Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

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Version of record first published: 24 Sep 2006

To cite this article: Valeriu Bivol & Stefan Robu (2000): New Compositions from Photosensitive Copolymers for Information Processing and Storage, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 353:1, 373-385

To link to this article: http://dx.doi.org/10.1080/10587250008025675

Mol. Cryst. and Liq. Cryst., 2000, Vol. 353, pp. 373-385
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New Compositions from Photosensitive Copolymers for Information Processing and Storage

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In this work we present a number of new compositions from photosensitive copolymers for information processing and storage. A number of donor-acceptor systems from carbazolyl containing polymers, in particular from carbazolyletilmethacrylates (CEM) and oktylmethacrylates (OMA) copolymers sensitized by threenytrofluorenone (TNF) derivates and additives of photochromatic substances from indolynospirobenzpyran row are investigated. The introduction in photoplastical layers 6–10 % of the photochromatical additives is increased by photosensitivity of donor-acceptor systems in 5–6 times. The greatest sensitization effect has 8'-nitro-1,3,3-three methylindolynospirobenzpyran.

The appreciable sensitization effect is reached at drawing of photoplastical layers on an injection films from chalcogenide glass semiconductors. Developed on the basis of photopolymer CEM:OM donor-acceptor systems have photosensitivity 10^{-6} J/sm^2 at 80–85° C that on 2–3 order is higher than usual systems without injection. From received compositions of photopolymers were obtains photothermoplastical carriers for registration optical information. A detailed experimental study of the kinetics of photodarking and photobleaching in photochromatic polymer films is presented in this work. As a photochromatic polymer films we have obtained photochrom 1,3,3-three methyl-6(8)-nytroindolynospirobenzpyran in butilmethachrylat-styrol copolymer, which were taken in different percentage correlation. On the base of this results were elaborated the information media for holographic image registration with resolution up to 5000 mm^{-1}.

In this work we present also the results concerning the possibilities of strengthening of polymer media with the scope to improve mechanical properties of the relief image (hardness, strength, adhesive stability) and the possibilities to make copies by hot stamping method. Layers were prepared from copolymers, which contain chemically active liaisons of 4-aminostyrol or hlycedylmethacrylat. The thermoplastic layers with relief images can be cross-linked under the action of UV-light or under the action of chemical agents. As a result the polymer layers with the relief image become mechanical hard, strength, adhesive stable, without solubility in organic solvents and with stability to high temperature. The second polymer matrix on the 4-aminostyrol and hlycedylmethacrylat thermoplastic layers can be used for the multiplication of the copies on the special thermoplastic material.

Carbazolylalcylmethacrylats with oktylmethacrylats copolymers have appeared rather suitable for create of new media for use in quality of photoresist. By us were received, tested and investigated as a photoresists media photopolymer layers from carbazolylalcylmethacrylats with oktylmethacrylats copolymers. On the created photoresists layers from copolymers CEM:OMA the diffraction holographic gratings diffraction efficiency 25 % and resolution capability 1500 mm-^{1} were obtained.

Keywords: compositions; copolymers; additives; photoresist; registration; storage

INTRODUCTION

Recently in the literature the more and more strengthened attention render to organic photothermoplastic carriers of the information being in most cases by donor-acceptor systems [1]. The donor as a rule serves carbazolyl or other polymer containing π-electronic systems – carbazolyl nucleus and in quality of acceptor use various low molecule connections containing an electron-acceptor groups forming with carbazolyl nucleuses a complex with carry of charge.

It results in occurrence in carbazolyl layers a new band of absorption and internal photoeffect in seen and near IR-areas of a spectrum, as provides registration of the holograms. With the purpose of search higher sensitive systems by us were investigated opportunity of additional sensitization of PP layers by additives and injection underlayers.

It is known [2] that the photochromatic layers based on polymer materials which contains additions from different organic photochromatic substances have been used in holographic image registration. The aim the present work was to synthesis and investigate photochromatic materials based on nytroindolyno-spirobenzpyran and antratsenoxazin dye-stuff common formula polymers.

During the last years the methods of optical registration of information are used in high technology equipment. These methods include also holographic registration on the layers of chalcogenide vitreous semiconductors (CVS) thin films [3] and sensitive photothermoplastic media (PTM) [4]. The method for metallic matrix preparation is very complex and the technological problems based on the reaction between the CVS and electrolyte cause many difficulties. With the view to facilitate the multiplication of hologram copies, which were initially recorded on CVS or others substrates, the images were transferred by the method of hot stamping on the thermoplastic layers, prepared form copolymers or other compositions, which contain chemically active liaisons of 4-aminostyrol I or hlicedylmethacrylat II.

Carbazolylalcylmethacrylats (CM) with oktylmethacrylats (OMA) copolymers have appeared rather suitable for create of new media for use in quality of

photoresist. As is known [5] carbazolyls polymers from vynilcarbazolyl with oktylmethacrylats, and also N-polyepoxypropylcarbazolyl, in addition containing electron-acceptor additives of a iodophorm type and others under action of a ultra-violet irradiation are exposed to a photochemical transformations, that conducts at the end to deep structurisation of a photopolymer layers. Structurisation of layers is accompanied by change of coloration of the irradiated sites, their solubility in the organic solvents, increasing of mechanical durability and adhesives properties of a material. Is established, that spatial cross-linked is carried out by means of a free radical-kations arising as a result of occurrence carbazolyl nucleuses with molecules of iodophorm [6].

With the purpose of expansion of a class of used materials in the given area of photolithography, and also for exception of lacks of the above mentioned polymers, by us were received, tested and investigated as a photoresists media photopolymer layers from carbazolylalcylmethacrylats with oktylmethacrylats copolymers.

Experimental Results and Discussion

For realization of researches on creation of new donor-acceptor systems by us were used copolymers CEM:OMA of composition 60:40 мol% and known under the literature N-polyepoxipropylcarbazolyl for comparison. For sensitization of photoplastical layers were used a number of sensitizers from a line of polynytrofluorenone in particular 2,4,7-threenytrofluorenone (TNF), N-fenilamino-2,4,7-threenytrofluorenone (FTF) and ditsianomethylen -2,4,7-threenytrofluorenon (DTF) containing donor-acceptors group.

For creation of donor-acceptor photoplastical systems a solution of photopolymers in 10 % toluol concentration with the 5-20 % additives of sensitizer and 0-12 % of photochromium from weight of photopolymer previously prepares. After complete dissolution of all components the solution carefully is filtered and is used for drawing PP layers. Drawing of PP layers was carried out on flexible polyethylentereftalat film on special watering installation, previously metallized by Al, Cr or SnO_2 thin layers, having a transparency 90-95%. After drying of PP layers in air and in the drying chamber at 40 degrees within 3-5 hours samples become suitable for realization of researches. During technology of obtaining of PP layers it is necessary to maintain the thickness of the order 2,5 microns.

Measurement of electrophotographic sensitivity (EFS) is carried out by potential relaxation at illumination by coherent light with the 100 Lx on the frame. Research of electrophotosensitivity by potential relaxation from sensitizers concentration in photopolymer (Fig.1) and from temperature (Fig.2) has shown, that the greatest photosensitivity have PP layers sensitized by 12-14 % of TNF or DTF. As the contents in photopolymer the 14-15 % of sensitizer follows from figure results in decrease of photosensitivity because of strong growth of dark conductivity of PP layers. At the large sensitizers contents PP layers lose an optical transparency because of cristallization of sensitizer in a polymeric layer.

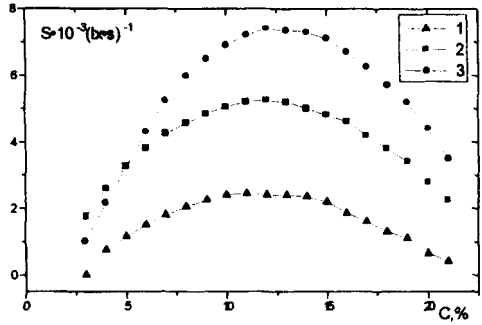

FIGURE 1 Dependence of electrophotosensitivity of CEM:OMA photopolymeric layers from concentration:
1 – FTF; 2 - TNF; 3 - DTF

For all donor-acceptor systems the dependence of photosensitivity from temperature was studied. With growth of temperature the sensitivity of all PP layers gradually decreases. The strong recession of photosensitivity occurs in the field of transition of photopolymer from high elastic condition in fluid-viscous. So, from a Fig.2 is appreciable, that the sharp recession of photosensitivity for PEPC layers occurs at T~55-60° C, and for CEM:OMA copolymers at temperature higher than 75° C.

With the purpose of increase of photosensitivity of PP layers they in addition were sensitized by 4-12 % of photochromium (PC) additives from indoleniny's

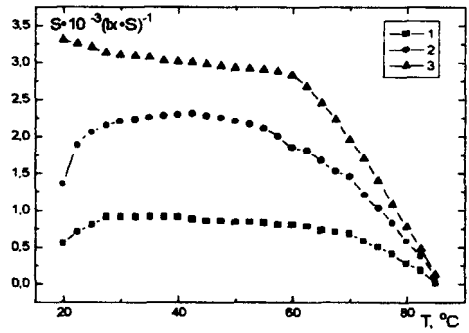

FIGURE 2 Dependence of electrophotosensitivity of photopolymeric layers containing 12 % of sensitizers from temperature:
1 - FTF; 2 - TNF; 3 - DTF.

class. For sensitization by us were used 1,3,3-threemethylindolynospiroantratsenopyran (PC-1), 6' and 8'-nytro-1,3,3-threemethylindolynospirobenzpyran (PC-2 and PC-3) and others. The thickness of PP layers was 2,5 microns.

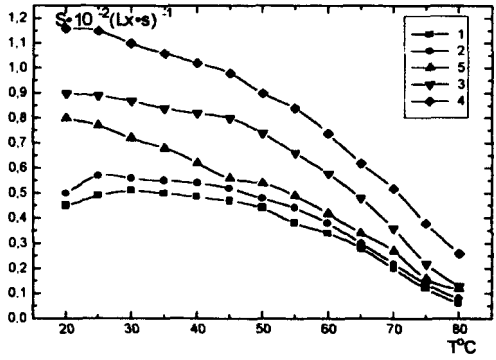

FIGURE 3 Dependence of electrophotosensitivity of PEPC photopolymeric layers with the various PC-3 contents:
1 - 0 %, 2 - 3 %, 3 - 6 %, 4 - 8-10 %, 5 - 12%.

The research of electrophotosensitivity dependence from temperature for

PP layers with the various contents of the photochomium additives has shown, that optimal concentration makes 6-10 % of weight of photopolymer (Fig.3). As follows from figure additional sensitization of PP layers, in particular from PC-3, raises sensitivity in 2-3 times. The greatest growth of sensitivity is observed in interval from room temperature up to temperature of a softening of photopolymer.

The registration on samples from a photopolymers has confirmed improving photographic sensitivity. Is placed, that the photographic sensitivity of the containing photochromium sensitizer carrier almost on the order is higher than sensitivity of the usual medium and makes 10^{-5} J/sm^2 with photographic contrast 0,6 - 0,8 units. The resolving power of a photoplastic layers CFM:OMA is higher than 800 mm^{-1}.

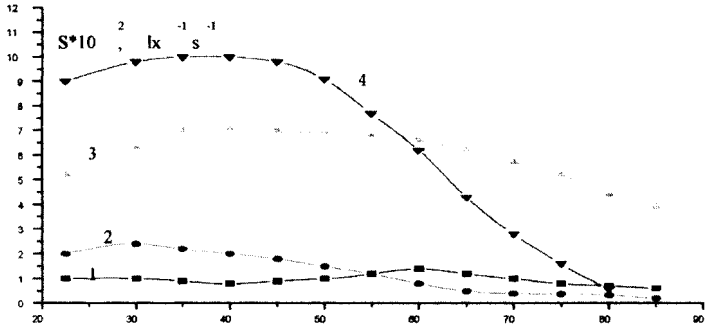

FIGURE 4 The temperature dependence of photosensitivity of photopolymers films without injection layer (1,2) and with injection layer (3,4).

To increase the photosensitivity the polymer layers were additional sensitized by use of injecting sublayers made from CVS. Evaluation of the electrophotosensitivity photopolymers layers with injector was carried out by the method of potential relaxation, by registration the time of decrease down to one half of the surface potential on the illuminated polymer layer.

Experimental investigations the photosensitivity (Fig.4) shown that the photopolymer layers with an injector substrates (3,4) in the interval of 20-100°C is 5-10 times higher than the photosensitivity of the films without an injector (1,2). We suppose that the enhancement of the photosensitivity in the polymer with injection layers is due to the injection of the charge carriers from the chalcogenide layer. These layers are characterized by the obvious growth of polyepoxipropylencarbazoly with a rich content of carbazolyl nucleus.

The photothermoplastic film structures can be used for recording of images, including holographic angles with the space frequency of 1000 mm^{-1} and with the diffraction efficiency of 8-10%. Its sensitivity for $\lambda = 0.5$ μm is more than 10-15 times than the value for the structures without injection layer.

The spectral and kinetic characteristics of photodarking (coloring) and photobleaching (relaxation) of photochromatic layers have been studied in details for elaboration of information media for holographic image registration with a resolution ~ 5000 mm^{-1}. The measurements were carried out with spectra-photometers SPECORD UV-VIS, SPECORD 61IR. It was determined that development time of photodarking process for polymer layers constitute about 20-25 s, and the relaxation time varies from several seconds to several hours and even more. These facts allow to use these films for information registration. The stability of photochromatic layers to UV-light in cycles "photodarking-photobleaching" was determined and the possibility to stabilized the photocromatic layers by aromatic oxiceeton additions and other stabilizers was studied. For preparing the photochromatic layers we have preliminary prepared the solutions-composition from copolymer styrol with butilmethacrulat (50:50 mol.%) and photochromatic substances in toluol. The content of additions constitute 6-8% from the quantity of copolymer.

The spectral characteristics in the visible and IR range of spectrum of polymeric photochromatic layers were study. The polymers are transparent in the visible range, but after ultra-violet illumination they become colored and exhibits a deep maximum of absorption in the range 550-600 nm (Fig.5, curve

1-3), which does not depend significantly on the position of NO_2-group in the structure of photochromatic substance. The most pronounced effect was observed for photochromatic layers of 1,3,3-threemethyl-6-indolinospirobenzopiran, that accumulate intensively the cherry color and the maximum absorption attains 100% (Fig.5).

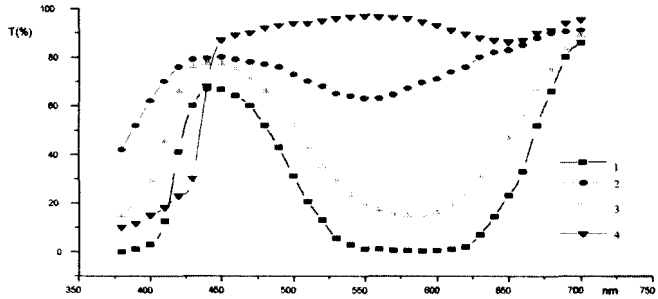

FIGURE 5 The spectral characteristic of photochromatic layers: 1 - 1,3,3-three methyl-6-nitroindolinospirobenzopiran I; 2 - 1,3,3-three methyl-8-indolinospiro-benzopiran II; 3 - Mixture I and II (1:1); 4 - 1,3,3-three methylindolinospiroantroxazin IY.

The study of spectral characteristics of photochromatic layers based on antratsen-oxazin dye-stuffs (curve 4) showed, that the maximum of absorption depends on the chemical structure of photochromatic layers. From the spectral characteristics we have evaluated the photodarking and photobleaching time. All layers have a time of colouring in the range of 20-30 s, but the relaxation time is different. For example, the oxazin layer (IY) has the relaxation time of several seconds, and benzopiran dye-stuffs has the relaxation time 24 hours.

The photodarking time and especially the relaxation time depend on the presence in the composition of the polymer layer of plastificator addition (5-10%). Fig.6 show the change of the optical transparency T_n/T_o in dependence on the relaxation time at room temperature. It can be seen that the layers which contain 5-6% of plastificator have the relaxation time much more long .

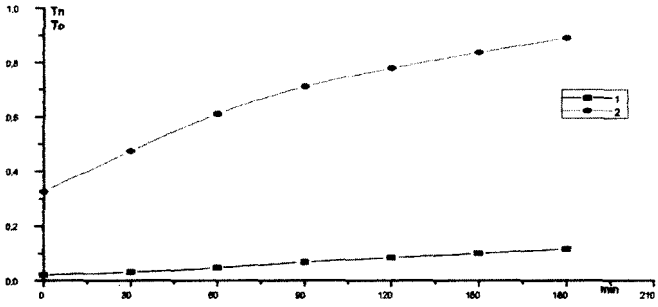

FIGURE 6 The dependence of transparency at 590 nm for the photochromatic layer without plastificator diontilftalat (1) and with 5 mas% of plastificator (2)

Investigation of photostability of photochromatic layers was carried out with an experimental set up similar to the spectrophotometer. The photochromatic characteristics and the photostability of photochromatic layers were evaluated from these measurements. As a criterion for the stability evaluation we considered the change of maximum current of the photodiode I_{fmax} which corresponds to relaxation level of coloring and I_{fmin}, which respectively corresponds to the level of darkness of layers (Fig.7).

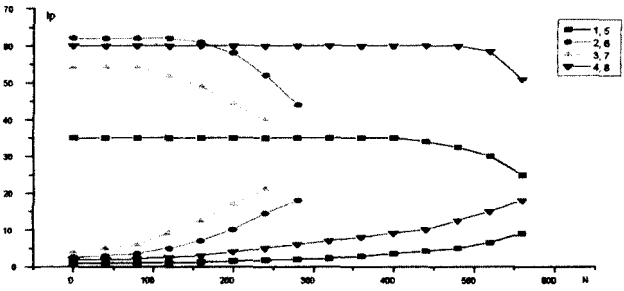

FIGURE 7 Changes in the photodarkening (1-4) and relaxation (1'-4') in dependence of the numbers of cucles (N) of UV-irradiation: 1,1' - photochrom IY; 2,2' - photochrom I; 3,3' - photochrom II; 4,4' - the stabilized photochrom I.

The investigation of the polymer layers photostability shows, that the maximum

stability in ultraviolet light have the layers made from photochrom IY (curve 1-1'), which attain ~500 total cycles of photodarking-relaxation. The indolynospirobenzopyrans' photochrom (curve 2-2' and 3-3') has a less photostability (~150 cycles), but it was possible to increase this stability by 2.5 - 3 times with different stabilizars (curve 4-4'). The effect of the photostabilizators concentration on the photochromatic characteristics of layers was studied. It was established that the optimal concentration for the photostability of photochromatic layers was about 2.0-2.5 %.

The stamping was carried out at the softening temperature of the thermoplastic layer 83 - 85°C for thermoplastic I and 65 - 67°C for thermoplastic II. The thermoplastic layers with relief images can be cross-linked under the action of ultraviolet light or under the action of chemical agents. As a result the polymer

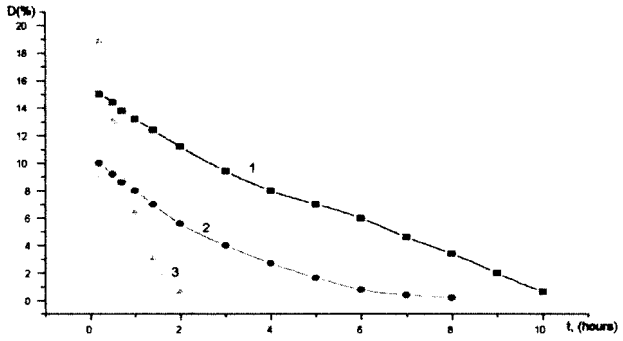

FIGURE 8 The dependence of absorption of the epoxygroup at 913 cm $^{-1}$ versus treatment time in $(C_2H_5O)_2BF_3$: 1- room temperature (d_{layer}=50 μm); 2- room temperature (d_{layer}=20 μm); 3- T=50°C(d_{layer}=55 μm)

layers with the image become mechanical hard, strength and adhesive stable.

The cross-linking process in both the cases was determined as a lost of solubility in organic solvents, or as a preservation of the relief image during a long time at high temperature without deterioration of the image characteristics,

and also with the Infrared spectroscopy, detecting the change in the intensity of the absorption band in the region at 913 cm^{-1}, which is characteristic for the epoxygroup (Fig. 8). As we can see on the Fig. 8, the increase of the temperature from 25°C to 50°C accelerates the cross-linking process more than by 4 times. The second polymer matrix based on the thermoplastic layers I and thermoplastic layers II can be used for the multiplication of the copies on the special thermoplastic material, prepared on the base of butadiene copolymers. The ability for multiplication of the second polymer matrix based on copolymers of hlycedilmethacrylat is higher and we can get the number of about 100 copies without significant changes of its characteristics.

Carbazolylalcylmethacrylats with oktylmethacrylats copolymers have appeared rather suitable for create of new media for use in quality of photoresist. Carbazolyls polymers from vynilcarbazolyl with oktylmethacrylats, and also N-polyepoxypropylcarbazolyl, in addition containing electron-acceptor additives of a iodophorm type under action of a ultra-violet irradiation are exposed to a photochemical transformations, that conducts at the end to deep structurisation of a photopolymer layers. Structurisation of layers is accompanied by change of coloration of the irradiated sites, their solubility in the organic solvents, increasing of mechanical durability and adhesives properties of a material.

With the purpose of expansion of a class of used materials in photolithography, by us were received, tested and investigated as a photoresists media photopolymer layers from carbazolylalcylmethacrylats with oktylmethacrylats copolymers. The photopolymer layers were made by a pouring method from solutions. The contents of iodophorm and others electron-acceptor additives was maintained within the limits of 5-10 % from weight of a photopolymer. The thickness of layers changed in a range 1-10 μm. The irradiation of polymeric samples was made by the mercury - quartz lamp PRK-4, and also by heating lamp, having a continuous spectrum of radiation and intensity 15,5 mW/sm^2. For all created photoresists media were studied photographic sensitivity and factor of contrast, and at holographic recording – diffraction

efficiency and resolution.

The numerous tests of samples have shown, that complete cross-linking (the latent structural registration of the image visually noticed on change of coloration) of copolymer layers occurs during 10 - 15 s at 4,0 - 5,0 $sm^2/mW \times s$, i.e. to speed in 2 times greater, than for polyvynilcarbazolyl or polyepoxypropylcarbazolyl layers. The photographic sensitivity of layers depends and on a thickness of a photopolymer (Fig.9). The increasing of a thickness from 2,0 up to 5,0 μm increases photosensitivity in 5-6 times. Researches of holographic characteristics of a photoresist layers was carry out on special installation with the help of Ion-Argon and He-Cd lasers. For want of

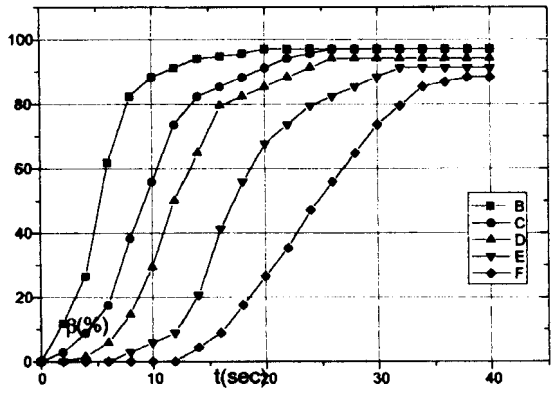

FIGURE 9 Change of a cross-linking degree (colouring) of a potopolymer layer from time of its irradiation at different thickness of a PP-layer, E_{irrad}=15,5 mW/sm^2; b - 6 μm; c - 4 μm; d - 3 μm; e - 2 μm; f - 1 μm.

it were investigated a kinetics of growth of diffraction efficiency in dependence from a doze of exposure, and conditions of solvents treatment, are defined holographic sensitivity, resolution capability and optimal diffraction efficiency of a photoresists layers. On the created photoresists layers from copolymers CEM:OMA the diffraction holographic gratings diffraction efficiency 25 % and resolution capability 1500 mm^{-1} were obtained.

Conclusions

The obtained results allow us to make the following conclusions.

1. Photothermoplastic media III based on copolymers carbazolyletilmethacrylat was developed. It has a photosensitivity more than 10^{-5} J/cm2 and a possibility to cross-link in BF_3 vapor. Is determined, that the plotting of photopolymer layers on injected sublayers from CVS reduces in increase of a photosensitivity at 1-2 order, reaching the value $10^{-6} - 10^{-7}$ J/cm^2. On the developed polymeric carriers the holographic images with holographic efficiency 12-15 % and resolution up to 1000 mm^{-1} were registered.

2. Optical properties and stability of indolinospirobenzopiran and indolinospiroantracenoxazin photochrom layers have been investigated for creation of a new information media with high (more than 5000 mm^{-1}) resolution and with stability up to 500 total cycles of photodarking-relaxation.

3. Thermoplastical media I and II from copolymer composition 4-aminostirol and glycedilmetacrilat are developed for registration and duplication of images. It was found that the optical information is transferred on polymer structure layer by stamping without losses, and the secondary polymer matrix showed no damage after ~100 cycles of duplication.

4. On the created photoresists layers from copolymers CEM:OMA the diffraction holographic gratings diffraction efficiency 25 % and resolution capability 1500 mm-^{1} were obtained.

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