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Light Fastness of Coloured Polymeric Materials

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The paper examines the photochemical phenomena underlying the photodegradation of dyes in coloured polymeric materials and determining the rate and degree of fading of the dyeings. Methods are described for assessing quantitatively the light fastness of coloured materials, and the principles of a scientifically based standardisation of methods for testing the light fastness of dyeings are discussed. The effects of the conditions of exposure and the physicochemical properties of the dye and the polymer matrix on the light fastness of the dyeing are also considered. A list of 106 references is included

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I. INTRODUCTION

Investigations of the action of light on coloured polymeric materials (films and fibres) are continually increasing every year. More than five hundred original papers have been published on this problem merely during the past five years. Such a wealth of publications is due to the increased ranges of dyes and polymer materials and the enhanced demands made on their light resistance.

The qualitative concept of the light fastness of a material is fairly definite. It implies the ability of the material to retain its initial properties under the influence of electromagnetic radiation in both visible and ultraviolet regions of the spectrum. In coloured materials both the dye and the polymer substrate undergo degradative processes under the influence of light.

In a coloured polymeric material both the polymer itself and the dye on it should have adequate resistance to light. If they differ markedly, the material will cease to function before its potential light fastness is exhausted. From this point of view an ideal material will be one in which polymer and colorant will have closely similar and high degrees of resistance to light.

The most obvious results of photodegradation are a change in the colour of the material and impairment of its mechanical properties. The changes in these properties during a given time of exposure are naturally most often chosen as criteria of resistance to light[1-4]. Despite the apparent obviousness and simplicity of such criteria, their practical use encounters very considerable and fundamental difficulties. A quantitative assessment of the colour of a material is already difficult because it must depend on subjective assessments by different observers. Certainly, the elaboration of formal systems of trichromatic coordinates, making possible the widespread use of instrumental estimates, shows promise. We must acknowledge the great importance of work[3,5-12] aimed at estimating objectively and instrumentally (photometrically) the change in colour undergone by coloured fibres during illumination.

No difficulty is presented by the quantitative evaluation of the mechanical properties of polymeric materials, since appropriate experimental methods have been well developed. However, the mechanical characteristics of a material are in general non-linear functions of time of exposure, so that results obtained for short exposures cannot form a reliable basis for prognostication[13]. Furthermore, little study has been made of the relation between chemical changes in the structure of a polymeric material and changes in its mechanical properties. It is therefore difficult to predict quantitatively the change in mechanical properties from the extent of chemical change, which causes the variation in the properties of the material[14].

The above comments make clear why the past years have seen an increase in the number of quantitative studies of photochemical processes occurring in coloured materials. Special mention may be made here of Refs. 15-22.

Information on the mechanism and the kinetics of the photodegradation of coloured polymer materials, revealing the factors determining their resistance to light, is of great interest for various fields of technology in which these materials (primarily films and fibres) are employed. The Soviet literature contains no reviews on the photostability of coloured polymer materials; among foreign publications the surveys by Giles[23] and by Brunnschweiler[2] may be noted. The present Review pays close attention to the main factors governing the resistance of coloured polymer materials to light, and summarises information on methods for its quantitative evaluation.

II. MONOCHROMATIC ILLUMINATION

1. Determination of Photostability from Quantum Efficiency of Photochemical Conversion

The change in properties of a coloured material under the influence of light is due to photochemical reactions occurring in the material. At least in principle, therefore, the light resistance with respect to any parameter can be related with a quantitative characteristic of the photochemical changes. The most rigorous of such characteristics is the quantum yield γ of a photochemical reaction, which is the reciprocal of the number of quanta of radiation absorbed in decomposing one reactant molecule or forming one product molecule. The quantum efficiency can obviously serve as a measure of the photostability. It is therefore useful to examine in greater detail the quantitative relation between quantum efficiency and the photochemical processes occurring in coloured polymers.

Wity monochromatic illumination the quantum yield[24] is calculated by definition from the relation

$$W = \gamma\Phi \qquad (1)$$

where W is the rate of the given chemical change and Φ the

rate of absorption of light, i.e. the number of quanta absorbed by the specimen in unit time. Formula (1) shows that the quantum yield γ is a coefficient of proportionality linking these two quantities.

If we denote by m the quantity of material undergoing conversion, we have

$$W = dm/dt . \tag{2}$$

Here m is the integral of the concentration x throughout the volume v of the specimen:

$$m = \int_{(v)} x\, dv . \tag{3}$$

If the concentration is the same throughout ($x = c$), then

$$m = cv \tag{4}$$

and, as is usual with homogeneous dark and also liquid-phase photochemical reactions with stirring, the rate W is proportional to the change in concentration in unit time:

$$W = v\, dc/dt . \tag{5}$$

When coloured polymer materials are illuminated, the concentration of absorbing centres varies non-uniformly through the thickness of the specimen, and the more general expression (2) must be used.

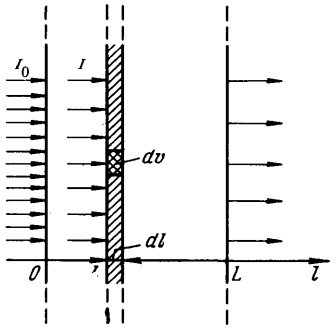


Figure 1. Diagram of plane-parallel specimen undergoing illumination.

The quantity of light absorbed by a specimen or one of its components can in principle be calculated by means of the Bouguer–Lambert–Beer law for a specimen of any shape and with any concentration distribution of absorbing centres. However, avoiding further complications and also with no loss of generality in the conclusions, we shall henceforward consider a specimen in the form of a plane-parallel layer of thickness L (a film) exposed on one side to a parallel beam of light perpendicular to the surface (Fig. 1). Here I_0 (in einsteins dm^{-2}) is the intensity of the light flux incident on the specimen, and I the intensity of the light flux reaching a layer at an arbitrary depth l.

In a multicomponent system every component is able to absorb light and undergo changes or cause changes in other components (stabilisation and sensitisation effects), which complicates Eqn. (1). For a binary polymer–colorant system, for example, the rate of photoconversion of the colorant is

$$W_c = \gamma_c \Phi_c + \gamma_c^p \Phi_p \tag{6}$$

where Φ_c and Φ_p are the rates of absorption of light by colorant and by polymer respectively, and γ_c and γ_c^p are the quantum efficiencies of conversion of the colorant resulting from the action of light absorbed solely by the colorant (Φ_c) and solely by the polymer (Φ_p). The corresponding formula for the rate of breakdown of the polymer is

$$W_p = \gamma_p \Phi_p + \gamma_p^c \Phi_c .$$

This last formula is used in studying the photodegradation of polymers sensitised by colorants[25–28].

Although in the present paper attention is paid mainly to revealing the kinetic mechanism of the breakdown of a colorant on a fibre, not of the fibre-forming polymer itself, the arguments and mathematical expressions given below can be successfully applied to quantitative evaluation of the photodegradation of the polymer[29].

If the absorbing centres of colorant and polymer are mutually independent, the Bouguer–Lambert–Beer law gives

$$\Phi_c = I_0 S \varepsilon_c' \int_0^L x_c(l) \exp\left[-\int_0^l (\varepsilon_c' x_c(l) + \varepsilon_p' x_p(l))\, dl\right] dl , \tag{7}$$

$$\Phi_p = I_0 S \varepsilon_p' \int_0^L x_p(l) \exp\left[-\int_0^l (\varepsilon_c' x_c(l) + \varepsilon_p' x_p(l))\, dl\right] dl , \tag{7a}$$

in which S is the surface area of the specimen, ϵ_c' and ϵ_p' (in $M^{-1}\ dm^{-1}$) are the natural molar extinction coefficients of colorant and polymer, and $x_c(l)$ and $x_p(l)$ are the concentrations of colorant and polymer absorbing centres at depth l. Equations (7) and (7a) cannot be integrated in the general case of arbitrary concentration distributions, which leads to great complications in kinetic investigations of photoreactions in solid polymers.

In the simplest case, if $x_c = c_c$ and $x_p = c_p$, we obtain

$$\Phi_c = I_0 S \frac{\varepsilon_c' x_c}{\varepsilon_c' x_c + \varepsilon_p' x_p}\left[1 - e^{-(\varepsilon_c' x_c + \varepsilon_p' x_p)L}\right] , \tag{8}$$

$$\Phi_p = I_0 S \frac{\varepsilon_p' x_p}{\varepsilon_c' x_c + \varepsilon_p' x_p}\left[1 - e^{-(\varepsilon_c' x_c + \varepsilon_p' x_p)L}\right] . \tag{8a}$$

The parameters

$$f_c = \frac{\varepsilon_c' x_c}{\varepsilon_c' x_c + \varepsilon_p' x_p} = \frac{D_c}{D_c + D_p} = \frac{D_c}{D} \tag{9}$$

$$f_p = \frac{\varepsilon_p' x_p}{\varepsilon_c' x_c + \varepsilon_p' x_p} = \frac{D_p}{D_c + D_p} = \frac{D_p}{D} \tag{9a}$$

(where D_c, D_p, and D are the optical densities (decadic or natural) of colorant, polymer, and specimen as a whole) define the fraction, absorbed by the given component, of the total quantity of light $\Phi = \Phi_c + \Phi_p = I_0 S(1-10^{-D})$ (on passing to decadic optical densities): i.e.

$$f_c = \Phi_c/\Phi , \tag{10}$$

$$f_p = \Phi_p/\Phi . \tag{10a}$$

The parameters f_c and f_p are often termed[30] "shielding coefficients", since they allow for the internal filtering effect of the second component.

When relations (10) and (10a) are incorporated, Eqn. (6) is written

$$W_c = (\gamma_c f_c + \gamma_c^p f_p)\Phi . \tag{6a}$$

When one of the components is photochemically inactive, e.g. if the polymer does not sensitise photodecomposition of the colorant ($\gamma_c^p = 0$), formula (6) becomes

$$W_c = \gamma_c f_c \Phi = \gamma_c \Phi_c \tag{6b}$$

which is convenient for assessing quantitatively the factors

influencing the light fastness of a colorant. If the colorant does not sensitise photodegradation of the polymer (i.e. $\gamma_p^c = 0$), the rate of breakdown of the latter is

$$W_p = \gamma_p f_p \Phi = \gamma_p \Phi_p . \quad (11)$$

It follows from (6a) that the light fastness of a colorant increases with decrease in W_c. Light fastness is therefore more conveniently characterised by the reciprocal of the rate of photoconversion

$$\tau_c = 1/W_c . \quad (12)$$

The parameters γ_c and γ_c^p represent in general the most important objective factors determining the light fastness of a colorant on a fibre, and enable a quantitative comparison to be made of the light fastness of different dyes on different kinds of fibres. However, τ_c will be a more rigorous characteristic of light fastness, taking into account not only quantum efficiency but also the rate of absorption of light by the sample.

When comparing the light fastness of different colorants by means of τ_c, we must pay special attention to the dependence of this parameter on the concentrations both of the colorant in the polymer and of the absorbing centres of the polymer. The concentration dependence of Φ_c and Φ_p is determined by the relations (7), (7a), (8), and (8a). The parameters γ_c and γ_c^p may also depend on concentration, as will be shown below. However, even without detailed analysis it is obvious that, for example, τ_c will be longer at a low colorant concentration than at a higher concentration of the same colorant (provided that no aggregation of the dye occurs, which would affect the rate of the photochemical processes), since in the former case values of Φ_c and hence of W_c will be smaller. With this definition of τ_c the light fastness of a given colorant will vary. Hence it is necessary to standardise the concentrations at which a comparison is made of the light fastness of different dyes, and this in turn requires knowledge of the specific dependence of rate of photoconversion on the concentration of colorant on the fibre.

2. Dependence of Rate of Photochemical Reactions on Concentration of Absorbing Centres

For photochemical reactions, in contrast to dark reactions, the concept of reaction order is usually devoid of meaning. According to Eqn. (1) the rate of a photochemical reaction is indeed determined by the product of the two quantities γ and Φ, each of which may be a complicated function of reactant concentrations. Only in the simplest cases, over comparatively short intervals of time, can the product approximate to a parabolic relation of the type

$$\gamma\Phi = kc^p \quad (13)$$

where k no longer has the significance of a rate constant, but is a proportionality coefficient depending in general on the reactant concentration.

If the action of monochromatic radiation on a sufficiently virogously stirred solution produces photoconversion of a dye or related compound, formula (1) leads to an equation of the type (provided that quantum efficiency is independent of reactant concentration) [31]

$$dc/dt = -\frac{\gamma I_0}{L}\frac{D_c}{D}(1-10^{-D}) \quad (14)$$

where c is the molar concentration of the dye, I_0 (in einsteins dm^{-2} s^{-1}) the intensity of the incident light flux, L (dm) the thickness of the layer of illuminated solution, $D_c = \epsilon_c c L$ the optical density of the dye, $D = D_c + D_{solv}$ the optical density of the solution, in which D_{solv} is the optical density of the solvent, and ϵ_c is the decadic molar extinction coefficient of the dye. At low optical densities $D < 0.1$ we have $(1-10^{-D})/D \simeq 2.3$ to within 10%, and the expression (14) then has the form of a first-order kinetic equation

$$dc/dt = -2.3\gamma I_0 \epsilon_c c = -k_1 c \quad (15)$$

with the rate constant $k_1 = 2.3\gamma I_0 \epsilon_c$. At high optical densities $D > 1$, we have $(1-10^{-D})/D = 1/D$ to within 10%, and the dependence of dc/dt on c is described by a hyperbolic function.

At optical densities in the range 0.01–2 different functional relations, easily approximated by power series, are obtained between W and c.[24,32] An important condition for a simple power form is that the photochemical reactant should be uniformly distributed through the thickness of the specimen. Only then is the concentration x constant through this thickness and proportional to the total quantity of substance m, while the rate of photoconversion is proportional to the change of concentration in unit time dx/dt. Conducting the photochemical reaction in a sufficiently vigorously stirred solution will guarantee the above condition.

In a coloured polymeric material—whether film or fibre—the condition of uniform distribution of absorbing centres (the optical densities of coloured materials are usually around unity) already breaks down at the start of exposure, owing to more intense fading of the dye in the surface layers. As a result, the dye concentration varies from point to point, and it is not possible to integrate Eqn. (14) for the general case. This feature of solid-phase photochemical processes has been ignored in certain publications [24,31,33]. The optical density ceases to be a linear function of thickness, and is given by the integral

$$D = \varepsilon \int_0^l x(l)\,dl,$$

where $x(l)$ is the local concentration, depending on the depth of that layer l. Yet it was concluded [31] that, if the local rate of photoconversion is proportional to the quantity of light absorbed (order of reaction with respect to absorbed light intensity $n = 1$), the local rate dx/dt and the observed total rate dm/vdt should coincide. It can easily be shown that this conclusion is in general incorrect.

On the assumption that there is no diffusion of photodecomposition products, we suppose that illumination of a film produces a colorant distribution represented by the equation

$$x_c = \sigma_c/a_c - b_c l \quad (16)$$

where σ_c, a_c, and b_c are empirical coefficients enabling us to describe the monotonic increase in colorant concentration with distance from the exposed surface. Assuming for simplicity that the polymer is non-absorbing, i.e. that $\epsilon_p' = 0$, we then find from Eqns. (6) and (7) that the mean observed rate per unit volume is

$$W_c/v = \frac{\gamma_c I_0 \epsilon_c'}{L}\int_0^L \frac{\sigma_c}{a_c - b_c l}\exp\left[-\int_0^l \frac{\epsilon_c' \sigma_c}{a_c - b_c l}\right] dl \quad (17)$$

or, after integration,

$$W_c/v = \frac{\gamma_c I_0}{L}\cdot\frac{\sigma_c \epsilon_c'}{a_c^\beta b_c \beta}[a_c^\beta - (a_c - b_c L)^\beta] \quad (18)$$

where $\beta = \epsilon_c' \sigma_c / b_c$. At the same time the local rate at

depth l is

$$W_c(l) = dx_c/dt = \gamma_c \epsilon_c' x_c I_0 e^{-\epsilon_c' \int_0^l x_c\, dl} = \gamma_c I_0 \frac{\epsilon_c' \sigma_c}{a_c^\beta}(a_c - b_c l)^{\beta-1}. \quad (19)$$

The ratio of rates (18) and (19)

$$\frac{W_c}{vW_c(l)} = \frac{[a_c^\beta - (a_c - b_c l)^\beta]}{Lb_c\beta\,(a_c - b_c l)^{\beta-1}} \quad (20)$$

obviously not only differs from unity but also depends on the depth l, which should in general be the case. It follows from the above discussion that experimental investigation of the dependence of the rate of photoprocesses (in particular fading) on the reactant concentration encounters considerable difficulties.

The most comprehensive investigations of the effect of colorant concentration on rate of fading in polymer films have been made by Giles and his coworkers [23,34-38]. Giles adopts as the main criterion of the light fastness of a dye its characteristic fading time t_f, which is the time required for the initial colorant concentration c_0 to decrease by a certain amount, e.g. by 10% or 50% ($t_{0.1}$ or $t_{0.5}$). Despite the simplicity and the convenience of the experimental determination of this criterion, its theoretical interpretation is in several cases difficult. The very definition of fading time already contains an ambiguity. The concentration of colorant in the test material becomes non-uniform as fading progresses, even if it had been uniform during coloration, and the concept of concentration for the specimen as a whole loses its meaning for optical densities exceeding 0.1. In most of Giles's experiments, therefore, t_f characterises not the time of decay of the initial colorant concentration (by a certain amount) but that of the optical density of the specimen or the mean colorant concentration.

The concept of total concentration is valid for low optical densities, and from (15) we then have

$$t_{0.5} = \ln 2/2.3\gamma I_0 \varepsilon_c = 0.3/\gamma I_0 \varepsilon_c\ . \quad (21)$$

This indicates that t_f is independent of c_0 for colorant concentrations corresponding to optical densities $D \leq 0.1$, and the graph of $\lg t_{0.5}$ against $\lg c_0$ should be a straight line parallel to the $\lg c_0$ axis, making an intercept of $-0.52 - \lg(\gamma I_0 \epsilon_c)$ on the $\lg t_{0.5}$ axis. Such a relationship was observed for small initial concentrations of colorant homogeneously distributed in a film [38]. If the light is monochromatic, such graphs can be used to determine γ for known I_0 and ϵ_c by extrapolation to $c_0 = 0$. However, Giles used polychromatic radiation in most of his experiments.

At optical densities exceeding unity we can no longer use Eqn. (14), obtained for stirred solutions, where the colorant concentration is constant throughout the thickness of the layer: instead, we must apply the equation

$$\frac{d}{dt}\int_0^L c\, dl = -\gamma I_0\ . \quad (22)$$

Introducing the mean concentration

$$\bar{c} = \int_0^L c\, dl/L \quad (23)$$

we obtain

$$d\bar{c}/dt = -\gamma I_0/L \quad (24)$$

which in effect is used by Giles for high optical densities. Here $d\bar{c}/dt$ is the observed total rate of photoconversion, which is related in extremely complicated fashion to the local rate (see above), so that the true order of the photochemical reaction cannot be assessed from this relation, as it is determined by the local rate.

The characteristic time can be defined in terms of the mean concentration, and in the present case

$$t_{0.5} = 0.5c_0 L/\gamma I_0\ . \quad (25)$$

The plot of $\lg t_{0.5}$ against $\lg c_0$ will then be a straight line of unit slope making an intercept $\lg(0.5L/\gamma I_0)$ on the ordinate axis. Giles obtained relations of this type in several cases for large initial concentrations [23,34-38]. With monochromatic illumination we can also determine γ from this relation. With polychromatic illumination a quantity equivalent to the product γI_0 should be the same, if γ is independent of colorant concentration, for low initial concentrations, when γI_0 occurs in the experimentally determined quantity $-0.52 - \lg(\gamma I_0 \epsilon)$, and for high initial concentrations, when γI_0 can be calculated from the experimental value of $\lg(0.5L/\gamma I_0)$.

It is in general impossible to calculate the fading time theoretically and relate it to the characteristics of coloured material and light source for the practically important range of optical densities $D = 0.1$–1.0, since this would require knowledge of the specific time variation of the distribution of absorbing centres through the thickness of the specimen. In the simplest case, when breakdown of the absorbing centres can be represented as the single reaction

$$A_1 + h\nu \rightarrow A_2$$

the distribution of the concentration of the reactant A_1 through the thickness at any instant can in principle be found by solving the set of non-linear equations in first-order partial derivatives (when A_2 does not absorb)

$$\begin{aligned} \partial x_1/\partial t &= -\gamma \varepsilon_1 I x_1 \\ \partial I/\partial l &= -\varepsilon_1 I x_1 \end{aligned} \quad (26)$$

in which x_1 is the concentration of A_1 at depth l, where the light intensity is I, and ϵ_1 is the molar extinction coefficient of A_1. The distribution $x_1 = f(l)$ would be obtained by solving Eqns. (26), but it is not yet possible to obtain a solution.

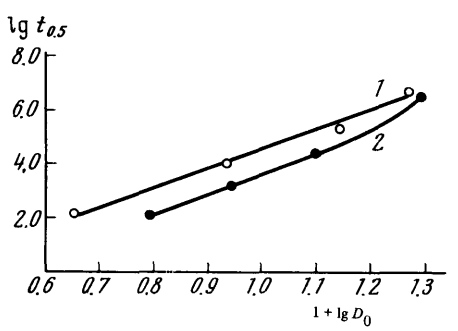


Figure 2. Dependence of characteristic fading time of the reactive dye Propionic Bright Red NZV exposed to PRK-2 lamp on initial concentration in cellulose film [25,26]: 1) covalently bound; 2) adsorbed.

With most coloured films and fibres the plots of $\lg t_f$ against $\lg c_0$ obtained by Giles [23,34-38] are only qualitatively consistent with the theoretical relation following from Eqns. (21) and (25). The slope of the linear portions of the curves at high initial concentrations usually differs from unity.

Giles explains such departure from the theoretically predicted behaviour by a purely geometrical factor—aggregation of the dye—which leads to a change in quantum efficiency with increase of concentration. It appears to the Reviewers that aggregation is only one of the possible causes.

Reactive dyes[39], which combine chemically (covalently) with certain functional groups in the fibre, are incapable of aggregation in the polymer substrate. Therefore the observed[25] increase in the light fastness of such dyes with increase in their concentration in the fibre cannot be explained by aggregation. Figs. 2 and 3 illustrate logarithmic plots of the characteristic fading time of reactive dyes against their concentration on cellulosic and polyamide films[25-27]. The appearance of a concentration effect with reactive dyes may be attributed to concentration-dependent self-quenching.

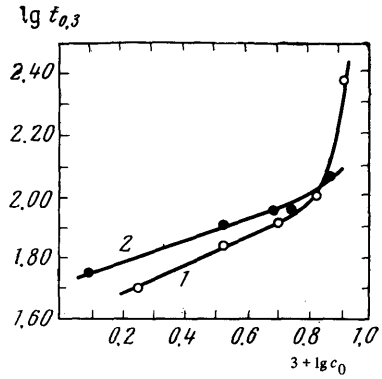


Figure 3. Dependence of characteristic fading time of the reactive dye Propionic Bright Red NZV exposed to BUV-30 lamp on initial concentration in a polyamide film[28]: 1) covalently bound; 2) adsorbed.

Analysis of the results obtained by Giles et al.[23,34-38] indicates that, although the characteristic time t_f is a convenient parameter for assessing the light fastness of a colorant, it is usually difficult to relate theoretically to photochemical parameters for the purpose of predicting light fastness.

A far more rigorous approach is to assess light fastness by means of the quantity $\tau_c = 1/W_c$ determined from the initial rates of fading at various colorant concentrations[17,26,27]. An advantage of this method is that the determination of quantum efficiency is independent of the concentration distribution of absorbing centres established during exposure. It is important merely that their concentration should be constant initially and not vary too rapidly with time. Furthermore, the quantum efficiency determined from the initial rate is independent of the accumulation of reaction products and is characteristic of the initially prepared system[28]. However, certain difficulties are encountered in determining light fastness from initial rates of fading.

1. In some cases the kinetics of fading determined for the initial period may change markedly with time. If two dyes have the same initial rate of fading and markedly different subsequent rates, for example, assessment of their light fastness from $\tau_c = 1/W_{c,0}$ will be incorrect. In this case the quantity τ_c determined from the initial rate cannot represent the real light fastness of the colorant.

2. Choosing the duration of the initial portion of the kinetic curve, along which the rate is calculated, is a very complicated matter. It is important that this section should correspond to a visually perceptible and practically important degree of fading of the dyeing. Fading is a superficial phenomenon in the sense that almost complete fading of a dyeing may be perceived, whereas the total quantity of colorant in the substrate has changed by at most 20–30%. It appears to the Reviewers that the most suitable characteristic time is $t_{0.1}$, and the initial rate in this method[17,26] should correspond to a diminution of the initial dye content by at most 10%.

III. POLYCHROMATIC ILLUMINATION

1. Calculation of Rate of Photodegradation of Coloured Materials

The large majority of investigations on photochemical changes in coloured materials have been made with polychromatic sources of ultraviolet radiation and visible light having various types of distribution of intensity with wavelength. This situation is primarily due to the practical requirement of forecasting light fastness in polychromatic sunlight and also to the simpler technique of polychromatic exposure.

Considering the principal quantitative relations determining light fastness under polychromatic illumination, we first assume that the effects of light of different wavelengths is additive and that sensitisation is absent. The total rate of photochemical conversion will then be the sum of the rates W_λ due to different portions of the incident spectrum. If this spectrum is discrete, consisting of several lines of wavelengths $\lambda_1, \lambda_2, \ldots, \lambda_n$, we have

$$W = \sum_{i=1}^{n} W_i = \sum_{i=1}^{n} \gamma_i \Phi_i \qquad (27)$$

where W_i, γ_i, and Φ_i are respectively the rate of conversion, the quantum efficiency, and the rate of absorption of light at wavelength λ_i. If, however, the radiant spectrum is continuous, extending from λ_0 to λ_m, we find that

$$W = \int_{\lambda} \omega_\lambda \, d\lambda = \int_{\lambda} \gamma_\lambda \, d\Phi_\lambda \, . \qquad (27a)$$

The quantities W_i and Φ_i correspond to Eqns. (1) and (7), while

$$\omega_\lambda = \lim_{\Delta\lambda \to 0} \frac{\Delta W}{\Delta \lambda} \qquad (28)$$

is the limit of the ratio in which ΔW is the rate of photoconversion due to the width $\Delta\lambda$ of the radiated spectrum at wavelength λ.

The quantity $d\Phi_\lambda$ is given by a formula analogous to (7):

$$d\Phi_\lambda = I_{0\lambda} S \varepsilon'_{c\lambda} \int_0^L x_c \exp\left[-\int_0^l (\varepsilon'_{c\lambda} x_c - \varepsilon'_{p\lambda} x_p) \, dl \right] dl \, d\lambda \qquad (7b)$$

where $\epsilon'_{c\lambda}$ and $\epsilon'_{p\lambda}$ are the molar extinction coefficients of colorant and polymer at wavelength λ, and $I_{0\lambda}$ is the spectral density of the radiation at the same wavelength. For

concentrations $x_c(l)$ and $x_p(l)$ constant through the thickness of the specimen Eqn. (7b) simplifies to

$$d\Phi_\lambda = \frac{D_{c\lambda}}{D_\lambda} I_0 (1 - 10^{-D_\lambda}) d\lambda \qquad (8b)$$

where $D_{c\lambda}$ and D_λ are the optical densities of the colorant and of the specimen as a whole at wavelength λ.

Since the change from summation to integration is clear from a comparison of corresponding formulae, we shall henceforward suppose for simplicity that the radiated spectrum comprises two lines at λ_1 and λ_2 (the extension to a larger number of lines is self-evident). The rate of photoconversion of the absorbing centres, when sensitisation or initiation occurs by the absorption of light by other centres, will then be (for the colorant)

$$W_c = \gamma_{c_1}\Phi_{c_1} + \gamma_{c_2}\Phi_{c_2} + \gamma^p_{i_1}\Phi_{p_1} + \gamma^p_{i_2}\Phi_{p_2}. \qquad (6c)$$

The initial rate of fading with a uniform distribution of the colorant is given by the expanded equation

$$W_{c_0} = I_{1_0} D^{-1}_{1_0} (1 - 10^{-D_{1_0}})[\gamma_{c_1} D_{c_{1,0}} + \gamma^p_{i_1} D_{p_1}] + I_{2_0} D^{-1}_{2_0} (1 - 10^{-D_{2_0}}) \times \qquad (29)$$

$$\times (\gamma_{c_2} D_{c_{2,0}} + \gamma^p_{c_2} D_{2_0})$$

in which the subscripts 1 and 2 relate to wavelengths λ_1 and λ_2, and the subscript 0 to the initial state.

Direct extrapolation of fading data obtained with a source having one spectral distribution (e.g. monochromatic) to a source having a different spectral distribution (e.g. polychromatic) is in general inadmissible, and would lead to especially marked distortions when colorants having different spectral characteristics are compared. Nevertheless, if the quantum efficiencies are known for different portions of the radiant spectrum, formula (27) or (27a) can be used to calculate the rate of photochemical conversion for any source and thus the conditions under which fastness ratings are determined can be standardised. When sensitisation occurs, Eqn. (27) for the simplest case of a binary system can be expanded to

$$W_c = \sum_{i=1}^{n} (\gamma_{ic}\Phi_{ic} + \gamma^p_{ic}\Phi_{ip}). \qquad (27b)$$

The fastness rating is then determined from the equation

$$\tau_c = 1/\sum_{i=1}^{n} (\gamma_{ic}\Phi_{ic} + \gamma^p_{ic}\Phi_{ip}) . \qquad (12a)$$

2. Standardisation of Methods of Fastness Testing

Formula (12a) contains all the parameters required to standardise the conditions for the determination of light fastness. As mentioned earlier, standardisation must be effected with respect to the initial rates of fading of the dyeing. The initial rate W_{C0} depends explicitly [Eqn. (29)] on the radiation intensities at the different wavelengths $I_{1,0}$ and $I_{2,0}$ and on the optical densities $D_{0,i}$ at these wavelengths.

Thus the main factor to be standardised is the spectral distribution of intensity of the light source. This condition is essentially satisfied automatically in all experiments on natural fading, since the same light source is used. If different sources are employed, the same values $I^{st}_{0,i}$ adopted as standard must be substituted, for all the test colorants, in an expression of type (29). Determination of light fastness from the initial rate $W_{c,0}$ will then be standardised with respect to the radiant flux.

Standardisation of the optical densities occurring in Eqn. (29) is a more complicated matter. Firstly, it is impossible to arrange that the optical densities for different substances should coincide at all wavelengths. Furthermore, the quantum efficiencies γ_i may depend on the optical density implicitly (through the colorant concentration). Therefore, although the change of optical density is most often used as a criterion of light fastness, comparison of different colorants with respect to light fastness is most correctly made at the same initial concentrations in the polymer. If the light fastness has been determined at different concentrations, values of D_{st} corresponding to the concentration adopted as standard with a specimen of standard thickness L_{st} must be substituted in a formula of type (29) in order to obtain comparable results:

$$D^{st}_i = \epsilon_i c_{st} I_{st} .$$

Dimensionally the light-fastness rating τ_c is the time required for unit molar change in concentration of the colorant in the coloured material under standard conditions. Thus it is in some measure a generalisation to rigorous conditions of the characteristic time concept widely used by Giles et al.[23,34-38].

IV. PHYSICOCHEMICAL PARAMETERS OF COLOURED MATERIAL DETERMINING ITS LIGHT FASTNESS

For the simple case of a binary system and an incident spectrum comprising two lines the light-fastness rating is related to the physicochemical parameters of the coloured material by the equation [see Eqns. (12) and (29)]

$$\tau_c = 1/(I_{1_0}\theta_1 + I_{2_0}\theta_2) \qquad (12b)$$

where the I_{0i} are the spectral characteristics of the source, and the

$$\theta_i = D_i^{-1}(1 - 10^{-D_i})(\gamma_{ic} D^p_{ic} + \gamma^p_{ic} D_{pi}) \qquad (30)$$

depend only on the spectral (D_i, D_{ic}, and D^p_{ic}) and other properties (γ_{ic}, γ^p_{ic}) of the absorbing medium at the given wavelength λ_i.

1. Spectra of Colorants and Polymers

According to Eqn. (12b) a decrease in any term $I_{oi}\theta_i$ produces an increase in light fastness. The problem of improving the light fastness of coloured fibres must therefore be attacked by analysing how these terms can be reduced. Since $I_{1,0}$ and $I_{2,0}$ are external parameters independent of the material (e.g. the time-averaged spectrum of sunlight or the spectrum of some standard source), τ_c can be lengthened only by diminishing the θ_i.

The absorption spectra of most dyes consist of an intense band in the visible, which determines the colour, and one or two bands in the ultraviolet[40] (Fig. 4). Dyes are usually most sensitive ($\lambda_{c,i}$ large) to the ultraviolet region of the solar spectrum. Hence, of two dyes possessing the same absorption bands in the visible, the one whose ultraviolet band is further displaced to wavelengths below 300 nm, i.e. to a region where the intensity of sunlight is low†, is the more stable, for the product $I_{oi}\theta_i$ is small. Thus the light fastness of a colorant can be enhanced by introducing substituents that shift the ultraviolet absorption band to a region where the source has low intensity.

† Solar rays having $\lambda > 290$ nm reach the surface of the Earth.

A theory of colour, relating the chemical structure of a colorant molecule with its spectrum, could be of great help in this respect. However, the development of such a theory, based on the quantum chemistry of the ground and excited states of polyatomic molecules[41-45], is far from complete. The controlled preparation of compounds having a specified spectrum can therefore be based only on intuition and semi-empirical rules.

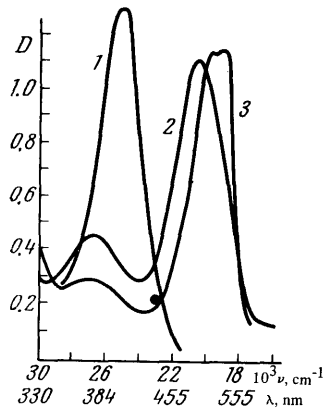


Figure 4. Absorption spectra of some reactive dyes in water[27]: 1) Reactive Yellow 2KT; 2) Reactive Scarlet 2ST; 3) Propionic Bright Red NZV.

An interesting phenomenological classification of the electronic spectra of various organic compounds has been worked out by Shigorin and his coworkers[45]. For an examination of a considerable quantity of data on absorption and luminescence spectra they formulated a rule governing the nature of the lowest energy levels responsible for long-wavelength absorption or emission: the nature of the lowest excited states (of $n\pi^*$ or $\pi\pi^*$ type) of complex molecules containing several interacting chromophoric systems is determined mainly by groups producing the smallest energy difference

$$h\nu = E_{S^*,T} - E_{S_0} \qquad (31)$$

between the lowest excited (S^*, T) and ground (S_0) electronic states. It follows that complex molecules containing different kinds of chromophoric groups should have different relative arrangements of singlet and triplet levels of $n\pi$ and nl types. On the other hand, the relative arrangement of electronic states is itself determined by the structure of the whole molecule. Hence, in order to explain the observed spectral luminescent properties of complex molecules containing $n\pi$ or nl electrons, it is necessary to know the relative arrangement of the five lowest electronic states —S_0, $S_{\pi\pi^*}$, $T_{\pi\pi^*}$, $S_{n\pi^*}$, and $T_{n\pi^*}$.

The spectrum of the polymer may have a significant effect on the light fastness of a colorant because of a shielding effect. Formula (12b) shows clearly that, if the polymer has no sensitising action ($\gamma_c^p = 0$), increase in the optical density of the polymer D_{pi} in the region of the ultraviolet absorption band of the colorant leads to an increase in the total optical density D_i, and hence a decrease in θ_i and an increase in τ_c. Absorption bands in the spectra of fibre-forming polymers (Fig. 5, curves *a* and *b*) usually lie in the far ultraviolet[13,46], so that their shielding effect is small under terrestrial conditions of exposure to sunlight ($\lambda > 300$ nm). In several cases, therefore, the shielding effect is strengthened by introducing into the polymer an ultraviolet absorber—a colourless additive having a strong absorption band in the region of the ultraviolet band of the colorant[23,46-50]—which produces an increase in D_i and hence also in τ_c.

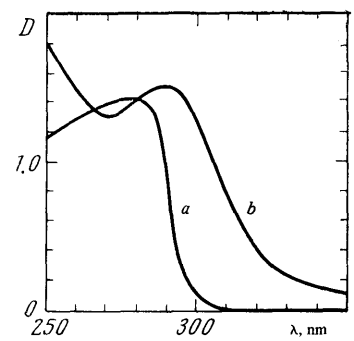


Figure 5. Absorption spectra of fibre-forming polymers[13,45]: *a*) poly(ethylene terephthalate); *b*) polyamide.

2. Factors Influencing the Quantum Efficiency of Photodecomposition of the Colorant

An obvious method for improving the light fastness of a colorant is to diminish either of the quantum efficiencies γ_c and γ_c^p. Quantum efficiency depends on several factors, whose significance can be most simply understood by using as a specific example data[15-17] showing that the photoreduction of azo-dyes can be represented by the scheme

0) $HX + h\nu \rightarrow HX^*$, $Q + h\nu \rightarrow Q^*$ } absorption of light
1) $HX^* \rightarrow HX$ (k_1)
1a) $Q^* \rightarrow Q$
2) $HX^* \rightarrow HX'$ (k_2)
3) $Q^* \rightarrow$ decomposition (k_3)
4) $HX' \rightarrow HX$ (k_4)
5) $HX' + Q \rightarrow QH + X^{\cdot}$ (k_5)

where HX is a reducing agent (e.g. phenylglycollic acid) simulating the polymer medium, Q is the colorant, HX* and Q* are excited states of reductant and colorant molecules, and HX′ is the active state of the reductant molecule initiating reaction (5), which produces fading of the colorant Q. Reaction (3) does not take place ($\gamma_c = 0$) under anaerobic conditions. With $D > 2$ the steady-state rate of fading is

$$W_c = -\frac{dQ}{dt} = I_0 S \frac{D_{HX}}{D_{HX} + D_Q} \cdot \frac{k_2}{k_1 + k_2} \cdot \frac{k_5[Q]}{k_4 + k_5[Q]} \qquad (34)$$

where D_{HX} and D_Q are the optical densities of reductant and colorant respectively, and [Q] is the concentration of the latter. Comparison of (34) with formulae (6), (7) and

(9) shows that

$$I_0 S \frac{D_{HX}}{D_{HX} + D_Q} = \Phi_p \ , \qquad (34a)$$

$$\frac{k_2}{k_1 + k_2} \cdot \frac{k_5[Q]}{k_4 + k_5[Q]} = \gamma_c^p \ . \qquad (34b)$$

Equation (34), obtained theoretically from a kinetic reaction scheme, agrees well with experimental results.

Formula (34b) gives the explicit dependence of γ_c^p on several factors, and is convenient for analysing their effects. According to this equation γ_c^p can be written as the product $\gamma_1\gamma_2$, where $\gamma_1 = k_2/(k_1 + k_2)$ characterises the ratio of the rates of processes involved in the conversion of the excited state HX* of the reductant, and

$$\gamma_2 = k_5[Q]/(k_4 + k_5[Q])$$

is the corresponding relation for the active state HX′. The transition of HX* and HX′ to the ground state (processes 1 and 4) may either be radiationless or involve radiation (luminescence). The larger the corresponding rate constants k_1 and k_4, the smaller obviously will be γ_c^p, which at the limit, when $k_1 \gg k_2$ and $k_4 \gg k_5$, will tend to

$$\gamma_{c(\text{line})}^p = \frac{k_2 k_5[Q]}{k_1 k_4} \ .$$

Here γ_c^p will be proportional to the colorant concentration, which will obviously lead to considerable simplification of the concentration dependence of W_c (on $c = [Q]$—see formula (13)). The relation between the parameters k_1, k_2, and k_4 is determined by competition among processes (1), (2), and (4), and depends on the structure of the excited states HX* and HX′. The quantity k_5 characterises the chemical reactivity of the state HX′.

If an acceptor A of electronic excitation energy (such as a diene) is introduced into the system, the excited state may be deactivated[46] by induced energy transfer:

$$\begin{matrix} 6)\ HX^* + A \rightarrow HX + A^* \ (k_6) \\ A^* \rightarrow A \end{matrix} \ .$$

The constant k_1 is then written

$$k_1 = k_1' + k_6\ [A]$$

where k_1' characterises as before all the processes yielding the ground state, both radiationless and involving quenching. At high values of the transfer constant k_6 the quantity γ_c^p will be small, which should enhance the light fastness of the colorant.

In several cases[46] additives (e.g. benzophenone, arylates with fused rings, etc.) may transfer energy efficiently to another molecule, i.e. they may be energy donors D:

$$7)\ HX + D^* \rightarrow HX' + D\ (k_7) \ .$$

The constant k_2 can then be written

$$k_2 = k_2' + k_7\ [D]$$

where k_2' as before characterises process (2). In this case γ_c^p will obviously undergo a greater increase the larger is the constant k_7.

In practice the polymer in which the colorant is distributed may itself be donor or acceptor of energy. It is interesting that the same additive may be either donor or acceptor depending on the chemical structure of the colorant. Introduction of an appropriate additive can obviously improve the light fastness of a colorant to a certain extent.

The direction of the energy transfer accompanying the interaction of two molecular species one of which is excited can be determined by the application of Vavilov's rule[51] to the electronic absorption and emission (luminescence) spectra. This states that energy is transferred efficiently to a molecule having an absorption band coinciding in position with the luminescence band of the excited molecule. The physical meaning is that the luminescence level of the donor D should lie roughly at the same height as the "absorption" level of the acceptor A (quantum-mechanical resonance).

Interesting semi-empirical rules have been established[52-56] between the spectral characteristics and the photochemical reactivity of a phosphor–matrix (organic additive–polymer) system. The photochemical reactivity and the mechanism of the primary step are determined by the nature and the relative positions of the excited electronic levels of the interacting species, as well as by structural features and their capacity for complex formation. The above workers were able to make a classification permitting qualitative prediction of the character of photochemical processes.

As has been stated above, the light fastness of coloured materials is determined, according to Eqn. (12a), by the quantum efficiencies of photodecomposition of colorant and polymer at various wavelengths and by the rates of absorption of light at the same wavelengths. The quantum efficiency of photodecomposition of a colorant, and hence its light fastness in a polymer matrix, depend most strongly on the following factors—(*a*) the state of the colorant in the polymer matrix, (*b*) the reactivity of the colorant under the conditions of exposure, (*c*) the chemical nature of the polymer matrix, (*d*) the nature of the colorant–polymer bond, (*e*) the humidity and the temperature of the surrounding medium and the material, and (*f*) the composition of the ambient atmosphere.

(*a*) State of Colorant in Polymer Matrix

A colorant can be distributed in a polymeric material either as single molecules or as aggregates of various sizes[23,34-39]. The light fastness of the dyeing is substantially affected by the state of the colorant in the polymer matrix, which depends on the chemical nature of the colorant, the physical nature of the matrix, and the dyeing conditions[23,34-39].

The electron microscopy of ultrathin regenerated cellulose films coloured with direct dyes has shown[35,37,57-59] that the dyes are present in the substrate as aggregates of various sizes, and that improved light fastness is obtained with dyes that form aggregates in the film. Unfortunately, no quantitative data have been published relating the size of the aggregates and the degree of aggregation of a colorant in a substrate to its light fastness. In general, however, aggregation of a dye in a polymeric material tends to enhance its light fastness, for the reasons indicated below.

1. Aggregation of a dye is accompanied by a decrease in the ratio of the surface area to the mass. Since light acts at the interface between the dye and the surrounding medium, the rate of fading W is proportional to this ratio S/m, and will diminish as the ratio becomes smaller.
2. In an aggregate the dye molecules are in more intimate contact with one another than is the case with a molecular distribution, and transfer of excitation energy will be more probable between the molecules in an aggregate than between the individual molecules.
3. The effect of self-shielding will be more strongly

developed when the dye is aggregated, although it is present even with a molecular distribution. Such a strong effect may lead to complete absorption of light in the upper layers of aggregates and hence abnormally slow photodecomposition of the dye.

It is known from the practical dyeing of textile materials that light fastness is enhanced by all factors promoting the formation of dye aggregates in the fibre. This applies in particular to the transition from fibres of more compact structure (cotton) to fibres of less dense structure (viscose rayon)[23], for the degree of aggregation of dyes increases with increase in the proportion of amorphous regions, where such aggregates are formed. Loosening the dense structure of cotton by mercerisation also improves the light fastness of a dyeing[23,39].

The effect of dye aggregation on light fastness has been somewhat overstated by Giles[23,34-38] in his attempt to reduce the behaviour of diverse and complicated systems on exposure to the breakdown or preservation of dye aggregates, on which basis he classifies all types of fading rate curves. Such a one-sided approach is completely unjustified, since, as the Reviewers have shown earlier, the dependence of the kinetics of the photodecomposition of dyes on their concentration and on their distribution in the matrix is extremely complicated. The non-universality of Giles's "aggregate" theory is especially clearly demonstrated by reactive dyes[25,26,39], which form covalent bonds with local active centres in fibres: i.e. they are incapable of aggregating in the substrate. Nevertheless, these dyes on cellulosic and polyamide substrates give fading curves[35,60] which correspond to aggregation of the dye according to Giles's classification.

(*b*) Reactivity of Colorant

Whereas the quantity of energy absorbed by a colorant molecule is determined by the spectral properties of colorants and polymer combined with the characteristics of the incident spectrum, the effect of this energy on the colorant, i.e. the direction and the depth of photochemical changes in the colorant, depends on its reactivity. Dyes of completely different chemical structure may have closely similar spectral characteristics. For example, yellow vat, azo, and nitro dyes, while having similar absorption spectra, will differ markedly in reactivity and hence in light fastness.

The chemistry of the photochemical breakdown of various classes and groups of dyes is the least studied aspect of the problem of light fastness. A few schemes have been suggested for the photodecomposition of azo[3,17,61], nitro[62-64], cationic[65-67], vat[18-22], and other classes of dyes. Most of them, however, are hypothetical, and their experimental demonstration was usually made under conditions remote from the conditions of use of coloured materials (the colorant was usually exposed in solution). The photodecomposition of a dye begins at the most reactive group in the molecule. For example, an azo-dye undergoes degradation at the azo-group, a nitro-dye at the nitro-group, a triphenylmethane dye at the central carbon atom, and a vat dye at a carbonyl group.

The light fastness of colorants depends not only on their reactivity under the conditons of exposure but also on the reversibility and irreversibility of the photoprocesses. Thus azo-dyes undergo irreversible breakdown at the azo-group; oxidation–reduction of vat dyes under the influence of light, on the other hand, is a reversible change, so that vat dyes have exceptionally high light fastness.

Despite the specific character of the mechanism of the photodecomposition of different classes and groups of dyes, in all cases the reactions involve either oxidation or reduction[32,40]. As oxidative mechanism of photodegradation is assumed and confirmed for the vast majority of dyes, a reductive mechanism being involved only in the fading of dyes on substrates of protein character[23].

Evidence that photodecomposition takes place by an oxidative or a reductive mechanism has been found in an analogy[23,68-71] between the behaviour of dyes under illumination and in dark redox reactions: the rates of the dark redox reaction and of photodecolorisation of the dye show the same correlation dependence on the Hammett σ constant. However, the attempt to relate the rate of photochemical reactions with the Hammett σ constant by analogy with dark reactions cannot be regarded as soundly based, since the colorant molecules involved in dark reactions are in the S_0 ground state, whereas those involved in photoreactions are in the completely different quantum-mechanical states S^* and T^*.

In the Reviewers' opinion an oxidative mechanism is most plausible for the photodecomposition of dyes in a polymer matrix (fibre or film), since all the conditions of exposure promote the formation of oxidising agents from substances present in the surrounding atmosphere or in the material itself. Among such oxidants may be oxygen in its various forms, peroxy-compounds formed by photodegradation of the fibre polymers, and other oxidising agents contained in the atmosphere of industrial towns. One source of peroxide compounds is water contained in the material itself and in the surrounding atmosphere.

(*c*) Chemical Nature of Polymer Matrix

Since light acts both on the colorant and on the polymer matrix in which the latter is distributed, the chemical and physical nature of this matrix cannot fail to affect the rate of photodecomposition of the dye. Different photochemical reactions yielding different products, which are involved in breaking down the colorant, occur in the matrix under the influence of light depending on the chemical structure. Thus the ultraviolet irradiation of coloured cellulosic and polyamide fibres gives rise to peroxy-compounds capable of decolourising dyes[9]. Models of polyamides of low molecular weight, e.g. *N*-pentylhexanoamide, on exposure to ultraviolet radiation form[72] an amide hydroperoxide having the structure $-CH_2.CO.NH.CH(OOH).CH_2-$.

Protein substrates, on the other hand, exhibit reducing properties on exposure, these being due to such amino-acids as tryptophan and histidine[23,70]. The explanation is that dyes fade by different mechanisms on protein and on non-protein substrates. The rate of fading of the same colorants (e.g. azo-dyes) is considerably lower on a protein fibre than on cellulosic fibres. It appears to the Reviewers that protein substrates, several of whose amino-acids develop reducing properties, retard the photo-oxidative degradation of dyes, probably by reacting with oxidants.

(*d*) Nature of Colorant–Polymer Bond

Different types of bond—hydrogen, van der Walls, coordinate, ionic, and covalent—may be formed between the colorant and the macromolecules of the polymer matrix. The type of bond, which depends on the chemical nature of colorant and polymer, will influence the light fastness of the system to the extent that the bond can promote the

transfer of excitation energy from the colorant molecules to the polymer macromolecule (improvement of light fastness) or from the macromolecule to the colorant molecules (impairment of light fastness). Energy transfer between two components in direct contact is theoretically possible, since even in the absence of contact between molecules (removal to 100 Å) the effect of concentration-dependent self-quenching operates[31,32,67].

Transfer of excitation energy between dye and polymer could occur most simply if they were linked by a chain of conjugated double bonds, i.e. if a single chromophoric system were formed between dye and polymer. However, such coloured polymers have not yet been prepared. Even reactive dyes, which form a more stable covalent bond with the polymer than do other classes, do not yield a single chromophoric system with the substrate.

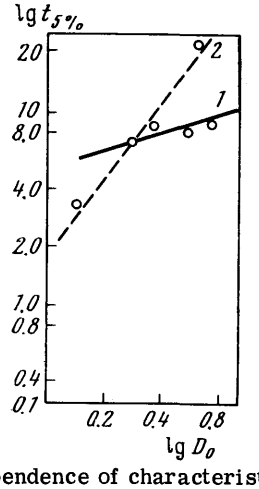


Figure 6. Dependence of characteristic fading time of Pararosaniline on initial optical density of films[23]: 1) regenerated cellulose; 2) polyacrylonitrile.

The effect of the nature of the bond is evident with cationic dyes: dyeings produced on cellulosic fibres by means of a third component (a mordant) have poor light fastness, whereas the same dyes exhibit considerably better light fastness on polyacrylonitrile fibres (ionic bond)[23] (Fig. 6).

With reactive dyes the covalent bond formed with a cellulosic fibre has a favourable influence on the light fastness, but only at low concentrations[27]. The light fastness of reactive dyeings on polyamide fibres is less affected by the covalent bond[25]. Fig. 7 illustrates the concentration dependence of the light fastness $t_{0.1}$ for the reactive dye Propionic Bright Red NZV in two forms (covalently fixed and adsorbed) on cotton cloth[27]. Only in the adsorbed form does the dye undergo aggregation with increase in its concentration in the fibre, and this aggregation effect begins to prevail over the favourable effect of the covalent bond.

(*e*) Effect of Humidity and Temperature of Atmosphere and of Textile Material

Under practical conditions of the exposure of coloured textile materials variations of the temperature and humidity of the surrounding atmosphere and of the material are interrelated, so that they can be studied separately only under laboratory conditions.

Effect of temperature. Hedges[73] investigated the effect of temperature on the fading of dyes on cotton and wool in atmospheres differing in relative humidity, and found that the activation energy of decomposition of the dye is 2 kcal mole^{-1}. Since the primary steps of photoexcitation have an activation energy close to zero[40], subsequent secondary photoreactions of decomposition must depend on the ambient temperature.

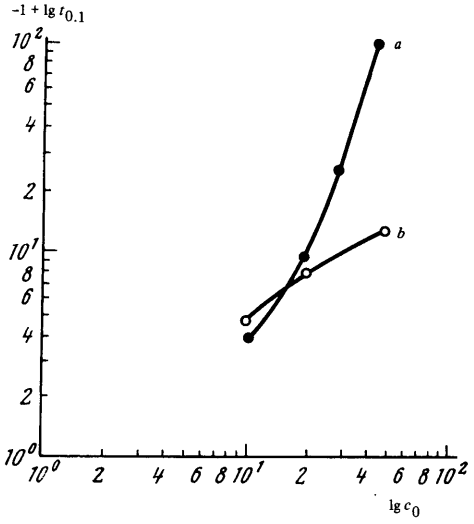


Figure 7. Dependence of characteristic fading time of the reactive dye Propionic Bright Red NZV on its initial concentration on cotton cloth[27]: *a*) hydrolysed form of dye; *b*) covalently bound form of dye.

Raising the temperature usually affects the results of light-fastness testing indirectly, the rate of fading being somewhat lower because of the diminished moisture content of the specimen. This effect is apparent with hydrophilic fibres[23]. The opposite effect is sometimes observed on hydrophobic fibres: i.e. raising the temperature causes a sharp acceleration of fading.

Investigations by the Standards Committee of the American Association of Textile Chemists and Colorists revealed[74,75] that the rates of fading of many dyes on synthetic fibres, when exposed in a Fade-Ometer and in sunlight, increase sharply with rise in temperature of the black panel (the surface temperature of a black specimen on exposure). Similar results were obtained by Friele and Selling[76].

It was suggested[23] that, in the absence of moisture on a hydrophobic fibre, (i) dye aggregates break down under the influence of atmospheric oxygen, and (ii) polar groups of the dye molecules become more accessible to attack by atmospheric oxygen, hydrogen bonds being absent between dye and water. However, these hypotheses are not supported by the experimental results. It is especially difficult to accept the last suggestion, since traces of moisture are retained as monolayers in fibrous material even at a very high temperature (up to 200°C)[77].

(*f*) Effect of Moisture in the Atmosphere and in the Specimen

The effect of moisture on the rate of fading of dyes is well known, and affects the reproducibility of light-fastness testing under natural conditions, when the intensity of irradiation varies and hence the atmospheric humidity and the moisture content of the specimen [78,79]. Increase in humidity usually accelerates degradation of the dye by light. In several cases a linear relation is observed between the light fastness and the moisture content of the specimen. The formula

$$F = K\sqrt{T}(w + c)$$

was suggested [73] to link the rate of fading of a dye, expressed as percentage decomposition F, with the temperature T °K and the moisture content w% of the specimen, K and c being constants. Lead showed [80] that the fading of dyes on wool is sharply accelerated at relative humidities of 45–80% in the surrounding air.

Despite the large number of results establishing that the light fastness of fibre dyeings is extremely sensitive both to the ambient humidity and to the moisture content of the fibrous material itself, from which quantitative relations have been elicited between them [81], the reasons for such sensitivity have not yet been finally clarified. The above mechanism of the deterioration of coloured polymers under the influence of light suggests that the role of water as a supplier (source) of species (oxygen, hydrogen, peroxide, etc.) that actively decompose the dye is extremely important and specific to various colorants and fibres. In general, however, water will be involved, either directly or indirectly, in photodecomposition of the colorant and of the fibre itself.

Assuming a photo-oxidative mechanism of breakdown for most colorants under actual conditions of use (atmospheric humidity and oxygen), we can suppose that the main function of water is to produce peroxy-compounds. Photochemical formation of a peroxide in the presence of colorants, oxygen, and water has been demonstrated with basic and vat dyes, which have a sensitising effect [73-78,80,81,83-87]. The formation of hydrogen peroxide has been shown also with dyes having no sensitising activity, but the quantity of peroxide isolated is considerably smaller in this case. The suggested [61-65] mechanism of formation of hydrogen peroxide can be reduced to the scheme

$$Q^S + h\nu \rightarrow Q^{S*} \rightarrow Q^T$$
$$Q^T + O_2^T \rightarrow Q^+ + O_2^-$$
$$O_2^- + H^+ \rightarrow HO_2$$
$$2HO_2 \rightarrow H_2O_2 + O_2^T,$$

where S and T denote singlet and triplet states, and the asterisk indicates an excited state of the colorant molecule Q. The resulting peroxide is able to break down not only the colorant but also the fibre itself [78,79].

Nevertheless, even when the moisture content of the fibre is very low (~5%) and the colorant content is 0.3–2%, each molecule of the latter is associated with 50–300 molecules of water: i.e. the excess of water present relative to the dye is such that further increase in the water content of the fibre should have no effect on the photochemical reactions. The actual situation, however, is quite different. Although calculations show [23] that the rate of fading should become constant at a very low moisture content (< 0.1%), in practice the rate has not become constant even at a content of 40%.

This can be explained by the fact that the relative humidity of the air in direct contact with the specimen is a very important factor influencing the light fastness of a dyeing. The humidity in this boundary zone is usually considerably lower than that of the total volume of surrounding air. McLaren [81] made a comprehensive investigation of the relation between the humidity of the surrounding air, that of the air in the boundary layer, the moisture content of the fibre, and the light fastness of the dyeings. He introduced the special concept of effective humidity, corresponding to that of the air in the boundary layer, and established a link between the effective humidity and the duration and intensity of irradiation of the specimen.

The effective humidity should be one of the exposure parameters to be standardised.

(*g*) Effect of Composition of Atmosphere

The deterioration of coloured fibres under the influence of light must be regarded as involving photochemical processes occurring in a system comprising fibre, the colorant, and the surrounding medium. Therefore the composition of this atmosphere should and does play an extremely important part in fading. Since oxidation, reduction, and hydrolysis lead to breakdown of colorants on the fibre, any pollutant of the atmosphere must be regarded as being possibly involved in these fading processes. The composition of the atmosphere is of paramount importance in the functioning of coloured materials in the open air and in light-fastness testing under natural conditions, i.e. in tests of fastness to light and weathering. However, it will be shown below that the composition of the atmosphere may also have an effect in accelerated tests under fading lamps.

Among pollutants of interest in connection with their effect on the action of light on coloured fibres are oxides of nitrogen, sulphur dioxide, carbon dioxide, ozone, and aldehydes. All these chemically active substances are present in the atmosphere, in which their contents may vary within wide limits depending on the type of locality (urban or rural), its geographical position, the season of the year, and the time of day. The Table lists the concentrations of the above substances in the atmosphere at three sites in the USA [88].

Pollutant concentrations in atmosphere of rural and urban localities of the USA.

Pollutant	Concentration, ppm by vol.		
	rural	Los Angeles	Chicago
Oxides of nitrogen	0.01	0.26	0.22
Sulphur dioxide	0.03	0.05	0.25
Carbon dioxide	—	23.00	16.00
Ozone	0.06—0.11	0.21	0.005
Aldehydes	—	0.3	—

The first to observe the effect of atmospheric composition on the rate of fading of dyes was Lazerev [88,89], who found an exponential relation between rate of deterioration and the oxygen content of the atmosphere.

The Table shows that the atmosphere of industrial towns has a well defined acidic character, which may promote the photodecomposition of dyes. These pollutants may break

down dyes even in the absence of light, i.e. by dark reactions, but illumination promotes their degrading action.

Sulphur dioxide enters the atmosphere of industrial towns from the combustion of coal containing up to 4% of sulphur. A considerable quantity accumulates from the use of coal as fuel (e.g. in Chicago), and the atmosphere is reducing in character, since sulphur dioxide is a strong reductant. When petroleum is used as fuel, oxidising products accumulate in the atmosphere. The main source of oxides of nitrogen is the exhaust from cars [90]. Ozone is present in the atmosphere of towns and of rural localities; its content varies with height above the Earth's surface [90].

Sulphur dioxide, nitrogen dioxide, and aldehydes absorb ultraviolet radiation of wavelengths 280–300 nm, and the excited molecules are involved in a series of successive reactions entailing formation of ozone. In contrast to sulphur dioxide, activated nitrogen dioxide reacts reversibly with oxygen, which may lead to the accumulation of ozone in the atmosphere even at low concentrations of N_2O_4.[91]

The products of the combustion of petroleum in diesel engines contain aldehydes, which in turn, in the presence of ozone and under the influence of light, form peroxides [92].

As already noted, sulphur dioxide is able to reduce dyes on the fibre. Azo-dyes are especially sensitive to the action of this gas, which breaks down the azo-group. Therefore azo-dyes are most fugitive to light and least durable on wool, since this fibre has enhanced affinity for sulphur dioxide, and absorbs it from the atmosphere [93–95].

Aminoanthraquinone blues, violets, and reds, as well as certain disperse azo-dyes, are very sensitive to the action of oxides of nitrogen [97]. Rowe and Chamberlain [98] established that the decomposition of aminoanthraquinone colorants under these conditions results from diazotisation of primary amino-groups and nitrosation of secondary amino-groups, together with oxidation, the direction of which depends on the nature of the colorant. The fastness of disperse dyes to light in an atmosphere of oxides of nitrogen is inversely proportional to their ability to form salts [99]. Under these conditions disperse dyes are most sensitive to illumination on cellulose acetate, polyester, and to a less extent polyamide and polyacrylonitrile fibres [100]. The effect of the nature of the fibre probably depends on its ability to adsorb oxides of nitrogen.

Ozone also activel. .ccelerates the photochemical decomposition of disperse and other classes of dyes [101–103]. Breakdown of the former is attributed [103] to electrophilic attack by ozone on aromatic amino-groups, so that the rate of fading should depend on the nucleophilic strength of the nitrogen atom in arylamine dyes. In fact changes in the structure of the dye, tending to diminish the electron density on the nitrogen, make the latter less susceptible to attack by an electrophilic reagent, whether ozone or oxides of nitrogen, and improve the light fastness [104–106].

The rate of breakdown of a dye on illumination in an atmosphere containing ozone depends on the distribution of the dye through the fibre, and decreases with increase in the depth of penetration into the fibre [103]. This is probably due to the role of diffusion in the effect of ozone: the accessibility of the dye to all attacking reagents, including ozone, decreases with distance from the fibre surface. Heat-treatment of a coloured cellulose triacetate fibre, like its surface hydrolysis, increases the light fastness in an atmosphere containing ozone [88], which also is probably due to diminished accessibility of the dye.

Since ozone is formed in ample quantities when xenon lamps are used, measures must be taken to remove it from the atmosphere in which the specimen is exposed.

* * *

Several fundamental conclusions can be drawn from an analysis of the literature surveyed.

1. Measurement of the initial rate of photodegradation of polymer and dye should form the basis for the quantitative assessment of the light fastness of coloured polymeric materials.
2. Interaction of polymer and colorant (both stabilising and sensitising) must be taken into account in assessing the light fastness of coloured polymers.
3. The main factors influencing the light fastness of a coloured polymer depend on the quantum efficiencies of photoreactions of polymer and colorant and on their rate of absorption of light.
4. Coloured polymer materials can be protected from the action of light by lowering the quantum efficiencies of the photoreactions of colorant and polymer and by diminishing their rates of absorption of light.

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