Spatial Distribution, Light Resistance and Light Stabilization of Dyestuff Molecules in Polymeric Matrices

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The distibution of the dyestuff and stabilizer molecules in the polymeric matrices of cellulose hydrate and polyamide were investigated. Also considered were such distributions in the specimens of the textiles made of natural and artificial fibers with the help of the diffusional and sorptional method. The comparison of these results with the coloration light resistance in the investigated systems was then made. The luminiscence method was used to determine the local concentrations. The analysis of the experimental results has been carried out with the assumption of the equally probable molecular distribution of the low-molecular admixtures across the volume in the certain zones of the polymeric matrix. A measure of the distribution heterogeneity is the specific volume of these zones reative to the polymetric matrix volume. It has been established that the molecules of the dyes and stabilizers are not evenly distributed across the polymeric matrix volume. The volume of the distribution zones of the low-molecular admixtures (determined by the material structure, admixture nature and introduction method) can comprise up to 5% of the matrix volume. The close spatial distribution of the dye and light stabilizer is the determining condition of the efficiency of the stabilizing action.

The investigation of mutual distribution of the dye and light stabilizer molecules in the diffusional saturation of the specimens made of solutions was carried out with both the model systems (industrial films of cellulose hydrate/CH/ and polyamide/PA/ПК-6 washed off from admixtures) and real textile materials of a different nature.

KEY WORDS Light resistance, dyes, textile fibers.

EXPERIMENTAL

Industrial active azodyes, dispersed dyes, nickel dibutyldithiocarbonate/NBTC/, Grade chemically pure/c.p./as well as ethyl alcohol-rectificate were used without additional cleaning. Xenthene dye Rhodamine 6G (R6G) was chromatographically cleaned. Stablé nitroxyl radical (SNR)-2,2,6,6-tetramethyl-4-oxypiperidine-1-oxyl was cleaned by recrystalization from an ether-hexane mixture (2:1). The CH (~28 μm) and PA (~60 μm) films were washed out of admixtures by boiling in distilled water for 1 hour.

The dyeing of the films and textiles with the textile dyes was carried out using the methods corresponding to the dye and polymer nature. Rhodamine 6G and NBTC were introduced from the ethanol solution into the CH film and from the

water-alcohol (2:1) mixture into the PA film. The film cleanliness as well as the admixtures were spectrophometrically controlled with the use of an "Specord-UV-Vis" apparatus. The SNR concentration was determined by the ESR spectra using radiospectrometer ESR B, produced by IChPh, Acad. Sci. USSR. The luminiscence measurements were made with a spectrofluormeter similar to the one described by Anisimov *et al.*[1] Irradiation was carried out at 20°C by the light high pressure mercury lamp DPW-1000, distinguishing the required spectral area with the help of light filters. The tests for determining the light resistance were carried out using a "Xenotest-450" instrument, made by the German company Heraeus.

RESULTS AND DISCUSSION

Let us consider the luminescence method of investigation of the admixture mutual distribution in the polymetric matrix, using as an example the systems of dye-Rhodamine 6G, light stabilizer — nickel dibutyldithiocarbonate (NBTC) in the films of celulose hydrate (CH) and polyamide (PA). Figures 1a and b show the relations of the relative intensity of the R6G fluorescence and the light stabilizer concentration in these systems. The quenching of the dye fluorescence by the NBTC molecues (S-S energy transfer, sufficiently effective overlapping of the donor emission spectrum and the absorption spectrum of the energy acceptor) takes place according to the long-acting inductive resonance mechanism, and in the conditions of the equally probably distribution of the investigated admixture molecules across the volume in the polymeric matrix should be described by the known equations[2]:

$$I/I_0 = \sqrt{\pi}xe^{x2}(I - \Phi/x/);\tag{1}$$

$\Phi/x/$ -- function of errors, $x = 2/3\pi^{3/2}R_0^3 n$

$$R_0^6 = \frac{9000 \cdot \ln 10 \cdot \chi^2 \cdot \eta_0}{128 \cdot \pi^5 \cdot n^6 \cdot N} \int_0^x f_D(\bar{v})\varepsilon_A(\bar{v}) \frac{d\bar{v}}{\bar{v}^4}\tag{2}$$

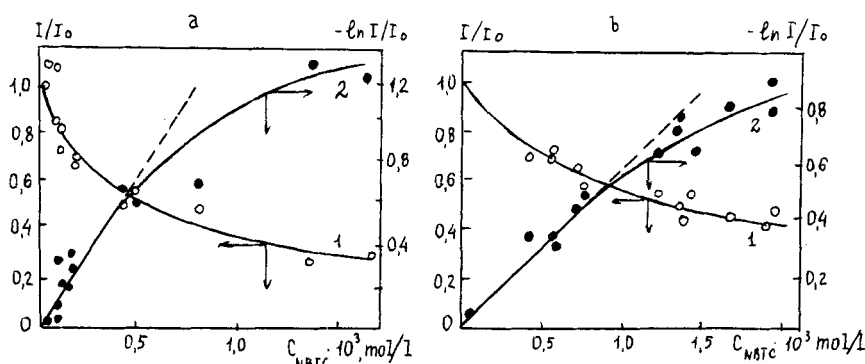
FIGURE 1   The relations of the relative intensity of the R6G fluorescence (2.5·10⁻³ mol/l)(1) and NBTC concentration in the CH (a) and PA (b) films as well as the semi-logarithmic anamorphoses of these relations (2). $\lambda_{excite} = 365$ nm.

where: η—luminescence quantum efficiency of energy donor in the absence of acceptor; $\varepsilon_A(\bar{\nu})$—molar coefficient of acceptor extinction; $f_D(\bar{\nu})$—spectral distribution of donor luminescence $\int f_D(\bar{\nu})\, d\bar{\nu} = 1$; n—medium refraction coefficient; χ^2—orientating factor (for accidental distribution $\chi^2 = 2/3$); N—concentration of energy acceptor.

The calculation carried out with Equation (2) using the spectral luminescence characteristics of the donor and energy acceptor resulted in the value of the characteristic radius of the energy transfer ($R_0 = 16$ Å). The quantitative comparison of the calculated results with the experimental values is made using the known (following from Equation (1)) relation between R_0 and the energy acceptor concentration corresponding to a half-quenching: $R_0 = 6.4 : \sqrt[3]{c_{1/2}^D}$. Accordingly, we obtain $c_{1/2}^D = 6.4 \cdot 10^{-2}$ mol/l. Thus, the quenching efficiency of the R6G fluorescence by the light stabilizer in the considered systems exceeds the calculated one by more than 100 times in CH and 50 times in PA.

We should note that neither CH or PA have their own levels of electronic excitation, suggesting the participation of the polymeric matrix in energy transfer by the mechanisms of the real or visual excitations. Hence, the single explanation for the difference in the results of the experimental and theoretical calculation is the invalidity of the assumption introduced into the calculation about the equally probable accidental distribution of the donor and energy acceptor molecules across the polymeric matrix volume.

The luminescence method, as the method giving the integral characteristic of mutual arrangement of the donor and energy acceptor molecules in the matrix volume, requires the introduction of certain model conceptions for the quantitative description of the results to be obtained. *Zone model.* Assume that the sorption centres of the dye and light stabilizer molecules are located in the definite zones of the polymeric matrix whose volume (v) makes up a definite portion of the total matrix volume ($v = \alpha \cdot V$), where: V is the volume of polymer, and the light stabilizer molecules have an equally probable distribution across the volume of these zones. Within the limits of the particular model the difference in the results of the experiment and calculation is determined by the difference between the molecular local concentrations: energy acceptors (C_1) and concentrations calculated for the whole volume of the polymeric matrix (C_Σ). The relation between them is found from the ratio of the scales using the concentration of the process efficiency of liminescence quenching:

$$C_1 = \alpha^{-1} \cdot C_\Sigma = \frac{C_a^T}{C_a^E}\, C_\Sigma$$

$$\alpha = C_a^E / C_a^T$$

where: C_a^E and C_a^T are, respectively, the experimentally and theoretically determined concentrations of the energy acceptor corresponding to the equal levels of the donor luminescence quenching.

Parameter α determined as the ratio of the volume of the polymeric matrix zones filled by the admixtures molecules to the matrix total volume. Thus the specific

TABLE I

Specific volumes of filling zones (%) for NBTC
and NP in CH and PA

Polymer Stabilization	CH	PA
NBTC	0.8	2
NR	2	3.5

volume of the filling zones is the quantitative characteristic of the mutual distribution of the dye and light stabilizer molecules within the limits of the particular model. The data on the specific volumes of the filling zones for the NBTC and NR light stabilizers in CH and PA relative to the R6G dye are given in Table I.

The zone model of molar distribution of the low-molecular admixtures in the polymers supposes the strict observation of Equation (1) for the relation of the quenching efficiency and energy acceptor concentration in the whole volume of the used concentrations. Thus the parameter should not depend on the level of donor luminescence quenching selected for estimating this parameter. It is this condition finally which detemines the applicability of the particular model. To verify the fulfillment of this condition use the fact the Equation (1) can be replaced with a sufficient degree of accuracy ($\sim 10\%$ to quenching extent $\sim 9C\%$) by Perren's equation: $I/I_0 = e^{-V_c D}$ accepted in the description of the exchange-resonance energy transfer. Figures 1a and b present the semi-logarithmic anamorphoses of the relations of the quenching efficiency and concentration of the stabilizer molecules. As seen in the figure, the linearity of these relations is satisfactorily observed below the quenching level equal to 0.5, at relatively low concentrations of the light stabilizer molecules (to $5 \cdot 10^{-4}$ mol/l in CH and to 10^{-3} mol/l in PA). The further observed essential deviation of the experimental dependence from the linear ones points to the necessity of making more precise individual conceptions.

Such precision can be introduced into the basic positions of the zone model through the ideal of the concentration of the sorption centers in the zone and, correspondingly, the maximum level of filling the zones with the energy acceptor molecules. In this case an increase in the concentration of the light stabilizer molecules in the solution through the process of diffusional saturation of the specimens after filling the zones results in filling less active sorption centers in the remaining volume of the polymeric matrix, with these molecules not participating in quenching the excited states of the dye molecules. This natural assumption completely corresponds to the experimental data on the sorption isotherms of the light stabilizer molecules: the linear section is separated at the low concentrations of the light stabilizer, and the long non-linear section is also seen with the monotonously decreasing sorption coefficient with an increase in the NBTC concentration in the solution. The data about the comptitive sorption of the dye and light stabilizer molecules by the polymeric specimens are additional confirmation of a limited number of the active sorption centers in the certain zones of the polymeric matrix. Figure 2 shows the relations of the R6G dye absorbed by the CH film and NBTC concentration in the solution. As shown in the figure, the concentration of
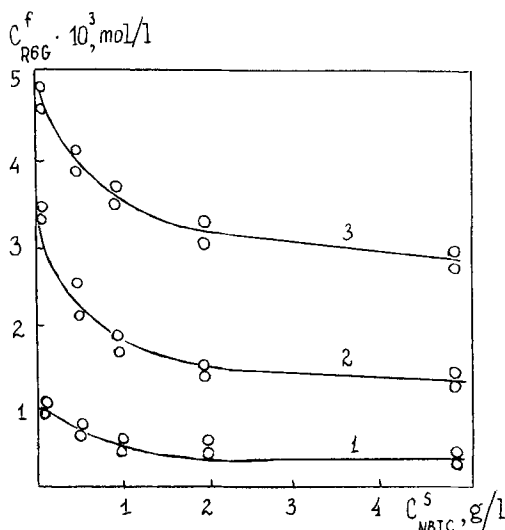
$$C_{R6G}^f \cdot 10^3, mol/l$$

FIGURE 2 The relation of the R6F concentration in the CH films and NBTC concentration in the solutions containing $1.1 \cdot 10^{-4}$ mol/l (1), $5.5 \cdot 10^{-4}$ mol/l (2) and $2.2 \cdot 10^{-3}$ mol/l of R6G. Reference solution, boiling, 30 min.

the dye molecules in the film essentially decreases with an increase in the NBTC concentration, while conversely increasing with a decrease in the dye concentration.

The total number (calculation on the matrix total volume) and concentration of the sorption centers in the zones are easily estimated from the maximum obtainable levels of the dye luminescence quenching, initial inclination of the semi-logarithmic anamorphoses in the relations of the quenching efficiency and concentrations of the energy acceptor molecules and values of parameter α. These values are equal to $\sim 10^{-3}$ mol/l and 10^{-1} mol/l for CH, $\sim 2 \cdot 10^{-1}$ mol/l for PA, respectively. (The limit levels of the quenching were estimated from extrapolating the experimental data in accordance wth the expression $I/I_0 - \Delta = \exp(-\gamma C)$, where Δ is the maximum obtainable level of quenching.)

The luminescence method of the spatial distribution investigation can ce applied not only to the binary systems of dye-light stabilizer, but also to the molecular distribution of the dye proper. The base here is the phenomenon of self-quenching of the dye molecular fluorescence with the exchange interaction. This phenomenon is well known and comprehensively studied for the liquid-phase systems.[3] Figures 3a and b present the relations of the fluorescence intensity of the R6G dye and its concentration in the CH and PA films. Beginning at relatively low concentrations $(3:5 \cdot 10^{-4}$ mol/l), these relations deviate from the linear ones in spite of the fact that the optical densities of the specimens on the wave length of the excited light did not exceed 0.1 within the whole used range of the concentrations (the condition of the linear relation of the absorption coefficient and dye concentration). A relative decrease in the effective quantum efficiency of fluorescence is not associated in this range of the concentrations with the formation of the non-luminescent stable associates of the dye molecules.

In this particular case when the luminescence quenching is determined by the
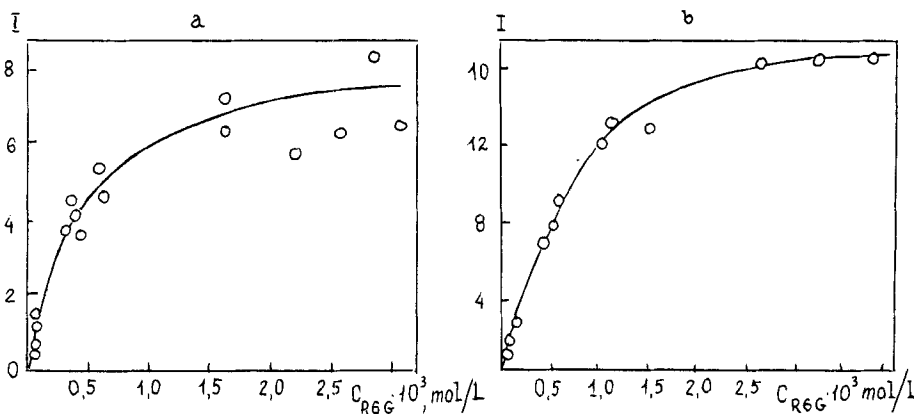
FIGURE 3   The relation of the relative intensity of the R6G fluorescence and dye concentration in the CH (a) and PA (b) films. λ_{excite} = 365 nm.
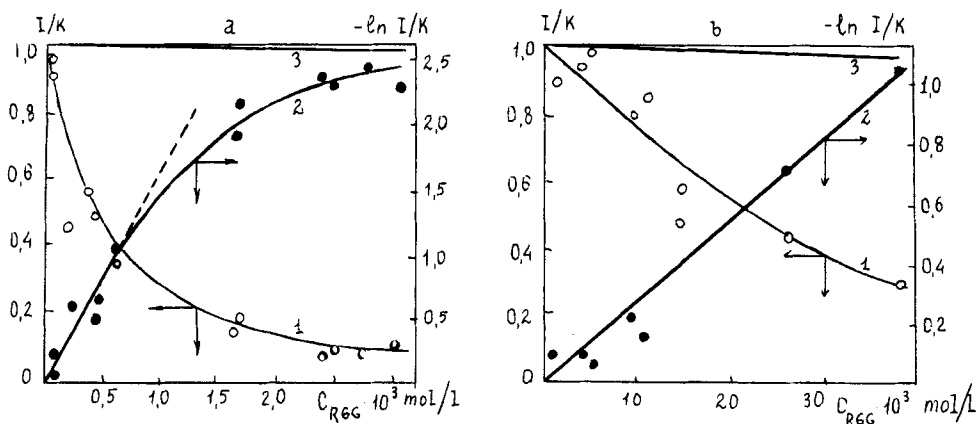

FIGURE 4   The relation of the relative intensity of the R6G fuorescence and dye concentration in the CH (a) and PA (b) films (1) as well as the semi-logarithmic anamorphoses of these relations (2). Also the theoretical relation (3) for the relative intensity of the R6G fluorescence. λ_{excite} = 365 nm.

exchange interaction (i.e., the contact of the interacting molecules, Perren's equation (I/I_0 = exp($-Vc$)) can be used to describe the relation of the quenching efficiency and concentration, and at the same time the radius of the action sphere can be determined from geometric relations. (The estimate of the sphere radius for the R6G molecules leads to value 15 Å). Figure 4 gives the relations of the relative quantum efficiency of the R6G dye fluorescence and its concentration in the polymeric matrices and anamorphoses of these relations in the coordinates of Perren's equation. The same figure presents the theoretical relation of a change in the P6G relative quantum efficiency and its concentration. Using calculations analogous to those shown above for the volumetric portion of the distribution zones of the dye molecules (determined by the starting sections of the given relations) gives values of 0.7% for CH and 2% for PA relative to the volume of the whole polymeric matrix. These values are on the order of the estimates made for the

molecular distribution of the NBTC light stabilizer in the same matrices. (It is interesting to note that earlier, in investigating the mechanism of the light stabilizing action of 2-oxybenzophenones in the PP photo-initiated oxidation by the analogous method, it was shown that the volume of the distribution zones of the photoinitiator and light stabilizer molecules makes up 2% of the total volume of the polymer.[4]

The qualitative behavior of the obtained relations is similar to the previous one. In introducing R6G into the CH films beginning from the dye concentration of $\sim 10^{-3}$ mol/l a sharp deviation of the experimentally determined relation from the theoretical one is observed, indicating the filling of the peripheral polymeric matrix areas relative to the zones of the primary distribution by the dye molecules. We may also estimate the concentration of the dye sorption centers in the zones of the primary distributions as 10^{-1} mol/l. (The analogous data for PA were not obtained: a further increase in the dye concentration resulted in its association in this case).

The comparison of the spatial distribution of the reactive dyes covalently linked with the polymeric matrix and the same hydrolysed dyes retained in the matrix by the forces of the sorption interaction is of interest to practical workers. Earlier literature is mostly filed with ideas about the fact that the reactive dyes are distributed more evenly across the volume of the polymeric matrix than simply the absorbed dyes.[5] The conducting of the similar investigaton appeared possible because in practice the reactive azo-dyes and their hydrolized form, while non-luminescent in the usual conditions at room temperature, sharply increase the quantum yield of the proper luminescence in decreasing temperature to 77°K.

Figure 5 shows the relations of the relative quantum efficiency of luminescence and concentration for bright-red reactive azo-dye 6C and its hydrolized form in the CH film as well as the anamorphoses of these relations in the coordinates of Perren's equation. Within the limits of the experimental accuracy these relations are not distinguished, i.e. the distributions by volume of the reactive dye and its hydrolized
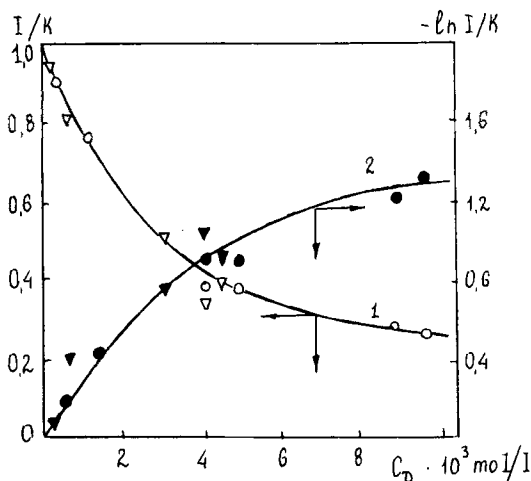

FIGURE 5 The relation of the relative fluorescence intensity of the 6C brilliant red reactive dye, its concentrations in the CH film (1) and semi-logarithmic anamorphoses of these relations (2). $\lambda_{excite} = 365$ nm.

form molecules practically coincide. In the existing technological methods the fixation of the dye in the polymeric matrix with the formation of the covalent links of dye-polymer is therefore less important than the dye fixation in the primary sorption centers of the matrix. As a matter of fact, the volumes of the distribution zones of both the dye proper and its hydrolized form coincide and make up ~1.5% of the total volume of the polymeric matrix (the estimation by the initial linear section of the semi-logarithmic anamorphoses). The estimation of the concentration of the sorption centers in the zones of the primary filling is ~$2 \cdot 10^{-1}$ mol/l.

The data on the spatial molecular distribution of the dyes in the different polymeric matrix (films and fabrics) are summarized in Table II.

The data presented in the table, besides of a pure scientific interest as the characteristic of the spatial heterogeneity degree of the polymeric matrices relative to the different types of the sorption centers, are also of great importance for the practical light stabilization of the low-molecular admixtures absorbed by the polymeric matrix, in particular, the dye molecules. Indeed, the well selected light stabilizer absorbed in the same zones as the dye molecules stabilized by it can have a local concentration of up to $5 \cdot 10^2$ times (capron, active dye) its gross concentration; an increase in the gross concentration cannot also result in an increase in the effects of light stabilization at the same time since the surplus molecules absorbed in the peripheral zones in the conditions of the limited movement cannot take part in the process.

Consider now the immediate relation between the efficiency of luminescence quenching of the dye molecules and an increase in their light resistance in the presence of the light stabilizers. As an example, Figure 6 shows the relations of the relative intensity of the R6G fluorescence, relative initial rate of photodestruction of the dye molecules and the light stabilizer concentration in the PA film. As shown in the figure, these relations practically coincide for the particular system, i.e. the efficiency of quenching the R6G excited states by the NBTC molecules completely detemines the effect of light stabilization.

A different situation is observed for the same pair of dye-light stabilizer in passing to the CH matrix (Figure 7). In this case a decrease in the relative initial rates of photodestruction of the R6G molecules markedly exceeds the efficiency of the dye fluorescence quenching. It is obvious that other directions of light stabilization are also realized in this system together with the light stabilizing action of the NBTC molecules according to the mechanism of quenching the chemically active excited states of the dye molecules. In particular, as shown elsewhere,[6] the photodestruction

TABLE II

Specific volumes of the dye distribution in polymeric films and textile materials (% of the matrix volume)

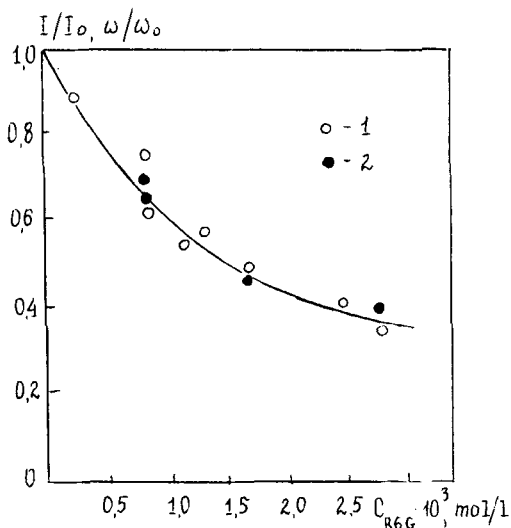| Dyes	Films		Fabric			
	CH	PA	Cotton	Silk	Capron	Wool
Reactive bright red 6C	1.5	—	3.4	9.8	0.2	—
Rhodamine 6G	0.7	2.0	0.4	1.5	0.4	0.5
Sulforhadomine B	—	—	1.2	3.7	0.7	2.0

FIGURE 6 The relations of the relative intensity of fluorescence (1), relative initial rate of the R6G photodestruction ($1.8 \cdot 10^{-4}$ mol/l) and NBTC concentration in the PA film. λ_{excite} = 365 nm. Exposure: Xe-lamp, Pyrex, $\lambda > 300$ nm.
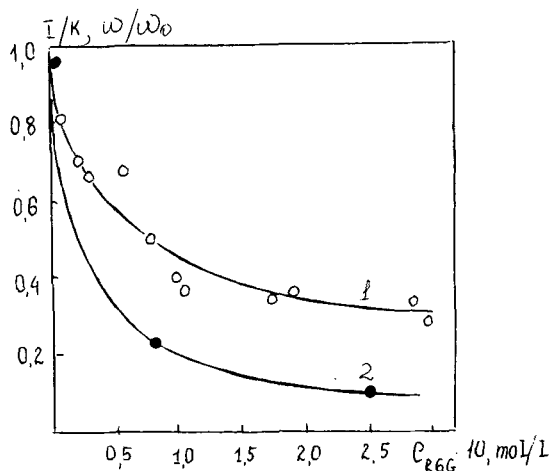

FIGURE 7 The relation of the relative intensity of fluorescence (2), relative initial rate of the R6G photodestruction ($8 \cdot 10^{-4}$ mol/l) and NBTC concentration in the CH film. λ_{excite} = 365 nm. Exposure: Xe-lamp, Pyrex, $\lambda > 300$ nm.

of the dyes in the polymeric matrix can with a great probability run with the participation of the medium free radicals when the dye acts as a real sensibilizer of the free radical transformations at the photochemical stage of the process. It is known that the NBTC molecules can act as inhibitors of the free radical transformations of polymers.[7] Hence, taking into consideration the high ($1 \cdot 10^{-1}$ mol/l) local NBTC concentration in the zones of the dye molecule distribution it seems logical to attribute an additional (relative to the quenching of the photochemically

active excited states) effect of light stabilization to the NBTC-inhibiting action in the conditions of realizing the free radical mechanism of the dye destruction in the system.

The examples of mutual spatial distribution of the dye and light stabilizer molecules considered above in the polymeric matrices have reflected the situation favorably from the viewpoint of possible effects of light stabilization when the zones of distribution of the light stabilizer coincide, or at least include the zones of distribution of the dye molecules. The similar situation is seldom approached. So an.attempt to use NBTC for stabilizing the dyeing of woolen textiles with xanthene dyes (R6G, sulforhodamine B, practically important system) has failed. It appears that in this system the distribution zones of the dye and light stabilizer molecules generally do not cross each other. The NBTC introduction up to the concentrations of $5 \cdot 10^{-2}$ mol/l does not lead to any significant decrease in the dye luminescence intensity. The result is a complete absence of the light stabilizing action.

The wider investigation carried out in the literature[8] has shown that the luminescence quenching of the dye molecules by the light stabilizer molecules (if this process is allowed by the physical parameters) is the necessary condition of realization of the light stabilization effect. It is not excluded that the luminescence method of the spatial distribution investigation can be the most acceptable for the primary screening of the potential light stabilizers of the dyeing in the concrete systems.

Moreover, the investigations of the mechanism of the light stabilizing action of the dispersed dyes in the process of photodestruction of polyamide have shown that the described method can also be used for the primary screening of the PA potential light stabilizers from the class of the dispersed dyes since the real effect is shown only by those dyes which are rather effectively absorbed in the location zones of the PA luminescence centers, i.e., where the process of photoinitiation of the matrix free radical transformation occurs /9/.

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