

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

Muksit Ahamed Chowdhury¹, B S Butola² and Mongala Joshi³

¹Department of Textile Engineering, Ahsanullah University of Science & Technology, Dhaka-1208, Bangladesh.

^{2,3}Department of Textile Technology, Indian Institute of Technology Delhi, New Delhi-110016, India.

Corresponding Author Email: muksit.iitd@gmail.com

Abstract: Light fastness of thermochromic colorants, which shows reversible change in colour with temperature, is of great importance for different textile and non-textile application. Light fastness of commercial thermochromic colorants was determined by measuring the colour 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. Significant improvement of photostability was observed when UV absorber and HALS were used in combination.

Key Words: Thermochromic colorants, Light fastness, UV absorber, HALS.

1. INTRODUCTION

Thermochromic colorants which show reversible colour 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 colourless 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 colour development or colour loss. On cooling, the solvent solidifies and the system reverts to its original colour [1-4].

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 stabilising additives to enhance photostability is also reported.

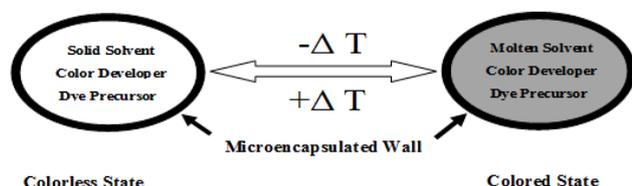


Fig.1: Reversible change in color with temperature.

2. Materials and methods

2.1 Materials

2.1.1 Fabric Particulars

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

Warp count	: 60Ne
Weft count	: 50Ne
Ends/inch	: 130
Pick/inch	: 103
Areal Density	: 106 g/m ²
CIE Whiteness Index	: 70.0
Absorbency	: < 3s

2.1.2. Thermochromic Colorants:

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

TABLE 1: Commercial Thermochromic Colorants

Thermochromic Colorant	Activation Temp. (°C)
Americos Thermochromic Red	27
Americos Thermochromic Yellow	25
Americos Thermochromic Light	27
Americos Thermochromic Green	26

2.1.2 UV Absorber & HALS:

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

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. By using such materials, the protection can be relatively long-lived [5-6]. Improvements in the light fastness of photochromic and natural colorants have been reported using these products [7-8]. 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)

Hindered Amine Light Stabilizer (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

is the original colour strength for a particular colorant before exposure on the Xenotest.

As illustrated in Figures 3, the colour strength (K/S) of the colorants decreases fairly quickly on exposure on Xenotest. Red colorant has better photostability than blue, green and yellow colorants. 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 stabilising 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 Hindered Amine Light Stabilizer (HALS). There is some literature [5-6] about the use of such additives to photostabilise photochromic or natural colorants, but no literature was available regarding improvement in light fastness of thermochromic colorants for textile applications.

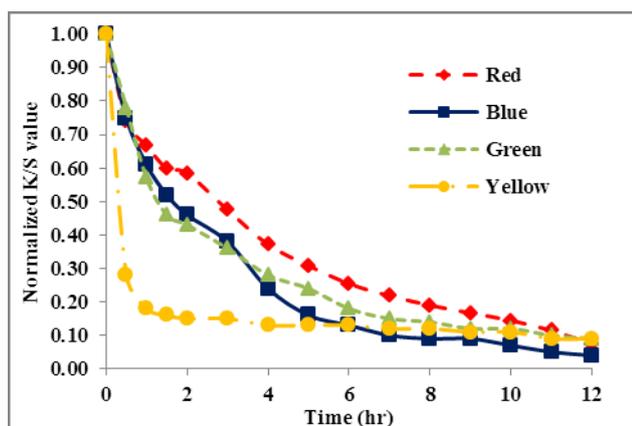


Fig. 3: Normalized photostability curves for thermochromic red, blue, green & yellow colorants.

3.2 Improvement of light fastness using UV absorber & HALS:

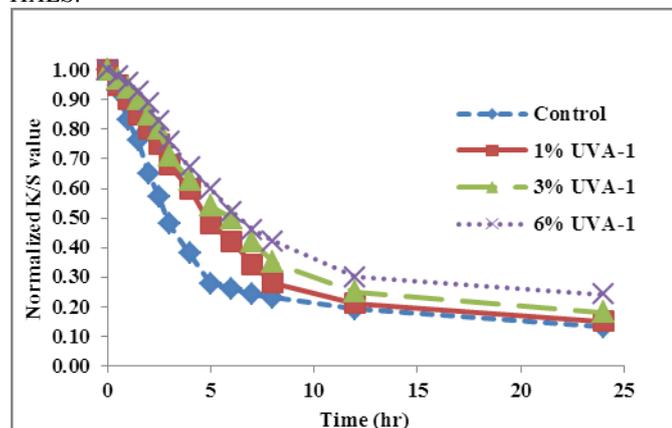


Fig. 4: Effect of UVA-1 on photostability of red colorant

The results in Tables 3 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 $(K/S)/(K/S)_0 = 0.5$. 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. Upto 3% concentration of either UV Absorber, there is only 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.

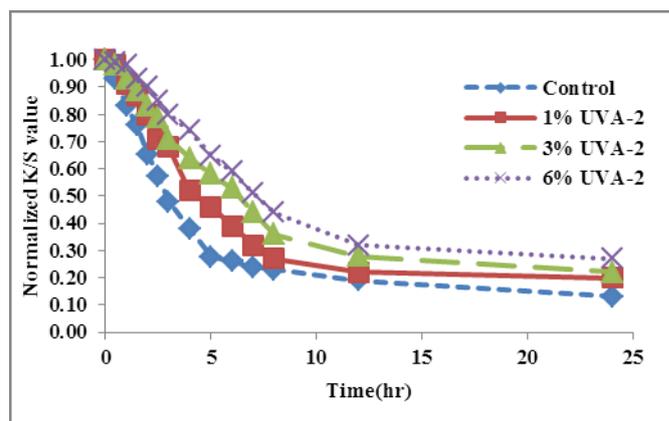


Fig. 5: Effect of UVA-2 absorber on photostability of red colorant

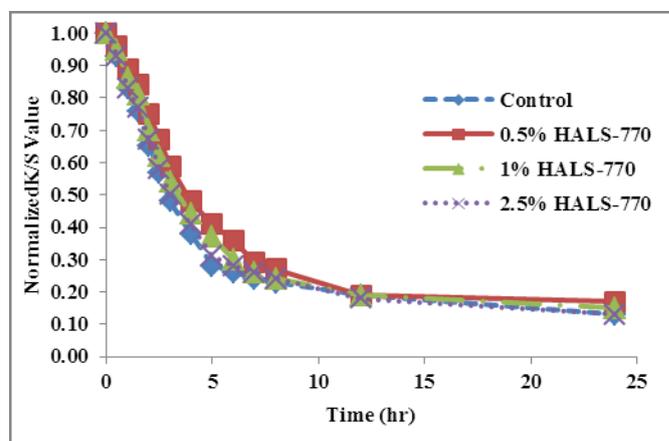


Fig. 6: Effect of HALS-770 on photostability of thermochromic colorants.

The application of hindered amine light stabilisers (HALS) as a photo stabiliser is well established and they are widely used in polymer stabilisation. Unlike UV absorbers, which basically protect the colorant 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 long-lived. 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. More over at higher concentration, it 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 [8]. 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 [9]. 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	0%	0.5%	1%	2.5%
HALS-770	170	230	210	180
HALS-791	170	270	180	180

UV absorber and HALS 791 & 770 were also applied in combinations as they are known to show synergistic effect. As UV absorber were found to perform better at higher concentration and HALS at lower concentrations, different combination of UV absorbers & HALS were prepared using high concentration of UV absorbers and low concentration of HALS. The results in Tables 8 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 @ 6% and HALS-770@ 0.5% photostability was increase by four times. Though the improvement of light fastness in these approaches are not sufficient for particular application, further study need to be carried out using different types UV absorber and HALS.

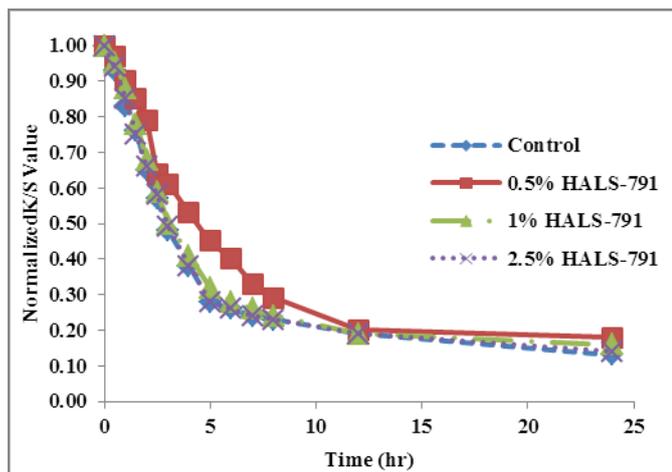


Fig. 7: Effect of HALS-770 on photostability of thermochromic colorants.

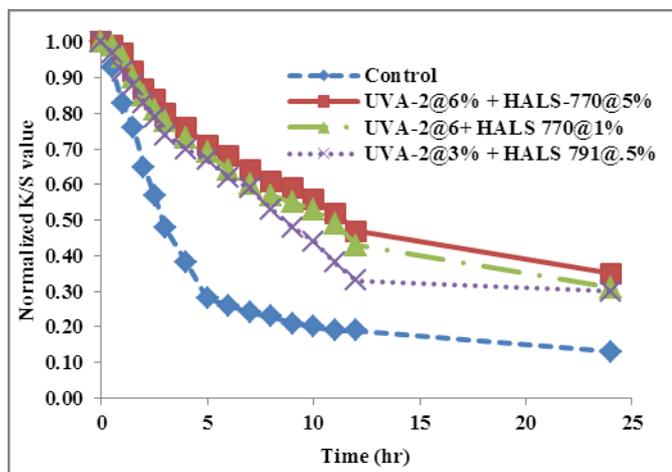


Fig. 8: Effect of mixed UV absorber & HALS on photostability of thermochromic colorants.

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 @ 0.5%	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

4. Conclusions:

Unlike traditional dyes, there are some complexities involved in the assessment of the performance of thermochromic colorants which shows stimuli-responsive dynamic colour 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 photocoloration 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*, 26(1), pp1-8, 1996.
4. R R Mather, "Intelligent Textile", *Review of Progress in Coloration and related Topics*, 31 (1), pp36-41, 2001.
5. J Pospisil and S Nespurec, "Photostabilization of coatings. Mechanisms and performance", *Progress in Polymer Science*, 25(9) pp1261-1335, 2000.
6. M McCusker, "A UVA/HALS Primer: Everything you've ever wanted to know about light stabilizers-Part I", *Metal Finishing*, 97(5), pp51-53, 1999.
7. H Oda, "Improvement of light fastness of natural dye: effect of ultraviolet absorbers containing benzotriazolyl moiety on the photofading of red carthamin", *Coloration Technology*, 128, (2), pp108-113, 2012.
8. 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.*, 127 (5), pp275-281, 2011.
9. Color fastness to light, AATCC Test Method 16-2004, *AATCC technical manual*, vol. 80, 2005.
10. 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*, 86 (1-3) pp247-252, 1995.
11. F Gugumus, "Current trends in mode of action of Hindered Amine Light Stabilizers", *Polymer Degradation Stability*, 40 (2), pp167-215, 1993.