fastness of the colorants. There are many different reaction pathways open to the light-excited colorant molecule, such as ionisation, dissociation into free radicals, oxidation, reduction, isomerisation, etc. It has also been proposed in literature that degradation of organic polymers may occur by the formation of charge transfer complexes between the polymer and oxygen or due to the formation of superoxide or singlet oxygen or various radical intermediates [17]. HALS may deactivate these species by direct transfer of energy from the polymer to the HALS, or by deactivation of the polymer–oxygen complex by formation of a HALS–oxygen charge transfer complex [10]. As HALS were not found effective in improvement of light fastness of this colorant, it indicates that the photodegradation of this colorant might not due to the formation of superoxide or singlet oxygen and various radical intermediates.

Table 4. Effect of HALS on the Time (min) for 50% Photodegradation of Red Colorant after Exposure to the Xenotest

HALS	**Control**	**0.5%**	**1%**	**2.5%**
HALS-	170	230	210	180
HALS-	170	270	180	180

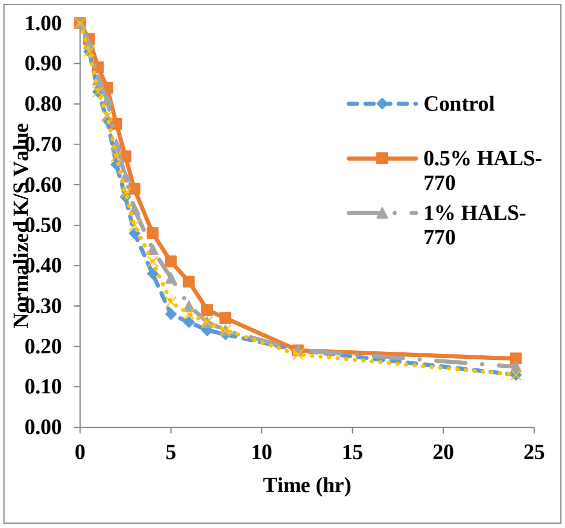

Figure 6. Effect of HALS-770 on photostability of red colorant,

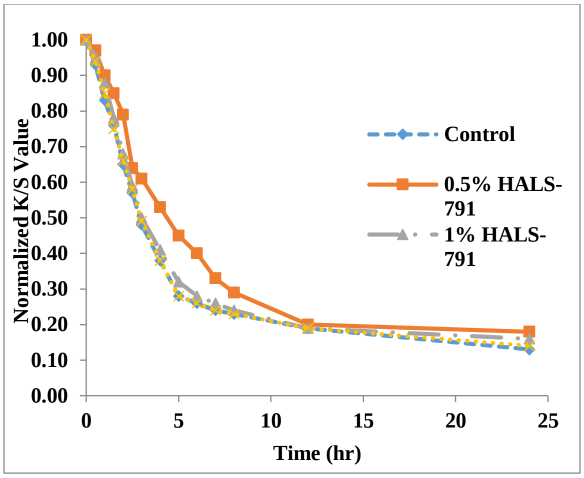

Figure 7. Effect of HALS-791 on photostability of red colorant,

Table 5. Effect of mixing UV Absorber & HALS on the Time (min) for 50% Photodegradation of Red Colorant after Exposure to the Xenotest

UV absorber & HALS concentration	**Time (min)**
Control	170
UVA-2 @3% + HALS 791 @ 0.5%	440
UVA-2 @3% + HALS 791 @ 1%	390
UVA-2 @3% + HALS 770 @ o.5%	500
UVA-2 @3% + HALS 770 @ 1%	430
UVA-2 @ 6% + HALS 791 @ 0.5%	570
UVA-2 @ 6% + HALS 791 @ 1%	520
UVA-2 @6% + HALS 770 @ 0.5%	670
UVA-2 @6% + HALS 770 @ 1%	610

UV absorber and HALS 791 & 770 were also applied in combinations as they are known to show synergistic effect. As UV absorber was found to perform better at higher concentration and HALS at lower concentrations, different combination of UV absorbers & HALS were prepared using high concentrations of UV absorbers and low concentration of HALS. The results in Tables 5 show the effect of the combination of UV absorber and HALS on the photostability of red colorant in terms of the time required for

50% photo degradation; i.e. the Xenotest exposure time required for the colorant to reach $(K/S)/(K/S)_0 = 0.5$. Results show that in combination, UV absorber & HALS perform better in improving photostability of thermochromic colorants. In case of UVA- 2 at 6% and HALS-770@ 0.5% photostability was increased by four times. Though the improvement of light fastness in these approaches are not sufficient for particular applications, further study need to be carried out using different types UV absorber and HALS.

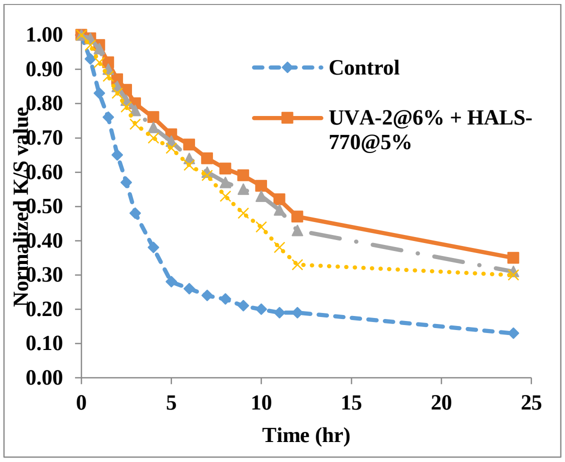

Figure 8. Effect of mixed UV absorber & HALS on photostability of red colorant,

Conclusions:

Unlike traditional dyes, there are some complexities involved in the assessment of the photostability of thermochromic colorants which shows stimuli–responsive dynamic color change properties. The level of light fastness found for assessed commercial colorants are not sufficient for many applications and thus an attempt was made to improve the light fastness of thermochromic colorant using UV absorbers and HALS. The incorporation of UV Absorbers was found to increase the photostability to a modest level, although the effect was specific to particular UV absorber ⁄ colorant combinations. As the UV absorber shields the colorant particle from UV light, their use led to a consistent reduction in the degree of photodegradation of the colorant. However, the incorporation of HALS, which is free radical scavengers, was not found satisfactory. But when UV absorber and HALS are used together considerable amount of improvement was found due to their synergistic effect.

References:

1. M. A. Chowdhury, M Joshi and B S Butola, “Thermochromic and Photochromic Colorants for Textile Applications”, *Journal of Engineered Fiber and Fabrics*, Vol. 9(1), pp 107-123, 2014.
2. M. A. Chowdhury, B S Butola and M Joshi, “Application of thermochromic colorants on textiles: Temperature dependent colorimetric properties of Thermochromic Colorants”, *Coloration Technology*, Vol. 129(3), pp 232-237, 2013.
3. D. Aitken, S M Burkinshaw, J Griffiths and A D Towns, “Textile Applications of Thermochromic system”, *Review of Progress in Coloration and related Topics*, Vol. 26(1), pp1-8, 1996.
4. R. R. Mather, “Intelligent Textile”, *Review of Progress in Coloration and related Topics*, Vol. 31 (1), pp 36-41, 2001.
5. E. P. G. Gohl and L D Vilenskly, Textile Science, 2nd edition, Longman Cheshire; 1983.
6. A. F. Little, “An Investigation into Textile Applications of Photochromic Dyes”, PhD thesis, Heriot Watt University, 2008.
7. P. Gijsman, J Hennekens and D Tummers, “The mechanism of action of hindered amine light stabilizers”, *Polymer Degradation and Stability.* Vol. 39(2), pp 225–233, 1993.
8. D. J. Carlsson, “Antioxidant Mechanism of Hindered Amine Light Stabilizer”, *Makromolekulare Chemie Macromolecular Chemistry and Physics.* Vol. 8, pp79–88, 1984.
9. P. Gijsman, “New synergists for hindered amine light stabilizers”,

Polymer Degradation and Stability, Vol. 43(5), pp 1573-1579, 2002.

10. F. Gugumus, "Current trends in mode of action of Hindered Amine Light Stabilizers", *Polymer Degradation and Stability*, Vol. 40(2), pp 167-215, 1993.
11. J. Pospisil and S Nespurec, "Photostabilization of coatings. Mechanisms and performance", *Progress in Polymer Science*, Vol. 25(9) pp 1261-1335, 2000.
12. M. McCusker, "A UVA/HALS Primer: Everything you've ever wanted to know about light stabilizers-Part I", *Metal Finishing*, Vol. 97(5), pp 51-53, 1999.
13. H. Oda," Improvement of light fastness of natural dyes: effect of ultraviolet absorbers containing benzotriazolyl moiety on the photofading of red carthamin", *Coloration Technology*, Vol. 128, (2), pp 108-113, 2012.
14. A. F. Little and R M Christie, "Textile applications of photochromic dyes. Part 3: factors affecting the technical performance of textiles screen-printed with commercial photochromic dyes" Color. Technol., Vol.127 (5), pp 275-281, 2011.
15. P. Thaigarajan and G Nalankilli, "Improving lightfastness of reactive dyed cotton fabric with antioxidants and UV absorbers", *Indian Journal of Fibre & Textile Research*, Vol. 38, pp 161-164, 2013.
16. Color fastness to light, AATCC Test Method 16-2004, *AATCC technical manual*, vol. 80, 2005.
17. C. Salemi, G Giusti and R Guglielmetti, "DABCO effect on the photodegradation of photochromic compounds in spiro[indoline-pyran] and spiro[indoline-oxazine] series", *Journal of Photochemical and Photobiology A: Chemistry*, Vol. 86 (1-3) pp 247-252, 1995.