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EFFECT OF ULTRAVIOLET LIGHT ON THE PROPERTIES OF DYED COTTON CELLULOSE

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Abstract: *Textile dyes have been reported of causing various stages of contact dermatitis. Reactive dyes are widely applied in dyeing cellulose fiber based textiles (100% cotton), skin fibers (hemp, flax), regenerated cellulose (cellulose acetate, viscose), protein fibers (natural silk, wool). The human body comes in contact daily with such compounds. This aspect is important for elucidating their biological effects on the human body, in correlation with physico-chemical properties. Dyes are chemical compounds containing chromophore and auxochrome groups. Authors herein report results concerning the influence of UV irradiation with* $\lambda > 300$ *nm on the structure and properties of different colored textiles. Subjects to study were textiles painted with four azo-triazine based dyes which were exposed to 100 h UV irradiation time and irradiation dose values up to 3500 J cm*$^{-2}$*. The five azo dyes were: reactive orange 13, reactive red 183, reactive yellow 143, reactive blue 204 and reactive red 2. Structural modifications as a result of irradiation were undertaken by UV-Vis spectroscopy. It was observed that during UV exposure there occurred partial dyes detachment from the textiles, accompanied by glucosidic units and dye photodecomposition by C–N bond scission and degradation of aromatic entities and azo based chromophores. Color modifications were also investigated. Color differences significantly increased with the irradiation dose for all the studied samples.*

Key words: *azo-triazine dyes, cellulose, ultraviolet protection, photodegradation.*

1. INTRODUCTION

Natural fabrics generally provide poor skin protection due to the low absorption of UV radiation [1]. The protection provided by is dependent on a series of factors, such as fiber type, color, structural characteristics, dyeing intensity and optical brightening agents or UV absorbers, if any [2], [3]. Most textiles are usually exposed to varying doses of sunlight. Solar light intensity generates important photochemical processes [4]. Textiles assure protection against visible light, for which sunscreens offer much less protection than for UV light [5]. A compound turns colored after absorbing specific electromagnetic radiations in the visible region. The entities existing in the coloring substance, which are responsible for electromagnetic radiation absorbtion and which reflect in the visible region are chromophores [6]. The UV radiation represents 5% of the total incident sunlight reaching the earth surface (visible light 50%, IR radiation 45%). Even in such a low proportion, UV radiation exhibits the highest quantum energy. Light is electromagnetic in its nature.

The human eye distinguishes visible light in the range 380–700 nm [7]. Dyes absorb electromagnetic radiation of in the visible spectrum range. The human eye detects visible radiations only for the corresponding complementary colours. ***Fig. 1*** indicates the different spectrum regions with their corresponding wavelengths.

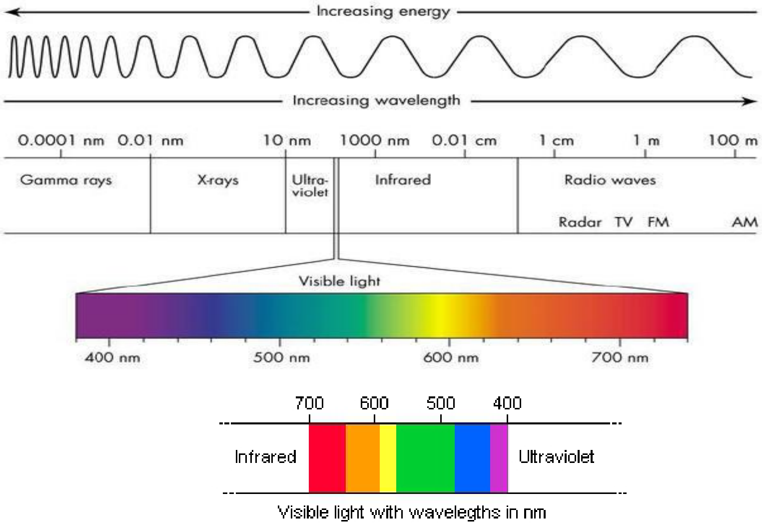


Fig. 1: *Regions of electromagnetic spectrum [8]*

Cellulose (***Fig. 2***) is comprised of glucose units linked through oxygen atoms. About 94 % of cotton is comprised of cellulose. What is remained includes 1.3 % protein, 1.2 % pectic substances, 0.6 % waxes and 4 % of other components. Of the three hydroxyl groups on the cellulose ring one is primary and two are secondary. Most reactions occur at the primary hydroxyl groups.

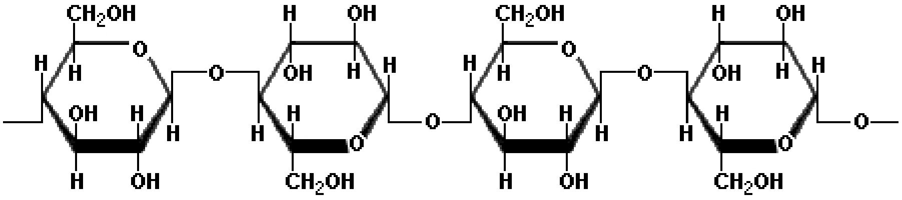


Fig. 2: *Chemical structure of cellulose fibers [8]*

When cellulose is modified with different cationic and anionic groups, its molecular chains are modified. This determines changes in the chemical and physical properties of cellulose fibers. Also, chemical modification enhances cellulose fibers reactivity. Several classes of dyes, such as direct, azo and reactive ones may be successfully applied on cellulose substrates. Applications of cationic dyes have not gained widespread success. Since the stability of the fabric-dye complex may affect human health, the behavior of the fabrics painted with reactive azo-triazine dyes under the action of UV radiation with $\lambda > 300$ nm represents the subject of this paper.

2. EXPERIMENTAL

2.1. Materials and methods

Five azo dyes, reactive yellow 143 (RY-143), reactive blue 204 (RB-204), reactive red 183 (RR-183), reactive red 2 (RR-2), reactive orange 13 (RO-13) were used as received. The fabric samples were exposed to light, using a middle pressure mercury lamp HQE-40 type, having a polychrome emission spectrum in the field of 240-370 nm, with 30 mW/cm^2 intensity. Utilization of filters permits exposure to greater proportions of UV and at lower wavelengths than in the case of borosilicate filters. The upper temperature during the light cycle was 40-45 ^{0}C. The surface color difference (ΔE*) was measured using a Pocket Spec Color (USA) color comparison spectrophotometer. The surface color difference was calculated using the CIEL L* a* b* system. The color change as a function of UV treatment was calculated using Eq. (1).

$$\Delta E_{ab} = \sqrt{(L_2^* - L_1^*)^2 + (a_2^* - a_1^*)^2 + (b_2^* - b_1^*)^2} \quad \textbf{(1)}$$

where L*, a* and b* represent the lightness, yellowness and redness, respectively.

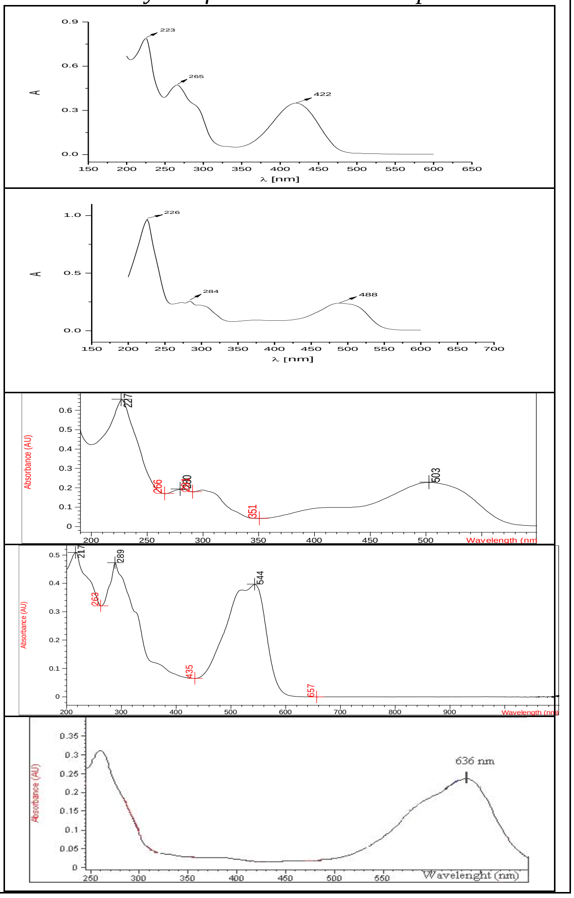
3. RESULTS AND DISCUSSION

Table 1 shows that color differences significantly increased with the irradiation dose for all the studied samples.

Table 1: *Variation of chromatic coefficients with irradiation dose*

Fabric type	Irradiation time (h)	L*	a*	b*
RY-143	0	69.90	-12.57	64.79
	25	61.06	-10.99	63.25
	50	69.82	-9.25	56.12
	75	60.30	-7.91	50.38
	100	61.26	-6.99	49.68
RO-13	0	49.41	33.83	40.82
	25	41.91	22.98	29.23
	50	45.05	21.29	26.92
	75	48.64	17.09	22.86
	100	49.35	15.35	21.43
RR-183	0	30.83	48.52	36.36
	25	28.16	44.19	32.97
	50	33.56	41.97	30.98
	75	29.66	40.55	29.30
	100	30.32	39.04	27.62
RR-2	0	29.07	48.26	24.03
	25	25.19	46.42	20.09
	50	29.63	42.10	17.05
	75	27.31	42.54	14.62
	100	27.40	39.25	11.90
RB-204	0	19.64	17.74	-33.33
	25	18.37	14.06	-28.72
	50	18.85	11.25	-23.20
	75	18.40	8.88	-19.83
	100	20.17	8.35	-19.06

Fig. 3: *UV-Vis spectrophotometric quantitative analysis of nonirradiated samples*



The increasing of irradiation time and dose decreased chromatic coefficients values in the case of fabrics painted with all studied dyes. Samples accumulated blue and green chromophores during irradiation. It is possible for structural dye changes during irradiation to lead to simultaneous hypochrome and bathochrome displacements of the absorption maxima, thus colouring the sample in complementary colors (blue and green).

Fabrics dyied with RY-143 and RO-13 showed a darkening tendency (Eq. (1)), simultaneously with an insignificant variation of the L^* values of the fabrics painted with RR-2 and RR-183. This was explained by accumulation of blue and green chromophores, because of cellulose substrate photo-oxidation reactions. Changes in UV-Vis spectra as a result of irradiation supported these observations. It may be observed from ***Fig. 3*** that the absorbtion maximum of the used dyes is located at the following wavelenghts: RB-204: λ_{max} = 636 nm; RR-183: $\lambda_{max.}$ = 503 nm; RR-2: λ_{max} = 544 nm; RY-143: λ_{max} = 422 nm; RO-13: λ_{max} = 488 nm. UV-Vis spectra were recorded in order to identify specific absorption maxima of each dye. Even the cellulosic fabric could undergo some photo-oxidative degradation during UV exposure, the dye acting as a photo-sensitizer. It is known that the UV radiation may cause free radicals generation which are able to initiate photo-degradative reactions in the cellulosic materials such as depolymerization, dehydroxylation, dehydrogenation, dehydroxymethylation and the release of hydrogen, carbon monoxide, and carbon dioxide.

4. CONCLUSIONS

UV radiation influence on coloured dyed fabric has been studied. This was made with polychromatic light ($\lambda > 300$ nm). Structural changes during UV irradiation were monitored. Changes consisted especially in the resulting of carbonyl and aromatic entities from dye structures due to photo-oxidative processes. Color modifications were also investigated. Color differences significantly increased with the irradiation dose for all the studied samples.

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