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# Dichromated gelatin layers for holographic registration (review)

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The physicochemical properties of light-sensitive materials based on dichromated gelatin (DCG) are considered. The chemical and physico-chemical processes occurring in the „gelatin-water" system during the production of the layer and recording of holograms are described. Various technologies for DCG layers formation are presented, as well as the most common options for their use in holography, such as the creation of hologram optical elements and holographic displays.

**Keywords:** gelatin, dichromated gelatin, ammonium dichromate, holographic optical elements, methylene blue, diffraction efficiency.

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## Introduction

The use of gelatin with admixtures of chromium acid salts as a photosensitive medium for recording holograms was first proposed in 1968 [1]. The author of this article has found that maximal diffraction efficiency (DE) of holographic gratings on dichromated gelatin (DCG) layers for the low spatial frequencies ($\sim 100\,\mathrm{mm}^{-1}$) and small thicknesses ($< 1\,\mu$m) was 33%, and for higher spatial frequencies ($1000-3000\,\mathrm{mm}^{-1}$) and higher thicknesses ($1.3-3\,\mu$m) it was amounting to $80-90$% which is close to the theoretically predicted limits for the thin and volume holographic structures. The holographic information in this case, according to the author, was recorded due to formation of a surface relief caused by gelatin etching in water, or the movement of its volumes due to the occurrence of tension forces during dehydration with isopropanol.

DCG layers, along with silver halide photoemulsions, are conventionally considered as one of the leading recording media in holography owning to their high optical properties that are close to ideal [2]. On these layers, which have a high resolution of over $3000\,\mathrm{mm}^{-1}$, it is possible to create highly efficient holographic structures with a thickness of fractions to thousands of micrometers and obtain both, thin and volume holograms with high selectivity and very low noise level [3–5]. The material can be used to record both reflective and transmission holograms, and DE of volume holograms can approach the theoretical limit — 100%.

The holographic sensitivity of a DCG layer is several orders of magnitude inferior to the sensitivity of silver halide photographic materials [3,4] (table 1). In addition, layers without sensitizers have a limited spectral range of photosensitivity ($350-530$ nm).

The main component of a DCG layer is gelatin, which largely determines the properties of the material [5]. Gelatin is colorless, odorless, tasteless, insoluble in organic solvents, environmentally friendly, easy to handle, cost-effective, and has good transparency, biodegradability, and other useful properties. Gelatin properties such as viscosity, gel strength, softening, and melting point can be altered by ultraviolet radiation, heat, chemicals, and ultrasound. Gelatin is characterized by high compatibility with a wide range of substances from simple mineral salts (silver halides, bichromates, etc.) to complex organic compounds (for example, dyes). Gelatin films have good light transmission properties at wavelengths from 350 to 2000 nm. The addition of a sensitizer dye allows gelatin to be sensitive to a wide range of electromagnetic radiation from UV to middle-IR. Unsensitized gelatin is sensitive to the effects of short-wave UV, IR and ionizing radiation of sufficiently high power. DCG properties depend also on another layer component — ammonium dichromate (ADC) and its quantitative ratio with gelatin.

Some holography tasks require ensuring the optical quality of the surface of a layer used, for example, for the manufacture of holographic optical elements (HOE) on planar or non-planar substrates. HOE, including those made on DCG layers, are used in optical instrumentation as gratings for spectral devices, lenses, light filters, mirrors, as well as in optical image processing devices [6,7].

The use of HOE makes it possible to reduce the complexity of optical systems, significantly reduce their size and weight, which is important for their use in space [8,9]. Telescopes that need to be launched into space (in order to increase the viewing range and focusing, which are not limited by fluctuations in the Earth's atmosphere) are

**Table 1.** Typical and minimum values of energy sensitivity of gelatin-based photosensitive media

| Energy sensitivity, J/cm$^2$ | DCG | Silver halide photoemulsion |
|---|---|---|
| Typical | $50-500 \cdot 10^{-3}$ | $50-150 \cdot 10^{-6}$ |
| Minimal | $0.5-10 \cdot 10^{-3}$ | $0.5-10 \cdot 10^{-6}$ |

limited in weight and size by glass and polycrystalline glasses mirrors. On the contrary, a lightweight, flexible holographic lens that could be folded up for launch and unfolded in space can reach tens of meters in diameter. The unique properties and extensive capabilities of HOE attract the attention of researchers involved in development of space-borne optoelectronic telescopic systems (SOETS). This is explained by the fact that the designed optoelectronic systems may be improved due to the ability of HOE to simultaneously perform the functions of several optical elements, such as a beam splitter, a spectral filter, and a shaping optical system. If HOE are used in SOETS this also allows improving the resolution, field of view and etc.

Holographic diffraction gratings are commonly used in practice [3,10]. They are easy to fabricate, cheaper than ruled ones, and have no defects associated with errors in the optical and mechanical systems that control the movement of the diamond cutter.

DCG layers are unstable to external factors: air humidity, ambient temperature fluctuations, mechanical damage, and dust contamination of the surface, which leads to deterioration of optical characteristics. To ensure stability of optical characteristics of HOE on DCG in various storage and operating conditions, protective coatings are applied on the layer. For example, a layer of polymer glue is applied to the optical surface of HOE from DCG layer side, a cover silicate glass is placed on it, followed by curing of polymer glue [11].

As at the initial stages of holography development, a holographic art in the three-dimensional media continues to be improved using Yu.N. Denisyuk method for DCG layers, which makes it possible to obtain highly effective real images of three-dimensional objects. The history of holographic art development in USSR, as well as a huge contribution of Soviet engineers and scientists in continuous improvement of the holographic art is described in [12,13]. Among them the following researchers have contributed to the use of DCG layers: Sh.D. Kakichashvili, V.A. Vanin, G.A. Sobolev, O.B. Serov, L.V. Tanin, M.K. Shevtsov and a number of other researchers. Their art holograms have been repeatedly exhibited at national and international holographic art exhibitions [13,14]. The use of artistic color holograms in museum technologies is also gaining popularity. Examples of the current state of holographic art abroad are given in [15–17].

The author of article [18] who uses holography as an artist demonstrated the color holograms with a size of $1.2 \times 1.5\,m^2$ created on DCG layers. The holograms were recorded according to Denisyuk method in opposite directed beams. In paper [19] the work of a Japan researcher was outlined describing him using the holograms on $35 \times 40\,cm^2$ DCG layers for his architectural installations. Recent achievements in the field of DCG holograms synthesis and other their applications in holographic art are presented by M.K.Shevtsov in his report [20] at the last International Conference on Display Holography in Seoul in 2023.

The benchmarks of the research are the studies of chemical and physical-chemical processes occurring in „gelatin-water“ system during fabrication of DCG layer and recording of holograms, as well as methods for the layer structure formation and photochemical treatment technologies.

## 1. Mechanism of holograms recording on DCG layers

The mechanism of holograms recording on DCG layers has been studied in sufficient detail and continues to be investigated [4,21–24]. It is known that the structure of gelatin can change when exposed to radiation or chemical treatment, while undergoing structuring or destruction. Light from the ultraviolet or blue-green region of the spectrum can cause formation of cross-links in DCG layer in the presence of bichromates (crosslinking of gelatin molecules). This crosslinking is known as a tanning process. After exposure, the irradiated part of the layer becomes insoluble in water, while the non-irradiated part can be easily removed by water, resulting in formation of a relief interference pattern.

There is also another process where DCG layer is initially chemically tanned to such an extent that the unexposed layer does not dissolve with water. After exposing the interference pattern, the hologram is washed with water to swell the gelatin and remove the bichromate that has not reacted with light. Next, the hologram undergoes rapid dehydration in baths with an initial concentration of isopropyl alcohol in water (IA) of more than 50–60% and further up to 100% in order to complete the development process. The hologram is recorded both, on the surface and across the layer. Due to the pre-tanning at the washing stage, gelatin does not dissolve and is not removed. Instead, gelatin absorbs water and swells growing in volume. The swelling and growing in volume occurs unevenly. The swelling decreases with the growing hardening of the gelatin layer. More exposed gelatin is more hardened, and the heterogeneous distribution of light intensity corresponds to the distribution of the layer swelling. If, during rapid dehydration in the isopropyl alcohol, water is removed from gelatin at a rate exceeding the normal shrinkage rate, the resulting spatial heterogeneous volume increase persists.

As a result, the known methods for producing DCG layers differ in the degree of tanning of gelatin matrix during the layer fabrication process. The layers may be differentiated as tanned and non-tanned ones. For the non-tanned DCG layers the gelatin-based layer with chromium acid salt is assumed to be fabricated without any chemical or thermal tanning before exposure. Sensibilisation or sensitization of the layer occurs during fabrication of photosensitive composition by introducing dichromate salts into a gelatin solution. Chemical or thermal tanning prior to exposure leads to the formation of tanned layers.

The primary photochemical reaction of electron transfer in the layer caused by light absorption by a complex of donor (gelatin) and acceptor (chromium ion) molecules occurs through at least two channels [24]. Having absorbed the light quantum, the chromium ion $Cr^{6+}$ in the emulsion is reduced to $Cr^{4+}$ and $Cr^{5+}$. The ions $Cr^{4+}$ spontaneously transit over time to $Cr^{5+}$ or, as a result of dark reactions (tanning without light), to $Cr^{3+}$, which is the main tanning agent of gelatin. $Cr^{5+}$ ions are stable and transform into $Cr^{3+}$ only under the action of water during development. In the aqueous solution a „helix-coil" transition process is initiated. This process takes time. After DCG layer is exposed, apart from the optical data recording due to transformation of chromium ions $Cr^{6+}$ to $Cr^{5+}$ and „helix-coil" transitions, $Cr^{6+}$ ions start to diffuse into the light-exposed areas. A gelatin layer exposed to high-intensity light will have a more intensive tanning than gelatin exposed to less light energy. As a result of the subsequent stage of dehydration in alcoholic solutions, local inhomogeneities (pores, microcracks) are formed, the location of which exactly corresponds to the interference pattern when recording a hologram [4,21–23].

In the solution, the gelatin molecules are predominantly in a conformational state of a coil [22,24,25]. The center of the latent image in DCG is a section of the gelatin macromolecule, which changes from a helix to a coil under the action of chromium ion photoexcitation. When the exposed layer is developed, there is a significant reduction in the size of the latent image's center. The maximum resolution of DCG layer therefore depends on the energy of exposure and the mode of development and reaches $0.2\,\mu$m. Modulation of refractive index is associated with a large number of diverse processes — from a intramolecular „coil-helix" transition to a purely mechanic cracking of the layer during fast dehydration in the isopropyl alcohol.

When the temperature of the solution goes down the solution starts the gelation, the coil-helix transition occurs, and the conformation of a collagen-like helix is formed. If a gelatin solution with dichromate salts is gelled, the coil-helix conformational transition slows down.

## 2. Technology of DCG layers formation

The initial technology of pouring the DCG layers is described in paper [1]. There are a number of more recent studies on the development of methods for the formation of DCG layers. There is a well-known technique for creating the fundamentals of fabrication and treatment of a highly sensitive, low-tanned DCG layer with high holographic parameters [26]. In this study, based on a comprehensive holographic and physical-chemical study, the formulation of DCG composition and the layer pouring technology were improved, including pouring on non-planar substrates, as well as in production conditions. The author has studied the dependence of holographic parameters on the composition and types of gelatin, and quantified the optimal composition of DCG layers, including concentration of additives that increase photosensitivity and DE. A method has been proposed and developed for obtaining a recording medium that ensures the required optical quality of the photosensitive layer surface on a glass or polymer substrate of various geometric shapes, which is very relevant for HOE fabrication. In the DCG layer proposed by the author based on 6−10% gelatin solution with an additive of ADC of up to 10% of dry gelatin weight there's a small addition of glucose in the amount of 0.1% of dry gelatin weight, which results in higher photosensitivity.

In the author's application [27], researchers propose a way to increase holographic sensitivity by more than 3 times. Instead of the known method of fabrication of an non-tanned DCG layer, where DCG matrix is formed by pouring the substrate with a gelatin solution with introduced dichromate salts followed by further gelling and drying, the authors sensitize the gelatin layer in a solution of dichromate salts after the gelatin layer has been already gelled and dried. At the same time, the presence of a helix structure of gelatin molecules makes it possible to optimally interact with chromium ions when bichromate salts are introduced than with a coil structure, which is observed when bichromate salts are introduced into a gelatin solution. The method described in [27] makes it possible to expand the scope of DCG use as a recording medium in holography, since increasing the sensitivity of photographic material opens up the prospect of fabricating the large-sized holograms (both in holographic art and in hologram optics) without increasing the radiation power of exposing lasers. Additionally, the gelatin layer fabrication takes place under white light conditions, which is much easier for the manufacturer. The obtained DCG layers can be preserved for a long time without sensitization and they become sensible only before use. At the same time, the possibility of layers aging over time disappears and the reproducibility of the results increases.

Similar option of dry gelatin layer sensitization by its bathing in ammonium dichromate solution is described in [24]. It was found that maximal DE of about 83% is reached at ABC concentration of 2% in the solution. It's worth noting that authors used partially or completely inoperative plates PFG-03M for sensitization (produced by OJC „Slavich" Company, Pereslavl-Zalessky).

This research dates back to a technology of DCG layers fabrication (described back in the 70s of the twentieth century in [28–30]) using commercial silver halide photographic materials Kodak 649F and Agfa 8E75 HD. To obtain a pure gelatin layer, the authors of the widely known monograph [28] recommend dissolving silver halide contained in an undeveloped photographic plate in a fixing solution and rinsing it in water and methanol. For sensitization of the photographic plate they suggest to bath the plate in 5% aqueous solution of ADC for 5 min and further slowly dry it in the dark during 4−6 h. Sensitized photographic plates can be stored for several months at a temperature of 10°C in the refrigerator.

## 3. Use of DCG layers for manufacture of HOE

Numerous studies have been performed to study the use of DCG layers for fabrication of HOE. Article [31] outlines in detail the key stages to fabricate high optical quality HOE on DCG layers with thickness from several micrometers to 100 $\mu$m. The technology of the layers pouring was developed late in 1970s in GIPO (Kazan). The process of layer formation before complete drying can be adjusted over time. According to Denisyuk's scheme, on these layers the selective hologram mirrors and narrow-band filters were registered distinguished by a wide range of applications from visual indication on the aircraft windshield to spectrum splitters and solar energy conversion devices. Volume-phase gratings have been fabricated that outpaced their relief-phase competitors in terms of DE magnitude. For optical telecommunication systems, grating prisms (grisms) have been manufactured to align DE for various polarizations of incident radiation, which are a combination of two prisms and a volume-phase transmission grating between them.

The thesis [32] outlines the use of untanned thick layers of DCG to create highly effective HOE for the ultraviolet, visible and near-infrared spectral regions (UV-Vis spectral regions). The counter-directional scheme of Yu.N.Denisyuk was used to make selective hologram mirrors and narrow-band filters. Hologram gratings were recorded in converging beams. The author has conducted systematic comprehensive studies of environmental impact on the optical characteristics of HOE obtained on thick (up to 250 $\mu$m thick) non-tanned DCG layers for all links of the technological chain (application of a photo layer on a substrate, exposure, physical and chemical treatment, etc.).

The authors of paper [33] theoretically and experimentally analyzed the potential of using holographic mirrors recording to create a spectrum splitter with spatial separation of two wavelengths in the spectral range of 290−330 nm when using non-tanned DCG layers fabricated according to [24]. These layers have a higher sensitivity compared to layers made using other known techniques. A significant increase in the efficiency of using HOE is achieved by combining several functions in one element. It is possible to use DCG layers with a thickness of no more than 25 $\mu$m.

Patent [34] describes a specific recording technique on a DCG layer. According to the authors, the method can be used in various sections of applied holography, for example, for making souvenir holograms, clock faces, advertising, optical design. This is due to the complex registration scheme of a mirrored hologram presented in the patent, according to which the direction of propagation of the reconstructed light beam is perpendicular to the hologram plane.

In the article [35], a technique is proposed for obtaining hologram mirrors on DCG layers which reflect light in a wide range of wavelengths. The need for such mirrors is due to the fact that in some applications (including display holography) there is a necessity to create holographic structures that are not selective with respect to the spectral composition of the reconstructing light. The authors associated the appearance of the „non-selectivity" effect during conventional recording of holograms in counterdirected beams by Lippman-Denisyuk method with the unique properties of DCG. The strong absorption of light in the photosensitive medium thickness at some wavelengths used for recording leads to a gradient in the optical thickness of the gelatin structure. In other words, after full treatment, the DCG hologram represents a set of layers with different spatial frequencies („multilayer structure"), which causes a good reflection of light from the holographic mirror in a wide spectral range.

The issues related to fabrication of planar and spherical hologram mirrors based on a thick layer of bichrominated gelatin using Denisyuk method were reviewed by the authors of paper [36]. The mirrors are designed to work as part of an ocular system of night vision goggles. In this paper, we used a method for transferring a DCG layer from a commercially produced PFG-04 plane photographic plate to a convex surface of a spherical substrate.

In papers [37–39], based on Gabor hologram, a new type of holograms was developed and studied allowing to compensate for the distortions peculiar to such a simple axial hologram. In particular, an axial holographic screen based on a non-supporting thick-layer hologram was proposed, which does not skip the zero order, does not create a halo and a conjugate image, unlike holograms obtained using the same optical scheme on thin layers of halide-silver photoemulsions. [40]. For screen recording a self-developing glycerine-containing DCG which is 0.10−1.15 mm thick was used. Such a screen can be used for image projection systems through a holographic screen, used, for example, as simulators. The effect of light concentration in the field of vision is noted. The possibility of registering a screen with one wavelength, and reconstructing and projecting an image with another, including white light, is demonstrated.

In papers [41,42], a modification of DCG layers treatment technology is proposed for the fabrication of high-frequency thin relief-phase holographic gratings operating on transmission, which are recorded using a holographic scheme in converging beams. The method is based on the use of glacial acetic acid (GAA) as an etching reagent after the destructive impact of the short-wave UV radiation with a wavelength of less than 270nm [43]. In this study they used both, commercially produced PFG-04 (produced by JSC „Slavich" Company, Pereslavl-Zalessky) with a thickness of up to 26 $\mu$m and holographic sensitivity of 2500 J/m$^2$, and the laboratory wetted DCG layers with a thickness of 0.7 to 11 $\mu$m similar to the way described in [1].

In contrast to the described technology used in halide-silver photo-emulsions, [41] there's a direct change in physical chemical properties of gelatin in DCG layers during holographic recording of the interference pattern due to selective light tanning by He-Cd laser radiation with a wavelength of 0.44 $\mu$m [42] in the presence of bichromates and subsequent water treatment. In this experiment, holographic gratings with a spatial frequency of up to 1600 mm$^{-1}$ were recorded using a symmetrical optical scheme with two converging flat beams. At the same time, structuring took place, i.e., the occurrence of a large number of cross-links in the maxima of the interference pattern intensities. The DCG areas tanned by photolytic method are less susceptible to the damaging effects of short-wave UV radiation with a wavelength of less than 270nm [43]. Then, the samples of the gratings were bathed in a 2% solution of sodium sulfite, water rinsed and dried. After that, the samples were irradiated by a short-wave UF-radiation of the mercury-quartz lamp DRT-220 during 20−25 min. At the same time, less hardened areas of gelatin lying in the minima of the interference pattern were destroyed more strongly under the influence of UV radiation. As a result of the subsequent short-time etching, these areas were removed from the surface of the layer first. The surface gelatin layer was etched in the glacial acetic acid and isopropyl alcohol during 10 s. The etching was interrupted by placing the sample into a bath of 100% isopropyl alcohol. The experimental findings are provided in the Table 2.

The samples of relief-phase holographic gratings on PFG-04 demonstrated high DE at a spatial frequency of 1600 mm$^{-1}$ up to 67%, and the gratings on the laboratory-grown DCG layers had DE of 50 mm−64% with a thickness of 0.7−5.6 $\mu$m.

The possibility of transferring the holographic structure, originally recorded on DCG layers, to a polymethyl-methacrylate (PMMA) substrate was also shown [44]. By improving the treatment modes and selecting developing formulations based on methyl isobutyl ketone, it was possible to create PMMA relief-phase holographic gratings with a high DE of about 25% and a maximum depth of surface relief of about 1 $\mu$m. 1 $\mu$m [44].

The proposed improved DCG treatment technique helps to increase the range of recorded spatial frequencies during the formation of relief-phase holographic structures and thereby expands the scope of DCG application in holography. The use of UV irradiation and nonequilibrium manifestation (short etching) leads to formation of effective high-frequency relief-phase structures with low angular selectivity, which can be used in diffraction optics. High DE values can also be obtained on gratings with an ultra-small thickness of fractions of a micrometer, which contributes a cost-effective use of the fabricated photosensitive material, reducing aberrations and distortions of the holographic image due to inhomogeneities inside and on the surface of the photosensitive layer. The advantage of the new treatment technique is its applicability to commercially available photographic material PFG-04 based on DCG. Thus, the application potential of a material traditionally used in holography in a new quality as a thin medium for recording hologram optical elements with low angular selectivity is shown.

Formation of a strong surface relief on DCG layers can be carried out not only by applying selective photo destruction of gelatin exposed to short-wave UV radiation, but also using other purely chemical methods. For instance, in papers [45] the authors used the radiation of neodymium laser ($\lambda = 468$ nm) or the near-UV light of the mercury lamp for tanning (structuring) of DCG thick layers. Solutions of the papain enzyme in water were used to etch gelatin in less exposed areas. The spatial periodic structures were studied obtained by a contact type copying of Ronchi gratings with low spatial frequencies from 4 to 10 mm$^{-1}$ onto the 50 $\mu$m thick DCG layers. The use of papain made it possible to increase the depth of the surface relief by almost 7 times compared to the samples treated in water and bring it to a value of about 15 $\mu$m. According to the authors, the obtained ultra-deep spatial- periodic structures can be effectively used in the infrared wavelength range. $\lambda = 1{-}15\,\mu$m.

The review article [46] discusses the use of holographic lenses (HL) to concentrate solar energy into a focal point or focal line, where it can be converted into electrical or thermal energy. The possibility of using photosensitive media, including DCG layers, for HL fabrication is estimated. Despite the fact that DCG has manifested itself as a universal material for recording holograms with high DE and optical quality and can be used on rigid or flexible substrates, flat or curved surfaces, the low sensitivity of DCG, as well as its toxicity, according to the authors, may limit its use in holographic solar concentrators.

DCG layers application in the integral and planar optics was discussed in a number of studies [47,48]. For example, the authors of the study jcite47 have fabricated a multiplane 32-channel optical bus for interconnection in local area networks and parallel computer systems. For this purpose, a combination of a single-mode waveguide on a glass substrate with volumetric holographic gratings recorded on DCG layers was used. Another example is the use of DCG layers to make planar holographic lenses that can be used to obtain images [48]. The planar holographic lenses described in this paper are featuring high DE (over 50%), low aberrations and low selectivity with respect to the incident angle ($\sim 16^\circ$). Such lenses may be included in a series of compact image producing systems.

## 4. Thick-layered photo-sensitive materials based on DCG

Of particular interest are thick-layer photosensitive materials that allow recording 3D holograms with a number

**Table 2.** Summary table of experimental data for treating the samples of relief-phase gratings on DCG photosensitive layers. Samples fabricated in the laboratory as per method [1] are marked by asterisk

| Type of photographic material | Layer thickness, $\mu$m | Type of etchant | DE, % for $\lambda = 0.63\,\mu$m |
|---|---|---|---|
| * Lab. DCG as per Schenkoff | 0.7 | $H_2O$ | 50 |
| | 1.1 | Mixture of GAA and IA in the ratio of 1:1 | 41 |
| | 1.94 | Mixture of GAA and IA in the ratio of 1:3 | 48 |
| | 5.7 | Mixture of GAA and IA in the ratio of 1:1 | 64 |
| | 11 | Mixture of GAA and IA in the ratio of 1:3 | 28.4 |
| PFG-04 | 26 | $H_2O$ | 54 |
| | 26 | Mixture of GAA and IA in the ratio of 1:1 | 67 |

of unique properties compared to a 2D hologram [49,50]. Among these properties, it is necessary to note the high angular and spectral selectivity, the absence of a conjugate image, the possibility of image reconstruction in white light, etc. [49–51]. This allows using 3D holograms in the development of such areas as three-dimensional imaging, optical memory, etc.

Papers [52–54] describe the examples of creation and use of thick-layered photo-sensitive DCG materials operating in real time. One of the first articles on the use of BCG layers in real time (without additional photochemical treatment) was published in 1984 [55]. The article outlined potential usage of the undeveloped DCG layers with DE of $0.1-0.7\%$ under exposure $200\,\text{mJ/cm}^2$ for the optical data processing. It was also noted that the presence of DCG layers in a humid atmosphere for several hours leads to a higher diffraction efficiency.

Treatment of a hologram recorded on a DCG layer requires presence of water in an amount sufficient to manifest the hidden image. In the first case, a sandwich structure was created where DCG was located between the two glass plates [52]. The process of making a gel-like layer was similar to the well-known DCG wetting technology [1]. The main difference was that the hologram was recorded directly in the wetted layer. The layer itself was quite a dense gel with a thickness of 1 to 5 mm, where a hologram can be recorded in the same easy manner as with a solid DCG film.

In the second case, [53] dry DCG layers containing glycerin were produced and studied for recording the 3D holograms. After drying in the air the layers thickness in the air was from 100 to $600\,\mu$m. For the first time, the introduction of a certain amount of glycerin into DCG to increase the proportion of reactive water molecules was described by the authors in [56,57]. Glycerin is miscible with water in any ratio. Glycerin in the layers increases the number of water molecules that can develop a hidden image due to the presence of hydrogen bonds. The introduction of glycerol into DCG layers, in addition to self-development, makes it possible to increase photosensitivity and expand spectral sensitivity into the long-wavelength region of the spectrum. Layers of a self-developed dichromated gelatin with admixtures of glycerin of up to 95% of the dry gelatin weight, which are $5-10\,\mu$m in thickness after drying, were described earlier in papers [58]. It has been shown that optimal concentration of free water in the layer to achieve maximum sensitivity is provided when $90-95\%$ glycerin by weight of dry gelatin is introduced into DCG.

To study the diffraction properties of the two versions of a three-layer self-developing DCG the holographic gratings were recorded by symmetrical optical scheme with He-Cd-laser ($\lambda = 0.44\,\mu$m) radiation of 16 mW. The holographic parameters of the gratings on the glycerin-containing DCG layers turned out to be better than on gel-like layers. Maximal achievable DE was $15-40\%$ depending on the layer thickness and ABC concentration. Sensitivity of thick glycerin-containing DCG layers was about $6-10\,\text{J/cm}^2$, which is close to the sensitivity of a thick-layer gel-like gelatin ($10\,\text{J/cm}^2$). Glycerin-containing DCG is characterized by an almost endless storage time for recorded holograms, unlike gel-like DCG, which had a lifetime of recorded information of several hours.

Both types of DCG layers are easy-to-fabricate materials that can be used to record 3D holograms, as well as to conduct a number of model experiments to study various holographic recording schemes. In particular, the gel-like material was used to register the so-called selective selectograms [59]. However, the low DE value of holograms and the limited lifetime of recorded information introduce certain limitations in its application.

Glycerin-containing DCG layers were used to produce such a HOE as a one-dimensional diffuser [60], which effectively diffuses light in one plane and was used, for example, when registering unsupported selectograms. The material was also used for recording and multiplication of the 3D axial holograms [61], including shift-like speckle-holograms [62].

When super-thick DCG layers are synthesized (over 0.5 mm) a problem of their „drying“ arises, which takes quite much time (more than three days) and accompanied by thickening, or „maturation“, of the colloidal medium. In [63], the use of laser annealing in the emulsion synthesis was considered which is distinguished by powerful infrared radiation with a wavelength of $1.06\,\mu$m for „drying" and thickening of colloidal layers of millimeter thickness. The authors experimentally demonstrated the possibility of improving the properties of self-developing DCG when exposed to IR laser radiation. The use of laser annealing for structuring, in addition to reducing the layer synthesis time, led to higher DE and improved uniformity of properties throughout the entire volume of the system, which is critical for layers with a thickness of $1-5$ mm. And, in general, laser annealing was used as an additional tool for the process control.

Optical sensitization of chromated colloidal systems is used to expand the spectral sensitivity of DCG by introducing a dye with maximum absorption in the desired spectral region. The main difficulty in selecting a sensitizer is the low solubility of a number of dyes in the presence of ammonium dichromate. From a practical standpoint, it is interesting to expand DCG sensitivity range into the red region of the spectrum to use layers when recording holograms by a He-Ne laser. As described in [64], the eigen sensitivity of DCG to radiation in red spectrum is very low (about $15-150\,J/cm^2$ for the layers about $10-30\,\mu$m thick).

As shown in the article jcite25, the eigen sensitivity is provided due to chromium ion complexes localized in the core region of the gelatin macromolecule globule. Therefore, in order to ensure maximum photosensitivity to radiation in the red spectral range, it is necessary to use DCG layers with a globular structure. The author has developed methods for synthesizing globular DCG layers that make it possible to improve the characteristics of hologram optical elements.

The largest number of publications on the sensitization of DCG layers to red radiation relates to the use of methylene blue (MB) as a dye [65–69]. By adding MB to conventional DCG layers with a thickness of $20\,\mu$m it is possible to increase the sensitivity (i.e. diminish the required exposure energy) by almost 3 orders. However, the sensitivity of DCG to red light remains at least one to two orders of magnitude less than when using blue and green laser light to record the holograms.

MB sensitizer also precipitates in the aqueous solution of ABC. Experimental data show that the successful functioning of the DCG+MB system is associated with the need to maintain at least 9.0 pH in the solution. Maintaining 9.0 pH of the solution can be achieved by adding certain amounts of ammonium, as well as by ensuring that after wetting and thickening, the layers remain covered with glass until the experiment is carried out.

The study [54] outlines the fabrication technology for the red spectrum sensitive DCG layers both, made as a sandwich structure and having an open surface. The interference pattern of the two plane waves detected by He-Ne laser radiation at a wavelength of $0.63\,\mu$m the gratings' DE was measured using a symmetrical scheme. In the experiment, the following parameters were varied: angle of convergence of the interfering rays from 15 to 35°, power density of recording radiation, concentration of potassium bichromate (PBC) from 20 to 60% of the weight of dry gelatin, and concentration of MB. Holographic characteristics were recorded every 24 h after wetting of layers. The layer thickness varied from 0.9 to 1.2 mm. In 24 h the thickness decreased by $15-20$%. Maximal DE of 26, 23, 18, 9 and 2% was obtained for the convergence angle 17, 20, 25, 39 and 35° respectively. Maximal DE of 29% at the concentration of potassium bichromate of 60% was obtained for the 1.3 mm thick layer.

The developed material, which is sensitive in the red region of the spectrum, allows obtaining a real-time image reconstructed by a hologram. This allows it to be used to study the recording features of holograms. The material is easy to prepare, cheap, and has good reproducibility of parameters and characteristics.

Wider sensitivity to the green region of spectrum was described, for instance, by the authors of paper [70]. They obtained bright holograms using argon laser radiation with a wavelength of 514 nm, using post-exposure annealing at 100°S. Due to the use of thermal curing in the presence of glycerin, the photosensitivity of DCG to green light had more than a threefold rise. For the DCG-based photosensitive material produced by JSC „Slavich" PFG-04, the authors of the article [71] also recommended heat treatment at a temperature of 100°C (tanning in the thermostat at 100°C for $0-60$ min depending on the shelf life of the plates). In this paper, an example of using a DCG-based photosensitive material in real time is described, where DCG was used as a sensitizer. In the experiment, holographic gratings were recorded using a symmetrical optical recording scheme by argon laser radiation with a wavelength of 532 nm Diffraction efficiency of gratings was measured by counting with He-Ne-laser with a wavelength of 633 nm. With DCK concentration of 1%, thickness of layer of $10\,\mu$m, irradiation energy of $18\,J/cm^2$ and angle between the converging beams 2.2° the diffraction efficiency reached 19%. According to the authors, an increase in the sensitivity, DE, and service life of the material can be achieved by adding glycerin, dye, or using a shorter wavelength during recording, as well as by irradiating the material with UV and introducing a development procedure.

The authors in [72], through sensitization of DCG using MB to the red light, demonstrated that by using 647.1, 514.5, 476.5 nm wavelength lasers, the full-color reflective holograms may be obtained in one layer with high diffraction efficiency (about 80%). The authors presented a simplified method of DCG fabrication, where the layers can be dried without the use of ammonium. The developed technology of preparing layers can be used in visual holography.

## Conclusion

This article highlights the relevance of using photosensitive DCG materials in holography and its applications. The latest research in the field of DCG layers allows us to consider this photosensitive medium as a promising material for recording optical information, manufacturing various holographic optical elements, creating holographic displays and other practical applications.

### Conflict of interest

The authors declare that they have no conflict of interest.

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