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Improving light fastness of natural dyes on cotton yarn

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Abstract

The objectives of this study were to evaluate the light fastness of selected natural dyes (madder, weld and woad) and the effect of some commonly used antioxidants and UV absorbers on the light fastness of these dyes.

The photofading rate curves of madder and weld fixed on cotton correspond to type II fading rate curves described by Giles. These results are in concordance with those of Cox-Crews. The woad presents a type III fading rate curve, similar to the indigo fading rate curve presented by Cox-Crews.

A poor light fastness of the three natural dyes in comparison with synthetic ones is established beyond question. Nevertheless, the use of some additives can improve this default of natural dyes. In all the cases, the use of UV absorbers or antioxidants improved the light fastness of dyed fabrics. The most effectives were the vitamin C and the gallic acid.

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Keywords: Madder; Weld; Woad; Light fastness; Antioxidants; UV absorbers; Natural dyes

1. Introduction

Since prehistoric times, natural dyes have been used for many purposes such as the coloring of natural fibers wool, cotton and silk as well as fur and leather. The dyes were also used to color cosmetic products and to produce inks, watercolors and artist's paints.

The use of natural dyes to color textiles declined rapidly after the discovery of synthetic dyes in 1856, until they were virtually unused by 1900. Most natural dyes have poor to moderate light fastness, while synthetic dyes represent the full range of light fastness properties from poor to excellent. The first systematic tests of the light fastness of dyes were made by Dufay about 1730. The modern system for the light fastness testing was introduced by the Deutsche Echtheiskommission in 1914, who adopted the principle, now in use in many countries, of exposing the test pattern alongside a set of standard patterns of graded fastness.

The light fastness is influenced by internal factors: the chemical and the physical state of dye, the dye concentration, the nature of the fibers, the mordant type.

- *The chemical structure* of a dye molecule is divided in two parts: the main skeleton (chromophore) and the substituent groups (auxochromes). In general, the skeleton seems to determinate the average light fastness properties of a dye, while substituent groups usually alter the light fastness properties of a particular dye within a class in minor ways.

  The analysis of the natural dyes listed in Color Index revealed that almost 50% of all natural dyes used to color textiles are flavonoid compounds. Most of the remaining natural dyes fall within three chemical classes – anthraquinones, naphtoquinones and indigoids. Although flavonoid compounds are not very light fast, anthraquinones and indigoids are

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noted for their excellent light fastness. However, the light fastness of anthraquinones is decreased as the number of hydroxyl substituent groups is increased. Other aspects of chemical structure may affect the light fastness, such as the symmetry of the dye molecules: symmetrical dye molecules usually exhibit greater light fastness than non-symmetrical dye molecules, and larger dye molecules generally provide faster dyeing than smaller ones.

- *The physical state of dye* is generally more important than the chemical structure. The more finely dispersed the dye is within the fiber, the more rapidly it will fade. Fibers with large aggregates of dye are more light fast, since a smaller surface area of the dye is exposed to air and light.

A useful way of probing the interrelationship between the physical state of a dye within a fiber and its light fastness is by examination of fading rate curves. In 1965, Giles [1] described five types of fading rate curves which are typical of synthetic dyes (Fig. 1). Type I is a fading rate which decreases steadily with time, but rarely occurs in practice; the dye is probably molecularly dispersed throughout the fiber. Type II fading initially occurs at rapid rate followed by slower fading at a constant rate; dyes are present in aggregates inside the fiber substrate. Most synthetic dyes exhibit a type II fading rate curve. Type III is a fading rate curve characterized by a linear or constant rate of fading. This type of fading occurs most often with pigments and fast dyes that form larger aggregates inside the fibers. Type IV is a fading rate initially darken, followed by a slow fading rate. This type of fading occurs in a few fast dyes. Type V is a fading rate that steadily increases with time and is observed occasionally with azo dyes on cellulose; there is a continued breakdown of large dye particles to small dyes particles.

Fading rate curves can be useful because they can give qualitative information about the physical state of dye within the fiber. They may also be useful in determining colorant formulation or dye concentration necessary to match faded materials. For these reasons, the fading rates of numerous synthetic dyes and some pigments have been studied. However, quantitative fading rate curves for most natural dyes have not been established. In 1987, Cox-Crews [2] studied the fading rate curves of some natural dyes, such as cochineal, fustic, madder, weld, turmeric and indigo. The fading rate curves were constructed from color difference measurements made using a tristimulus colorimeter. The 12 dye/mordant combinations evaluated in this study exhibited fading rate curves similar to either type II or type III described by Giles; type II: fustic (alum or tin mordant), madder (alum or tin mordant), turmeric (alum or tin mordant), weld (alum or tin mordant); type III: cochineal (alum or tin mordant), fustic (chrome mordant), indigo.

- The light fastness of a dyed fiber usually increases with increasing *dye concentration*, the main cause being an increase in average size of the submicroscopic particles which the dye forms in the fiber [1].
- Light fastness of dyes textiles is related to *the chemical structure and physical characteristics of the fiber* itself. Cumming et al. [3] attributed the fading on cellulose to an oxidative process, whereas on protein fibers the process has a reductive nature. Padfield and Landi [4] stated that indigo is much more light resistant on wool than on cotton; the reverse is true for madder. An oxidative pathway is involved in the fading of indigo dyed cotton. As fading on non-protein substrates is reductive, the indigoid chromophore which is resistant to photoreduction shows high fastness on wool [5].
- The fastness of a mordant dye depends on *the mordant and mordanting method*, because different metal dye complexes are formed, which may differ in their stability to light and also because the metal may have a positive or negative catalytic effect on the photochemical degradation of the dye [6].

  Cox-Crews [7], in a study on 18 yellow natural dyes, concluded that the mordant is more important than the dye itself in determining the light fastness of colored textiles. Use of tin and alum mordant results in significantly more fading than when chrome, iron or copper ones are used.

External factors such as the source and the intensity of illumination, the temperature and the humidity, the atmospheric pollution, can affect the reaction as well.

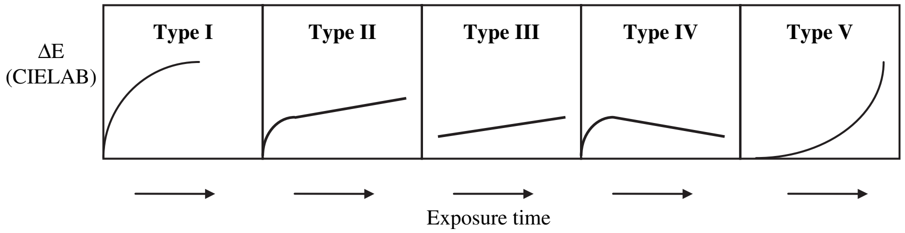


Fig. 1. Giles' diagrams of fading rate curves (percent change in concentration versus time).

◆ *The light source* (the nature of the incident light) is very important during the photofading process; fugitive dyes are faded mainly by visible radiation, while dyes of high light fastness are faded mainly by UV radiation [8]. Gantz and Sumner [9] stated that UV radiation is a major factor in the fading of the more light fast dyes, particularly yellows and oranges. Use of a UV filter has been shown to afford some protection to natural dyes [4].

◆ Under the normal conditions of exposure to light, both *temperature and humidity* affect the rate of fading of dyed textile materials. It was found that a drop in relative humidity from 65 to 45% had very little effect, but a further decrease up to 25% caused a significant reduction of fading [10].

◆ *Atmospheric contaminants*, such as sulfur dioxide and oxides of nitrogen and ozone, are known to react with dyes even in the absence of light.

◆ Some *substances, other than the colorant*, may be present on the fiber and may affect the fastness properties. For example, after treatment of silk with tannic acid and treatment of cotton with myrobolans, before and after dyeing, improves the fastness properties of most natural dyes. On the other hand, presence of substances such as starch and gums might accelerate the fading process [6].

UV absorbers are additives used to prevent the photodegradation of polymeric materials by UV-rich sunlight and artificial light. These additives absorb UV radiation and reemit it as fluorescent or infrared radiation. The energy of the excited molecule which causes photodegradation is released as thermal energy [11].

The UV absorbers must have the following characteristics: high absorptivity of the radiation between 290 nm and 400 nm, stability to long-term light exposure, molecular dispersion for optimum screening activity, and chemical inertness to other additives in the substrate. Researchers have investigated the usefulness of UV absorbers in reducing color alteration from two general perspectives: direct application of UV absorbers to fibers and use of UV filtering materials over the light sources [12].

The major classes of commercial ultraviolet-radiation stabilizers include derivatives of 2-hydroxybenzophenone, 2-(2*H*-benzotriazol-2-yl)-phenols, phenyl esters, substituted cinnamic acids and nickel chelates.

Gordon Rose et al. [13] studied the use of ultraviolet light absorbers for protection of wool against yellowing. They demonstrate that the substituted benzophenones are effective in protecting wool; the maximum protection was obtained from water-soluble UV absorbers, using dye-bath techniques.

Without going into the history of UV absorbers or reviewing the many structures that have been studied, it can be stated that substituted benzophenones are the most effective compounds that have been found to date. Since a hydroxyl group ortho to a carbonyl is characteristic of stable ultraviolet absorbers we could conclude that this structure is associated with the stability and internal energy conversions of these molecules [9].

Antioxidants, also called inhibitors of oxidation, are organic compounds that are added to oxidizable organic materials to retard autooxidation and, in general, to prolong the useful life of the substrates. Relatively few chemical classes are effective as antioxidants. Those in common use today are hindered phenols, secondary aromatic amines, certain sulfide esters, trivalent phosphorous compounds, hindered amines, metal dithiocarbamates and metal dithiophosphates. Antioxidants are classified as either radical trapping (chain breaking) or peroxide decomposing, terms that describe the mechanism by which they function. As radical trapping antioxidants we can cite gallic acid and its esters, tocopherols and some vegetal polyphénols (quercitin, myricetin, vanillic acid, cafeic acid, ferulic acid…). As synergists we can cite ascorbic acid (vitamin C) and erythorbic acid. As metal chelating agents we can cite citric acid, lactic acid and lecithin [14].

2. Experimental

2.1. Materials and chemicals

In our study we used aerial parts of weld (*Reseda luteola* L.) and woad (*Isatis tinctoria*) collected in Ariege (South of France) and madder roots (*Rubia tinctoria*) purchased from Kremer Pigmente (Germany). These dyes were selected because they were widely used for red (madder), yellow (weld) and blue (woad) colors in European, American and even Asian textiles until the 19th century.

The cotton yarn was obtained from commercial sources.

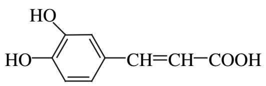
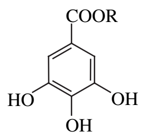
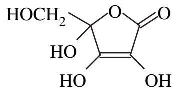
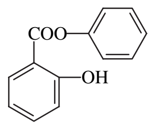
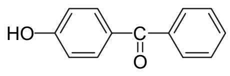
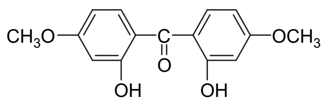
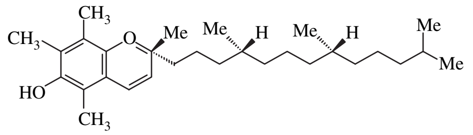
The antioxidants and the UV absorbers used for treating the cotton before exposure to irradiation were obtained from commercial sources (Acros Organics, Sigma–Aldrich, Fluka). Their structures and their purity are presented in Table 1.

2.2. Dyeing

Dyeing of the fabrics were performed at 70 °C; for weld and madder a pre-mordanting bath was necessary, using an alum mordant. For woad, we used a classical vat bath ($Na_2S_2O_4$/NaOH).

After dyeing, the samples were rinsed in distilled water, scoured in Deuterzoil soap solutions, rinsed again in distilled water and then air dried.

Table 1
Antioxidants and UV absorbers used in this study

Substance	CAS No.	Structure	Origin	Purity (%)
Cafeic acid: 3-(3,4-dihydroxy-phenyl)-2-propenoic acid	331-39-5		Fluka	97
Gallic acid: 3,4,5-trihydroxybenzoic acid	149-91-7		Aldrich	97
Vitamin C: ascorbic acid	50-81-7		Fluka	99.5
Phenyl salicylate: 2-hydroxybenzoic acid phenyl ester	118-55-8		Fluka	98
Benzophenone: 2-hydroxybenzophenone	117-99-7		Acros	99
Uvinul D49 Benzophenone 6: 2,2′-dihydroxy-4,4′-dimethoxybenzophenone	131-56-6		Aldrich	98
Vitamin E: α-tocopherol			Aldrich	98

2.3. Antioxidants and UV absorbers incorporation

The UV light absorbers and the antioxidants were applied by placing the cotton yarns in a solution of the substance (1 g/L), at 70 °C, under 30 min steering. For gallic acid, vitamin C and cafeic acid we used aqueous solutions; for the others we used a water/ethanol mixture (9/1 v/v).

After treatment, the samples are washed and then air dried.

2.4. Light exposure

The dyed samples of cotton (12 × 4 cm) were stapled on to white card, a portion (4 × 4 cm) covered with card and aluminum foil, and the combination introduced inside the fading apparatus – Sun Test CPS+(Atlas Materials), having a Xenon arc lamp (type NXE 1500) and a UV filter, under a 550 W/m^2 illumination. Exposure was conducted for different periods (1, 2, 6, 12, 24, 36, 48 h), at a temperature of 25 ± 2 °C and at relative humi-dity of 65 ± 5% alongside with a Standard Blue Scale.

2.5. Color measurements

Color changes in the specimens were measured using three different methods: the Standard Blue Scale, the Gray Scale and a colorimetric method. First of all, the photofading of the textile proofs, after exposure in the SunTest, were compared with eight wool standards (Standard Blue Scale), which submitted the same treatment. In France, the textile yarns must have a 3–4 light fastness, according to the Standard Blue Scale.

A second measurement consisted in the attribution of a photofading degree using an ISO Gray Scale.

A third measurement was made according to a colorimetric method. Color changes in the specimens were measured at intervals during exposure using a Minolta colorimeter. The tristimulus values, X, Y and Z under illuminant were converted to CIELAB coordinates. The color difference (ΔE CIELAB) values between the original and the faded portions were calculated for each exposure period [9].

3. Results and discussions

In 1965, Giles described the five types of fading rate curves which are typical of synthetic dyes. In 1987, Cox-Crews constructed the fading rate curves of some natural dyes and compared them with Giles's five types of fading. Madder and weld, with either tin or alum mordant fixed on wool, showed a type II fading and indigo showed a type III fading.

In the first part of this study we tried to determine the fading rate curves of the three natural dyes fixed on cotton yarn. Fig. 2 shows these fading rate curves constructed from color difference measurements.

Madder and weld, two natural mordant dyes, fade rapidly at first, followed by slower fading at a constant rate, so we have a type II fading rate curve. This type of fading suggests that a small portion of the dye remains molecularly dispersed within the fiber, but most of it forms aggregates [1,2,15].

The woad, one of the few natural vat dyes, exhibited a type III fading rate. The results are convergent with those of Cox-Crews which studied an *Indigofera tinctoria* extract, richer in pigment than *Isatis tinctoria* (woad). The woad fading rate curve suggests that the dye formed large aggregates inside the fiber which reduce the surface area of the dye accessible to oxygen, light and moisture [1,2,15].

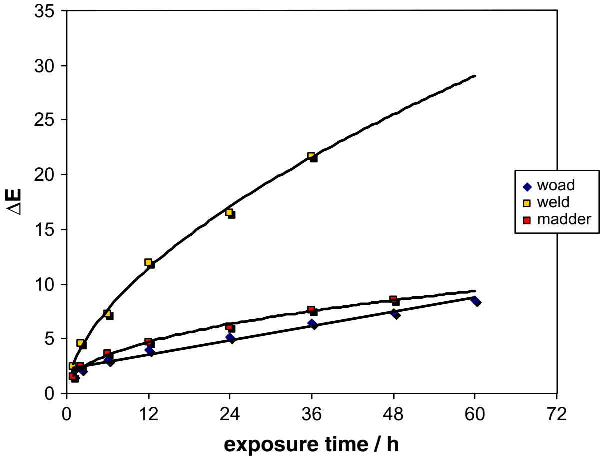


Fig. 2. Fading rate curves of weld, madder and woad fixed on cotton yarn.

The madder coloring compounds are anthraquinones – at least 19 components in a liquid extract. The most important of which are alizarin, purpurin, ruberythric acid and lucidin-primeveroside. Generally, the anthraquinone dyes have a good light fastness; for the hydroxyanthraquinones, the fastness decreases as the number of hydroxyl groups increases.

The coloring constituents of weld are luteolin, luteolin-7-glucoside, luteolin-3′,7-diglucoside and apigenin. The light fastness of these compounds is also dependent on the number and position of substituents (auxochromes) [16].

The coloring matters of woad are indigotin and indirubin. Indigotin is a symmetrical dye molecule. In addition, indigoid dyes have good light fastness properties and their light fastness is relatively independent of substituent groups. These factors, combined with the physical state of the dye, may explain its superior light fastness compared to other natural dyes.

Madder and woad are more light fast than weld. This fact can be explained by the state of dye inside the fiber: indigotin is in form of relatively large particles of insoluble colorant and anthraquinones aggregate into large particles in the fiber, forming metal-complexes. Giles et al. [17] stated that the fastness of alizarin may be due partly to an absorption spectrum shift caused by the dye–metal complex formation. Van Beek presumed that the metal ions quench the excited states, therefore their presence in a system usually increased the stability toward light [18].

The size and the form of the aggregates determine the extent of the exposed air–dye interface, and this in turn determines the rate of photodegradation. Giles [15] presumed that the characteristics of the aggregates influence fading by influencing the aggregate lattice energy – the energy to break away a dye molecule. No certain experimental evidence is available for this hypothesis.

In the second part of this study we tried to improve the light fastness of these three natural dyes, using UV absorbers and antioxidants.

First of all, the incorporation of these additives must not change the color of the dyed samples. However, the

Table 2
$L*$, $a*$ and $b*$ (CIELAB) values for the treated and untreated samples of woad dyed cotton

Sample treatment	$L*$	$a*$	$b*$
Woad untreated	59.52	−10.38	−16.98
Woad/gallic acid	60.63	−7.61	−13.87
Woad/vitamin C	64.80	−7.38	−13.58
Woad/cafeic acid	62.47	−5.57	−10.07
Woad/α-tocopherol	58.07	−9.01	−17.06
Woad/phenyl salicylate	63.33	−6.35	−12.95
Woad/2-hydroxybenzophenone	67.43	−6.40	−5.94
Woad/2,2′-dihydroxy-4,4′-dimethoxybenzophenone	60.75	−9.07	−16.63

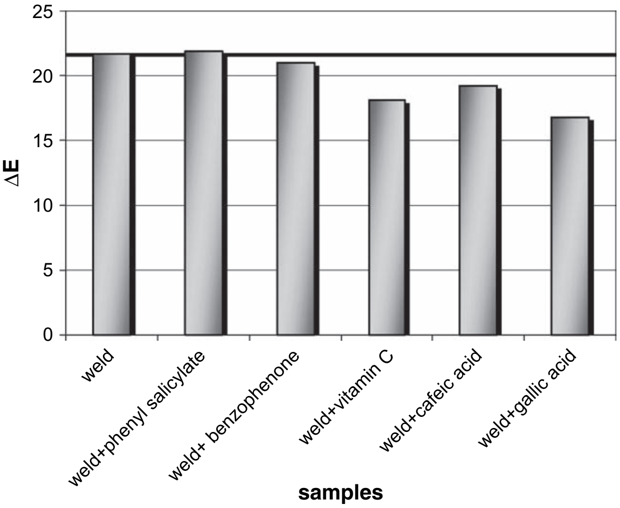


Fig. 3. Color difference for treated weld samples after 36 h of exposure.

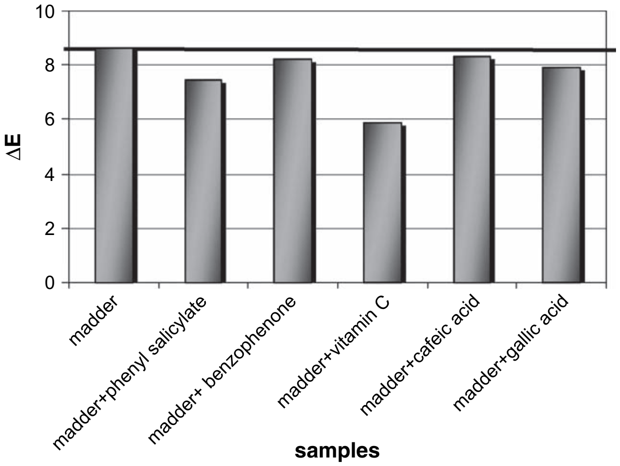


Fig. 4. Color difference for treated madder samples after 48 h of exposure.

values $L*$, $a*$ and $b*$ (CIELAB) of the treated and untreated samples of woad dyed cotton, presented in Table 2 show that, in general, the treatment brings certain changes; all of the three values ($L*$, $a*$, $b*$) increase, which means brighter and more yellow colors. For woad, the 2,2′-dihydroxy-4,4′-dimethoxybenzophenone and the α-tocopherol, did not bring a color change, after their fixation on the dyed cotton yarn.

For weld and madder, the incorporation of UV absorbers or antioxidant substances does not bring important changes to the photofading process; the results are presented in Figs. 3 and 4. The fading rate curves of the treated samples look alike to the fading rate curve of the untreated dyed cotton yarn. Nevertheless, we can observe that for the weld, the antioxidants (gallic acid, vitamin C and cafeic acid) are more effective than the UV absorbers (2-hydroxybenzophenone and phenyl salicylate). The most efficient additives were gallic acid and vitamin C for weld, and vitamin C and phenyl salicylate for madder. The fact that the UV absorbers are inefficient on weld dyed cotton suggests that this natural dye is very susceptible to fading by the visible light. This hypothesis is sustained by the studies of Cox-Crews on the color of museum light filters. She stated that for weld, madder and fustic, the use of yellow UV filters is more appropriate than the use of clear ones because apparently they absorb the damaging radiation for these dyes [19].

For woad, all the UV absorbers and antioxidants, except phenyl salicylate, showed a great improvement in the light fastness of the dyed cotton yarn. The most efficient additives (after 48 h of exposure) were vitamin C, 2,2′-dihydroxy-4,4′-dimethoxybenzophenone, α-tocopherol and gallic acid. The results are presented in Fig. 5.

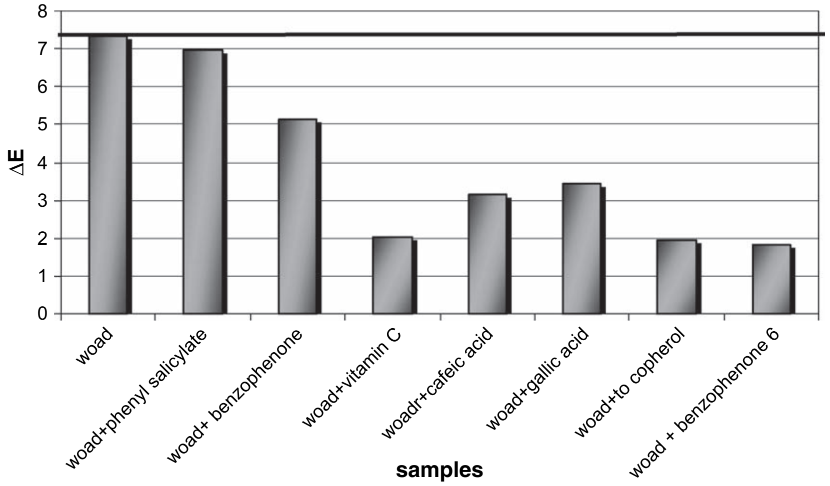


Fig. 5. Color difference for woad treated samples after 48 h of exposure.

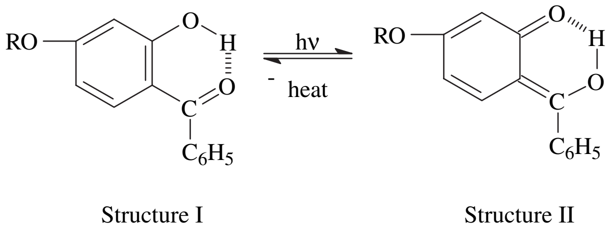


Fig. 6. Photochemistry of the 2-hydroxybenzophenones.

The photochemistry of the 2-hydroxybenzophenones, presented in Fig. 6, has been more extensively studied than that of the other classes of ultraviolet absorbers. It is known that the structure I is rapidly converted to a "photoenol" (II) by absorption of light, and that the structure II reverts to structure I with loss of energy as heat, with almost 100% efficiency. The existence of the intramolecular hydrogen bond in both I and II structures accounts for the rapid and efficient phototautomerism [11].

In their study, Coleman and Peacock [20] showed that the hydroxybenzophenones are efficient on wool but not very efficient on cotton. Van Beek [18] stated that the application of benzophenones is only useful for dyes which are not sensitive to visible light and even then, the improvement is in general not greater than one grade of fastness.

Our study showed that the 2-hydroxybenzophenone is not an efficient UV absorber for the three chosen natural dyes fixed on cotton. Nevertheless, the 2,2′-dihydroxy-4,4′-dimethoxybenzophenone seems to be more efficient than the 2-hydroxybenzophenone in the case of the woad dyed cotton yarn. The difference between the 2,2′-dihydroxy-4,4′-dimethoxybenzophenone and the 2-hydroxybenzophenone activities may be explained by the differences in adsorption: the 2,2′-dihydroxy-4,4′-dimethoxybenzophenone presents a strong absorption in the near ultraviolet, attributed to a conjugate chelation between the *ortho*-hydroxy and the carbonyl group.

The phenyl salicylate presents a very low absorption in the solar ultraviolet region. However, after exposure to sunlight for a time, it shows an increase in absorption in the 290–400 nm region, and after sufficient exposure, its spectrum resembles those of 2-hydroxybenzophenones. The phenyl salicylate owes its effectiveness to a light-catalyzed rearrangement that converts it to 2-hydroxybenzophenone (Fig. 7). Unfortunately, other products are also formed, and the conversion to effective stabilizers is only 50–70% efficient [11].

Our study showed that the phenyl salicylate is inefficient in all the given cases.

The poor light fastness of the three natural dyes is established beyond question. Nevertheless, the use of some additives can improve this default of natural dyes.

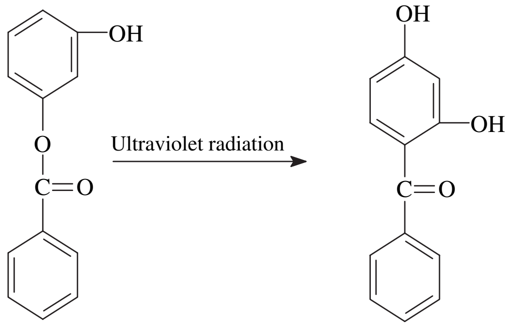


Fig. 7. Photochemistry of phenyl salicylate.

The UV light is an important cause in the fading of practically all dyes, in the weakening of fibers and fabrics, and in the photodegradation of many other substances. UV absorbers and antioxidant molecules have been applied to many substances and have been successful in many cases in neutralizing the destructive attack of UV light. However, many more studies on their application to fibers will be necessary before maximum effectiveness can be attained.

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