

We are IntechOpen, the world's leading publisher of Open Access books Built by scientists, for scientists

6,900

Open access books available

185,000

International authors and editors

200M

Downloads

Our authors are among the

154

Countries delivered to

TOP 1%

most cited scientists

12.2%

Contributors from top 500 universities



WEB OF SCIENCE™

Selection of our books indexed in the Book Citation Index
in Web of Science™ Core Collection (BKCI)

Interested in publishing with us?
Contact book.department@intechopen.com

Numbers displayed above are based on latest data collected.
For more information visit www.intechopen.com



Light-Sensitive Media-Composites for Recording Volume Holograms Based on Porous Glass and Polymer

O.V. Andreeva and O.V. Bandyuk

*The National Research University of Information Technologies, Mechanics and Optics
Russia*

1. Introduction

Volume holography, or holography in three-dimensional media, dates back to Yu. N. Denisyuk's works (Denisyuk, 1962), who implemented the idea of hologram recording in a three-dimensional medium by means of recording a hologram in counterpropagating beams, using traditional silver-halide light-sensitive materials. Adaptation of traditional photomaterials for purposes of image (pictorial) holography consisted in reconstruction of Lippman photographic layers with the size of light-sensitive grains less than 25 nm and use of photochemical processing techniques that allow obtaining amplitude-phase high-efficiency holograms in the visible region (Denisyuk & Protas, 1963).

Three-dimensional holograms with Klein parameter (Q) that describes the degree of three-dimensionality of a hologram grating on order of 10 (Kogelnik, 1969), obtained on traditional photomaterials of thickness on order of 10 μm , are referred to as 3D-thin holograms. Hologram gratings with $Q > 1000$ are commonly considered 3D-volume holograms. To meet the condition, the thickness of the recording medium should be by 2-3 orders of magnitude greater than in the case of 3D-thin holograms and amount to a value on order of millimeters.

Recording 3D-volume holograms made use at different times of different recording media: crystals, photochromic glasses, etc., their main features in high demand in 3D-volume holography being large thickness and negligible shrinkage. Yet it became clear that the available media fail to meet the set of requirements placed on media for hologram recording, and foremost, for recording static holograms, intended to be used as hologram optical elements and holograms for long-term information storage. The need to develop the theoretical and experimental research in the field of volume holography called for creation of recording media of great thickness and with corresponding properties. Creating such media required new approaches to their development and corresponding measurement techniques for parameters.

The present section introduces media for 3D-volume holography, which were created on the basis of principles developed in 80s-90s of the XX century (Sukhanov, 1994a). The media demonstrated the potentiality of the implementation of the proposed theoretical principles of creation of volume recording media in practice and also proved conducive to refining parameter measurement techniques for volume holograms, to studying and understanding

the relationship between physical-chemical processes of manufacturing technology for light-sensitive samples of volume recording medium and parameters of obtained holograms.

2. Light-sensitive media for volume hologram recording: Basic requirements and principles of design

2.1 Basic requirements to recording media to construct static volume holograms

The interest to static volume holograms with thickness of several millimeters is due, mainly, to their use in research and in creation of holographic optical elements (HOE) of various purposes with unique parameters (Sukhanov et al., 1984; Ludman et al., 1997; Popov, et al., 2000; Luo, et al., 2008). Requirements to materials for recording of such holograms are rather specific and cannot be met when using traditional light-sensitive materials.

Recording media for construction of static 3D-volume holograms should have the following properties:

- high spatial resolution (greater than 3000 mm^{-1});
- large physical thickness (100-10000 μm);
- high physical and mechanical performance;
- sensitivity in the wavelength region of present-day lasers;
- transparency at the operating wavelength ($\tau > 0.5$);
- non-destructive reconstruction of recorded information.

Of greatest practical interest are media with photo-induced alteration of refractive index, which are suitable to record high-efficiency phase holograms, a special place among them belonging to media with latent image. Such media are most preferable in creation of HOE, as the recording process generates holograms of low efficiency, so-called "latent image" that leaves the recorded interference pattern undistorted. High efficiency of recorded holograms is in the case achieved through multiple magnification of modulation amplitude of a latent image hologram with the help of post-exposure treatment.

2.2 The principle of composite structure

The most natural way of realizing light-sensitive media with great physical thickness and high physical and mechanical performance is creation of medium-composite. The requisite set of parameters is in the case ensured by virtue of the medium components fulfilling different functions. Rigid framework has the necessary physical and mechanical properties and ensures the negligible shrinkage of samples; light-sensitive composite situated inside the framework ensures the properties needed for hologram construction (Sukhanov, 1991, 1994b).

The principle of creating the composite structure of light-sensitive medium by using a rigid framework was implemented in two ways. Firstly: the framework is created and formed independently; the light-sensitive composite is introduced into finished mold of the sample. The way was followed in realization of recording medium (RM) on the base of porous glasses with different light-sensitive composites (Sukhanov et al., 1988), one of them being the AgHal-based composite. Under such manner of RM realization, the framework effect on photochemical properties of samples is minimal and results from interaction of light-sensitive composite with the internal surface of the framework. Secondly: the framework is created and formed simultaneously with the light-sensitive composite – formation of sample-composite and rigid framework takes place at the same

time. The manner was implemented by using organic dye phenanthrenequinone (PQ) as a light-sensitizing agent and forming the rigid framework by means of radical polymerization of composite on the base of methylmethacrylate monomer (MMA). The properties of the framework itself in such a RM are not limited only to maintenance of sample rigidity; the frame plays a certain part in recording, enhancement and fixation of holograms.

2.3 The dispersion refraction principle

The approach to creation of volume light-sensitive media, proposed in work (Lashkov & Sukhanov, 1978) and termed the dispersion refraction principle, consists in the following. It is necessary that the impact of light caused a sharp change of the absorption band of the material in the spectral region very far away from the operating wavelength range of recording radiation. The change of the absorption band is accompanied by change of dispersion, which leads to photo-induced refractive index appearing in the operating spectral range. Sensitivity of created RM in given wavelength interval can be ensured by using sensitized phototransformations. The change of refractive index due to the above causes was proposed to term as sensitized dispersion refraction. Purposeful use of given principle allows selecting substances with corresponding spectral parameters and calculating the possible modulation amplitude of constructed hologram. The principle became the base for realization of the first volume polymeric medium “Reoksan”, whose light sensitivity is due to sensitized photo-oxidation of compounds of anthracene structure (Sukhanov, 1986, 1994a). It was used to create a medium with diffusion enhancement and is applicable to description and analysis of photophysical processes in most media intended for recording and reading the information in the optical spectral range.

2.4 The diffusion enhancement principle

The principle of diffusion enhancement supplements previous ones and opens up new opportunities to combine properties of the framework and light-sensitizing agent, thus setting direction of the search for new substances and photochemical and photophysical processes in creation of volume light-sensitive materials. According to the principle, particles of light-sensitizing agent of medium-composite should have no binding with the rigid framework: when a latent image hologram is recorded, two antiphase gratings are formed in such medium, one of them being made up of photochemically transformed molecules (photoproduct), the other one (supplementary to the first) being made up of light-sensitive particles remaining unchanged (unexposed). The formation of two antiphase gratings is a necessary, but not a sufficient condition: the main special feature of the principle is that after the medium exposure the photoproduct particles should be rigidly bound to the framework (here, unexposed particles remain unbound). The hologram recorded, the particles, unbound to the framework (free), diffuse with the passage of time, spreading uniformly across the sample bulk and causing the supplementary grating to degrade and the photoproduct grating to “develop” (be enhanced), since particles are not subject to diffusion.

This principle was successfully implemented in practice by using polymeric medium on the base of polymethylmethacrylate with PQ (Cherkasov et al., 1991; Veniaminov et al., 1991, 1996; Steckman et al., 1998; Lin et al., 2000, 2006; Luo et al., 2008; Liu et al., 2010; Yu et al.,

2010). Attempts to implement the principle using other compositions was less successful. However, experts consider the principle today among the most promising in creation of volume recording materials for holographic memory (Ashley et al., 2000; Shelby, 2002; Liu et al., 2010).

3. Study of volume light-sensitive media using recorded holograms

Volume recording media of about a millimeter thickness for holography exhibit, as a rule, very small values of modulation amplitude of optical parameters ($\Delta n \approx 10^{-3} \div 10^{-5}$) and small spatial size (fractions of a micron) of behavior of physico-chemical processes, taking place under impact of radiation and post-exposure treatment. These particular properties make it difficult to use standard instruments and procedures in study of such media and their changes under impact of radiation and other factors. The basic technique for research into volume RM parameters is the holographic one – investigation of media through construction of holograms and study of their parameters. The technique comprises task-oriented alteration of controlled variables in recording and post-exposure treatment of holograms; measurement of hologram parameters at each stage of their construction; theoretical analysis, enabling to correlate the changes of hologram parameters with experimental conditions and RM parameters.

As a test object, we used hologram-gratings, which were theoretically analyzed with the help of coupled wave theory (Kogelnik, 1969). This theory is an indispensable tool in study of RM using recorded holograms, as it allows relating the measured hologram parameters with the amplitude of modulation of optical characteristics of a medium.

The work dealt with phase and amplitude-phase transmission hologram-gratings with different thicknesses and constants, constructed, as a rule, in a symmetrical (or close to that) configuration of interfering beams relative to the sample surface. Main measured holographic parameters were the diffraction efficiency (DE) and selectivity contour of holograms, constructed under different recording and post-exposure treatment conditions.

Diffraction efficiency (η) of a hologram was defined as the ratio of diffracted beam intensity (I_d) to the sum of beam intensities behind the hologram: $\eta = I_d / (I_d + I_0)$, where I_0 is the intensity of the zero-order diffraction beam. Maximum values of DE for a hologram are attained at reconstruction under Bragg conditions. According to the coupled wave theory, the DE of a volume phase hologram-grating at reconstruction under Bragg conditions can be represented by the formulas: $\eta = \sin^2 \varphi_1$ for transmission holograms and $\eta = \tanh^2 \varphi_1$ reflection holograms. Phase modulation amplitude, φ_1 , is defined by the expression:

$$\varphi_1 = \pi n_1 T / \lambda \cos \theta \quad (1)$$

where n_1 is the amplitude of variation of the first harmonic of refractive index of the medium; T is the hologram thickness; λ is the radiation wavelength; 2θ is the angle of diffracted beam (I_d) to zero beam (I_0). This equations relate the measured parameter of transmission hologram (η) to RM parameters (n_1 , T) and experimental conditions (λ , $\cos \theta$). Fig. 1a shows dependences of DE on the magnitude of phase modulation for phase transmission (curve 1) and reflection (curve 2) holograms in the variation range of phase modulation of media under study ($0 < \varphi_1 < 2\pi$).

In the presence of the amplitude component, the DE of an amplitude-phase transmission hologram is defined taking into account that the modulation amplitude of the first harmonic of hologram absorption index (α_1) and the average hologram absorption index (α_0). Fig. 1a presents the dependence (curve 3) for the case $\alpha_1 = \alpha_0 = 0.05$. The oscillatory nature of dependence $\eta(\varphi_1)$ is seen to persist. The data on Fig. 1a characterize variation of DE of holograms at their reconstruction under Bragg conditions. To describe the deviations from Bragg conditions, mismatch parameter (ξ) is used. Dependence of hologram DE, or diffracted beam intensity, on mismatch parameter ξ is the selectivity contour of a hologram. One recognizes the spectral selectivity contour of a hologram – dependence $I_d(\lambda)$ at $\theta = \theta_{Br}$ and the angular selectivity contour of a hologram – $I_d(\theta)$ at $\lambda = \lambda_{Br}$. The halfwidths of spectral and angular selectivity contours, $\Delta\lambda$ and $\Delta\theta$, are a measure of hologram selectivity. Comparison of selectivity of hologram-gratings with different DE by measured values of $\Delta\lambda$ and $\Delta\theta$ is appropriately done in the variation range of phase modulation of a medium $0.1\pi < \varphi_1 < 0.5\pi$, where the halfwidth values for a selectivity contour are practically independent of the DE of a hologram and are defined by its constant and thickness.

As have been noted, the dependence of DE of transmission volume holograms on phase modulation value (φ_1) is of oscillatory nature. Here, for phase holograms without absorption, $\varphi_1 = k\pi \pm \sin^{-1} \sqrt{\eta}$, where $k = 0, 1, 2, 3$; therefore, different sections of DE variation range (as indicated on Fig. 1a) are to correspond to different formulas for calculation of φ_1 by measured values of η . Fig. 1b shows selectivity contours of transmission phase holograms with DE = 50% (at reconstruction under Bragg conditions), which were obtained at different values of phase modulation amplitude. It is clearly seen that φ_1 for high-efficiency transmission holograms can be unambiguously found by DE values only with account of selectivity contour shape as opposed to thin-layer holograms, where, as a rule, $\varphi_1 < 0.5\pi$. The study of amplitude-phase holograms should involve not only the hologram selectivity contour (the dependence of diffracted beam intensity on parameter ξ), but also the dependence of intensity of zero beam that passed the hologram without changing the direction, on parameter ξ (Fig. 1c).

Dependences $I_d(\xi)$ and $I_0(\xi)$, given on Fig. 1 (b,c) for hologram-gratings with different values of phase modulation, display unsymmetrical nature of dependence $I_0(\xi)$ of amplitude-phase holograms (Fig. 1c) as opposed to phase holograms (Fig. 1b). Thus, symmetry of dependence $I_0(\xi)$ with respect to Bragg conditions is evidence of absence of the amplitude component in the hologram under study, which is necessary for correctness of calculations and estimation.

When the coupled wave theory is used to analyze experimental results, account is to be taken of the measurements of hologram parameters taking place, as a rule, in the air, and the formula-defined relationship of the studied parameters being established inside the medium. Comparison of experimentally measured hologram parameters to those calculated theoretically for given experimental conditions allows finding the amplitude of modulation of optical parameters of the medium in a hologram and their variation in processes under study as well as estimating some other characteristics, e. g., the uniformity of the light-sensitive agent distribution in the sample bulk, the effective hologram thickness against the geometric dimensions of the sample and so on.

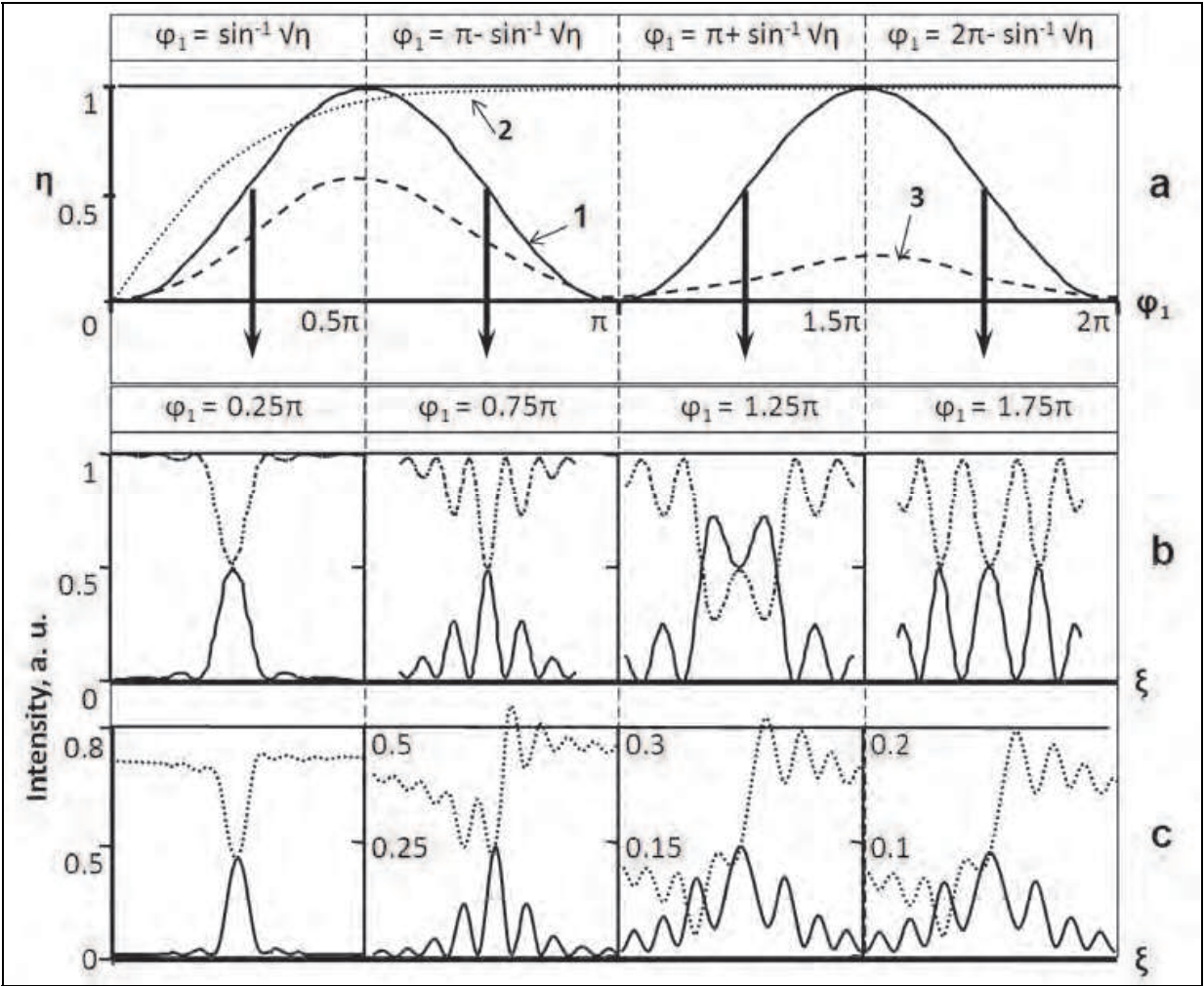


Fig. 1. a - dependence of diffraction efficiency (η) on phase modulation amplitude (φ_1) for volume phase transmission (curve 1) and reflection (curve 2) holograms; amplitude-phase transmission hologram with absorption index $\gamma_0 = \gamma_1 = 0.1$ (curve 3). b, c - intensity distribution in diffracted (solid lines) and zero (dotted lines) beams at deviation from Bragg conditions (ξ) at reconstruction of transmission phase hologram (b) and transmission amplitude-phase hologram (c) at $\gamma_1 = \gamma_0 = 0.1$ with phase modulation: 1 - $\varphi_1 = 0.25\pi$, 2 - $\varphi_1 = 0.75\pi$, 3 - $\varphi_1 = 1.25\pi$, 4 - $\varphi_1 = 1.75\pi$.

4. Light-sensitive AgHal-porous glass medium-composite

4.1 AgHal-porous glass samples: Manufacture and main features

The rigid framework of porous volume media provides porous glass, obtained from two-phase glass by treating samples in acid and alkali solution. The need to secure the requirements to rigid matrix during development of recording media led to creation of samples NPG-17 with stable and reproducible parameters, which are obtained from initial two-phase glass DV-1 by the developed technology. Samples NPG-17, used to create RM, are polished plates or disks 1-3 mm thick. The average pore diameter is 17 nm, the pore-occupied free volume of a sample is $(52 \pm 4) \%$. The light absorption in the short-wave region by air-dry samples is quite considerable because of scattering by porous structure and absorption by framework components (see Fig.2, curves 1). Under impregnation of

pores with an immersion liquid, a 1 mm thick sample exhibits high transparence practically in all visible region (see Fig.2, curves 2).

The light sensitivity of porous silver-containing recording medium is provided by the silver-halide component with gelatin as a protective colloid. Light-sensitive component is formed as a solid-phase shell that is rigidly bound with framework walls (see Fig.2c,d), while central regions of internal framework cavities remain unfilled, thus forming a network of through capillaries, which provides access for liquid and gaseous chemical agents. The synthesis of light-sensitive composite is performed directly inside a sample with the use of KBr, KJ, AgNO₃ and gelatin solution. The synthesis process is typical for manufacturing high-resolution RM.

The solid-phase shell occupies less than 10 % of the total volume of an air-dry sample. Under impregnation of water solutions, the shell swells and fills the entire internal pore volume without changing its localization relative to framework walls, to which it is rigidly bound. In synthesis of AgHal, the size of formed particles and the variation of their localization in the course of post-exposure treatment cannot exceed the maximum size of porous ducts, which amounts when using matrices NPG-17 to 20 nm. The feature makes AgHal-porous glass (AgHal-PG) media fundamentally distinct from AgHal film plates, where it is practically impossible to create an ensemble of particles with limitation of maximum sizes and to ensure their rigid localization during the hologram construction.

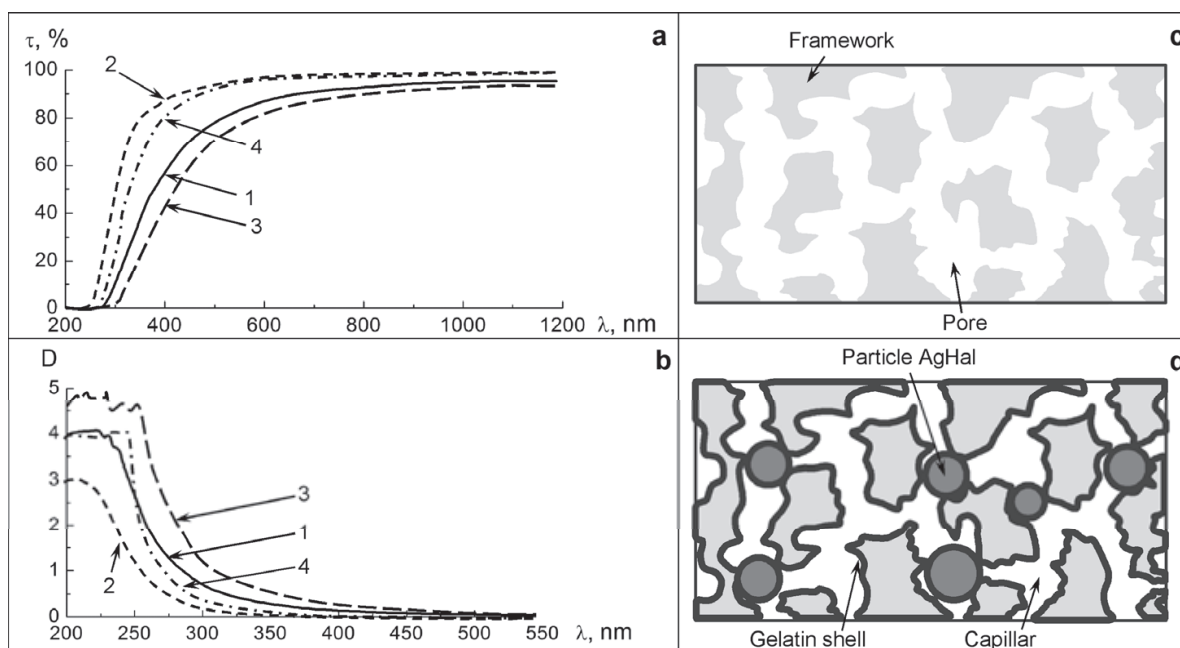


Fig. 2. Spectral dependence of transmission (a) and optical density (b) of porous samples in air (curves 1, 3) and in water immersion (curves 2, 4); 1, 2 – a sample NPG-17 of thickness 1 mm; 3, 4 – a sample with gelatin shell of internal capillaries: measurements in the air are relative to the air; those in water are relative the water. Schematic drawing of the cross-section of porous glass (c) and light-sensitive medium AgHal-PG (d).

Unsensitized samples of medium-composite are sensitive in the intrinsic light sensitivity of AgHal in spectral region $\lambda < 510$ nm. The developed synthesis process allows performing optical sensitization of AgHal composite with the use of dyes for the visible and near IR regions. During experiments, hologram recording with the use of Ar-ion laser (488 nm) was

assured by intrinsic sensitivity of AgHal and that with the use of He-Ne laser (633 nm) was due to optical sensitization. Hologram parameters were measured in the red (633-655 nm) and near IR regions (1.5 μm).

4.2 Basic stages of hologram construction process on samples of AgHal-porous glass

The stages of hologram construction on samples of AgHal-PG medium are typical for holograms on traditional AgHal media: pre-exposure treatment of samples (e. g., impregnation of an immersion into a sample to reduce scattering); exposure; development; additional post-exposure treatment - stop bath, fixation, bleaching and so on; rinsing; drying. The network of through capillaries allows using water solutions for pre- and post-exposure treatment of porous samples, but essentially retards and modifies the physico-chemical processes, developed to construct holograms on traditional AgHal materials.

Recording. During hologram recording in a medium under effect of radiation, formation of the so-called “latent image”, typical for AgHal media, takes place. Latent image centers (LIC) cause practically no changes in optical properties of the sample and form a hologram that has, immediately after recording, low diffraction efficiency ($< 1\%$). LICs are as a rule also the development centers that determine the formation of developed particles. Fig. 3a (curve 1) shows angular selectivity contours of “latent image” hologram. The width of measured contours is in agreement with the theoretical values, found for a hologram with constant-depth amplitude modulation, but the sidelobes exceed the calculated values. The fact is evidence that the LIC concentration near the sample surface is somewhat higher than on average in the sample.

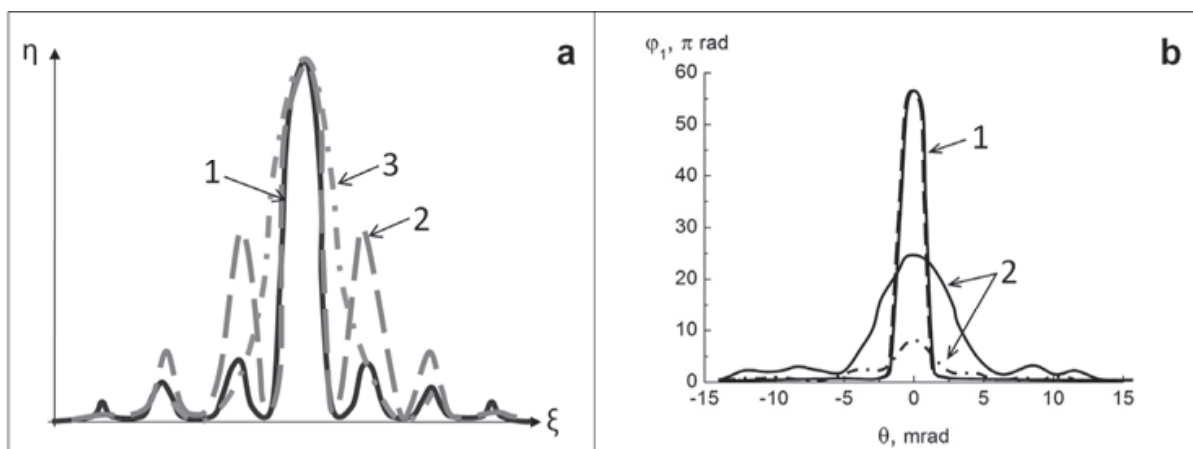


Fig. 3. Angular selectivity contours of holograms at different stages of their construction: a - a hologram at the latent image stage (curve 1), after development (curve 2), after thickness reduction owing to grinding away of surface layers of the sample (curve 3); b - developed hologram (curve 1) after the bleaching stage (curve 2) in air-dry condition (solid curves) and in water immersion (dashed curves).

Development. The basis of the elaborated process of development was taken to be that of construction of holograms on film plates with the use of developer PRG-1. The elaboration of the process of hologram construction took account of special features of the elaborated process of synthesis of light-sensitive component in nano-porous matrix and minimized the effect of the chemical activity of quartz-like framework on silver recovery process. A

modification of developer PRG-1 was proposed, which was used in the performed experiments: anhydrous sodium sulfite – 0.2 g, hydroquinone – 0.2 g, KBr – 0.15 g, water – 100 ml. Development time is 8-20 hrs at temperature 20 °C. Stop bath is dipping in 0.2 % solution of citric acid for 30 min. Rinsing is in distilled water for 20 hrs. Drying is at room temperature.

Developed particles of AgHal-porous glass medium-composite, like those of AgHal film plates, represent particles of recovered metallic silver of colloid structure. Fig. 4a presents attenuation spectra of developed film plates PFG-03 (curve 1) and AgHal-PG (curve 2) after development to formulation PRG-1 so as to obtain developed silver particles of colloid structure. Curve 3 represents attenuation spectrum of diluted water preparation of Ag-PG sample of type 2, which is dispersed (powdered) and spread in water solution.

As seen from the given results, all attenuation spectra are of highly marked selective nature with a maximum in the short-wave part of the visible region ($0.39\div 0.43\text{ }\mu\text{m}$), which is evidence of colloid structure of studied particles, close in shape to a sphere. When comparing spectra, a shift of the maximum of attenuation spectra of Ag-PG samples to the short-wave region is clearly seen, which is evidence of reduced average developed particle size in AgHal-PG as compared to film plates PFG-03.

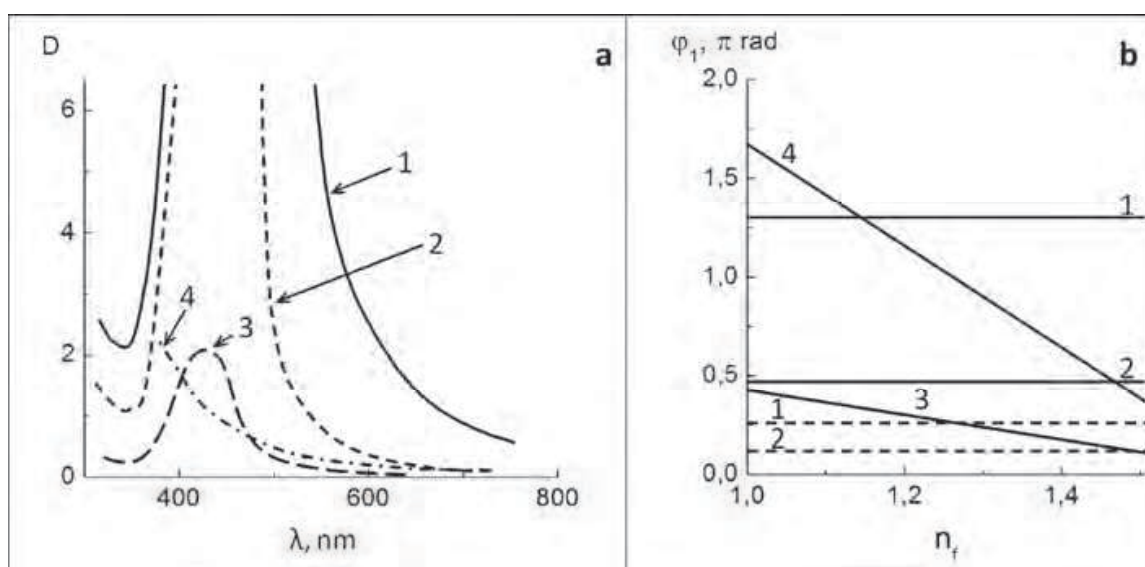


Fig. 4. a - attenuation spectra of AgHal media after the development stage with creation of particles of colloid structure (curves 1-3) and after the bleaching stage (curve 4): 1 – film plate PFG-03); 2 – AgHal-PG samples with thickness 0.3 mm; 3 – preparation of dispersed sample 3, diluted with water; 4 – AgHal-PG sample after the bleaching stage. b - phase modulation amplitude ϕ_1 of PG-holograms as function of the filler of the free volume of pore n_f for $\lambda = 0.63\text{ }\mu\text{m}$ (solid curves) and $\lambda = 1.5\text{ }\mu\text{m}$ (dashed curves): AgHal-PG after development (1,2) and after the bleaching (3); porous glass with dichromated gelatin (4).

The development process results are affected by a lot of factors, related to the conditions of performing the synthesis of light-sensitive composite and hologram recording, i. e. “life history” of samples prior to their development. The angular selectivity contours holograms on Fig. 3b (curve 1) demonstrate the influence – of immense interest is the possibility to obtain a developed hologram contour, having no sidelobes. Angular selectivity contours of developed holograms (see Fig. 3a, curve 2) have as a rule higher sidelobes, which is

evidence of increasing non-uniformity of hologram modulation amplitude across the sample depth in the course of development. Grinding away of surface layers of the developed sample allows constructing a hologram less thick, but more uniform in distribution of modulation amplitude (Fig. 3a, curve 3).

Bleaching. The bleaching process, when colloid particles of metallic silver are transformed to those of silver halide, transparent in the visible region (see Fig. 4a, curve 4), changes also the hologram structure due to changes of optical parameters of the components and their distribution across the sample depth, which is manifested in alteration of the selectivity contour of the bleached hologram as compared to the initial developed hologram (Fig. 3b, curves 2). Impregnation of an immersion into free volume of pores of bleached holograms causes their DE to lower, which is to be kept in mind as the use of bleached holograms without impregnation of immersion is often impossible because of noticeable scattering as compared to unbleached ones.

4.3 Investigation of developed samples and Ag-porous glass holograms

Developed Ag-PG holograms are amplitude-phase ones: they exhibit absorption in the visible region, especially high in its short-wave part, which strongly affects the potential of usage and application of such holograms. The presence of amplitude modulation is evidenced by non-symmetric dependence of $I_0(\delta\theta)$ on conditions of hologram reconstruction, namely, $I_0(-\delta\theta) \neq I_0(+\delta\theta)$ at $\lambda = 0.63 \mu\text{m}$. The amplitude modulation decreases noticeably with growing wavelength of reconstructing radiation (see Fig. 4b) and at $\lambda = 1.5 \mu\text{m}$ the Ag-PG hologram can be considered a purely phase one, which is evidenced by experimentally measured $I_0(\delta\theta)$ and $I_d(\delta\theta)$: dependence $I_0(\delta\theta)$ is symmetric and typical for a phase hologram, $I_0(-\delta\theta) = I_0(+\delta\theta)$.

The relation between amplitude and phase components in such holograms is determined by spectral dependence of permittivity (ϵ) of developed silver particles, which is in the case of finely dispersed particles different from the corresponding dependences for bulk silver. This was the reason for performing theoretical estimates and calculations of spectral dependences of effective optical parameters of porous model medium, containing Raleigh silver particles, and parameters of constructed Ag-PG holograms (Sukhanov et al., 1996).

According to calculations based on using the concept of limitation of free path length of electron in a small particle (Kreibig, 1970, 1978, 1981), composite medium has the minimum width of attenuation band at the size 15-20 nm of its constituent silver particles that have no defects of crystalline structure. Free path length (l) of electron in a particle of such ideal medium is $l = 8 \text{ nm}$. The value of free path of electron in silver particles, composing a real medium with attenuation spectrum shown on Fig. 4 (curve 3), is found to be $l = 2 \text{ nm}$.

This free path value is not an estimate of the average particle size, as in addition to size there are other unmanageable factors: contamination, crystalline structure defects etc. But it is quantity l that determines the effective optical constants of a medium, which are used in further calculations to estimate the parameters of AgPG holograms. Comparison of effective optical parameters of “ideal” (with particles $l = 8 \text{ nm}$) and real (with particles $l = 2 \text{ nm}$) media with identical structure parameters, whose calculated values are given on Fig. 5a, shows the attenuation spectrum of real medium to be essentially wider than that of the “ideal” one, whereas the change of refractive index due to the presence of silver particles (Δn_{Ag}) is practically the same and is determined by their concentration, C_{Ag} , (the quoted calculations used the volume silver concentration in the medium equal to 10^{-4}).

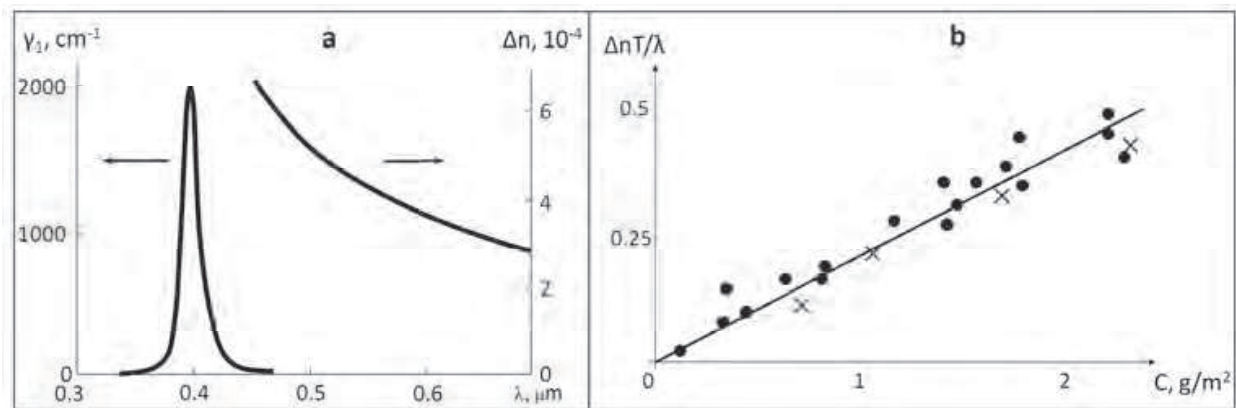


Fig. 5. a - theoretically found spectral dependences of optical constants of porous model medium, due to the presence of “ideal” silver particles ($l = 8 \text{ nm}$) and “real” particles ($l \approx 2 \text{ nm}$); γ and Δn are, respectively, absorption constant and refractive index. b - dependence of phase incursion ($\Delta nT/\lambda$), due to the presence of silver particles in the medium, on silver coverage, C , of the studied sample: experimental measurements with the use of developed holography film plates PFG-02 (dots); calculations by measured attenuation spectra with the use of dispersion Kramers-Kronig relations (crosses).

The dependence of diffraction efficiency of transmission amplitude-phase hologram gratings, formed by colloid silver particles, on silver concentration, given on Fig. 6, is of oscillatory nature because of presence of strong phase modulation and is dependent on the operating wavelength and optical properties of its constituent silver particles. The given data show the maximum values of DE of transmission AgPG holograms to be attained at a certain value of silver concentration: as the wavelength grows, so do both the maximum values of DE and the silver concentration needed to attain them. The DE values for holograms in a porous medium with ideal particles can be thought of as a theoretical limit for parameters of Ag-PG holograms.

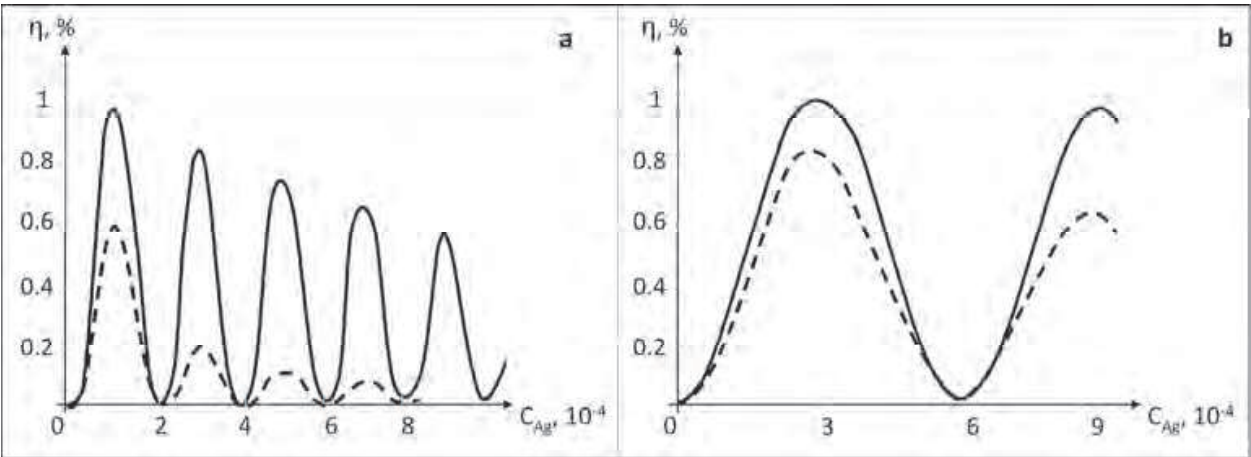


Fig. 6. Theoretically calculated dependences of DE of transmission Ag-PG holograms on developed silver concentration C_{Ag} for porous medium 1 mm thick with ideal ($l = 8 \text{ nm}$, solid curves) and real ($l \approx 2 \text{ nm}$, dashed curves) particles: $\lambda = 0.63 \text{ }\mu\text{m}$ (a) and $\lambda = 1.5 \text{ }\mu\text{m}$ (b).

The presence of direct proportionality of refractive index of developed RM, containing colloid silver particles, on developed silver concentration, is confirmed by measurements of

refractive index of developed high-resolution AgHal materials (film plates PFG-02) in the red region $\lambda \sim 650$ nm. Experimental measurements, their results given on Fig. 5b, were performed under different conditions of formation of developed particles and at different developed silver concentrations; the resulting dependence can be represented by the empirical formula:

$$\Delta n_{\text{Ag}} T / \lambda = 0.28 C \text{ (g/m}^2\text{)} \quad (2)$$

where Δn_{Ag} is the change of the medium refractive index due to the presence of silver particles; T is the medium thickness; C is the surface silver concentration (silver coverage in g/m^2), measured by rhodanine method. Eq. (2) enables estimation of developed silver concentration by measured values of phase incursions in the red region $\lambda \sim 650$ nm due to the presence of colloid silver particles, without refinement of their optical parameters.

Experimental measurements of a hologram at $\lambda = 1.5 \mu\text{m}$ are performed in the absence of the amplitude component and allow finding the phase modulation of a hologram at given wavelength, which allows estimating the spectral dependence of amplitude and phase modulation of the studied Ag-PG hologram, $\varphi_1(\lambda)$ and $\gamma_1(\lambda)$, by using known wavelength dependence of optical constants of real medium. Calculations of angular selectivity contours of amplitude-phase holograms at $0.63 \mu\text{m}$, carried out by experimentally found phase modulation at $\lambda = 1.5 \mu\text{m}$, have shown satisfactory agreement with the results of experimental measurements.

This situation enables using known value φ_1 (0.63 - $0.65 \mu\text{m}$) to estimate the concentration of silver, forming given hologram, with the help of empirical dependence Eq. (2). The performed calculation have shown the volume concentration of silver, forming the Ag-PG hologram, to be $C_1 = (1 \div 3) \cdot 10^{-4}$, which corresponds to surface concentration $1 \div 5 \text{ g/m}^2$, comparable to a similar value in developed holographic film plates PFG-02 and PFG-03. It should be noted that average hologram absorption γ_0 (hence average silver concentration in the sample, C_0) exceed the estimates found by values γ_1 and C_1 due to the presence of veil, formed by colloid silver particles, which take no part in hologram construction, yet lead to an increase of sample absorption in the spectral region of the absorption band of colloid particles.

4.4 Distinctive features of AgHal-porous glass medium-composite in hologram construction

The proposed version of light-sensitive porous medium-composite on the AgHal base significantly enhances the potential of using traditional AgHal media in holography, which is evidenced by its main features.

1. Porous glasses are close in physical and mechanical properties to silicate glass, have close thermal expansion coefficient, and are shrink-proof. Upon placing air-dry samples into liquid medium and using water solutions in post-exposure treatment, geometrical dimension of the framework remain unchanged, while local deformations of solid-phase shell inside a pore are substantially less than light wavelength, lack any regular pattern and cause no distortion of hologram structure. The experiments were carried out with samples in the shape of plane-parallel plates or disks 1-3 mm thick.
2. Size of light-sensitive particles and those forming a finished hologram cannot exceed the maximum size of porous framework ducts. When using matrices NPG-17, the size amounts to 20 nm.

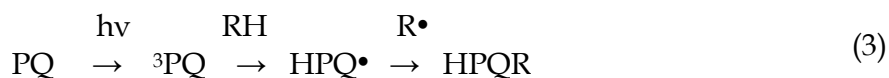
3. Light sensitivity of unsensitized samples across the spectrum is limited by intrinsic sensitivity of AgHal ($\lambda < 510$ nm) and amounts to 10^{-3} J/cm² when recording holograms at 488 nm with DE = 10 %. The possibility to perform optical sensitization of AgHal-PG was demonstrated and samples, sensitive in the red region, were obtained: holograms with DE = 50 % were constructed when recording by He-Ne laser radiation ($\lambda = 633$ nm) at exposure 10^{-2} J/cm².
4. Formation of low-efficiency holograms (DE < 1 %) during recording leaves the structure of recorded interference pattern undistorted, and substantial hologram enhancement is possible in the course of post-exposure treatment.
5. Post-exposure treatment is performed with the use of traditional photochemical water solutions owing to the presence of through capillary network. Formulation can be modified, conditions of running the processes can be optimized, and new stages can be introduced.
6. Impregnation of an immersion into free volume of pores to reduce light scattering by porous samples is possible both at stages of recording and operation of constructed holograms. When using holograms formed by colloid silver particles, impregnation into free pore volume of an immersion with refractive index close to that of the framework (water, acetone, alcohol, CCl₄) produces practically no change in their phase modulation (the change lies within the experimental error), as distinct from holograms, obtained with the use of bleaching or dichromated gelatin.
7. Concentration of developed silver in the samples is close on order of magnitude to the corresponding parameter in AgHal film plates ($1 \div 5$ g/m²). The distance between particles that form a finished hologram is several times their diameter.

5. Polymeric material Difphen

5.1 The principle of action

There are at present several modifications of polymeric light-sensitive media on the base of phenanthrenequinone (PQ), which implement the diffusion enhancement principle. The authors devised the technology to obtain a material, whose samples have certain holographic and physical-mechanical parameters, conditioned by modes of sample synthesis and hologram construction. The name Difphen (from words DIFfusion and PHENanthrenequinone) allows singling given material out of variety of other modifications of PQ-based polymeric medium with diffusion enhancement.

Samples of material Difphen (like some other materials of given group) represent a solid solution of organic dye PQ, uniformly distributed in polymethylmethacrylate (PMMA). Light sensitivity of the material results from capacity of PQ to bond to polymer under irradiation, transforming into 9,10-disubstituted derivative of phenanthrene (HPQR) according to schematic diagram (Chercasov et al., 1991):



where ${}^3\text{PQ}$ is the triplet-excited PQ molecule, $\text{HPQ}\cdot$ is the semiquinone radical, RH и $\text{R}\cdot$ are, respectively, the polymer molecule and radical.

Samples of recording medium $1 \div 5$ mm thick are obtained by means of bulk polymerization of PQ solutions in methylmethacrylate (MMA) between molding glass plates. Fig. 7a

(curve 1) shows PQ absorption spectrum, measured in a sample with concentration $8,5 \cdot 10^{-3} \text{M}$, with clearly defined long-wave maximum of absorption in the visible region ($\lambda = 405 \div 410 \text{ nm}$). Under the impact of radiation, PQ changes its chemical structure, while the formed photoproduct (semiquinone radical) bonds to a PMMA molecule and loses its mobility. Absorption spectrum of photoproduct differs from that of PQ: the long-wave maximum vanishes (Fig.7a, curve 2). The dissimilarity of absorption spectra of PQ and its photoproduct preconditions the difference in their refraction indices and determines the efficiency of recorded latent image hologram (without effect of post-exposure treatment) at given wavelength.

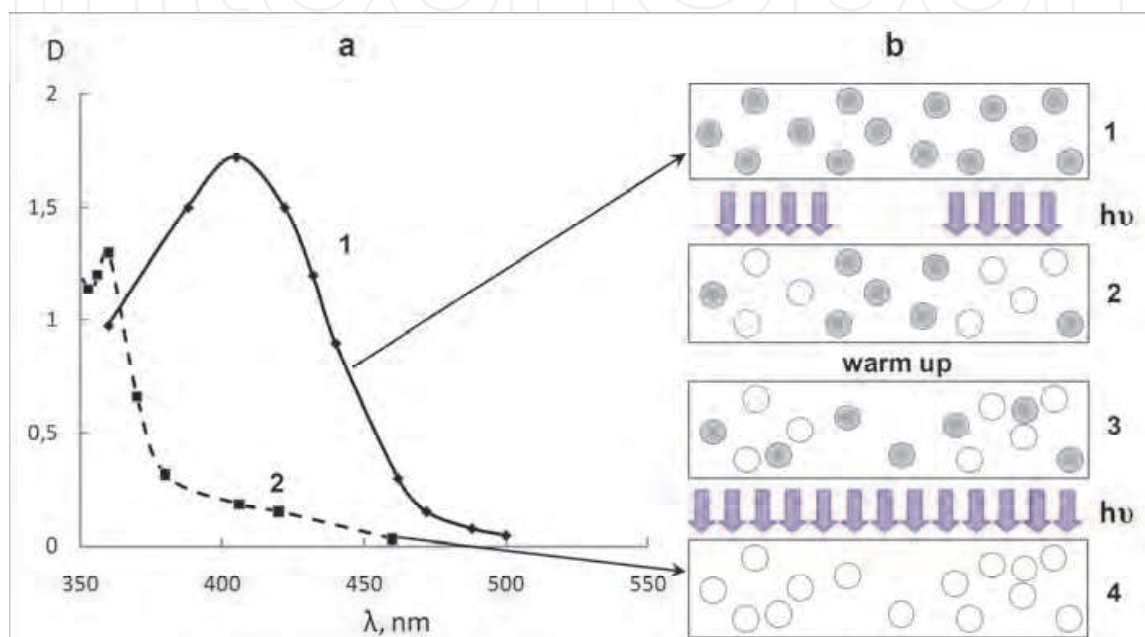


Fig. 7. a – absorption spectra of PQ (curve 1) and photoproduct (curve 2) in polymeric matrix. b – diagram to explain hologram construction process in polymeric medium with diffusion enhancement: distribution of molecules of PQ (○) and photoproduct (●) across the sample bulk in the initial state (1), after recording of hologram-grating (2), after warm-up (3), after fixation (4).

The process of post-exposure warm-up leads to redistribution of concentration of unexposed PQ molecules uniformly in the sample bulk, which ensures enhancement of recorded interference pattern, formed by photoproduct, that is, hologram “development”. The sample after fixation becomes non-light-sensitive, the unreacted PQ, distributed uniformly across the sample volume, transforms into non-light-sensitive photoproduct with the same distribution, therefore, the fixation process leaves n_1 unchanged. The presence of photoproduct molecules in the medium makes the maximum values of n_1 of constructed hologram dependent on recording radiation intensity, spatial frequency of interference pattern being recorded and initial PQ concentration.

Thus, hologram construction on given material includes the following basic stages:

- hologram recording by radiation with wavelength $400 < \lambda < 530 \text{ nm}$;
- warm-up of samples for 50 hrs at temperature 50°C ;
- hologram fixation by incoherent radiation with wavelength in the PQ absorption region $\lambda = 430\text{-}490 \text{ nm}$.

The work used samples obtained by means of casting polymerization in the shape of disks with diameter 20-40 mm and thickness 1-4 mm. Fixation of samples under study was affected by radiation of mercury lamp at 436 nm or that of “blue” LED with maximum of radiation band at 470 nm. Schematic diagram of information recording in such medium is shown on Fig. 7b by the example of constructing a hologram-grating.

5.2 Relation of holographic characteristics to conditions of sample synthesis

To obtain a medium with required holographic characteristics, it is necessary to know the effect of synthesis conditions on constructed hologram parameters and be in a position to purposefully change and control them.

The performed experiments have shown the quality of constructed holograms to be strongly affected by physical and mechanical properties of samples, which are determined by their hardness, and the most important holographic characteristic, determined by synthesis conditions for medium samples, to be the dependence of diffraction efficiency, of recorded holograms on post-exposure warm-up time. The data given on Fig. 8a, curve 1, show a typical dependence, which is specific for optimal synthesis conditions and can be approximated with two straight lines, as shown on the figure (dashed line).

The first dashed line describes the DE growth from the beginning of post-exposure warm-up (the DE value for latent image hologram) to attainment of the maximum values of DE, its slope being defined by PQ diffusion rate at given warm-up temperature (that is, degradation rate of the grating, formed by PQ unreacted with light). The second dashed line describes the hologram behavior after the maximum values of DE are attained and is, for the optimal synthesis samples, parallel to the abscissa axis. The intersection point of dashed approximation straight lines defines the characteristic sample warm-up time, t_{ch} , necessary to attain the maximum efficiency of recorded holograms.

With synthesis conditions, leading to “soft” sample structure, a latent image hologram has high DE values, quickly attains maximum efficiency at warm-up, is unstable and partially degrades at elevated temperature (Fig. 8a, curve 2). With synthesis conditions, leading to “hard” sample structure, PQ molecule diffusion proceeds too slowly, and high values of phase modulation are unattainable under a reasonable temperature-time regime of post-exposure treatment (curve 3). The clear-cut dependence of characteristic sample warm-up time on sample synthesis conditions allowed dividing all studied samples into three main groups: optimal synthesis samples, “soft” synthesis samples, and “hard” synthesis samples. Because of necessity to estimate the hardness of samples, a procedure was devised to allow relating physical and mechanical properties of samples to synthesis conditions and holographic process parameters.

Hardness was found by resistance to indentation of diamond pyramid into a material (Vickers test). The said procedure is notable for its relative simplicity, reproducibility and is supported with standard industrial instruments. Samples were tested with the help of PMT-3 hardness tester. Measured for each sample was the diagonal of the diamond pyramid indent in the material, its length depending on the sample hardness. It is the diagonal length, expressed in relative units (tied up with the use of a specific instrument), that is denoted as hardness index, K_h .

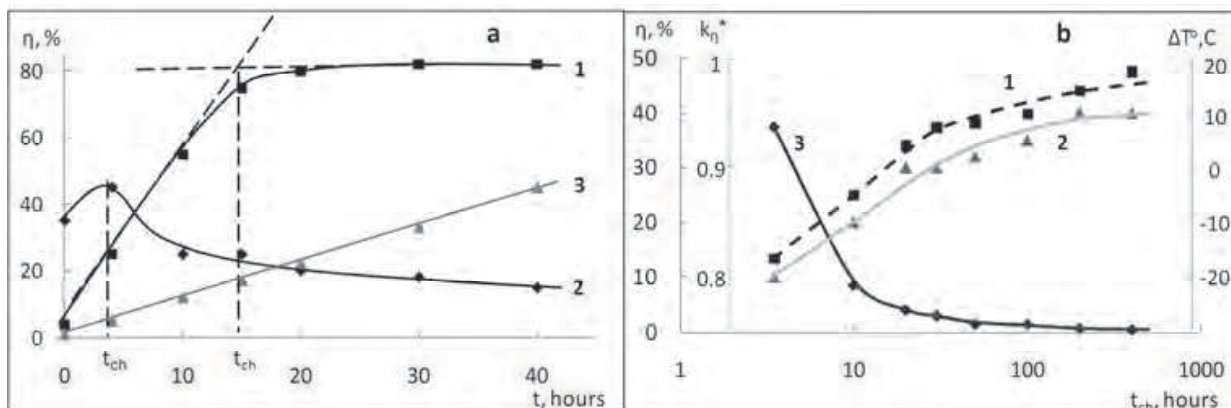


Fig. 8. a – dependence of diffraction efficiency η of holograms, recorded on samples of different synthesis, on post-exposure warm-up time (t_{ch} is characteristic warm-up time); curve 1 – optimal synthesis, curve 2 – soft synthesis, curve 3 – hard synthesis, spatial frequency of hologram 640 mm^{-1} . b – dependences of relative hardness index K_h^* of samples (curve 1), deviations of synthesis temperature from the given one ΔT (curve 2), latent image hologram DE (curve 3) on characteristic warm-up time t_{ch} of recorded holograms.

Measurements of K_h for samples with different warm-up conditions and shelf lives (up to 10 years) have shown that there is limiting value $(K_h)_{lim}$, which defines the maximum possible hardness of samples, manufactured by given process. This allowed estimating the degree of sample hardness with the help of relative hardness index $K_h^* = (K_h)_{lim}/K_h$ (curve 1 on Fig. 8b). Sample synthesis conditions were varied by changing some parameters: polymerization initiator concentration, PQ concentration, temperature-time regime of polymerization etc. Fig. 8b (curve 2) shows the dependence of impact of deviation of synthesis temperature from the optimal one ($\Delta T = T - T_{opt}$) on characteristic sample warm-up time to be in very good correlation with similar dependence $K_h^*(t_{ch})$.

Dependence $\eta(t_{ch})$ of latent image holograms (Fig. 8b, curve 3) supplements the notion of existence of a rather narrow range of parameters of sample synthesis, wherein one can obtain holograms with required characteristics: stable parameters in the course of operation, low efficiency of latent image holograms, and high efficiency after warm-up under given temperature-time regime. Samples, obtained under optimal synthesis conditions, are seen from the data of Fig. 8b to exhibit a certain degree of hardness, which allows carrying out preliminary sample quality control without staging a labor-consuming holographic experiment. (Diamond pyramid diagonal is no longer than tenths of a millimeter, which allows making hardness measurements without deterioration of the working sample.)

The fact of existence of limiting values of hardness for studied material samples along with measurements of sample hardness at each stage of hologram construction process have shown that post-exposure sample warm-up can be divided into two basic stages: warm-up-1 till specified hologram parameters are achieved (at temperature 50°C) and warm-up-2 till limiting values of sample hardness are achieved (additional warm-up at temperature $60\text{--}65^\circ\text{C}$, which is higher than at warm-up-1, but below the vitrifying point). Warm-up-2 can take place both before and after sample fixation under conditions that leave hologram parameters unchanged.

5.3 Main characteristics

5.3.1 Modulation transfer function

Resolving power of recording material under study is from traditional viewpoint determined by dimensions PQ molecules, whose diameter is less than 2 nm. Hologram-gratings on given material were obtained at maximum spatial frequency about 3000 mm^{-1} with efficiency over 80% (Sukhanov, 1994a), yet it can be said with certainty that the potential of the material in recording of interference structure of high spatial frequency is far from exhausted.

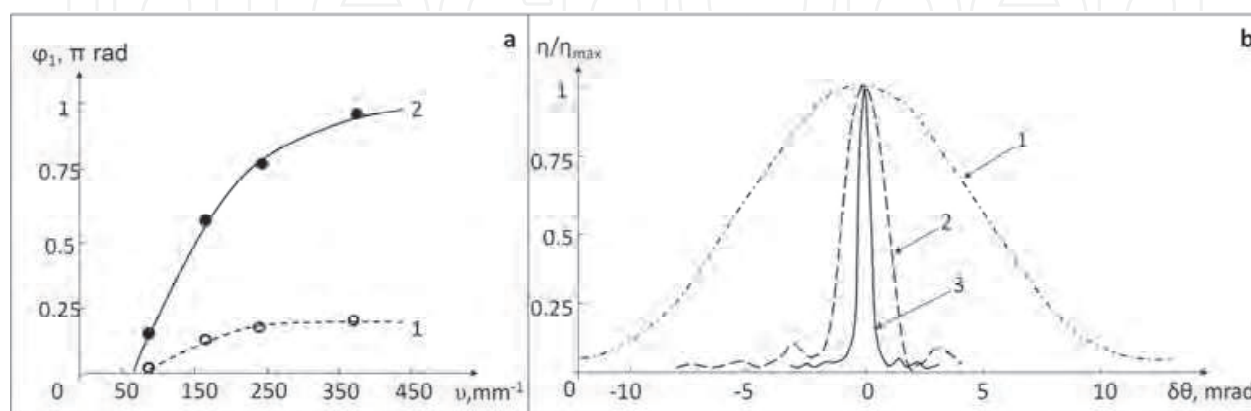


Fig. 9. a – dependence of phase modulation of transmission hologram-gratings ϕ_1 on spatial frequency of recorded interference pattern ν : 1 – latent image hologram (after exposure); 2 – hologram after complete cycle of post-exposure treatment. b – angular selectivity contours of transmission holograms with different spatial frequency, recorded with $\phi_1 < 0.5\pi$: 1 – $\nu = 70 \text{ mm}^{-1}$, 2 – $\nu = 320 \text{ mm}^{-1}$, 3 – $\nu = 1100 \text{ mm}^{-1}$.

Maximum attainable phase modulation amplitude of hologram-gratings, recorded in a medium with diffusion enhancement, depends on grating constant, post-exposure warm-up conditions and is defined by diffusion rate of PQ molecules, which leads to a decrease of phase modulation in the region of low spatial frequencies.

Measurement results for parameters of holograms, recorded in spatial frequency region $70 \div 350 \text{ mm}^{-1}$, are given on Fig.9a. Phase modulation of latent image holograms (curve 1) is less than 0.2π and practically independent of spatial frequency at $\nu > 200 \text{ mm}^{-1}$. For holograms with completed post-exposure treatment cycle (curve 2), phase modulation increases with growing spatial frequency. Thus, it can be concluded that material Difphen with sample thickness on order of 1 mm allows obtaining transmission hologram-gratings with DE over 70 % ($\phi_1 > 0.3\pi$) in spatial frequency region $\nu > 100 \text{ mm}^{-1}$. When dealing with higher spatial frequency region, the maximum attainable values of hologram phase modulation are strongly affected by factors, determined by the manner of treatment and conditions of hologram recording, such as stability of recording scheme, design features of hologram attachment and so on. Contours of angular selectivity of hologram-gratings with different spatial frequency are given on Fig. 9b and demonstrate agreement with theoretically calculated contours for hologram-gratings of given thickness.

5.3.2 Dynamic range

When using optimal-synthesis samples of material Difphen, the exposure range, wherein the linear mode of recording of latent image holograms can be ensured, is limited by values

$H < 1 \text{ J/cm}^2$, as seen from the data of Fig. 10a that shows exposure dependences of hologram parameters after completion of recording (curve 1) and after completion of post-exposure treatment cycle (curve 2). At $H > 1 \text{ J/cm}^2$, the recording process is of non-linear character, as high-efficiency latent image holograms are formed.

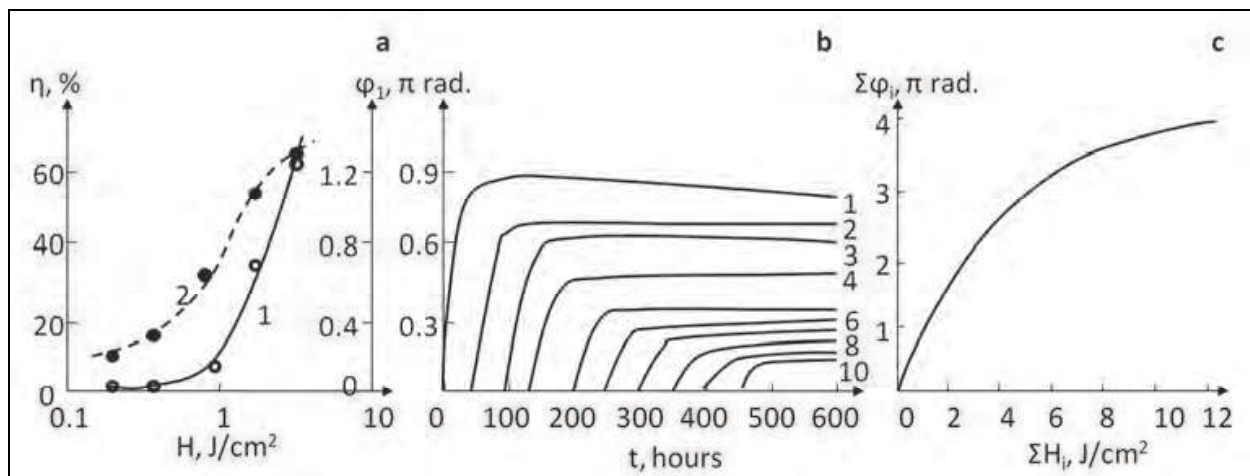


Fig. 10. a – exposure dependences of hologram parameters: diffraction efficiency η after completion of recording (curve 1) and phase modulation ϕ_1 after completion of post-exposure treatment (curve 2); spatial frequency 640 mm^{-1} . b – dependence of phase modulation amplitude ϕ_1 of superimposed holograms, recorded on the same sample section, on sample warm-up time; for each hologram $H_i = 0.8 \text{ J/cm}^2$ (holograms are numbered according to order of recording, $i = 1, 2, 3, \dots, 10$). c – dependence of total phase modulation of multiple hologram $\Sigma\phi_1$ on total exposure of recorded holograms ΣH_i .

The performed experiments on recording of a single hologram on samples 1 mm thick have shown attainability of high enough values of modulation amplitude of the medium, in excess of π radians. Limitations in the case are due to impossibility to obtain latent image holograms with low DE, rather than dynamic range.

Dynamic range of volume RM can be estimated and used in superimposed hologram recording. The potential was demonstrated by superimposed recording of more than 1000 low-efficiency holograms on the same sample section with the view of using it as archive memory (Steckman et al., 1998). Specifics of superimposed recording of high-efficiency holograms is linked with deterioration of holograms, constructed in a medium with non-uniform distribution of light-sensitive particles due to recording of previous holograms. The features of given material allowed overcoming the drawback by way of construction of superimposed holograms with individual post-exposure warm-up: recording 1 – warm-up; recording 2 – warm-up and so on. Fig. 10b shows dependence of phase modulation of superimposed holograms, constructed by angular multiplexing technique, on total time of sample warm-up. Each hologram, regardless of recording number, is recorded in a medium with uniform distribution of PQ in the sample bulk: PQ concentration falls with hologram number growing, which leads, as seen on Fig. 10b, to smaller attainable values of phase modulation of single hologram.

Of much interest in studying the volume RM is quantity $\Sigma\phi_1$, which is a sum of values of phase modulation of all superimposed holograms that constitute given multiple hologram, and describes the dynamic range of used light-sensitive medium. Fig. 10c shows

dependence of total phase modulation of superimposed holograms on their total exposure, obtained in experiment on construction of 10 superimposed holograms with individual warm-up. The dependence describes the dynamic range of used RM, being a kind of characteristic curve of light-sensitive material. Maximum values of total phase modulation, attained in the experiment, are as high as $\Sigma\phi_1 \cong 12$ rad, which was obtained on a sample 2.3 mm thick. With the use of polymeric media on the base of PMMA with PQ, other authors in work (Steckman et al., 1998) attained values $\Sigma\phi_1 \cong 4.8$ rad for a sample 3 mm thick, and in work (Lin et al, 2000) – $\Sigma\phi_1 \cong 14$ rad for a sample 8 mm thick. The cited works point out that $\Sigma\phi_1$ grows linearly with growing sample thickness. Comparison of experimental data in the cited works and those by the authors, testifies that using the individual post-exposure warm-up of superimposed holograms can increase dynamic range of the material and obtain higher values of $\Sigma\phi_1$ at given sample thickness.

5.3.3 Other characteristics

Modulation amplitude of refractive index in holograms. Experimental data on the magnitude of the amplitude of refractive index variation in a hologram and its dependence on wavelength of reconstruction radiation were obtained in study of hologram-gratings, recorded on optimal-synthesis samples of material Difphen with different thickness. Angular selectivity contour of hologram-grating under study was measured using lasers with different wavelengths; at each wavelength, phase modulation amplitude, ϕ_1 , was determined and modulation amplitude of the first harmonic of refractive index, n_1 , of a hologram was calculated by formulas of Kogelnik's theory. Fig. 11a shows calculation results for $n_1(\lambda)$ of studied samples. Dashed lines illustrate the process character and allow making some estimates. Modulation amplitude of refractive index of studied holograms in the visible region is within limits $n_1 < 10^{-3}$; dependence $n_1(\lambda)$ in the studied spectral range (473÷808 nm) displays normal behavior of dispersion, conditioned by absorption band of the material in the UV region.

The effect of ambient humidity variation on hologram performance. Polymeric RM on the PQ base are commonly considered to demonstrate negligible shrinkage, yet it is known that PMMA samples in atmosphere of increased humidity are capable of absorbing up to 1.5 % of water, which causes the sample thickness and average refractive index to change. Stability of hologram parameters at variations of ambient humidity was estimated by the change in the position of the maximum and in the shape of angular selectivity contour under conditions of different ambient humidity. Use was made of measurement design for angular selectivity contour of volume holograms with divergent radiation beam and data recording on CMOS-matrix. The collected data, processed according to devised procedure, are given on Fig. 11b.

In the study of holograms with width of angular selectivity contour 1.3 mrad, recorded on a sample ≈ 1 mm thick, the shift of contour maximum position at an abrupt change of ambient humidity from 85 % to 50 % at temperature 21 °C corresponds to a change of radiation diffraction angle by $0.1 \div 0.2$ mrad.

Stability of hologram parameters over a long period of time of storage (6÷9 years) and operation. During storage and observation time, the holograms stayed in a room with temperature (15-40) °C and were used for occasional experiments as optic circuitry elements, for students' laboratory works etc. Used as measured and controlled hologram parameters were DE and angular selectivity contour. The data show that over the time of storage and

operation of studied holograms there is no noticeable and systematic degradation of their parameters in a wide range of used exposures and spatial frequencies.

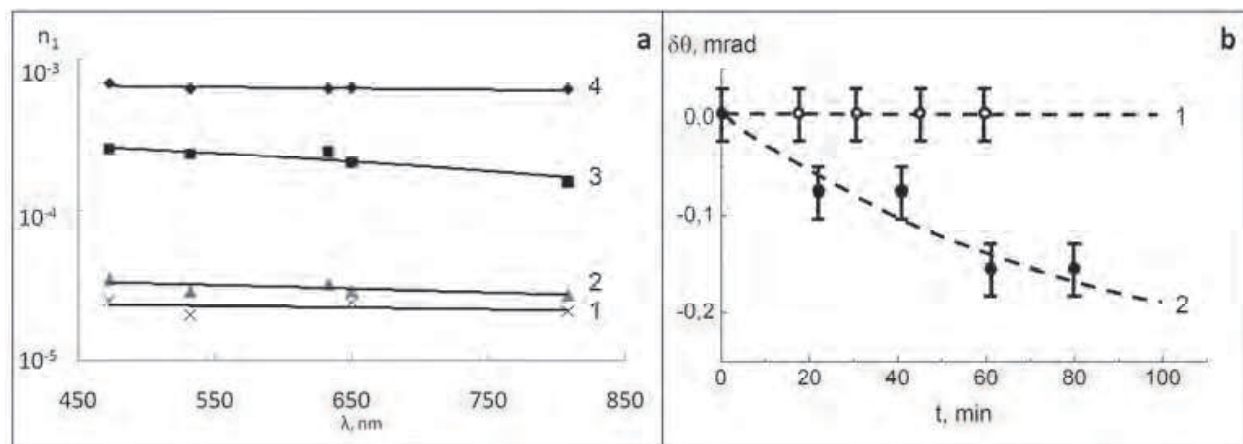


Fig. 11. a - wavelength dependence of modulation amplitude of the first harmonic of refractive index n_1 for holograms constructed on different samples of material Difphen: 1-3 – bulk-synthesis samples 2.3 mm, 2.0 mm, 1.3 mm thick, 4 – film sample 0.1 mm thick. b – position of the maximum of contour of studied hologram-grating under stable conditions (1) and at abrupt change in ambient humidity from 85 % to 50 % (2). Dashed lines illustrate the character of processes.

5.4 Film-type samples of material Difphen

Of great interest is to obtain samples of given material, which have thickness in the range $50\div 500\ \mu\text{m}$, since the available product line of RM for holography has such samples represented by isolated laboratory-made specimens (e.g., Mahilny et al, 2006). The devised technological mode is unsuitable to obtain samples about $100\ \mu\text{m}$ thick by means of bulk polymerization.

Film samples were obtained by the technique of pouring from solution, which is in some cases used to accomplish similar tasks under laboratory conditions. The basic components were PQ, PPMA and organic solvent. This resulted in homogeneous, uniformly colored films of size greater than $10\times 10\ \text{cm}$ and thickness from 80 to $350\ \mu\text{m}$, whose elasticity allowed samples of various shape to be cut out of them. Here, volume PQ concentration in film samples was several times that in bulk ones. Performed tests have shown that samples, manufactured by given process, retain light-sensitive properties after storing at room temperature for a year.

To carry out holographic tests of film samples, custom designed cartridges were used: hologram recording, post-exposure treatment and measurement of parameters proceeded in the stable-state mode of the film sample, fixed between glass plates to exclude local deformations. Measurement results for DE of hologram-gratings, recorded at $\lambda = 488\ \text{nm}$ at spatial frequency $360\ \text{mm}^{-1}$ with different exposures, have shown that values of DE on order of 50 % were achieved on test samples of film $180\ \mu\text{m}$ thick (measurements at $633\ \text{nm}$). In a number of cases, a decrease of hologram DE under fixation was observed, which never occurred in working with bulk samples.

Obtained film samples permitted to run hologram recording in the “latent image” mode (with low values of DE), enhance holograms in the course of post-exposure warm-up and fix

the constructed holograms. Comparative characteristics of bulk and film samples (with the same optical density at the recording wavelength), derived by using a unified procedure of holographic testing, are given in Table 1. Quantitative estimation of enhancement of hologram-gratings, Q , used the value of modulation amplitude of refractive index, n_1 , obtained after warm-up and after fixation relative to the value of n_1 of latent image hologram.

Sample type	Thickness, mm	Transmission ($\lambda = 488$ nm), %	DE ($\lambda = 633$ nm)	Enhancement, Q ($\lambda = 633$ nm)	
				After warm-up	After fixation
Bulk	1.45	~ 20	0.94	5.1	5.0
Film	0.18	~ 20	0.43	4.0	4.5

Table 1. Comparison of parameters of holograms, constructed on bulk and film samples of polymeric material with PQ (measurements at $\lambda = 633$ nm).

Investigation of stability characteristics of parameters of holograms, recorded on film-type samples with thickness on order of 100 μm , in the course of long-term storage and operation has shown that some studied holograms, recorded at exposures over 0.3 J/cm², exhibited a DE increase beyond the limits of predicted experimental errors (see Table 1). The effect of DE growth during storage of holograms, recorded on film samples, may be due to a host of causes, including, apparently, plastic nature of RM samples used.

Performed experiments have shown the fruitfulness of the devised approach to obtaining polymeric holographic film-type materials and the necessity to carry on the research and to improve parameters of film samples and procedure for their use with the view of creating an assortment of materials for hologram recording with wide spectrum of parameters.

5.5 Main special features of samples of volume polymer medium

Material Difphen belongs to the group of polymeric recording materials, implementing the diffusion enhancement principle, which is at present fruitfully used by various authors in a number of science and engineering projects. Material samples have certain holographic, and physical and mechanical parameters, determined by the devised modes of sample synthesis and of hologram construction. The following main special features can be noted.

1. Resolving power of material exceeds 3000 mm⁻¹ and is limited by PQ molecule size and photoproduct molecule mobility.
2. The modulation transfer function is untypical for traditional light-sensitive materials. In the low spatial frequency region (less than 50 mm⁻¹), hologram construction on given material is impossible; phase modulation amplitude of recorded holograms grows with increasing spatial frequency of a hologram. The use of such media can be very helpful in information recording that requires canceling the low-frequency component of spatial spectrum of radiation.
3. Feasibility of construction of latent image holograms and their subsequent enhancement under conditions of unchanged interference structure, formed at the recording stage, which ensures linearity of information recording in a wide dynamic range.
4. Wide dynamic range and feasibility of construction of high-efficiency superimposed holograms owing to the use of individual post-exposure warm-up.

5. Feasibility of producing samples of thickness from tens of microns to several millimeters.

6. Specifics of parameter measurements of high-selectivity volume holograms

6.1 Diffraction efficiency

Principal difficulties in measurement of parameters of high-selectivity volume holograms stem from the rigid requirements on the illuminating beam in its divergence (spatial frequency spectrum of radiation) and monochromaticity (radiation wavelength spectrum). To correctly find the maximum values of diffraction efficiency of a hologram under Bragg conditions, meeting the following conditions is necessary.

- Divergence of reading radiation beam ($\Delta\psi$) should be much narrower than angular selectivity of a hologram ($\Delta\theta$): $\Delta\psi < \Delta\theta$. The contour measured in the case is a convolution of the true angular selectivity contour of a hologram and the contour, defined by spatial frequency spectrum of the reading radiation beam (see Fig. 12a).
- Spectral distribution of reading radiation beam ($\Delta\lambda$) should be much narrower than spectral selectivity of a hologram ($\Delta\lambda$): $\Delta\lambda < \Delta\lambda$.
- At given experiment geometry and transmission hologram thickness (T) the region of overlap of zero and diffracted beams on the exit surface of the sample (A_{out}) with respect to that on the entry surface (A_{in}) should satisfy relationship: $A_{out}/A_{in} > 0.8$.

6.2 Angular selectivity contour

A very common measurement procedure for angular selectivity contour of volume holograms provides for angular scanning of parameters, i. e. rotation of a hologram relative to the reading beam when using collimated monochromatic laser radiation (Fig. 12b). Advantages of the technique are obvious:

- comparative simplicity of optical scheme for measurements; ease of data processing operation;
- possibility to carry out measurements in a strictly localized area of a hologram.

Drawbacks of the technique are less obvious, but render the measurements of high-selectivity holograms rather involved:

- rigid requirements on divergence and geometry of the reading radiation beam (see 6.1);
- long duration of measurements of a contour, which increases with growing accuracy of construction;
- complexity of forming a collimated radiation beam with divergence on order of fractions of a milliradian.

For a single measurement act to yield information, incorporating complete data of angular selectivity contour, use can be made of a divergent beam of monochromatic radiation (Fig. 12c) rather than collimated one. Hologram-reading radiation beam is to have spatial frequency spectrum ($\Delta\psi$) in an interval, greater than the width ($\Delta\theta$) of spatial spectrum of diffracted radiation. A radiation detector, placed into diffracted or zero beam, as Fig. 12c shows, records spatial distribution of beam intensity in given spatial domain. Used in practice to this end are CMOS-matrices (including matrices of digital cameras). Fig. 13 (bottom) shows distribution of intensity in diffracted (a) and in zero (b) radiation beams, recorded on camera matrix.

Advantages of the technique are:

- recording of selectivity contour takes place in a single measurement act;
- acquisition of information, using both diffracted and zero beams, and formation of optical scheme of an experiment to achieve necessary measurement accuracy;
- possibility to trace the dynamics of contour variation for the hologram under study both in rapid processes and in sufficiently slowly varying conditions.

Drawbacks of the technique are also obvious:

- labor intensity of data processing;
- necessity to stabilize and fine adjust the scheme elements for experiments.

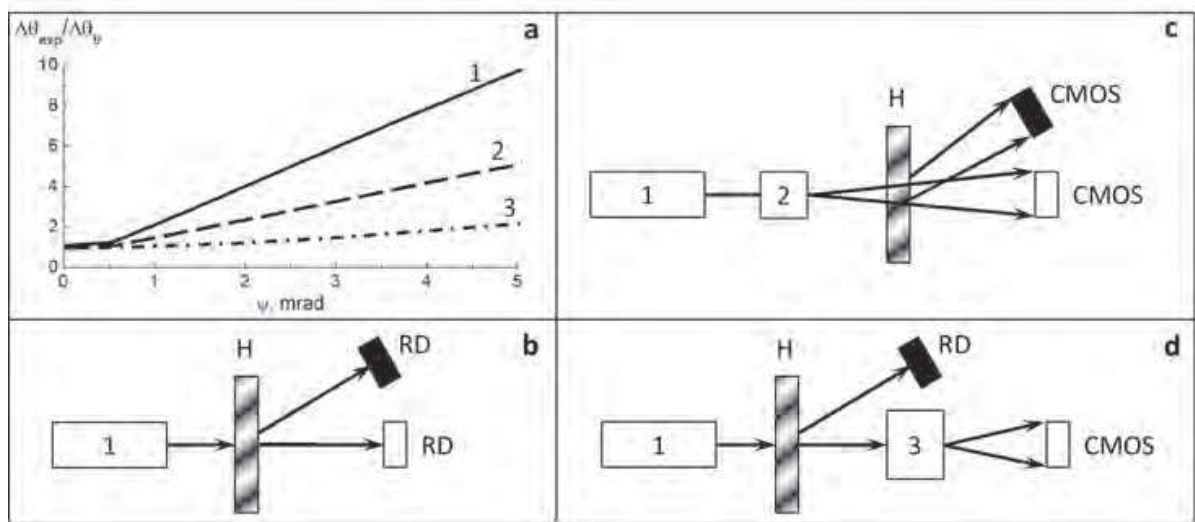


Fig. 12. a - effect of halfwidth of spatial spectrum of reading radiation ($\Delta\psi$) on ratio $\Delta\theta_{exp}/\Delta\theta_{tr}$ at different values of $\Delta\theta_{tr}$: 1 - $\Delta\theta_{tr} = 0.5$ mrad; 2 - $\Delta\theta_{tr} = 1$ mrad; 3 - $\Delta\theta_{tr} = 3$ mrad. $\Delta\theta_{exp}$ is the halfwidth of experimentally measured contour; $\Delta\theta_{tr}$ is the halfwidth of true contour of the hologram under study. b,c,d - schematic diagram of measurement of angular selectivity contour by collimated (b) and divergent (c) beams of monochromatic radiation; measurement of spectral selectivity contour by collimated radiation beam with a wide wavelength spectrum (d): 1 - radiation source, 2 - optical system for formation of divergent radiation beam; 3 - spectral instrument for expansion of wavelength spectrum in spatial frequencies; H - hologram; RD - radiation detector.

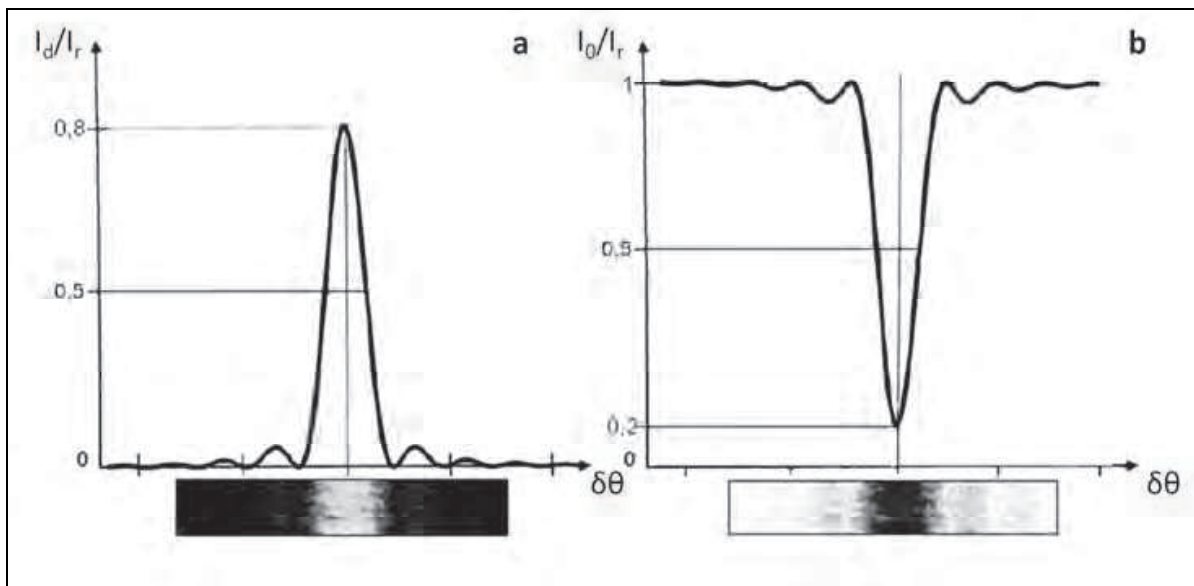


Fig. 13. Distribution of radiation intensity in diffracted (a) and zero (b) radiation beams, recorded on a camera matrix (bottom); processing result for experimental data (top).

6.3 Spectral selectivity contour

When measuring the spectral selectivity contour of a volume hologram according to schematic diagram, shown on Fig. 12b, the hologram is to be scanned with a collimated radiation beam of a wavelength, varying within the spectral range of the contour. At different times, this was carried out in different ways. In work (Denisyuk et al., 1970), the measurements involved a monochromator, with a collimated beam of radiation with a wide spectral range being formed in front of its entrance slit. In work (Sukhanov et al., 1984), the reading radiation wavelength was changed with the help of frequency-tuned dye laser with excimer pump: in this case, the laser radiation divergence was less than 0.5 mrad and the spectral width of scanning radiations was 0.01 nm. The halfwidth of spectral selectivity contour, measured in the present work for a reflection hologram, was $\Delta\lambda = 0.16$ nm (at DE = 80%). Such measurements, naturally, require special equipment and cannot be accomplished using standard techniques for measuring spectral characteristics of optical elements.

Applying the collimated laser radiation with wide spectral interval of wavelengths to measurement of the spectral selectivity contour of volume holograms was proposed by the authors and was implemented with the use radiation of femtosecond laser and semiconductor laser. The schematic diagram of measurements is given on Fig. 12d. A collimated beam of laser radiation with a wide spectrum illuminates hologram, which can be placed in positions “outside Bragg conditions” ($I_d = 0$) and “under Bragg conditions” (I_d is at the maximum for wavelength λ_{Br} within the reading radiation wavelength range).

A radiation beam, having passed a hologram with the direction unchanged (I_0), arrives at the entrance slit of spectral instrument (3 on Fig. 12d), the spatial pattern of wavelength spectrum expansion being recorded behind it on a CMOS-matrix as a spectrogram. With the hologram placed “outside Bragg conditions”, reading radiation spectrum is recorded (curves 1 on Fig. 14); with the hologram “under Bragg conditions”, spectrum of zero diffraction beam (curves 2 on Fig. 14) is recorded, in similarity to the distribution, given on Fig. 13c. Spectral selectivity contour of a hologram represents in this case a differential contour (curves 3 on Fig. 14), resulting from comparison of two spectrograms.

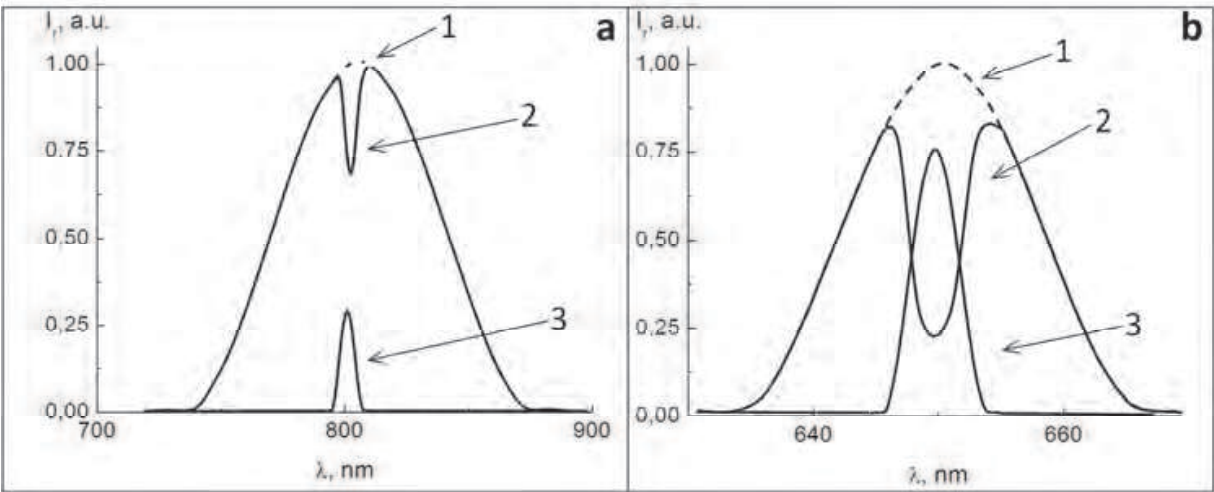


Fig. 14. Spectral distribution of intensity of laser radiation, passed the hologram outside Bragg conditions (curves 1) and under Bragg conditions of hologram reading (curves 2); spectral selectivity contour of a hologram (curves 3): a – femtosecond laser ($\lambda_{\text{max}} = 808 \text{ nm}$); b – semiconductor radiation source ($\lambda_{\text{max}} = 654 \text{ nm}$).

7. Conclusion

One of the cardinal problems of 3D holography is provision of research in the field with recording materials (Denisyuk, 1980). Volume recording media for holography are at present manufactured in laboratory conditions in the form of isolated specimens or small batches. Obtaining samples with stable and reproducible performance is, as the authors' experience shows, still possible even in such conditions.

The current studies reveal those properties of devised materials, which open up new application opportunities far beyond narrow professional use of recording media for holography. A number of special features of recording media, considered in the paper, can be quite in demand to accomplish unconventional tasks in various fields of science and engineering.

AgHal-PG-media exhibit a set of parameters, pertaining to commonly used traditional AgHal-media: possibility to achieve high sensitivity, the width of spectral sensitization, the variety of techniques of post-exposure treatment etc. The list of the most important parameters of silver-halide media is supplemented by AgHal-PG-media with new opportunities: obtaining samples with thickness of several millimeters; shrinkproof; limitation of the maximum particle size in the light-sensitive agent and post-treatment products.

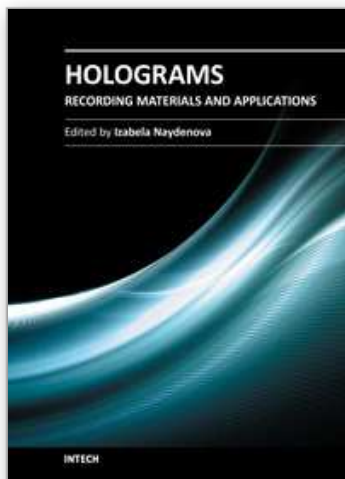
Polymeric medium with diffusion enhancement has a modulation transfer function, which is untypical for traditional light-sensitive materials and allows excluding the region of low spatial frequencies during the information recording. A no less important and rather unique property is the possibility to obtain the structure of high-efficiency hologram as a latent image at the recording stage and thus achieve a distortionless recorded interference structure in a wide dynamic range after post-treatment. It should be also noted that enhancement and fixation of holograms recorded on such a medium require no treatment in water solutions.

Advancement of volume holography and provision of this line of research with experimental base for comprehensive studies makes it necessary to investigate the processes taking place in the bulk of recording media during hologram construction, which, in its turn, calls for improvement of research techniques and methods to control the parameters of target processes.

Volume recording media and methodology of their investigation, presented in the paper, contribute in the authors' unpresuming opinion to the solution of the problems in question.

8. References

- Ashley, J. et al. (2000). Holographic data storage, *IBM J. Res. Dev.* Vol. 44(3), pp. 341-368
- Cherkasov, A.S. et al. (1991). *Opt. Spectrosc.*, Vol. 71(2), pp. 344-350
- Denisyuk, Yu.N. (1962). *Doklady AN SSSR*, Vol. 144(6), pp. 522
- Denisyuk, Yu.N. & Protas, I.R. (1963). *Opt. and Spectrosc.*, Vol.14, pp.721, USSR
- Denisyuk, Yu.N. et al. (1970). *Opt. Mech. Prom.*, Vol. 2, pp. 29-31
- Denisyuk, Yu.N. (1980). Holography and its prospects, *J. Appl. Spectrosc.*, Vol. 33, pp. 397-414
- Kogelnik, H. (1969). *The Bell System Technical Journal*, Vol. 48, No. 9, pp. 2909-2947.
- Kreibig, U. (1970). *Z.Phys. B, Condens. Matter*, Vol. 234, pp. 307-318
- Kreibig, U. (1978). *Z.Phys. B, Condens. Matter*, Vol. 31(1), pp. 39-47
- Kreibig, U. et al. (1981). *Surf. Sci.*, Vol. 106, pp. 308-312
- Lashkov, G.I. & Sukhanov, V.I. (1978). *Opt. Spectrosc.*, Vol. 44, pp. 590-594
- Lin, S.N. et al. (2000). *Opt. Lett.*, Vol. 25(7), pp. 451-453
- Lin, S. H. et al. (2006). Doped photopolymers for volume holographic applications, *Proceedings of SPIE*, Vol. 6314
- Liu, D. Yu. et al. (2010). Diffusional enhancement of volume gratings as an optimized strategy for holographic memory in PQ-PMMA photopolymer, *Optics Express*, Vol. 18, Issue 7, pp. 6447-6454. doi:10.1364/OE.18.006447
- Ludman, J.E. et al. (1997). Very thick holographic nonspatial filtering of laser beams, *Opt. Engng.*, Vol. 36(6), pp. 1700-1705
- Luo, Yu. et al. (2008). Optimization of multiplexed holographic gratings in PQ-PMMA for spectral-spatial imaging filters, *Optics Letters*, Vol. 33(6), pp. 566-568. doi:10.1364/OL.33.000566
- Mahilny, U.V. et al. (2006). *Applied Physics B: Lasers and Optics*, Vol. 82(2), pp. 299 - 302
- Popov, A., et al. (2000). Spectrally selective holographic optical elements based on a thick polymer medium with diffusional amplification, *J. Opt. A: Pure Appl. Opt.*, Vol. 2(5), pp. 494-499
- Shelby, R.M. (2002). Materials for holographic digital data storage, *Proceedings of SPIE*, Vol. 4659, pp. 344-360
- Steckman, G.J. et al. (1998). Characterization of phenanthrenequinone-doped poly(methyl methacrylate) for holographic memory, *Opt. Lett.*, Vol. 23(16), pp. 1310-1312
- Sukhanov, V.I. et al. (1984). Three dimensional hologram on reoxan as narrow band spectral selector, *Sov. Tech. Phys. Lett.*, Vol. 10, pp. 387-389
- Sukhanov, V.I. (1986). *Physics-Uspekhi (Advances in Physical Sciences)*, Vol. 148(3), pp. 541-543.
- Sukhanov, V.I. et al. (1988). *Opt. and Spectrosc.*, Vol. 65(2), pp. 282-284, (USA)
- Sukhanov, V.I. (1991). *Proceedings of SPIE*, Vol. 1238, pp. 226-230
- Sukhanov, V.I. (1994a). Porous-Glass as a Storage Medium, *Opt. Appl.*, Vol. 24(1-2), pp. 13-26
- Sukhanov, V.I. (1994b). 3-Dimensional Deep Holograms and Materials for Recording Them, *J. Opt. Technol.*, Vol. 61(1), pp. 49-56
- Sukhanov, V.I. et al. (1996). *Opt. and Spectrosc.*, Vol. 81(5), pp. 779-783, (USA)
- Veniaminov, A.V., et al. (1986). *Optics and Spectroscopy*, Vol. 60(1), pp. 142-147
- Veniaminov, A.V. et al. (1991). *Opt. Spectrosc.* Vol. 70, pp. 505-508
- Veniaminov, A.V. et al. (1996). *Opt. Spectrosc.* Vol. 81, pp. 617-621
- Yu, D., et al. (2010). Holographic storage stability in PQ-PMMA bulk photopolymer, *Optics Communications*, 283, pp. 4219-4223



Holograms - Recording Materials and Applications

Edited by Dr Izabela Naydenova

ISBN 978-953-307-981-3

Hard cover, 382 pages

Publisher InTech

Published online 09, November, 2011

Published in print edition November, 2011

Holograms - Recording Materials and Applications covers recent advances in the development of a broad range of holographic recording materials including ionic liquids in photopolymerisable materials, azo-dye containing materials, porous glass and polymer composites, amorphous chalcogenide films, Norland optical adhesive as holographic recording material and organic photochromic materials. In depth analysis of collinear holographic data storage and polychromatic reconstruction for volume holographic memory are included. Novel holographic devices, as well as application of holograms in security and signal processing are covered. Each chapter provides a comprehensive introduction to a specific topic, with a survey of developments to date.

How to reference

In order to correctly reference this scholarly work, feel free to copy and paste the following:

O.V. Andreeva and O.V. Bandyuk (2011). Light-Sensitive Media-Composites for Recording Volume Holograms Based on Porous Glass and Polymer, Holograms - Recording Materials and Applications, Dr Izabela Naydenova (Ed.), ISBN: 978-953-307-981-3, InTech, Available from:
<http://www.intechopen.com/books/holograms-recording-materials-and-applications/light-sensitive-media-composites-for-recording-volume-holograms-based-on-porous-glass-and-polymer>

INTECH
open science | open minds

InTech Europe

University Campus STeP Ri
Slavka Krautzeka 83/A
51000 Rijeka, Croatia
Phone: +385 (51) 770 447
Fax: +385 (51) 686 166
www.intechopen.com

InTech China

Unit 405, Office Block, Hotel Equatorial Shanghai
No.65, Yan An Road (West), Shanghai, 200040, China
中国上海市延安西路65号上海国际贵都大饭店办公楼405单元
Phone: +86-21-62489820
Fax: +86-21-62489821

© 2011 The Author(s). Licensee IntechOpen. This is an open access article distributed under the terms of the [Creative Commons Attribution 3.0 License](https://creativecommons.org/licenses/by/3.0/), which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

IntechOpen

IntechOpen