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Azo-Dye Doped Polymers as an Universal Light Polarization Sensitive Photo Material

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Abstract: The properties of the polarization sensitized material with the wide possibilities, on the basis of azo-dye doped polymers, are reviewed and analyzed shortly. Some experimental results obtained on these materials in the polarization holography and photography on the basis of Weigert's effect are briefly described. In particular, with the help of these materials, the results of holographic recording and reconstruction of the polarization characteristics of the light field have been significantly improved. Were obtained holographic diffractive optical elements with the highest diffraction efficiency, such as diffraction gratings and zone plates (Fresnel lenses), which have no analogues among the known ones. Was observed self-recording phenomenon in a dynamic holographic recording and recovery process. The prospects of using the given materials in the photography for obtaining polarimetric images of various objects, including celestial bodies, were shown.

Key words: Light sensitivity, polarization, isotropy, anisotropy, Weigert's effect, polarization holography, polarization photography.

1. Introduction

Anisotropic response of the photo plates of Ag-Hal and of some dyes at the influence of the linear polarized light at the first time was found and investigated by Weigert et al. [1-6]. Subsequently, Zocher and Koper [7], Thirunamochandran [8], and Petrova [9] published information on the gyrotropic response of Ag-Hal photographic plates to the effect of circularly polarized light, which has not been convincingly confirmed in studies by other authors to this day. Further extensive studies of the photo induced anisotropy were carried out by Kondo [10] among them based on polymers doped with different dyes. Kondo discovered many azo dyes that exhibited a relatively strong anisotropic response when exposed to linearly polarized actinic light. As it turned out, from the point of view of the Weigert's effect, water-soluble mono- and dis- azo- dyes turned out to be the most effective materials [1-6]

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Future studies of the Weigert's effect have been rare. They became more active and more intensively, only since 1972, which was associated with its use in holography.

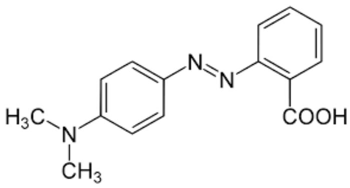
In 1972 by Sh. D. Kakichasvili was realized for the first time the holographic registration and reconstruction of the linear polarization of the light wave in Ag-Hal layers [11-13]. However Ag-Hal layers had disadvantages: low value of the Weigert's effect, low efficiency of holographic recording and unreversibility, i.e. one-time use of the given material. To improve the efficiency of the polarization holographic recording and improve the characteristics of obtained polarization holograms and holographic optical elements, was additionally studied the Weigert's effect in the polymers (gelatin, Poly Vinyl Alcohol—PVA) doped with the different dyes [14-16].

Materials and Methods: Modern research has shown that the most effective examples of such materials are mono- and disazo dyes methyl orange, chrysophenine, brilliant yellow, and others (Fig. 1). Water-soluble disazo-dyes similar to chrysophenine and brilliant yellow, which are doped into a gelatin or

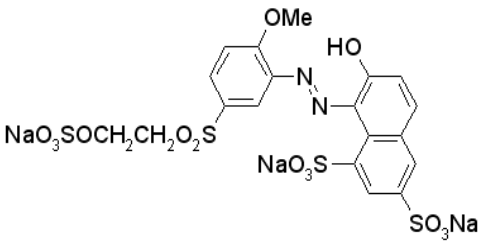
PVA matrix, turned out to be clearly effective in terms of the Weigert effect and polarization sensitivity [17, 18]. The main mechanism for the appearance of the Weigert effect in polymers dyed with azo-dye was taken to be photo cis(E)-trans(Z) isomerization [19, 20].

So, all studies show that the most effective materials in this regard are azo dyes, which have shown a high value of the Weigert effect (linear birefringence and dichroism in a wide range of 430-600 nm), reversibility and sufficient photosensitivity. Despite the similarity of the photo anisotropic properties of all azo dyes, one of the pronounced examples of such materials is the dis-azo-dye Mordant Pure Yellow (MPY), which is characterized by much higher sensitivity and anisotropic effect (Fig. 2). Therefore, all of the results listed and described below are related on the basis of this material MPY [14-18].

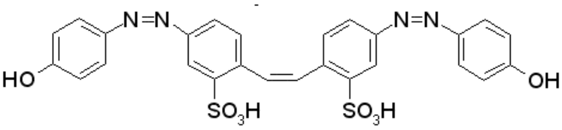
Review: In 1986-1987 on the basis of this material (MPY) the diffraction grating with anisotropic structure and with the highest diffractive efficiency (η = 100%) was obtained by the holographic method [21, 22]. Holographic recording was realized according to Leith-Upatnieks scheme by the registration of interference pattern of two plane light waves with identical intensity and with mutually orthogonal (left and right) circular polarizations [23]. The interference pattern in this case is a uniform, in intensity, light field modulated in orientation of linear polarization (Fig. 3). Accordingly the diffractive grating registered in the polymer doped by azo-dye represents oneself the holographic structure with periodical changing of linear anisotropy (Weigert's effect). At the light diffraction on such a grating, only two +1 and -1 diffraction orders with mutually orthogonal circular polarizations are obtained. Moreover, the ratio of their intensities is equal to the ellipticity of the incident polarized light. In fact, such a diffraction grating represents oneself a diffraction analogue of the polarization Fresnel prism and can be used for ellipsometric measurements [24].



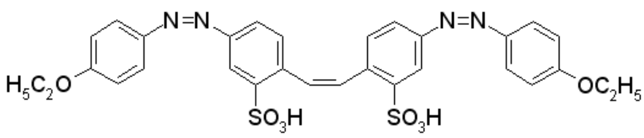
Methyl orange



Active orange yellow



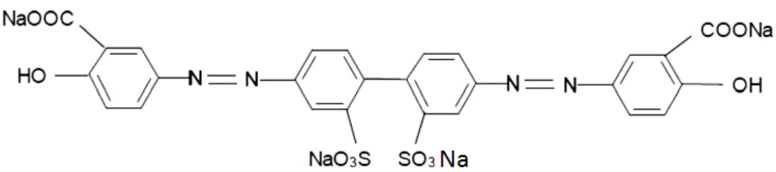
Brilliant yellow



Chrysophenine

Fig. 1 Mono- and dis-azo dyes: methyl orange, active orange yellow, chrysophenine, brilliant yellow.

Laser beam cis (E) form



Trans (Z) form

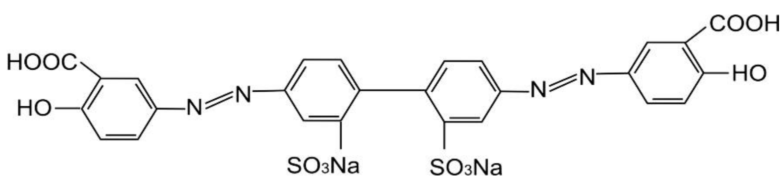


Fig. 2 Dis-azo-dye MPY in the cis (E) and trans (Z) forms.

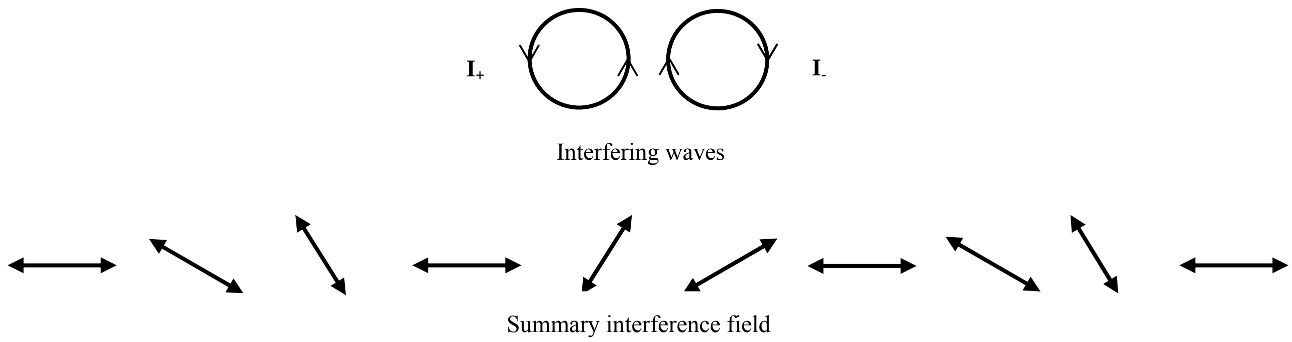


Fig. 3 Interfering waves with mutually orthogonal circular polarizations and their interference pattern.

Results and discussion: in 1989 was realized zone plate (Fresnel lens) with an anisotropic structure by the holographic recording on the basis of the same polarization sensitive material [25]. Anisotropy in this case is distributed radially, respectively, Fresnel zones. The scheme of holographic recording is shown in Fig. 4. Circularly polarized collimated beam of the He-Cd (λ = 441.6 nm) or Ar (λ = 488.0 nm) laser falls on the calcite lens. Calcite lens divides this beam into two linear polarized spherical waves with orthogonal linear polarizations and with different divergence. The λ/4 wave plate transforms the polarizations of these light waves in mutually orthogonal circular polarizations. The objective gives an image of the diaphragm in the plane of the recording material where these waves are completely overlapped. So the summary interference field on the plane of the registering material has a view as Fig. 3b, in difference that the period of anisotropy orientation, already, is distributed radials according to Fresnel zones:

$$r_m = \sqrt{m \frac{ab}{a+b} \lambda}$$

where a and b are radiuses of the wave fronts. The view of the obtained zone plate (Fresnel lens) in a polarizing microscope at crossed polarizer and analyzer in three different orientations (0°, 45°, 90°) relative to their axes is shown in Fig. 5. In Fig. 6 are shown polarization images of the anisotropic object obtained by such a Fresnel lens after polarization

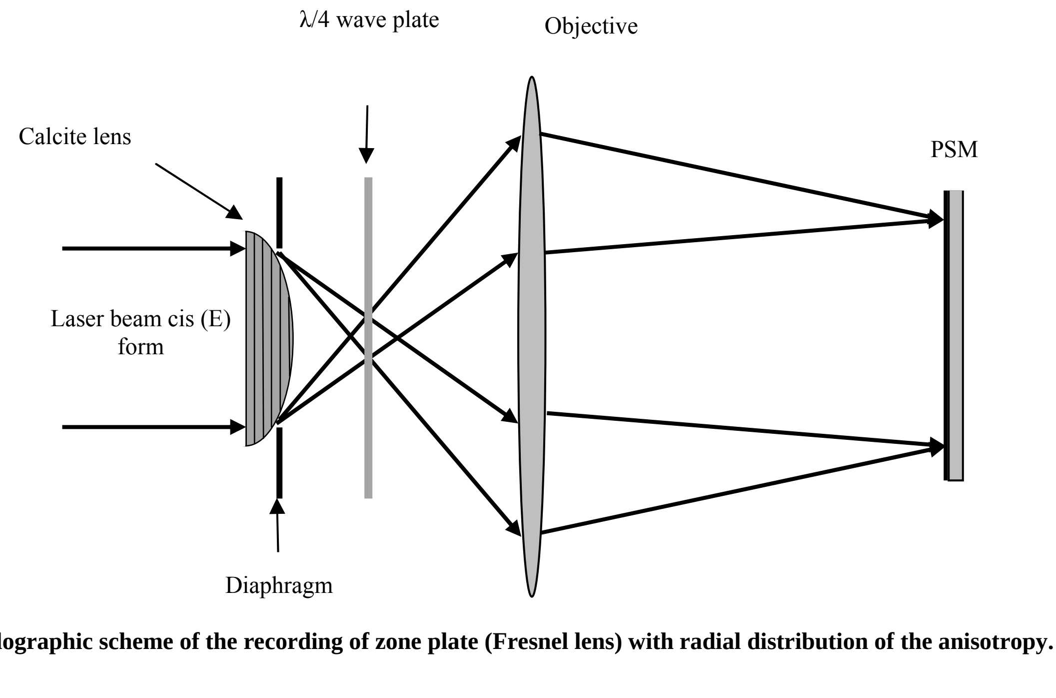
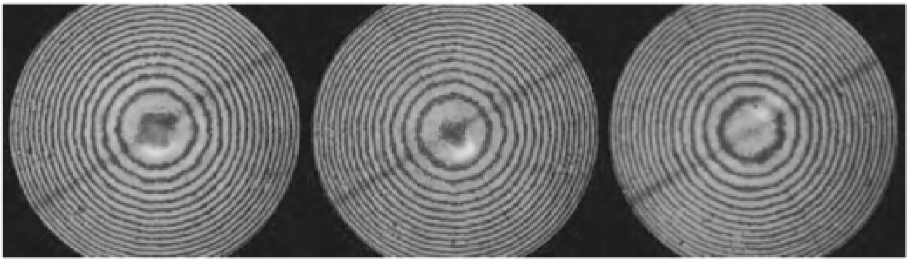
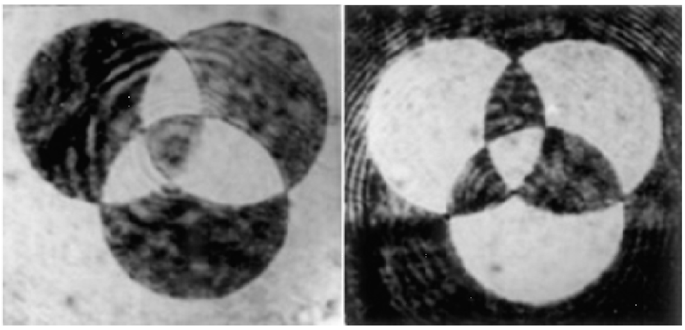


Fig. 4 The holographic scheme of the recording of zone plate (Fresnel lens) with radial distribution of the anisotropy.



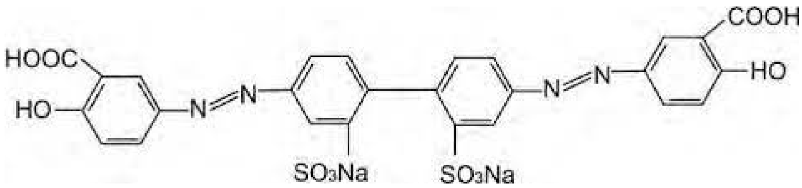
(a) (b) (c)

Fig. 5 The views of Fresnel lens with radially distributed anisotropy in the polarization microscope at the orientations 0°, 45°, 90°.

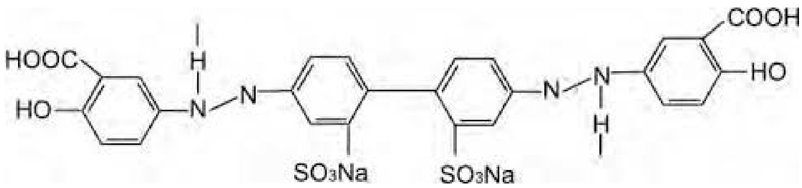


(a) (b)

Fig. 6 The polarization images of the anisotropic object obtained with one and the other side of the object by the holographic Fresnel lens with radial distributed anisotropy.



(a)



(b)

Fig. 7 The (a) initial and the (b) intermediate forms of the azo-dye MPY in the process of cis-trans (E-Z) isomerization.

analyzer when the object is illuminated by linear polarization plane wave of the He-Ne laser (λ = 632.8 nm) from the one side and the opposite side. As it is shown from Fig. 6 such a Fresnel lens inverts the polarization image of an anisotropic object that is important for the problems of optical image proceeding. It may be also an important optical element for development of new type polarization optical systems as microscopes and telescopes with the possibilities of polarization analysis.

In 2006 author proposed a new mechanism of the Weigert's effect in materials doped with azo dyes according to which the effect is caused not by complete transitions from cis to trans form (full E-Z isomerization) but by intermediate process when the double nitrogen bond is temporarily broken (Fig. 7). In this case, the chromophore bond N=N is temporarily transformed into an auxochrome bond

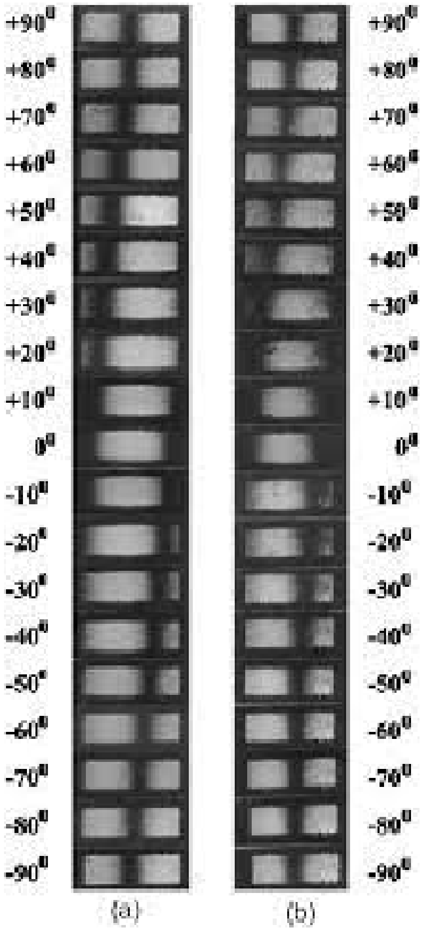


Fig. 8 The polarization images of the anisotropic object and its holographic reconstructed image after the polarization analyzer at the orientation angles ±90°.

N-H when exposed to actinic radiation. According to this point of view the MPY dye and other water soluble mono- and dis-azo-dyes must have much better characteristics between known dyes for obtaining polarization sensitive materials, which was confirmed in further research [26]. In the same year, the holographic recording in the general case of linear polarization of the object wave has been studied theoretically and experimentally on the same photosensitive medium. A simple analysis showed that it is possible to record and reconstruct the plane light wave with all possible linear polarization in this case. The experiment carried out quite well confirmed the results of the analysis (Fig. 8). The study was carried out for the first time in the case when the linear polarization is continuously changing over the cross section of the object wave, which is important for some practical applications in problems of optical memory and in the optical information processing [27].

On the basis of this material it was also investigated the possibility of creation of holographic chiral structure [28]. In particular it was realized holographic recording with two counter propagating plane light waves (λ = 441.6 nm) with mutually orthogonal circular polarizations. According to the theory the summary interference pattern of the recorded beams in this case represents oneself the chiral distribution of the electric vector of the light in the thickness of registering material. Because of anisotropic response of the material, obtained holographic structure has also chiral character and works similar to cholesteric liquid crystal. Specific characters of obtained chiral holographic mirror structure were:

(1) High spectral selectivity i.e. at the illumination by white light it reflects recorded wave only (λ = 441.6 nm).

(2) When such chiral structure is illuminated by a circularly polarized recording light wave, the reflected wave has its maximum intensity and the same polarization. With a gradual transition to orthogonal (opposite) circular polarization of the incident wave, the intensity of the reflected wave gradually decreases to zero and the beam completely passes through the structure (Fig. 9).

Subsequently, in 2007, it was discovered the phenomenon of the self-recording during the reconstruction of a light wave with the highly efficiency dynamic hologram in the process of holographic recording in a gelatin layer doped with the same azo-dye (MPY) [29]. The essence of this phenomenon lies in the fact that for some ratios of intensities of the recording waves, a sharp jump of the diffractive efficiency is observed at the overlapping, in the recording process, of the beam with low-intensity (Fig. 10).

At the same year was investigated the reversibility of the Weigert's effect in the azo-dye Mordant Pure

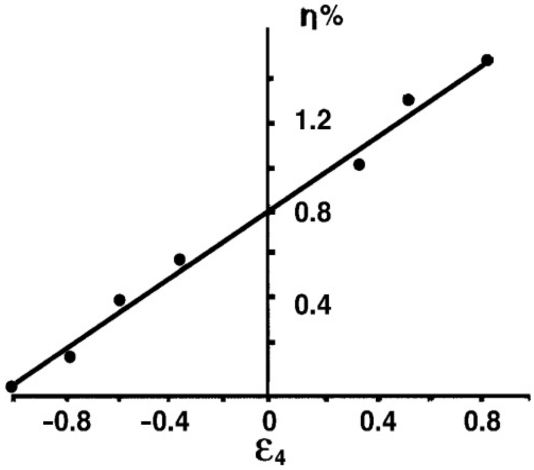


Fig. 9 Reflection efficiency of the holographic chiral structure in the changing of the ellipticity of the falling light.

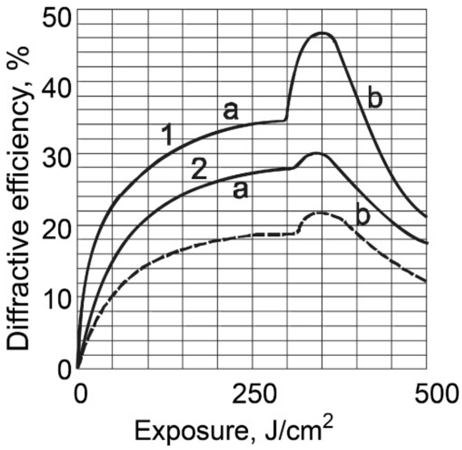


Fig. 10 Curves showing a self-recording effect.

Yellow (MPY) doped gelatin layer [30]. In particular, the dynamic process of multiple recording and erasing of anisotropy with linearly polarized actinic light (λ = 488.0 nm) was experimentally investigated. Multiple recording and erasing was performed with linearly polarized light through successive irradiation with mutually perpendicular polarizations (Fig. 11). Investigations showed out that the cyclicity of this material is practically infinite, without any signs of fatigue and a decrease in the magnitude of the Weigert's effect obtained. The results of the investigation were in good compliance with the possible mechanism of anisotropy generation in the azo-dye-colored materials proposed by Wardosanidze [26].

In addition to the above, it is much interesting also application of the given light-sensitive material in photography. In particular, a special property of this material is that unpolarized light causes in it, only an isotropic effect, which is practically not observed in the polariscope. However, when exposed to partially linearly or elliptically polarized light, significant anisotropy occurs, which is easily observed in the crossed polarizer and analyzer. This means that when photographing scattering or emitting objects on a carrier, in the form of anisotropy, only those parts of the object are recorded that give polarized or partially polarized light, and the unpolarized background is excluded. Thus, the obtained picture of anisotropy, in this case, practically is a polarimetric image of the object. The first works in this direction were made in 1989-1991, where the proposed method was called by me as a photo polarimetry [31, 32]. Fig. 12 shows the usual

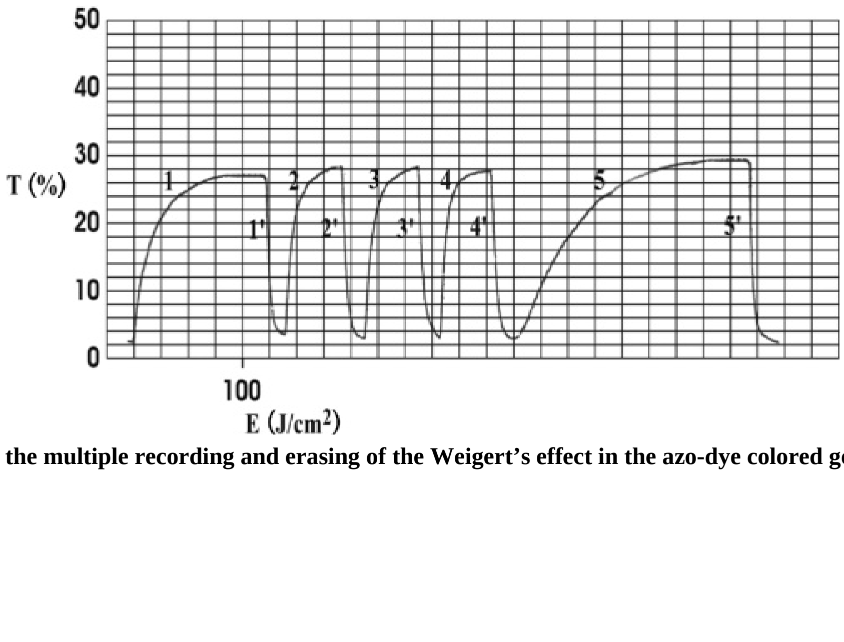
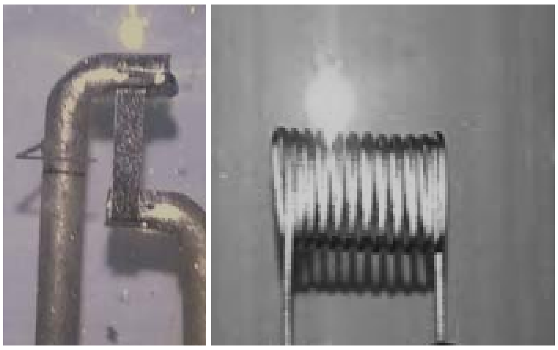
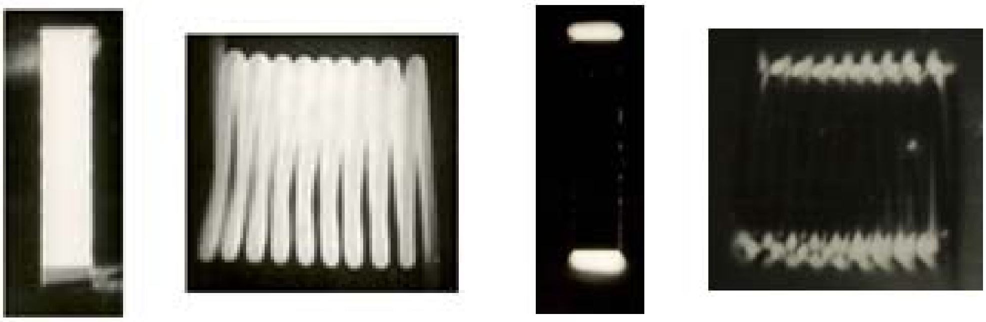


Fig. 11 Dynamics of the multiple recording and erasing of the Weigert's effect in the azo-dye colored gelatin (MPY).



(a)



(b) (c)

Fig. 12 The images of the filaments of incandescent lamps without glow (a), when glowing (b) and their polarimetric images obtained on the azo-dye (MPY) doped gelatin (c).

(a) (b)

Fig. 13 (a) The usual photo of the city landscape and (b) its polarization image obtained on the material MPY.

photos of the filaments of incandescent lamps without glow (before switching on, Fig. 12a), when glowing (after switching on, Fig. 12b) and their polarimetric images obtained on the azo-dye doped gelatin (Fig. 12c). Fig. 12c shows that a high polarization of the emitted light is observed at the edges of the luminous filament, which indicates the predominant polarization of the rays emitted only at an angle to the luminous surface.

Fig. 13 shows the usual photo of a city landscape (Tbilisi, Georgia) and its polarization image obtained on this material. In Fig. 13b is clearly visible partial polarization of Rayleigh scattering of the sky and partial polarization of inclined surfaces of rooftops and other fragments of the landscape.

(a)

(b)

Fig. 14 Polarized images of the sun, on gelatin stained with azo dye (MPY), obtained with a refractor telescope (a) in 1994-1995 and (b) in 2020-2021.

In 1994-1995 in Bulgaria at the Kirdzhal observatory, first experiments were carried out to obtain a polarimetric image of the sun and the solar corona on the basis of MPY. Obtaining a polarized image of the solar corona was not removed due to the low polarization sensitivity and limited dynamic range of the material. For the same reason and of the low quality of the material, the quality of the obtained polarization image of the sun was unsatisfactory (Fig. 14a, defects in the form of dots are visible) [33]. Subsequent improvements material in late 2020 and in early 2021 resulted in improvements in the quality of the polarized image of the sun (Fig. 14b). Fig. 14 shows the polarimetric images of the sun obtained on the (MPY) colored gelatin by the refractor telescope obtained in 1994-1995 (Fig. 14a) and in 2020-2021 (Fig. 14b, is publishing firstly). According to Fig. 14 the optical radiation of the sun is characterized by the partially polarization. Considering the characteristics of the polarization sensitivity of the given material, it can be said that the average degree of polarization of the emitted visible radiation of the sun is approximately 10^{-6}.

2. Conclusions

From the results described above, it can be concluded that the polarization sensitivity of polymers doped with azo dyes based on the Weigert's effect gives them the following advantages:

(1) Possibility of holographic recording and reconstruction of the polarization of the light wave and obtaining high efficient polarization (100%) holograms and holographic optical elements with specific characteristics.

(2) Holographic and photographic recording and reconstruction of statistical polarization structure of the unpolarized and partially polazrized light.

(3) The possibility of creation of the holographic diffractive optical elements with the anisotropic structure with advanced features.

(4) Some new processes (for example self-recording) in the investigation of dynamic processes of holographic recording based on the Weigert's effect.

(5) Photo polarization investigations in the image proceeding, microscope optics and astrophysics.

(6) Some new approaches in investigation of mechanisms of Weigert's effect.

Thus, polarization-sensitive materials, and especially azo dyes, can be of some use in various fields of scientific and applied optics and optical technology. However, it should be noted that these materials require improvement by modern technological methods. For example, in the case of azo dyes, it would be necessary to synthesize such non-equilibrium chemical structures that would lead to much higher polarization sensitivity and higher values of the Weigert's effect.

References

[1] Weigert, F. 1919. “Uber Einen Neuen Effect der Strahling in Lichtempfindlichen Schichten.” *Verhandl. Deutchen Physik. Ges*. 21: 479-83. (in German)

[2] Weigert, F. 1920. “Uber die spezifische wirkung der polarisierten shtrahlung.” *Ann. Physik.* 63: 682-725. (in German)

[3] Weigert, F. 1929. “Photodichroismus und photoanisotropie, I//Z.” *Phys. Chem.* 3: 377-88. (in German)

[4] Weigert, F. 1929. “Photodichroismus und photoanisotropie, II//Z.” *Phys. Chem.* 3: 389-404. (in German)

[5] Weigert, F., and Nakashima, M. 1929. “Photodichroismus und photoanisotropie, V//Z.” *Phys. Chem.* 4 (4): 258-76. (in German)

[6] Weigert, F., and Nakashima, M. 1930. “Photodichroismus und photoanisotropie, VI//Z.” *Phys. Chem.* 7 (1): 25-69. (in German)

[7] Zocher, H., and Coper, K. 1928. “Uber die Erzeugung optischer Aktivitatdurch Zirkulares Licht.” *Z. Phys. Chem.* 132: 313-9. (in German)

[8] Thirunamochandran, T. 1977. “Laser-Induced Circular Dichroism.” *Chem. Phys. Lett.* 49 (3): 536-8.

[9] Petrova, S. S. 2001. “Light-Induced Anisotropy and Gyrotropy in Polarization-Sensitive Media.” *Technical Physics* 46 (3): 351-3.

[10] Kondo, T. 1932. “Uber den Photoanisotropen Effect (Weigert-effect) an Farbstoffen, I//Z.” *Wissenschaftliche Photogr., Photophys. Und Photochem.* 31 (6): 153-267. (in German)

[11] Kakichashvili, Sh. D. 1972. “On the Polarization Recording of Holograms.” *Opt. & Spectr.* 33 (2): 324-7. (in Russian)

[12] Kakichashvili, Sh. D. 1974. “The Method of Phase Polarization Recording of Holograms.” *Quantum Electronics* 1 (6): 1435-41. (in Russian)

[13] Kakichashvili, Sh. D. 1978. “Polarization Holography.” *Advances in Physical Sciences* 126 (4): 681-3. (in Russian)

[14] Kakichashvili, Sh. D., and Shaverdova, V. G. 1979. “Photo Anisotropy in the Mordant Yellow Azo-Dyes.” *Journal of Scientific and Applied Photography and Cinematography* 24 (5): 342-5. (in Russian)

[15] Todorov, T., et al. 1984. “Polarization Holography. 2: Polarization Holographic Gratings in Photoanisotropic Materials with and without Intrinsic Birefringence.” *Appl. Opt.* 23 (24): 4588-91.

[16] Naydenova, L., et al. 1998. “Diffraction from Polarization Holographic Gratings with Surface Relief in Side-Chain Azobenzene Polyesters.” *J. Opt. Soc. Am. B* 15 (4): 1257-65.

[17] Petrova, S. S., and Shaverdova, V. G. 2006. “Study of Structural Factors Influencing the Weigert Effect in Azo Dyes.” *Optics & Spectroscopy* 101 (46): 549-54.

[18] Petrova, S. S., Chichinadze, N. M., and Shaverdova, V. G. 2005. “Kinetics of the Weigert Effect in Azo Dyes Embedded in Polymeric Matrices with Different Activities.” *Technical Physics* 50 (2): 227-31.

[19] Shatalin, I. D. 1989. “Mechanisms of Photoanisotropy in Photochemical Trans-Cis Isomerisation.” *Optics & Spectr.* 66 (2): 362-4. (in Russian)

[20] Ebralidze, T. D., Ebralidze, N. A., and Bazadze M. A. 2002. “Weigert’s Effect Mechanism Observed in Dyes.” *Appl. Opt.* 41 (1): 78-9.

[21] Kakichashvili, Sh. D., and Shatalin, I. D. 1986. “Polarization Holographic Gratings with High Diffractive Efficiency.” *Sov. Tech. Phys. Lett.* 12 (5): 277-80. (in Russian)

[22] Shatalin, I. D., Kakichashvili, V. I., and Kakichashvili, Sh. D. 1987. “Polarization Hologram with 100% Diffractive Efficiency (Polarization Kinoform).” *Sov. Tech. Phys. Lett.* 13 (17): 1051-5. (in Russian)

[23] Leith, E. N., and Upatnieks, J. 1962. “Reconstructing Wave Fronts and Communication Theory.” *J. Opt. Soc. Amer.* 52 (11): 1123-30.

[24] Born, M., and Wolf, E. 1965. *Principles of Optics*. 3rd ed. Oxford, London, Edinburgh, p. 936.

[25] Kakichashvili, Sh. D., and Wardosanidze, Z. V. 1989. “Zone Plate with Anisotropic Profile.” *Sov. Tech. Phys. Let.* 15 (17): 41-4.

[26] Wardosanidze, Z. V. 2006. “One More Possible Mechanism of Weigert’s Effect in Azo-Dye-Colored Materials.” *Applied Optics* 45 (3): 438-44.

[27] Wardosanidze, Z. V. 2006. “Holographic Recording in the General Case of Linear Polarization.” Optical Engineering: Coincident Beams 45 (8): 085801-1-6.

[28] Wardosanidze, Z. V. 2006. “Holographic Chiral Structure on the Basis of Weigert’s Effect.” *Applied Optics* 45 (12): 2666-71.

[29] Wardosanidze, Z. V. 2007. “Self-Recording Phenomenon in the Process of Reconstruction from a Highly Efficient Dynamic Hologram on Azo-Dye-Colored Material with Powerful Weigert’s Effect.” *Applied Optics* 46 (14): 2575-80.

[30] Wardosanidze, Z. V. 2007. “On the Reversibility of Weigert’s Effect in Azo-Dye-Colored Materials.” *Applied Optics* 46 (27): 6727-32.

[31] Kakichashvili, Sh. D., and Wardosanidze, Z. V. 1989. “Polarization Photography (Weigert-Photography).” Presented at XXVI Colloquium Spectroscopium Intenationale, Sofia.

[32] Wardosanidze, Z. V. 1992. "Polarization Photography at the Partially Polarized Light Flows/Photopolarimetry." *Sov. Tech. Phys. Let.* 18 (2): 52-6.

[33] Vardosanidze, Z. V., Kakichashvili, Sh. D., and Shopov, Y. Y. 1995. "An Attempt for Application of the New Photoanisotropic (Polarization) Materials for the Photography of the Sun." *Annales Geographyque* 1 (8): 241.