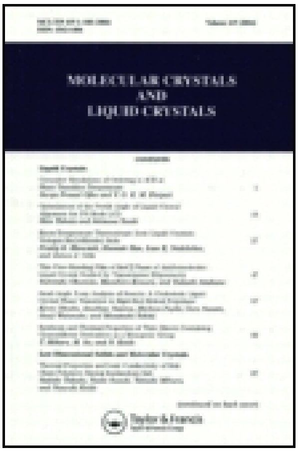

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Holographic Materials for Recording in the Blue Spectrum Region

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Holographic characteristics of commercial and new silver halide materials by recording of reflection holograms in the blue spectrum region have been studied. The conditions for the diffraction efficiency above 50% in commercial materials not sensitized to the blue region and the conditions for the synthesis of emulsions and the optical sensitization which allows to improve the sensitivity up to 8 times as compared with that of commercial materials have been determined.

Keywords Diffraction efficiency; holographic characteristics; optical sensitization; sensitivity; silver halide materials

Introduction

The development of the classical trends of holography (imaginary facilities, holographic interferometry, holographic optical elements) and the manifestation of new trends (holographic lithography, protective elements) are determined by the necessity to obtain high holographic parameters at the recording in the blue spectrum region. Recording media used for the holographic recording in the blue region (layers based on dichromated gelatin, photoresists [1–4]) do not comply with the requirements to the sensitivity put forward by a number of new challenges.

In this connection, the orientation toward silver halide materials considerably surpassing non-silver materials in sensitivity is visible. Holographic materials based on halide silver are widely used for recording in the red and green spectrum regions, which is related, to a great extent, to the availability of commercial materials (produced by OJSC «Slavich») sensitized to these regions. The objective of this work was to investigate the characteristics of commercial materials during holographic recording in the blue spectrum region and to develop new materials with the optical sensitization to the blue spectrum region.

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Experiment Methodology

The characteristics of the materials were studied by recording reflection holograms of flat waves. The layout of the installation for studying the holographic characteristics of the materials is shown in Figure 1. Holographic characteristics of materials were investigated when recording reflection holograms of plane waves at a wavelength of 442 nm from a helium cadmium laser GKL-40(I).

The radiation of laser 1 falls on mirror 2, then spread by lens 3 to isolate the uniform part of the laser beam. To exclude diffused light, the beam passes through diaphragm 4. Multiplier 5 is a thick glass plate with reflecting coatings applied onto its surface with reflection ratios close to 100 and 50%. Falling on a multiplier, light undergoes the multiple reflection, and several beams of various intensity fall on holographic plate 7.

Diffraction efficiency was measured at a wavelength of 633 nm during the expansion of an emulsion layer to provide the Bragg condition. Diffraction efficiency was determined as the ratio of the intensity of the diffracted beam to the intensity of the incident ration (Fig. 2).

For the treatment of exposed materials, we used the processes which ensure the formation of colloidal silver (GP compounds during a change in the consistency of ammonium rhodanate and potassium hydroxide) and the processes with bleaching which ensure the transfer of halide silver to transparent salts [4]. The treatment process without bleaching is as follows: the development in GP compound for 3–12 min, and the washing in water for 10 min. The treatment process with bleaching includes the development in CW C2 [4] compound for 3–6 min, the washing in water for 6–10 min, and the bleaching in compound PBU with amidol [4] for 7–10 min.

Experimental Results

Figure 3 presents the exposure curves of the diffraction efficiency (DE) for materials PFG-03 m (sensitized to the red spectrum region) and PFG-03c (sensitized to the red

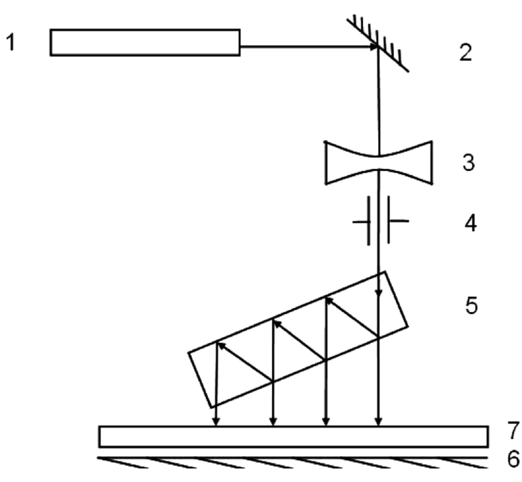

Figure 1. Installation layout for studying the holographic characteristics of materials. 1 – laser, 2 – mirror, 3 – lens, 4 – diaphragm, 5 – beam splitter, 6 – mirror, 7 – recording medium.

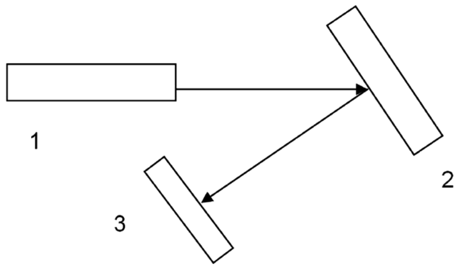

Figure 2. Installation layout for measuring the diffraction efficiency. 1 – laser, 2 – hologram, 3 – photoreceiver.

and green regions) obtained when treating in classical GP-2 compound and the optimal compound with the doubled consistency of ammonium rhodanate and potassium hydroxide. When treating in the optimal compound, the values of diffraction efficiency more than 40% were obtained, which is sufficient for solving a number of practical issues. The use of GP developers has an advantage related to a low labor intensity of the treatment process consisting of the stages of development and washing. However, during the reconstruction with radiation in the blue spectrum region, the diffraction efficiency is reduced by 2–3 times due to the high absorption of colloidal silver. In this connection, of the greatest interest are the processes with bleaching.

Figure 4 shows the exposure curves of the diffraction efficiency of commercial materials PFG-03 m and PFG-03c during the treatment in the developer CW C2 with subsequent bleaching in the PBU compound with amidol. We have obtained values of diffraction efficiency above 50% which are comparable with those attained on these materials, when recording in the red and green regions, but with reduced sensitivity.

In order to increase the sensitivity in the blue spectrum region, new materials based on the emulsion of the Russian Scientific Center Kurchatov Institute have been synthesized. Because a reduction in the wavelength of recording radiation imposes enhanced (toward increase) requirements to the resolution ability determined by the sizes of light-sensitive crystals of halide silver, the conditions for emulsification have been optimized. A reduction in the duration of emulsification, the use of a weak

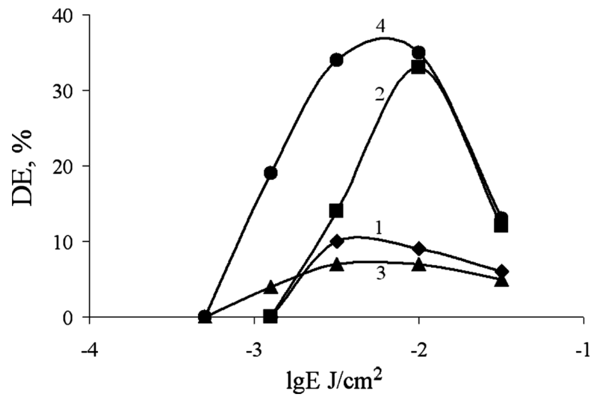

Figure 3. Exposure curves of the diffraction efficiency (DE) of materials PFG-03m and PFG-03c. Treatment: developer GP-2, 20 min (1, 3); GP_{opt}, 6 min (2, 4).

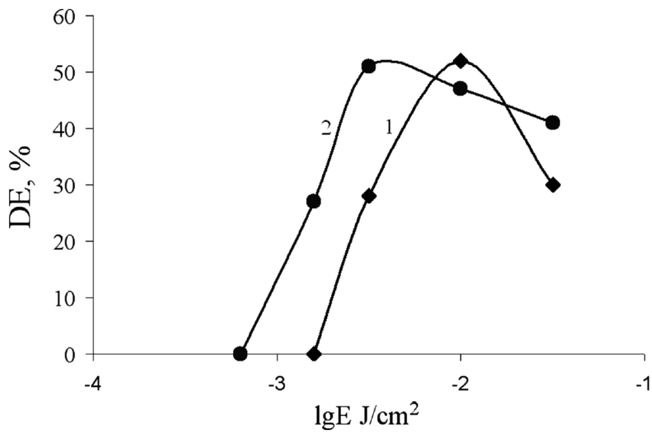

Figure 4. Exposure curves of the diffraction efficiency of materials PFG-03m (1) and PFG-03c (2). Treatment: developer CW C2, 3 min; bleacher PBU.

solution, a synthesis at high pAg values, and the introduction of a stabilizer (Sta-salt) have allowed obtaining the sizes of crystals of 10–20 nm. With a goal to the sensitizing to the blue spectrum region, a number of optical sensitizers have been investigated with the absorption band in this region. Characteristics of the optical sensitizers are presented in the Table 1, where $\Delta\lambda$ is the absorption band width and λ_{max} is the wave length corresponding to peak of absorption.

The consistency of working solutions and the quantity of the introduced sensitizer have been optimized to rule out the desensitization effect. The best results have been obtained for sensitizers MA-30 and 1610 upon their introductions in the following quantities: 0.0025 g of MA-30 sensitizer (M = 280.38) as an alcoholic solution per one gram of halide silver; 0.006 g of 1610 sensitizer (M = 251) as an alcoholic solution per one gram of halide silver.

Table 1. Optical sensitizers under study

No.	Full name	Design.	Empirical formula	λ_{max} (nm)	$\Delta\lambda$ (nm)
1	2π-dimethylaminostyrylbenz-thiazol	MA-30	$C_{17}H_{16}N_2S$	470	400–500
2	Triethylammonium salt 3,3^1-di-(γ-sulfopropyl)-5,5^1-dimethoxythiacyaninbetaine	6439	$C_{29}H_{41}O_8N_3S_4H_2O$	470	400–500
3	1,3-dimethyl-5(3^1-methylpyrrolidinilidene-2^1-ethylidene)-imidazolidinethionine(2)-O-H(4)	1610	$C_{12}H_{17}ON_3S$	460	400–540
4	3,3–diethylthiazolinocarbo-cyaniniodide/(π-toluene sulfonate)	109	$C_{13}H_{21}N_2S_2J$	470	400–520

Figure 5 gives the holographic characteristics of the new materials for the treatment in GP compounds. Is seen a high criticality to the developer composition and the development duration that may by connected with different structure of developed silver [5].

The results obtained in the treatment with bleaching, when transferring halide silver to transparent salts, are shown in Figure. 6. For comparison, we show the result which was obtained in the process of bleaching developed silver (treatment in SM-6 developer) in a compound based on iron nitrate. As a result of the optimization of the condition for the synthesis, optical sensitization, and treatment process, the values of diffraction efficiency of 40–50% have been obtained with a considerable (up to 8 times) increase in the sensitivity.

Thus, the executed investigations allow us to determine the conditions for obtaining high diffraction efficiency during the holographic recording in the blue spectrum region for commercial silver halide materials not sensitized to this region and to develop new highly sensitive holographic materials for the blue region.

Application of the Results

The determined possibility to obtain high values of diffraction efficiency in the blue spectrum region in commercial materials PFG-03c (worked out for the recording in the red and green spectrum regions) allows using these materials to make colored holograms by the recording on three wavelengths in the red, green, and blue spectrum regions. A possible application of the results is the fabrication of holographic protective elements. Presently, one of the most widely used protective methods is the use of iridescent holograms. However, the technological equipment for making the iridescent holograms is quite accessible, which enhances the risk of counterfeiting the protective elements.

The objective of our work was to work out the principles of a technology that would become an alternative to the technology of making the iridescent holograms. The technology is based on the making of a volume colored hologram in the recording at various wavelengths of the visible spectrum. Unlike the relief elements varying

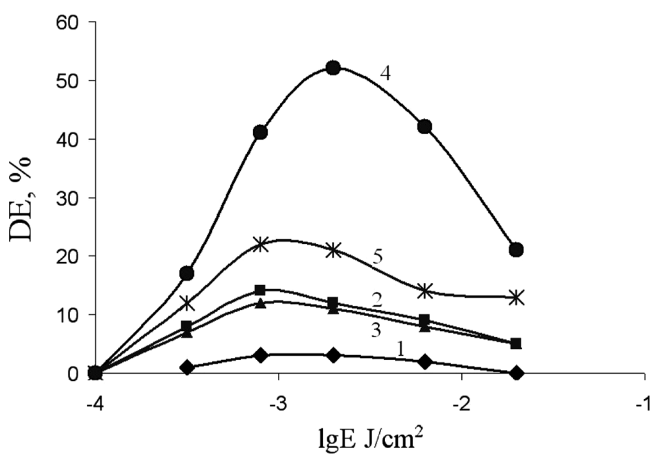

Figure 5. Exposure curves of the diffraction efficiency of new materials. Treatment: developer GP-2, 10 min (1) and 2 min (2) GP_{opt}, 3 min (3); 6 min (4), and 12 min (5).

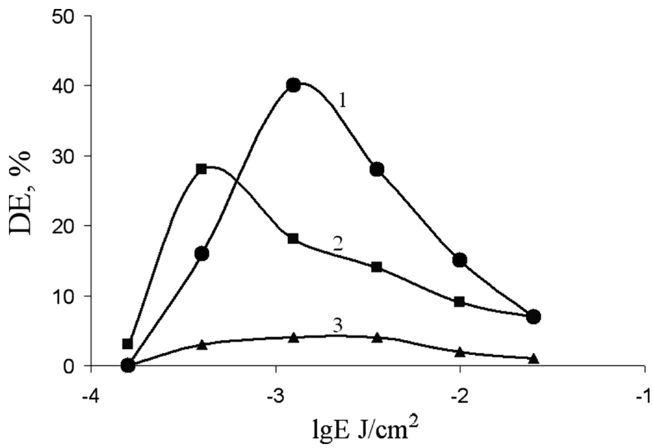

Figure 6. Exposure curves of the diffraction efficiency of new materials. Treatment: developer CW C2, 3 min (1) and 6 min (2); bleacher PBU.

color in a wide spectrum region, the elements based on a volume reflection hologram allow assuring the unidirectional reflection during the illumination by a white light source with the isolation of a narrow spectrum region (increased light purity and uniformity of the coloring of an image), which is a new protective sign (in line with the introduction of additional protective elements).

The advantages of this technology are as follows:

– the technology is less likely to be reproduced,
– possibility to obtain the characteristics (protective properties) of holographic elements which differ from the characteristics of iridescent holograms, including the reproduction of spectrally pure colors due to a high spectral selectivity of a volume hologram and the directivity of reflection,
– possibility to realize a great number of protective signs,
– increasing of the number of protective levels in one element,
– impossibility to alter a protective element (unlike the protection based on digital methods).

The use of the proposed treatment processes consisting of one stage (the development) or two stages (the development and the bleaching), unlike the hologram treatment processes used earlier which were based on the transfer of the developed silver to transparent salts, seems to be possible under conditions of the mass production due to their simplicity and the high light resistance of holograms.

When using the special recording schemes and sources of radiation, a helium-neon laser GI-15 R (0.63 μm), helium-cadmium laser (0.44 μm), and DPSS-laser KLM-532 (0.53 μm), the protective elements were obtained which restore the red, green, and blue colors during illumination by a white light source, as well as various images upon varying the angle of observation.

Conclusion

The conditions for high values of the diffraction efficiency in the recording of reflection holograms in the blue spectrum region in commercial materials developed for the recording in the red and green spectrum regions have been determined. New high-resolution materials for the holographic recording in the blue spectrum region have been developed. A possible use of the obtained results for the fabrication of color-changing protective elements based on a volume hologram has been demonstrated.

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References

[1] Pantelic, D., & Muric, B. (2001). Improving the Holographic Sensitivity of Dichromated Gelatin in the Blue-Green Part of the spectrum by Sensitisation with Xanthene Dyes. *Appl. Opt.*, *40*(17), 2871–2875.
[2] Malov, A. N., & Neupokoeva, A. V. (2006). *Holographic Recording Media based on Dichromated Gelatin*. IVVAIU: Irkutsk.
[3] Juodkazis, S., Mizeikis, V., & Misava, H. (2008). Tree-Dimensionel Structuring of Resists and Resins by Direct Laser Writing and Holographic Recording. *Adv. Polym. Sci.*, *213*, 157–206.
[4] Bjelkhagen, H. J. (1995). *Silver-Halide Recording Materials for Holography and Their Processing*. Springer: New York.
[5] Vorzobova, N. D., & Ryabjva, R. V. (2000). Pulsed Holographic Recording on Silver Halide Emulsions. *Sci. Appl. Photo.*, *42*(2), 107–111.