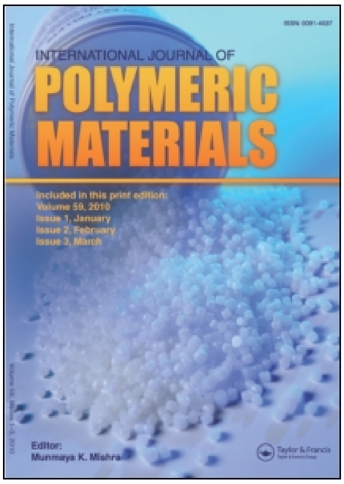

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Light Fastness Forecasting: Exposure to Various Irradiation Conditions

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A method to forecast light fastness of materials at various spectral conditions of irradiation has been developed. While the tests are carried out at a fixed set spectral conditions of irradiation, the forecast is not limited by the choice of light source and presence of light fastness in the specimens.

KEY WORDS Light fastness, forecast, irradiation spectrum.

RESULTS AND DISCUSSION

Along with a variety of sample testing procedures that affect the light fastness forecast, the researcher will also encounter the use of a variety of spectral conditions because of numerous natural factors. These include changes in location, latitude, and longitude of the test station, seasonal effects, presence of atmospheric ozone destructors, and so on. To take into account all of these factors is very difficult but also necessary because for quantum yields of dye photodegradation in polymer matrices is markedly changed with the wavelength of incident light (2–3 orders of magnitude at 30–40 nm).[1] Any attempts to adapt for this purpose the specially-selected specimens in order to determine the sample's true light fastness are futile. For example, the light fastness of the dye in polyamid cloth is changed with irradiation conditions from 1 to 7 units.[2] As far as possible the complete simulation of some "average" spectral conditions of exploitation combined with application the blue scale specimens is realized in practice but gives no guarantee for reliable light fastness forecast by exploitation.[3]

The reliable method on samples light fastness forecast at various spectral conditions of irradiation has been developed in the present work. Based on measurements carried out at some fixed set of irradiation spectral conditions, this method not only evaluates the light fastness but determines reliably (according to given confidence probability) an estimation error pointing out both a top and bottom limit for actual values of light fastness. As necessary it also allows for reliable evaluation of photodegradation quantum yield dependence on the wavelength of incident light.

To demonstrate the method we have chosen the wavelength interval from 290 to 500 nm. In order to realize irradiation spectral conditions corresponding to this interval we used a light source similar to that in "Xenotest" device (Xenon lamp). Its measured spectral structure $I_0(\lambda)$ is given in Figure 1, where λ denotes a wave-

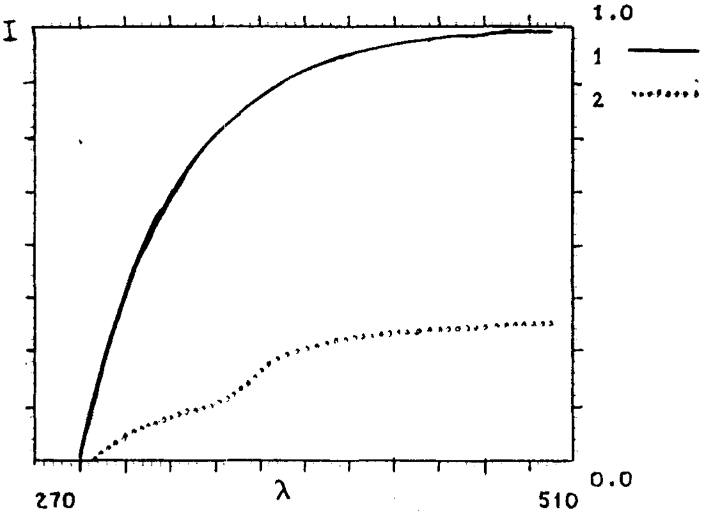

FIGURE 1 Spectral conditions of irradiation in tests (1) and exploitation (2).

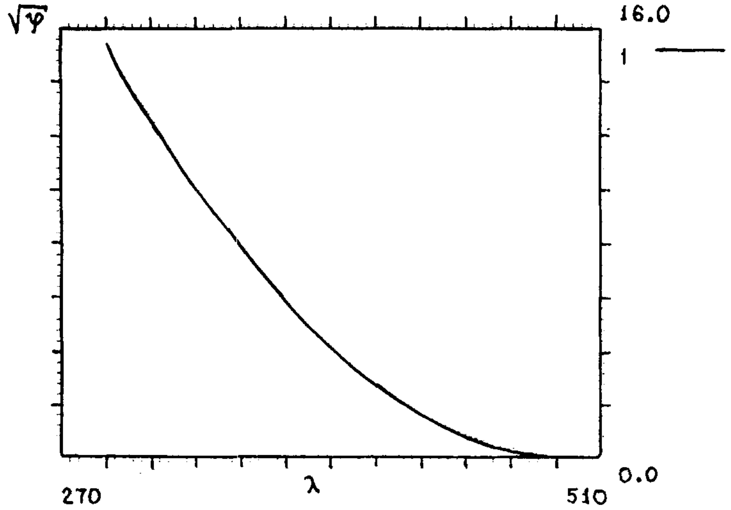

FIGURE 2 Change in the quantum yield of photodegradation process with the wavelength of incident light.

length. The curve N 2 in Figure 1 simulates irradiation spectral conditions as a forecast $I_{fc}(\lambda)$ and represents the average light spectrum in middle latitudes obtained within a year of observation.

To describe the change in simulated photodegradation quantum yield with the wavelength of incident light a function $\varphi(\lambda)$ is used. Figure 2 illustrates a typical dependence for the quantum yield of dye photodegradation in textile materials.

The following set of standard optical glasses of the same thickness (2 mm) given by catalogue[4] has been used to simulate the chosen spectral conditions: 1) CC9,

2) CC1, 3) CC15, 4) CC5, 5) C0, 6) YΦC1, 7)ΠC11 and 8) C3C24 (CO denotes a lack of glass).

Note that numeration of glass filters is not to be changed until the end. The set of filters (i.e. irradiation spectral conditions) has been chosen in accordance with a number of dye specimens which are used in standard unit estimation method of light fastness and allows to compare the quality of both proposed and standard methods.

The corresponding plots of transmissivities $\varepsilon_i(\lambda) = 10^{-2D_i(\lambda)}$ ($i = 1, \ldots, 8$) against the wavelength of incident light λ are shown in Figure 3a, where $D_i(\lambda)$ are the absorption factors as functions of λ^4 and $D_5(\lambda) = D_0(\lambda) = 0$ ($\varepsilon_5(\lambda) = \varepsilon_0(\lambda) = 1$).

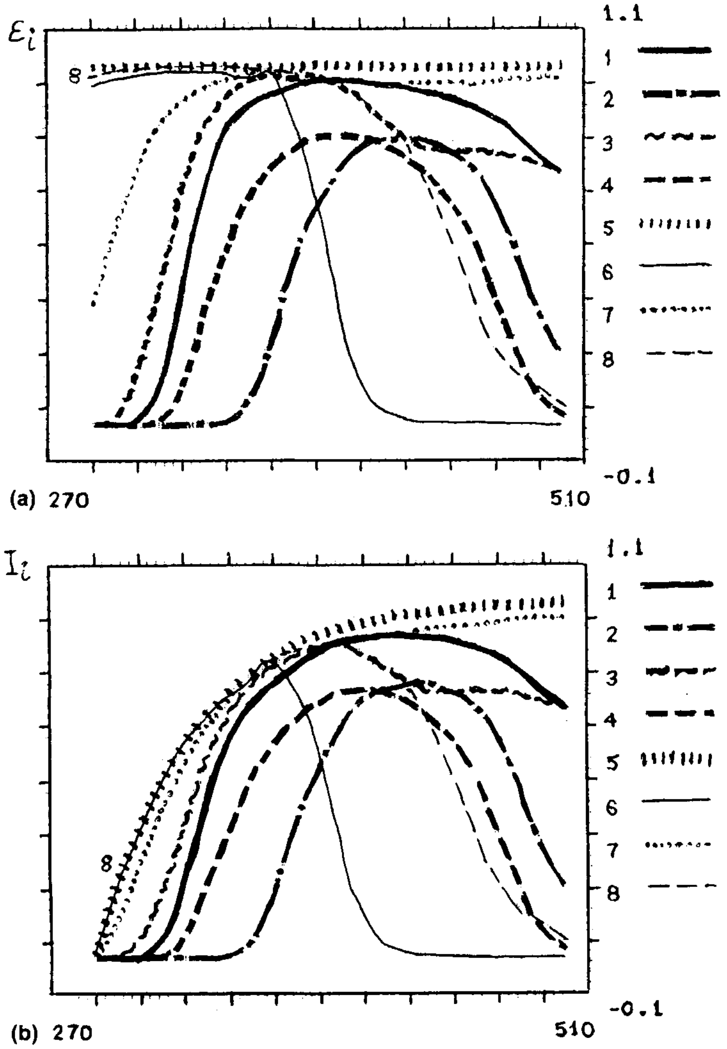

FIGURE 3 (a) Change in the transmissivities with the wavelength of incident light for fixed set of glass filters. (b) Spectral conditions of irradiation induced by fixed set of glass filters.

Abstract models describing the light effect on dye degradation processes are given in Reference 5. To get a better picture the additivity of the light effect was assumed. In this way the various irradiation spectral conditions $I_i(\lambda)$ necessary for light fastness forecast may be expressed by

$$I_i(\lambda) = I_0(\lambda)^*\varepsilon_i(\lambda), \qquad i = 1, \ldots, 8. \tag{1}$$

This is shown in Figure 3b, where the spectrum $I_0(\lambda) = I_5(\lambda)$ is given in Figure 1 (curve N 1).

Various models concerning dye decoloration kinetics which may be used in offered forecast method are also described elsewhere.[5]

To further clarify the principal scheme of method we have assumed only the exponential order reaction profile of dye decoloration process. This allows the decoloration kinetics to be described by means of the only argument—the initial decoloration rate W_i:

$$W_i = \int_{290}^{500} I_i(\lambda)^*\varphi(\lambda)\, d\lambda, \qquad i = 1, \ldots, 8. \tag{2}$$

where conventional units are used and $I_i(\lambda)$ are given in (1), $\varphi(\lambda)$ in Figure 2.

In view of (1), (2), and the model function $\varphi(\lambda)$ there were determined the corresponding set of dye decoloration kinetic plots illustrated in Figure 4 and initial rates of decoloration listed in Table I.

One can see the quantum yields of dye photodegradation in a range larger than 450 nm are too small (see Table I, Figure 3b and 4). This is clearly seen by comparison of the light effects resulted in spectra I_5, I_6, I_8 and I_7 given in Figure 3b. In particular, the spectra I_5 and I_8 correspond with each other in the range less

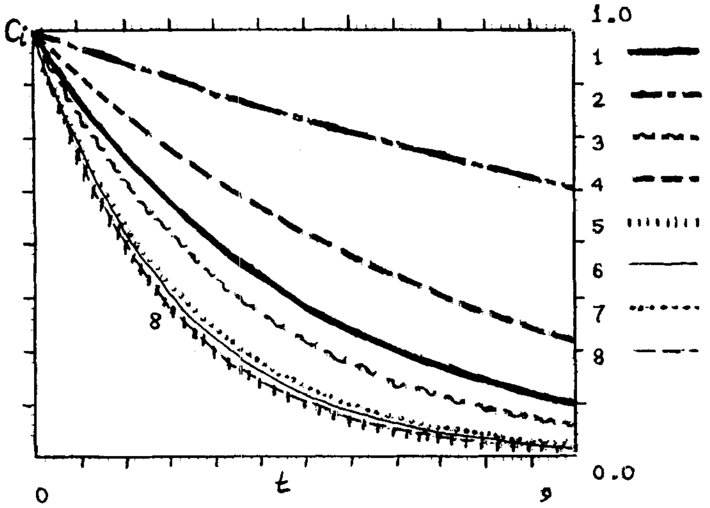

FIGURE 4 Kinetic plots of decoloration process for fixed spectral conditions of irradiation.

TABLE I

Initial rates of decoloration (see Eq. (2))

$W_1 = 22.861$; $W_2 = 5.125$; $W_3 = 28.815$; $W_4 = 14.315$;
$W_0 = W_5 = 46.508$; $W_6 = 42.312$; $W_7 = 39.762$; $W_8 = 45.762$.

than 370 nm, but along with considerable decrease in light intensity for spectrum I_8 larger than 370 nm the decoloration rates practically became even, while small differences between spectra I_5 and I_7 at whole wavelength range result in markedly different corresponding decoloration rates.

For the above-mentioned reasons we take $\varphi(\lambda) = 0$ at $\lambda > 500$ nm, allowing us to use Equation (2).

Thus we come close to the next mathematical problem in forecasting of dye light fastness:

To determine

1) the quantum yield of dye photodegradation at wavelength interval (295 nm − 500 nm);
2) the dye light fastness W_{fc} in sample at certain spectral condition of irradiation I_{fc}. (3)

Under the conditions are as follows:

$$1)\ W_{fc} = \int_{290}^{500} I_{fc}(\lambda)^*\varphi(\lambda)\, d\lambda,$$

$$2)\ W_i = \int_{290}^{500} I_i(\lambda)^*\varphi(\lambda)\, d\lambda, \qquad i = 1, \ldots, 8,$$

where one is supplied the values W_i (Table I), I_{fc} (the curve N 2 in Figure 1), I_i (the curves 1–8 in Figure 3b) to be evaluated under the known error (I_{fc}, I_i at the interval from 290 nm to 500 nm) and W_{fc}, $\varphi(\lambda)$ are unknown.

As the presence of experimental errors is an inevitable occurrence so problem (3) has to do with a variety of uncertainties discussed by Tikhonov.[6] Consequently any attempt to estimate the error of an approximate solution in a case of non-zero deviation as for input data (in our case—W_i, I_i, $i = 1, \ldots, 8$) will meet failure.

Solutions to such problems were examined[7] using a new method[8] to solve problems of applied mathematics, such as "estimates of error in approximate solutions." An IBM compatible program block has been engineered that is capable of obtaining error estimations of approximate numerical solutions which are tended to zero along with decreasing the experimental errors for input data. These methods and programs will be used in the present work to solve the problem (3).

The relative error equal to 2% created in random number generation has been used through the simulation of experimental conditions for decoloration rates values W_i (Table I). The wavelength interval (290 nm–500 nm) was divided on 42 equivalent subintervals each 5 nm long that simulated the error for irradiation spectral condition I_{fc} and I_i on problem (3). Figures 5 and 6 illustrate the result of forecast problem solution based on above-mentioned input data. Both the actual (the curve N 2) and forecast kinetic plots (the curve N 1) (and also dye decoloration) are bounded with confidence intervals at 95% as shown in Figure 5. Herewith the corresponding initial rates of decoloration (the light fastness) are as follows: $W = \int_{290}^{500} I_{fc}(\lambda)^{*}\varphi(\lambda)\, d\lambda = 8.438$—the actual value of light fastness, $W_{fc} = 8.810$—the dot estimation of light fastness, $(W_{min}, W_{max}) = (7.291, 10.238)$—the 95% confidence interval for W. The change in simulated integral quantum yield of pho-

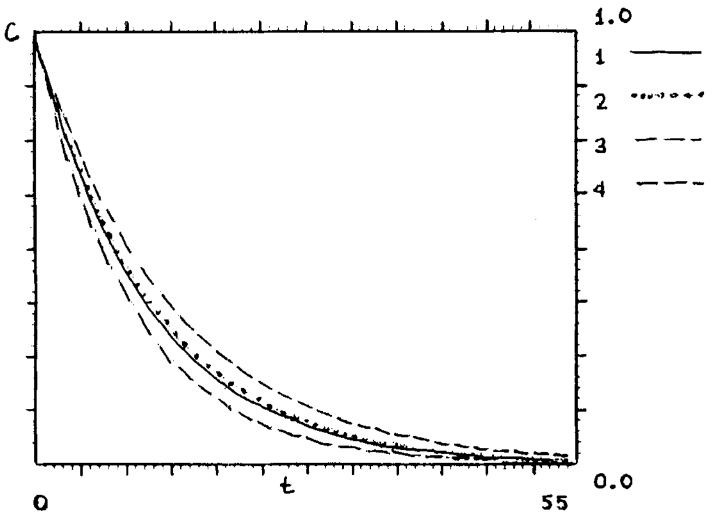

FIGURE 5 The forecast of decoloration process for spectral conditions of exploitation.

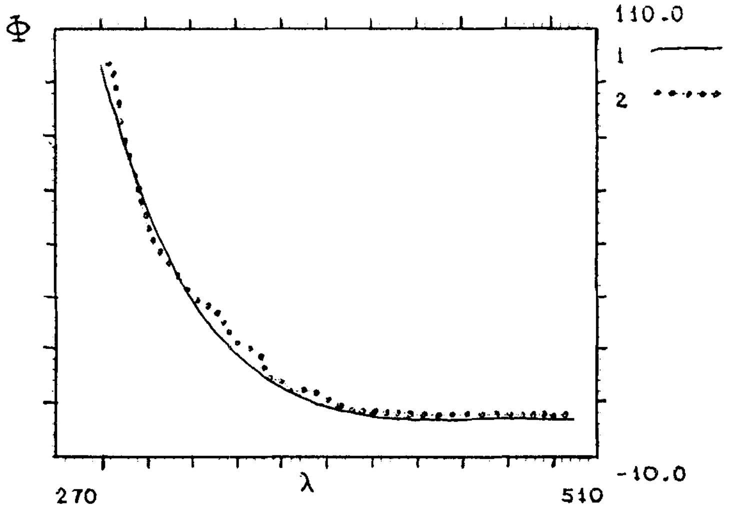

FIGURE 6 Change in integral quantum yield of dye photodegradation with the wavelength of incident light: the actual (1) and the calculated (2) one.

todegradation $\varphi(\lambda)$ (Figure 2) for both the actual $\Phi(\lambda)$ and calculated (forecast) $\Phi_{fc}(\lambda)$ cases is given in Figure 6, where

$$\Phi(\lambda) = \int_{\lambda}^{500} \varphi(\lambda_1)\, d\lambda_1, \qquad \Phi_{fc}(\lambda) = \int_{\lambda}^{500} \varphi_{fc}(\lambda_1)\, d\lambda_1.$$

Thus the engineered method along with applications software allows us to perform an impartial forecast on light fastness of colored materials at various spectral conditions of exploitation. If the decoloration process proceeds with a non-exponential profile, the formal argument specification described in Reference 5 may be used. This approach results in Figure 7, where the kinetic plots of decoloration process—the actual, calculated (forecast) and also photodegradation curves limited by the 95% confidence interval—are shown.

It should be emphasized that the present method is not limited by the choice of light source.

In conclusion we would like to note that engineered applications software also allows for solution of one of the most important problems of chemical kinetics: to reconstruct the reactivity distribution function in the case of monomolecular reaction, whose results may be applied for specification of the non-exponential decoloration process.

Then the change in concentration of reactive molecules c with time t is described by the equation

$$C(t) = \int_{k} \exp(-k^{*}t)^{*}f(k)\, dk, \tag{4}$$

where $f(k)$ is the density of the above-noted reactivity distribution induced by matrix microheterogeneity.

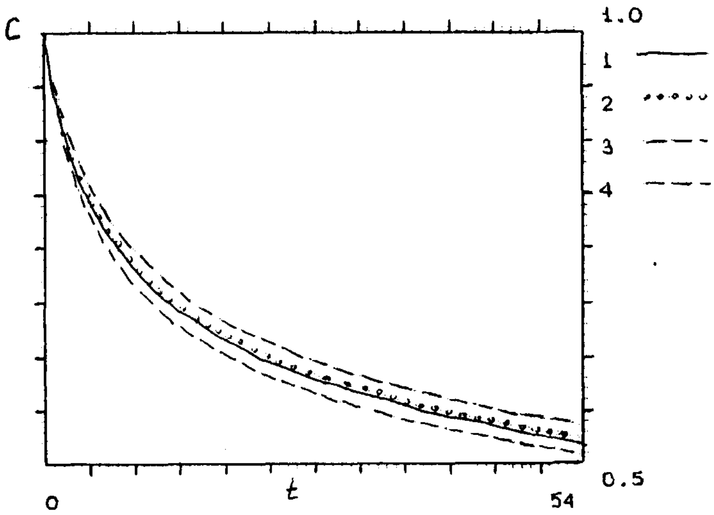

FIGURE 7 The forecast of non-exponential dye decoloration process for the spectral condition of exploitation.

Because the solution of Equation (4) and the related forecast problem on photodegradation process kinetics are completely analogous to those for problem (3), the applications software already designed for the previous problem can be applied to this new one as well.

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