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Preferential Orientation of Dye Molecules Detected at the Total Internal Reflection in the Unexposed Azo-dye-containing Gelatin Layer

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Abstract
The difference in the absorption of two orthogonal linear polarizations was first observed in the investigation of the total internal reflection from the interface azo dye doped gelatin layer - air. This means that there exists a predominant orientation of dye molecules in the emulsion layer. It is very important fact for the problems of adequately holographic registration of polarization characteristics of the light fields. It is especially important also in the creation of holographic diffractive structures with anisotropic structures. Experiment was performed for the actinic radiation of the He-Cd laser (λ = 441.6 nm) for two mutually orthogonal linear polarizations of the light: with oscillations of electric vectors parallel (P polarization) and perpendicular (S polarization) regarding to incidence plane. The result of investigation has shown the difference of total internal reflection for these polarizations at the initial stage of irradiation of azo-dye doped emulsion layer at the incidence angle of the light 45^0. The different values of the relative intensities of the total reflection (I_r/I_0) for the P and S polarizations (0.025 and 0.1 accordingly) indicate to the anisotropy of absorption of the light caused by predominant orientation of dye molecules (POM) in the layer. At the prolongation of exposure with the same wavelength the dichroism of the total internal reflection disappears because of photo transformation of the dye molecules responsible for Weigert effect in these materials.

1. Introduction

Azo-dye-containing polymers are one of the interesting photosensitive materials for the registration of light polarization [1-5]. Low scattering ($<10^{-5}$), sufficient photosensitivity (≈0.5 DIN), spectral range of sensitivity (350-550 nm), reversibility (unlimited number of cycles) and high value of the Weigert's effect make them one of the promising materials for polarization photography, polarization holography and for creation of holographic diffractive optical elements with an anisotropic structure [6-15]. The most known example of such a material is disazo-dye Mordant Pure Yellow used in the given work [16-27].

As the polarization sensitivity is an anisotropic effect (Weigert's effect) distribution of the orientation of dye molecules (absorbing oscillators) in the emulsion layer is very important. At the predominant orientation of absorbing oscillators (dye molecules) the photo-process will be having different efficiency at the different polarizations and at the different angles of incidence of the polarized light wave. Because of this it is very important the statistical homogeneity of the orientation of dye molecules for the adequate registration of the polarized light fluxes [6-15].

In spite of this the polymer layers containing azo dyes till now are prepared by conventional emulsion spill methods on the glass plate or by Lin method [16-28]. Consequently, in both of these cases the gelatin layer undergoes of sufficient strong changing during of sensitization and drying that should have some influence on the final distribution of orientation of dye molecules [30]. The initial linear dichroism of such layers detected at the total internal reflection, confirms the presence of preferential orientation of dye molecules (POM) in the emulsion layer.

2. Experiment

The scheme of the optical setup for investigation of the total internal reflection from the interface azo-dye containing gelatin layer-air is presented in Figure 1. Horizontally linearly polarized beam (**S** polarization) of the He-Cd laser (λ = 441.6 nm) 1 is expanded by a collimator 2. The polarization of one half of the collimated beam is changed to orthogonal one (P polarization) with the 90^0 quartz rotator 3. The usual isotropic glass plate 4 overlaps the second part of the collimated beam for equalization of the intensities in both parts of incident light. The prism of the total internal reflection 6 is placed with its short side perpendicular to the incident beam don't influencing on the states of P and S polarizations. The glass plate 7 which is covered by the azo-dye containing gelatin layer 8, has an optical contact with the uncovered surface to the base of the prism 6 by an optical glue. This excludes the Fresnel reflections from the interface of the prism and glass plate.

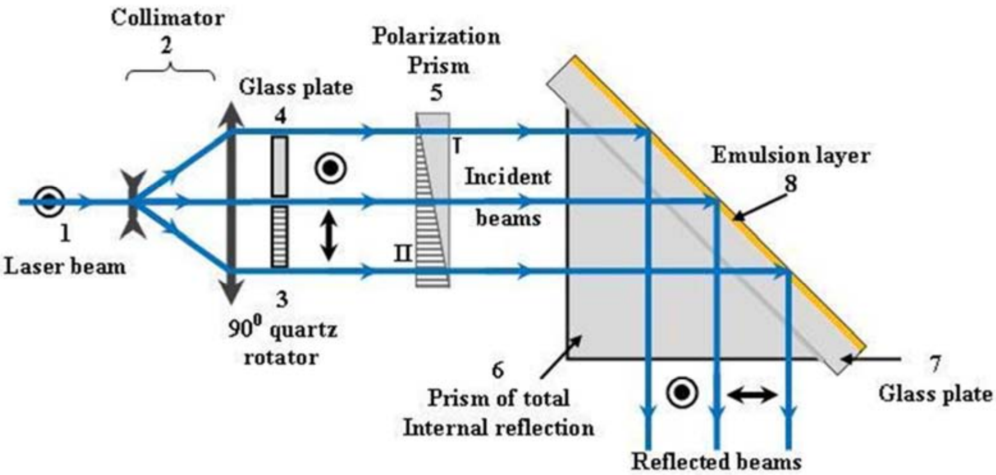
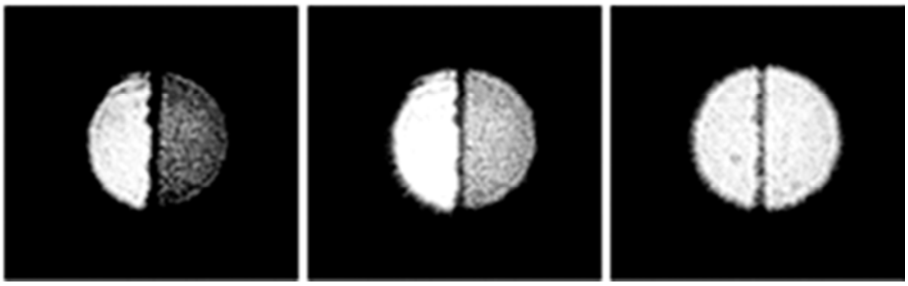


Figure 1. *The scheme of observation of the total internal reflection from the interface of the azo-dye containing gelatin layer-air.*

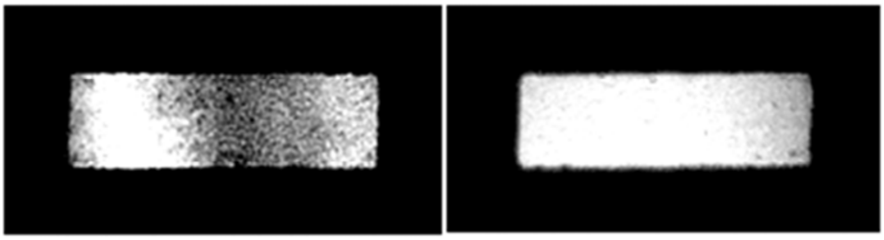
Because the used azo-dye material is photosensitive the observed picture of the total reflection is changing in the exposure process. The dynamic of changes in the picture of total internal reflection from the interface emulsion layer - air for the P and S polarizations were registered by the photo camera and chart recorder. The results of investigations are presented in Figure 2 - Figure 4. In Figure 2 the right and left parts of the images correspond to P and S polarizations, after total internal reflection, respectively. Figure 2 a corresponding to the reflected image at the initial stage of irradiation showing more low intensity for P polarization than for S polarization after total internal reflection. This difference is the result of inequality of light absorption for the P and S polarizations in the emulsion layer that confirms the existence of the initial linear dichroism of the investigated layer for such geometry of the optical scheme (Figure 1). This result indicates that most of absorbing molecules are oriented close to direction of electric vector of P polarization than to S polarization. Figure 2b and c correspond to the same image after 2 and 5 minutes of light influence, respectively. As it follows from Figure 2b and c here the process of enlightenment takes place that is well known for such materials [21]. At the same time the intensities of both parts (P and S polarizations) of the image are rising differently in the exposure process. Particularly, the intensity of P polarization after total internal reflection grows much faster than that of S polarization and they become almost equal at the end of exposure. Similar result was obtained for optical prism 5 with varying rotation of polarization (Figure 1, 3). This prism consists of two wedges of ordinary glass (I) and optically active quartz (II) that rotates the light polarization from 0^0 to 120^0 at the wavelength λ = 441.6 nm [11]. On Figure 3 is shown the image of this prism after total reflection from the interface emulsion layer - the air at the initial stage of irradiation. The dark area of image corresponds to P polarization. Figure 3b represents the same image after 5 minutes of exposure to actinic light what is in full accordance with the results shown in Figure 2. So, according to obtained results unexposed gelatin layers containing azo-dye prepared by the conventional methods are characterized with some inhomogeneity regarding to polarization of incident light.

The influence of linearly polarized actinic light causes the process of anisotropic enlightenment of the emulsion layer, the speed of which is more for P polarization than for S polarization [21] (Figure 4).



A b c

Figure 2. *The images of reflected P and S polarizations at the initial stage (a) after 2 minutes (b) and after 5 minutes (**c**) exposure by an actinic light.*



a b

Figure 3. *The images of the prism for polarization rotation after total reflection from the interface of the azo-dye doped gelatin layer-air at the initial stage (a) and after 5 minutes of exposure (b) by actinic light.*

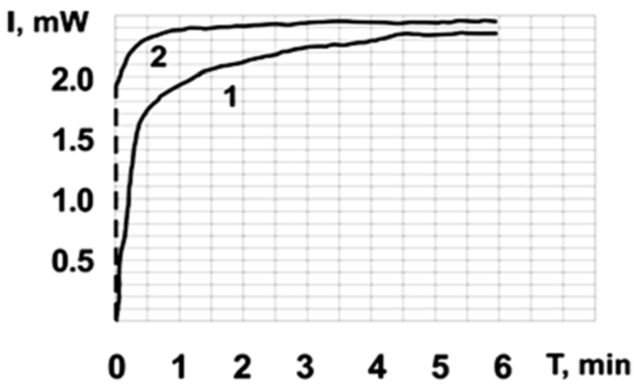


Figure 4. *The dynamics of enlightenment of the azo-dye doped gelatin layer at the total internal reflection during exposure by actinic light for P (curve 1) and S (curve 2) polarization.*

Intensities of P and S polarizations after total reflection on the initial stage are equal to 0.5mW and 2.0mW, respectively, and they reach of their maximal values 2.85mW and 2.95mW after 4.5 min of irradiation. According to Figure 4 the value of the enlightenment for the P polarization is approximately 2.5 times more than for S polarization. This means decreasing of the initial dichroism value for the total internal reflection from the interface emulsion layer - air in the irradiation process. Obtained results were used to calculate the dynamics of decreasing of mentioned dichroism.

The formula for calculation of the dichroism has a view:

$$D = \frac{K_s - K_p}{K_s + K_p} \tag{1}$$

Where

$$K_p = -\frac{1}{2d} \ln \frac{I_p}{I_0} \tag{2}$$

$$K_s = -\frac{1}{2d} \ln \frac{I_S}{I_0} \tag{3}$$

are absorption coefficients for P and S polarizations; I_0 is the intensity of the incident light; Is and Ip are the intensities of P and S polarizations after total reflection; d is the thickness of the emulsion layer. From the (1), (2) and (3) it follows:

$$D = \frac{\ln \frac{I_P}{I_S}}{\ln \frac{I_P \times I_S}{I_0}} \tag{4}$$

The dynamics of decreasing of the dichroism in the irradiation process is shown in Figure 5. Thus, the initial value of the dichroism has a significant value of 0.45 and decreases up to 0.03 during exposure process.

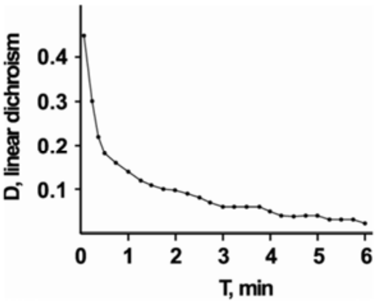


Figure 5. *Dynamics of linear dichroism of the total internal reflection in the emulsion layer during the exposure.*

3. Discussion

The structure of the molecule of azo-dye Mordant Pure Yellow has the following view [21]:

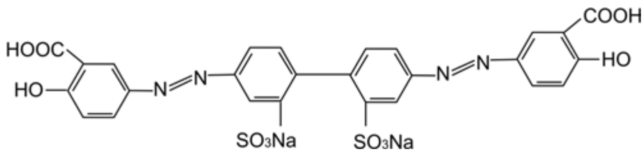


Figure 6. *The structure of the molecule of azo-dye "Mordant Pure Yellow".*

Two linear oscillators (chromophores) – N = N – determine the absorption anisotropy and photosensitivity of this molecule basically. The probability of absorption is proportional to $cos^2\Theta$, where Θ is an angle between of electric vector of light and of the absorbing oscillators of the molecule [10, 21]. So, the difference of intensities of P and S polarizations in the observed image after total reflection can be explained only by the initial predominant orientation of dye molecules (POM) in the emulsion layer. (Figure 2, 3).

Naturally, the conditions for absorption of both of P and S polarizations will be identical at the statistically homogeneous distribution of orientations of dye molecules because average value of Θ is equal for both polarizations. Therefore, most of dye molecules, at such geometry of optical setup (Figure 1), are oriented predominantly along to electric vector of P polarization before and after reflection. However, P polarization changes its direction at orthogonal after reflection (Figure 7). In this case most probable predominant orientation of the absorbing oscillators of dye molecules (POM) will be near to the normal of the plane of emulsion layer.

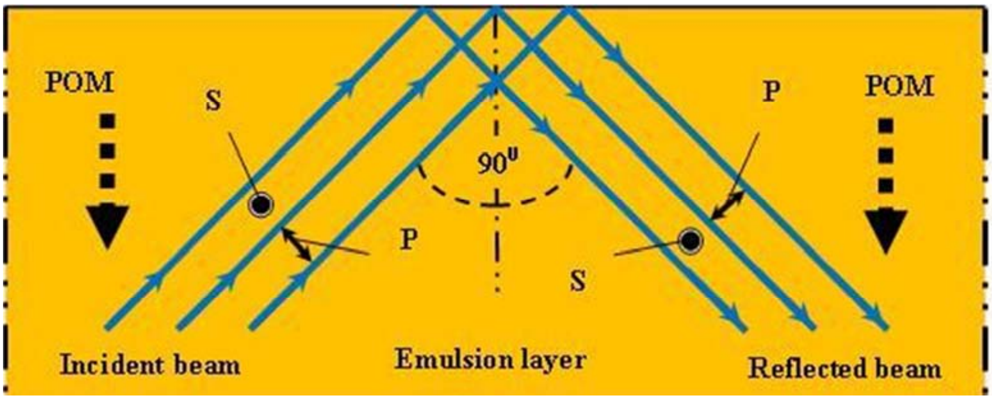


Figure 7. *The scheme of the incidence and reflection of P and S polarizations on the interface emulsion layer-air.*

In the opposite case, if the predominant orientation of dye molecules is (POM) close to the parallel of emulsion plane, the absorption for S polarizations should be higher than for P polarization. The image in Figure 2 should be opposite in that case.

Thus, for the most plausible explanation of obtained results, it can be assumed that the dye molecules are oriented predominantly perpendicularly to the surface of the emulsion layer.

Increasing in the intensities of the observed images is the result of anisotropic enlightenment of the emulsion layer because of transformation of azo-dye molecules at the influence of the actinic light (Figure 2-4) [21, 27]. From Figure 2-4 follows that P polarization provokes transformation of greater number of molecules than S polarization. As the probability of transformation of dye molecules is proportional to $\cos^2\Theta$ obtained results confirm additionally that the predominant orientation of dye molecules (POM) perpendicular to the surface of emulsion layer.

Similar results were obtained for emulsion layers containing other organic dyes with the linear molecules prepared by the same methods [28].

The preferential orientation of dye molecules (POM) above all must be the result of the great values of expansion and shrinkage of the gelatin (about 9 times) during the technology processes of preparation of the plates with emulsion layer. It's also possible the influence on the orientation of dye molecules of surface forces on the interfaces of the glass plate - emulsion layer and emulsion layer-air. It isn't excluded the influence on the orientation of molecules of the diffusion of dye molecules in the emulsion layer at the preparation of the plates by the Lin method [28].

4. Conclusions

It is obvious that the photosensitivity and the value of the Weigert's effect are the most important characteristics for polarization sensitive materials and among them for azo-dye doped materials. Both of these parameters are associated with many factors such as concentration of dye molecules, the force of the absorbing oscillator, of character of matrix, of presence of impurities including water, etc. [21, 29]. However the character of distribution of orientation of dye molecules in the emulsion layer should also influence on the processes of holographic registration of polarization [10, 11]. In particular, in the case of predominant initial orientation of dye molecules the photosensitive layer will have more selective character regarding to varying polarizations that will complicate the task of its adequate registration. From this point of view the obtained results may be useful for the polarization photography, polarization holography and for technologies of creation of passive and laser active diffractive optical elements with an anisotropic structure [30-34]. In authors opinion the achievement of the statistical character of the distribution of orientation of dye molecules in the photosensitive layer is very important, the possibilities of which will be investigated in the further.

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