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Effect of Post Heat-treatment on Spectral Shifts Photopolymer Reflection Holograms and Its Use for Creating Color Holograms

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The effect of post heat-treatment on the spectral properties of photopolymer reflection holograms scheme has been studied. It has been established that holograms with protective film retain a high diffraction efficiency of $\sim 90\%$ and do not have additional shrinkage during heat treatment for several days at a temperature of $80-90^\circ$C. The holograms without a protective film, removed after exposition, when heated in the temperature range of $40-110^\circ$C, show effective shrinkage up to 17% without compromising diffraction efficiency. Addiction the degree of shrinkage from the time of keeping the hologram at a given temperature is described by the function biexponential growth with saturation. The parameters of the approximating function are calculated. The characteristic shrinkage times in the temperature range of $40-110^\circ$C decrease from hours to minutes for fast components and from tens of days to tens of minutes for the slow component. Effect large shift of spectral response was used to create color-separated holograms. Color-separated holograms were obtained in two ways: two-layer version with shrinkage of one of the layers, single-layer version using photoresistive pattern and subsequent shrinkage.

Keywords: reflection photopolymer holograms, thermal shrinkage, spectral shifts, color holograms

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1. Introduction

Currently, holographic photopolymer materials (HPPM) [1–4] are being developed, which are used in art and security holography, data storage systems, holographic sensors and displays [5–9].

Both transmission and reflection photopolymer holograms are characterized by material shrinkage. Shrinkage occurs immediately at the time of recording due to monomer contraction during radical polymerization and in process of post-processing. In this case, the period of the recorded gratings decreases; in the case of recording a reflection hologram, shrinkage leads to a hypsochromic shift of the maximum of the spectral response. It is known to develop photopolymer compounds with small shrinkage [10,11], when the use of low molecular weight acrylate monomers is avoided and branched oligomer-like monomers separating siloxane units, oxirane monomers [12] are used. In particular, for water-soluble HPPMs based on acrylate monomers in polyvinyl alcohol, $\sim 3\%$ shrinkage was achieved when recording reflection holograms [13]. Similar values were obtained for commercial low-shrinkage acrylate compounds [14,15].

During photopolymerization, along with a decrease in the thickness of the photopolymer layer, there is a change in the density of HPPM and, as a consequence, the average value of the refractive index. Therefore, in [16] the concept of effective shrinkage is introduced, which takes into account both factors. In the work [17] a spectroscopic method for measuring the effective shrinkage of reflection photopolymer holograms directly during their recording, is proposed.

As a general rule, research on the shrinkage of photopolymer materials focuses on ways to achieve low shrinkage during photopolymerization and post-processing. The creation of HPPM with a high degree of shrinkage, in our opinion, is also of fundamental and practical interest. Controlled hypsochromic shift of the spectral response of a hologram over a wide spectral range can be useful for imparting unusual additional properties to art or security holograms. Studies in this direction are not presented in publications known to us.

The objectives of this work are: to determine the dependence of the evolution of spectral shifts of reflection holograms in HPPM on time at a given temperature; choice of thermal post-processing mode for reflection photopolymer holograms to achieve large values of their spectral shifts; implementation of color effects in two- and one-layer HPPM through the use of shrinkage.

2. Experimental part

2.1. Object under study

The study of the effect of thermal post-treatment was carried out in the HPPM, sensitive in the red region of

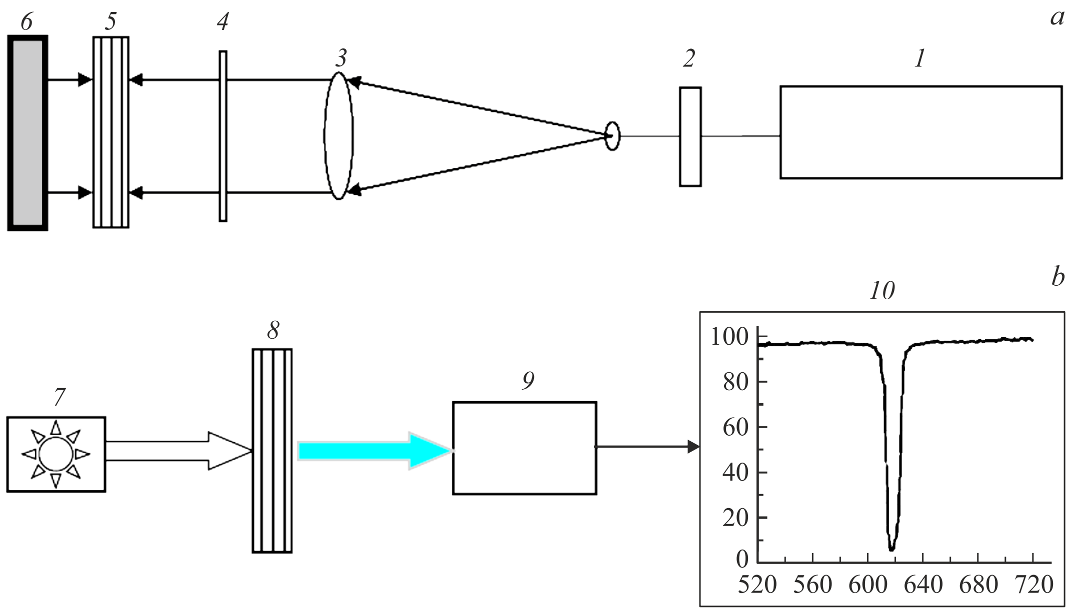

Figure 1. Schemes of installations for recording (*a*) and characterization (*b*) of volume reflection holograms: *1* is laser (CNILASER, MSL-FN-639, 200 mW); *2* is automated shutter (Thorlabs, SH05/M); *3* is two-lens collimator forming a parallel beam; *4* is neutral light filter; *5* is HPPM sample; *6* is mirror; *7* is halogen lamp for forming a probing beam of white light; *8* is reflection hologram; *9* is digital spectrophotometer (Avantes, AVASPEC-ULS2048CL-EVO); *10* is control computer and display.

the spectrum and described in [18,19]. The compound for obtaining HPPM contained the following main components: solvents, polymeric binder (polyvinyl acetate), Methylene Blue dye, co-initiator, acrylamide monomer polymerizing by free radical mechanism. The dye concentration concentration was selected taking into account the recommendations [20] so that the transmission at the recording wavelength of laser radiation was 35–45%. Prior to exposure, a protective polyethylene terephthalate (PET) film was rolled onto the photopolymer layer, which prevents the access of oxygen to the photosensitive layer, and also serves to protect the HPPM from mechanical damage and environmental influences. Based on this compound, single-layer and two-layer HPPM samples with a thickness of 20–30 μm were obtained, in which reflection monochrome holograms were recorded.

The thicknesses of the holograms and the additional photoresistive layer were measured using an MII-4 computerized interferometer (Diffraction, Novosibirsk, Russia).

2.2. Recording, post-processing and characterization of volume reflection holograms

The holograms were recorded using a laser with a radiation wavelength of 639 nm according to the Yu.N. Denisyuk scheme [20]; the recording object was a flat metal mirror with a reflection coefficient of $\sim$ 90%. The main elements of this scheme are shown in Fig. 1, *a*.

A parallel beam of laser radiation with a wavelength of 639 nm, a diameter of 10 mm and an intensity of 1 mW/cm^2, formed by a collimator, is a reference beam in this scheme and is directed to a photopolymer sample strictly along the normal; Further, the light beam passing through the HPPM is reflected from a mirror installed directly behind the photopolymer, thereby creating an object beam that interferes with the reference beam in the HPPM volume, resulting in a reflection hologram. The illumination energy is dosed using a shutter. Also, for recording holograms, a two-beam symmetric scheme for recording reflection holograms with a convergence angle of recording beams of 110° (in air) and a laser with a radiation wavelength of 639 nm [18]) was used. In this case, the calculated wavelength of the spectral response maximum is 691 nm.

Due to spurious reflections, spurious holograms are formed in addition to the main hologram, however, it has been experimentally established that their influence on the effects we are studying is insignificant.

After recording, the holograms were fixed by post-exposure of the entire sample with a halogen lamp. In addition to light post-processing, thermal post-processing was additionally carried out: by keeping the fixed hologram in a drying oven by Venticell at a given temperature and time. Holograms were subjected to thermal post-processing both with and without a PET protective film on the photopolymer layer. The measurement of the diffraction efficiency (DE) and the degree of shrinkage of the hologram was carried out on a installation, the scheme of which is shown in Fig. 1, *b*. The spectral properties of reflection holograms were determined by measuring the parameters of their transmission spectra (shape, width and depth of contours, wavelength at the transmission minimum, etc.).

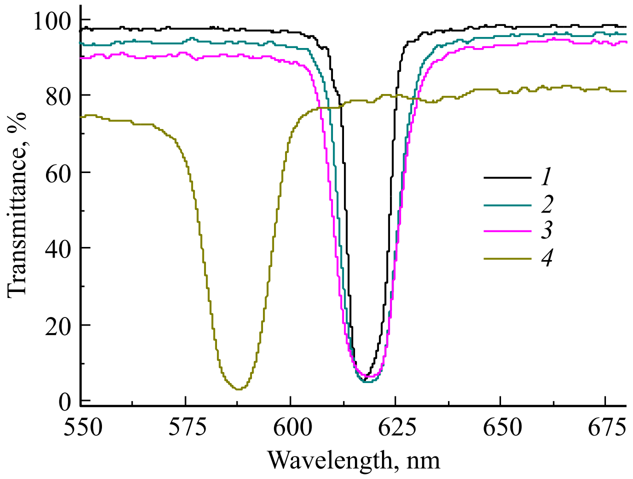

Figure 2. Transmission spectra of holograms at various times and temperatures (in brackets) of post-heat treatment: *1* — 0; *2* — 30 h (80°C); *3* — 16 h (90°C); *4* — 1 h (150°C).

For brevity of designation of the spectral response as a whole, we also use the term reflex.

3. Results and discussion

3.1. Influence of heat treatment on the spectral properties of holograms with a protective film

One of the parameters that determine the possibility of using holographic elements in practice is their resistance to temperature changes. Fig. 2 shows the change in the spectral response of a hologram with a layer thickness of 25 μm under successive exposure to temperatures of 80, 90, and 150°C.

The experimental values of the DE of reflection holograms were estimated using the formula

$$\eta_r = (1 - T_r/T_0) \cdot 100\%, \tag{1}$$

where T_r is transmission of the hologram at the wavelength of the minimum of the spectral response contour (reflex), T_0 is residual transmission of the HPPM sample outside the hologram region. For example, for a hologram with a layer thickness of 25 μm, with light transmissions T_r and T_0 equal to 5 and 95%, respectively, the diffraction efficiency is about 95%.

Shrinking rating of ΔS is related to the relative spectral shift of the reflective hologram and is calculated by the formula

$$\Delta S = \frac{\lambda_1 - \lambda_2}{\lambda_1}, \tag{2}$$

where λ_1 is the wavelength of the maximum of the initial reflex of the reflection hologram after recording, λ_2 is the wavelength of the reflex as a result of post-processing. Note that for a non-shrinking HPPM, the theoretically expected reflex wavelength λ_{ref} should coincide with the wavelength of the recording radiation, i.e. 639 nm, however, as mentioned above, in practice, immediately after recording, a hypsochromic shift of the reflection by approximately 20 nm is observed, which corresponds to the shrinking rating ~ 0.03.

From the data presented in Fig. 2, it can be seen that as a result of recording a hologram, post-heat treatment at 80°C for 30 h and additional heat treatment at 90°C over 16 h, there was an insignificant increase in the width at half-height of the spectral response of the hologram from 11 to 15 nm. Additional shrinkage of the hologram is not observed in this case. Heating holograms up to 150°C leads to an additional hypsochromic shift of the hologram reflection by 30 nm, as a result, the total effective shrinkage is $\sim$ 8% relative to the wavelength 639 nm, but the transmission decreases due to an increase in light scattering, which is presumably caused by the destruction of the polymer and low molecular weight components of the compound.

The experiments performed show that the recorded holograms with a protective film applied are resistant to thermal post-processing up to 100°C, retain a high DE and do not acquire additional shrinkage.

3.2. Effect of heat treatment on the spectral properties of holograms without a protective film

In contrast to HPPMs protected by PET film, the heat treatment of holograms with the Mylar film removed leads to significant hypsochromic shifts of holographic reflections even at low temperatures.

Fig. 3, *a* shows the spectra of the reflection hologram after the stages of recording, post-exposure irradiation with a halogen lamp, and subsequent heat treatment of the hologram with the protective film removed at 40°C.

Similar data on the kinetics of the shrinkage ranging were obtained for different temperatures. For two temperatures they are shown in Fig. 3, *b*. Shrinking rating at a given temperature tends to saturation over time. When describing shrinkage as a consequence of the relaxation of stresses in the polymer matrix that arose during the photopolymerization of HPPM, one should take into account the polyexponential nature of the stress decay in polymers with several different relaxation times [21]. With an exponential stress decay, the inverse function associated with the exponential is the asymptotically bounded exponential growth

$$y' = A\exp(-x/t) \Rightarrow y = A(1 - \exp(-x/t)). \tag{3}$$

Taking the exponential nature of the relaxation of the HPPM matrix upon heating and the corresponding increase in shrinkage, it should be assumed from the data obtained (Fig. 3, *b*) that in the region of limited temperatures 40–100° C, at least a biexponential pattern of shrinkage accumulation with a fast and a slow component is observed. Therefore, to approximate the increase in the spectral shifts of reflection holograms during shrinkage in time, the

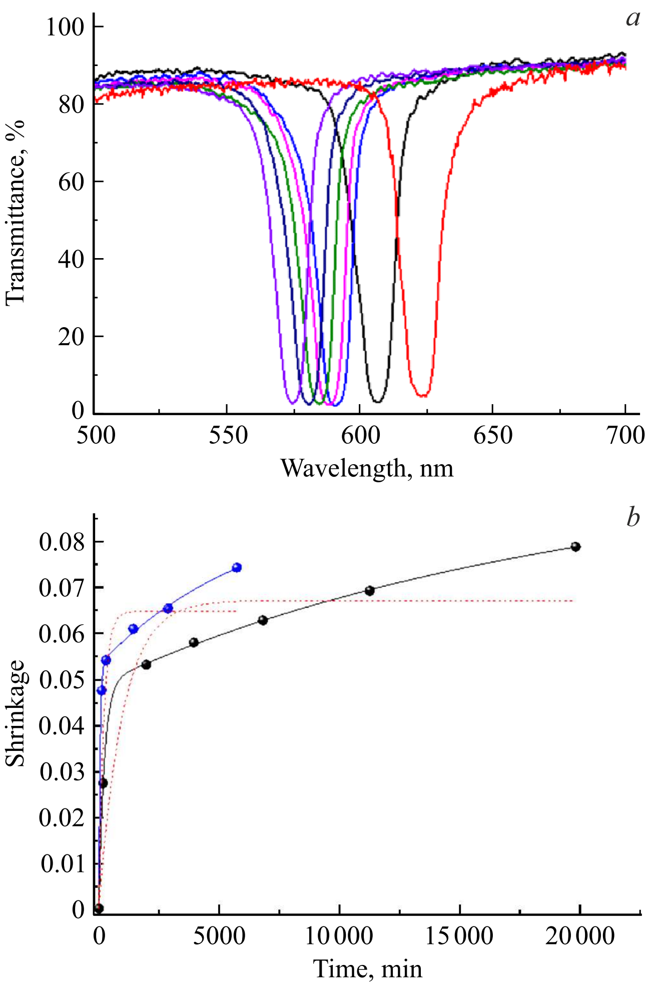

Figure 3. *a*) Diagrams of shifts in the transmission spectra of holograms as a result of post-heat treatment without a protective film at 40°C for several days. *b*) change in the degree of shrinkage of holograms as a function of exposure time at 40°C (black dots) and 85°C (blue dots), data approximation by the equation for biexponential growth (blue and black curves) and mono-exponential growth (red dashed curves).

function of biexponential asymptotically bounded growth was used.

$$y = A_1(1 - \exp(-x/t_1)) + A_2(1 - \exp(-x/t_2)), \qquad (4)$$

where $A1$, $A2$ are saturation levels, t_1, t_2 are characteristic times.

The calculated parameters of equation (4) are given in the table. Note that the sum of the coefficients $(A_1 + A_2)$ gives the maximum shrinkage at a given temperature.

It follows from the obtained approximation parameters by equation (4) that the amplitudes of fast and slow shrinkage processes for a low temperature of 40°C are approximately equal, but as the temperature rises, the ratio of the components changes to 3 : 1 in favor of the fast component. Total shrinkage as a percentage is 10–14%. The characteristic times of the fast and slow components naturally decrease with increasing temperature: t_1 from 3 hours at 40.60°C to a minute at 110°C, t_2 accordingly decreases from tens of days to tens of minutes. The greatest changes accelerating shrinkage occur at a temperature in the region of 100°C. When the hologram is heated at 150°C, a complete shrinkage of 12% occurs in one minute. A further increase in temperature leads to an increase in light scattering of the sample.

Shrinkage parameters based on the results of biexponential approximation

T, °C	A_1	t_1, h	A_2	t_2, h
40	0.05	3.7	0.047	324
60	0.064	3.1	0.013	70
85	0.053	0.95	0.025	57
95	0.07	0.06	0.047	0.43
105	0.082	0.07	0.037	0.58
110	0.1	0.02	0.03	0.11

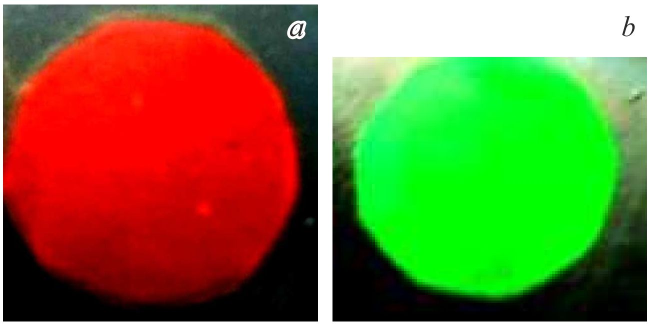

Figure 4. Photographs of reflection holograms before (*a*) and after (*b*) maximum shrinkage.

The maximum shrinkage value of 17% was observed for one of the samples when heated to a temperature above 100°C. Visually, when the spectral shift of the reflection is close to saturation, the color of the hologram changes from red to yellow-green, as shown in the photographs in Fig. 4.

Note that during the post-heat treatment of HFPM without a protective film to a temperature of 110°C, no deterioration in the diffraction characteristics of holograms is observed: the DE value is ~ 94%, the transmission beyond the absorption peak of the hologram is 85–90%. Moreover, for example, during heat treatment of a hologram at a temperature of 80–85°C for 2 days, an increase in the DE was observed with the hypsochromic shift, as shown in Fig. 5.

3.3. Creation of color-separated two-layer holograms by shrinking photopolymer layers

The effect of controlled shrinkage of HPPM without a protective film was used to create two-color holograms in versions of single-layer and two-layer HPPM, the construction schemes of which are shown in Fig. 6.

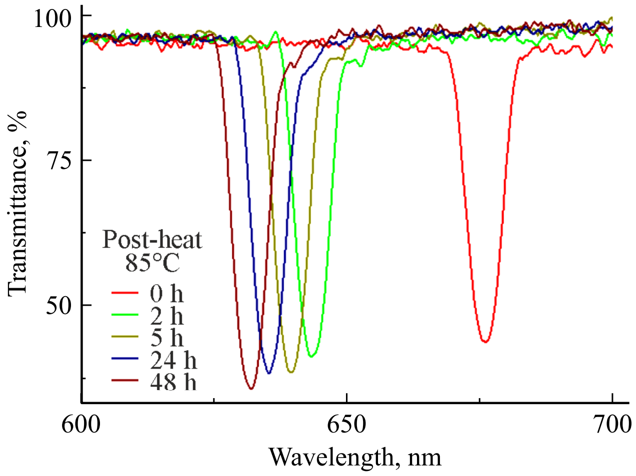

Figure 5. Spectral shifts of hologram transmission peaks in time at a temperature of 85°C.

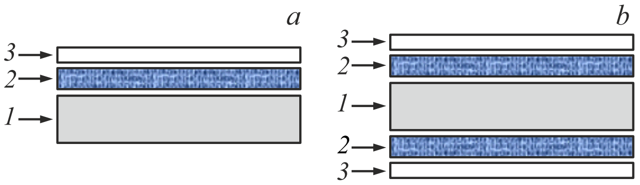

Figure 6. Structural diagrams of single-layer (*a*) and two-layer (*b*) HPPM: *1* is glass substrate, *2* — photopolymer, *3* is protective film.

Initially, the first reflection hologram was recorded on a single-layer sample, which was subjected to post-exposure processing; after that, a second HPPM layer with a protective film was applied to the back side of the glass substrate, the second hologram was recorded and post-exposure processed, then the protective film of one of the photopolymer layers was removed, then the entire two-layer structure was subjected to thermal post-heat treatment at 45°C. The spectral responses of the resulting two-layer color hologram before and after post-heat treatment are shown in Fig. 7.

It can be seen from Fig. 7 that after post-heat treatment, the holograms have a large spectral response width (FWHH are 12 and 9 nm), the DE of holograms obtained in each layer is ~ 85%, which is not always possible achieve in the case of single-layer two-color HPPM [16]. Compared to single-layer holograms, a decrease in transmission is observed due to an increase in light loss when passing through two layers. The shift of the reflex maximum of the reflection hologram with the protective film removed was ~ 36 nm. Note that after applying a protective Mylar film to the unrolled part of the HFPM and additional processing at 85°C for 24 h, the transmission spectrum of the two-layer hologram was identical to the initial one. Thus, the achieved spectral shift during controlled shrinkage of HFPM without a protective film can be fixed by a repeated protective coating and used to create two-layer color holograms. Since the width of the spectral reflection of the hologram is 12 nm, the possibility of fixing the spectral shift, in turn, creates the fundamental possibility of carrying out polychromatic separation of colors, fixing intermediate colors. At the same time, it is important to strive to obtain HPPM with the highest degree of shrinkage.

3.4. Creation of holograms with color separation image

Fig. 8, *a* shows photographs of a hologram of a mirror subjected to heat treatment at 50°C for 100 h with the PET film partially removed and a section of this hologram taken with an electron microscope (Fig. 8, *b*). In this case, the boundary between the red and green regions is clearly visible, which is associated with the difference of shrinkage for protected and unprotected regions of the hologram. Since, as a result, one initially monochrome layer is divided into two colors, this effect means obtaining a bi-chromatic color-separated image from a monochrome one.

The manifestation of difference shrinkage allows to separate the colors of an initially monochrome image, using a transparent stencil that protects certain places in the hologram. The effect of a hypsochromic shift in the spectral response of a hologram during thermal post-processing of HPPM without a protective film was used to obtain a color-separated image in monochrome holograms using photolithography and included the following main steps: deposition of a photoresist on an exposed HPPM, irradiation through a photomask, and development of non-irradiated areas of the photoresist (Fig. 9).

To create a color-separated image, a negative photoresist based on a hybrid light-sensitive material [22,23] was deposited on the photopolymer layer with the recorded hologram. The photoresist was applied by pouring until uniform spreading. A polyethylene terephthalate film with an applied letter image was used as a photomask. The photoresist was exposed with a CS-410 UV irradiator. After exposure, the photoresist was developed in a solvent bath for 20 s at room temperature. As a result, a relief with a thickness of ~ 100 μm was formed on the hologram. Then the heat treatment of the hologram was carried out in an oven at a temperature of 50°C for 5 days.

Fig. 10 shows photographs of a hologram with a photoresist after heat treatment and the boundaries of the polymerized and developed photoresist.

It can be seen from the photographs that in the region with the cured photoresist the hologram has a response in the red region of the visible spectrum, while in the developed regions of the photoresist the hologram has a response in the yellow-green region due to the spectral shift after heat treatment. The color of the image after shrinkage can be controlled by setting the holding time at a given temperature using the data given above.

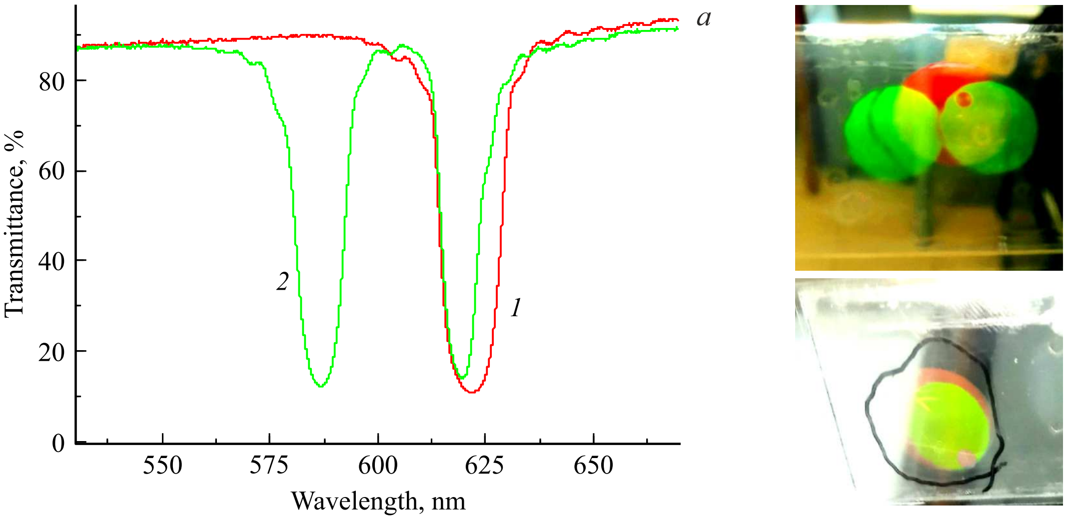

Figure 7. Transmission spectra of a two-layer hologram before and after post-heat treatment (*a*, curves *1* and *2*, respectively); photographs of a two-layer hologram (*b*).

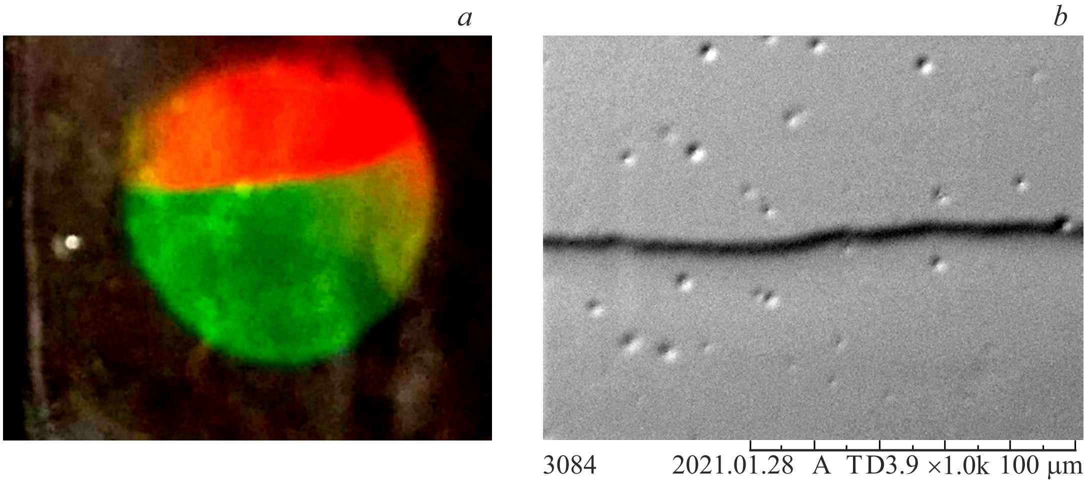

Figure 8. Photograph (*a*) and SEM image (*b*) of the hologram (the area with the applied and removed protective film) after post-heat treatment.

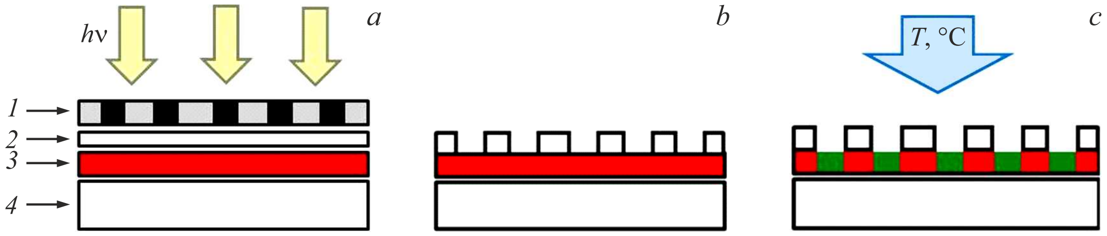

Figure 9. Stages of creating a combined color hologram using the photolithography method: irradiation (*a*), development (*b*), heat treatment (*c*); photomask with printed macro image (*1*), photoresist (*2*), HFPM with recorded hologram (*3*), glass slide (*4*).

Thus, the developed post-processing process makes it possible to create reflection holograms with a color-separated image when recorded by laser radiation at one wavelength using photolithography and subsequent thermally stimulated shrinkage.

Conclusion

The effect of thermal post-processing on the spectral characteristics of reflection holograms has been studied. It has been established that holograms with a protective

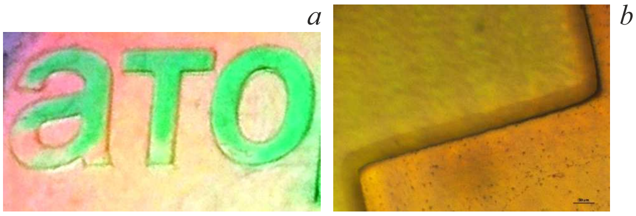

Figure 10. Photographs of holograms with photoresist: *a*) photo of the hologram after heat treatment, *b*) boundary of the developed photoresist.

PET film retain a high diffraction efficiency of 90% and do not acquire additional shrinkage during heat treatment for several days at a temperature of 80–90°C.

For holograms without a protective film, when heated in the temperature range 40–110°C, an effective shrinkage of up to 14% occurs without deterioration of their diffraction efficiency. The dependence of the degree of shrinkage on the holding time of the hologram at a given temperature is described by the function of biexponential growth with saturation. The parameters of the approximating function are calculated. The characteristic shrinkage times in the temperature range 40–110°C decrease from hours to minutes for the fast component and from tens of days to tens of minutes for the slow component.

The application of the effect of a large shift in the spectral response of a reflection hologram is shown to create color-separated images when recording a monochrome image at one wavelength of laser radiation. Color-separated holograms were obtained in two versions: a two-layer version with shrinkage of one of the layers, a single-layer version using a photoresist pattern and shrinkage. The effect of a large spectral shift of a photopolymer reflection hologram during post-processing is of interest in creating security holograms.

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