Manuel Ulibarrena
m.ulibarrena@umh.es

A new panchromatic silver halide emulsion for recording color holograms

About the author

Manuel received his PhD from the Universidad Miguel Hernandez in Elche, Spain, in 2003. For his project he studied the characteristics of the ultrafine BB640 emulsion in relation to holography. He is currently associate professor of non-destructive testing in the same university. He has been involved in holographic research since 1985, and his current area of interest remains silver halide holographic recording materials.

Introduction

All introductory text books about holography make a comparison with photography, saying that photography is a technique that is only capable for recording the intensity of the light scattered by a real object, while holography records both intensity and the phase of that light. What they fail to mention is that when one looks at a display hologram, the image is in most cases monochromatic, so in this case this advantage of holography over photography is completely true only when comparing black and white photography with monochromatic holography.

Today almost all photography is in full color. In order to make the advantage mentioned true for color photography, the holograms must be recorded in full color. This has been obtained in rainbow holography by multiplexing three rainbow holograms with different slit locations, so that an image color is obtained with a single laser and monochromatic recording material. But the color of image depends strongly on the relative position of the slit, and in any case this color is synthesized from three or more monochromatic holograms, with the object illuminated with a monochromatic source. So that although we can get good color, the color cannot be considered as “real”. True color holograms can only be obtained from the light scattered by an object illuminated by several different wavelengths. Two major practical problems are found when trying to make such a hologram.

The first one is related with the lasers. While red lasers (He–Ne or semiconductor lasers) are common in many holographic laboratories (they are cheap and easy to maintain) green and blue lasers are more difficult to find since they are more expensive (e.g. argon ion, frequency-doubled Nd–YAG) or have limited holographic performance (e.g. He–Cd).

The other problem is the recording material. Traditionally, the materials used for recording color holograms have been panchromatic silver halide emulsions, multiple layer dichromated gelatin and panchromatic photopolymers. For dichromated gelatin, with spectral sensitivity in the blue–green zone of the visual spectrum, the red gratings had to be recorded with very special procedures. The blue and the green holograms were recorded individually, not multiplexed, and the final multiple-band hologram had to be built up by laminating the three individual gelatin layers one over the other with complex and costly techniques [1]. In the late 80's and early 90's, commercial panchromatic photopolymers [2] emerged as an alternative to DCG [3]. Silver halide-sensitized gelatin processes with panchromatic emulsion PFG03-C have also been used, with high diffraction efficiencies for single wavelength recordings [4].

Silver halide holographic emulsions exhibit a better sensitivity than all the recording materials mentioned above. Nevertheless, although they have been used for recording multiplexed reflection holograms with different laser lines [5, 6], their usage has been limited by their relatively low index modulation capacity, as well as by their spectral sensitivities, since most of them are sensitized to a single spectral band only. Besides, the material is composed of ultra fine silver halide grains, with an intrinsic absorption band around 400 nm. Therefore, blue recordings do not work properly, since they have low diffraction efficiencies due to high levels of absorption and scattering. This led to the use of techniques involving recordings in more than one plate [7] or more than one recording material [8]. The use of monochromatic emulsions for multiplexing reflection gratings with different swelling factors between recordings has been also reported [9], although in this case we are again working with synthetic color. In all these configurations, emulsions were useful for display and artistic holography. In the mid 90's, new ultra fine grain panchromatic emulsions, especially Slavich PFG-03C, with a mean grain size of 10 nm—smaller than that of the emulsions previously available—boosted advances in these two fields [10]. More recently, results obtained with a non-commercial ultra fine grain panchromatic emulsion have been reported, with diffraction efficiencies for single exposure diffraction gratings higher than 50% [11].

There are several aspects that have to be considered when working with multiplexed reflection holograms with different wavelengths in silver halide materials. The first is the high scattering, mentioned above, that occurs in the blue part of the spectrum. This scattering can be reduced by working with ultra fine grain emulsions. In this study we used the new panchromatic ultra fine grain emulsion BBVPan, based on the existing family of BB emulsions, currently manufactured by Colourholographics Ltd, with a mean grain size of 20 nm. The second aspect is related to shrinkage or swelling of the emulsion after the plate is processed, since in reflection holography this is directly related to the wavelength of reconstruction, and this affects the final replay spectrum and color rendition of the grating. The last aspect is the effect of multiple exposures on a single emulsion, since this is associated with a reduction in the diffraction efficiency. This reduction has been historically evaluated as inversely proportional to the square of the total number of recordings [12].

Experiments

We recorded color reflection holograms using the new panchromatic ultra fine grain emulsion BBVPan, batch no. 174. In all our works with BB emulsions we have presensitized them in order to reduce the exposure times. Previous work in reflection holography with BB640 emulsions showed a response in the 604 nm range, instead of the expected 633 nm of the He–Ne laser, an effect caused by the presensitizing bath composed of a 3% triethanolamine (TEA)–water solution. TEA is an electron donor that increase the speed of photographic emulsions and photopolymers. But it is also known to be a swelling agent used to reduce the replay wavelength of the holograms, and has this additional effect when used in presensitization. We found that an additional water bath following the first TEA solution bath reduces the swelling effect. The soaking time in this second bath is important and has to be adjusted to obtain the proper wavelength at reconstruction.

In all the tests reported here, plates were presensitized by soaking for 2 min in a 3% TEA water solution, 7 min in a deionized water bath, drying with a photographic roll and warm air, and leaving in the exposure room for half an hour in normal laboratory conditions (20° and 60% RH) [13].

For the above characterization study, plates were exposed to single collimated beams in a Denisyuk configuration [14] using a blue He–Cd laser (wavelength 442 nm), a green frequency-doubled Nd–YAG laser (wavelength 532 nm), and a red He–Ne laser (wavelength 632.8 nm). The recording setup consists of an optical sandwich composed of a first surface mirror that reflects the incident beam back into the emulsion. The emulsion side of the plate is in contact with the mirror via an index matching fluid, and the glass side is in contact with an anti-reflection coated glass plate via another thin layer of index matching fluid to prevent internal reflections. The setup schematic is shown in figure 1.

With this configuration spatial frequencies of 7145 l/mm (blue), 5936 l/mm (green) and 4990 l/mm (red) were recorded (considering a refractive index of 1.579 for the unexposed emulsion). The sandwich was mounted on a computer controlled motorized holder which enabled us to record 9 gratings with different exposure energies on a 2″ × 2.5″ plate. The size of the plate was obtained by cutting each of the 4″ × 5″ plate into 4 pieces, since at the time we performed our study we had only 5 of these plates available.

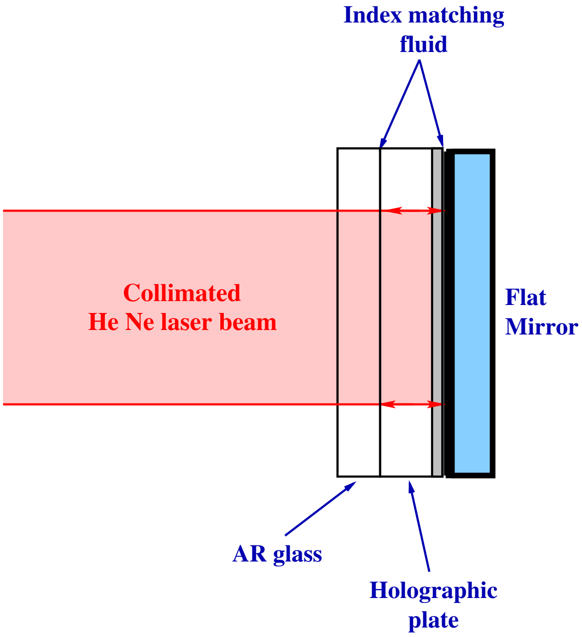

Figure 1. Recording setup used for the characterization study of the BBPan emulsions.

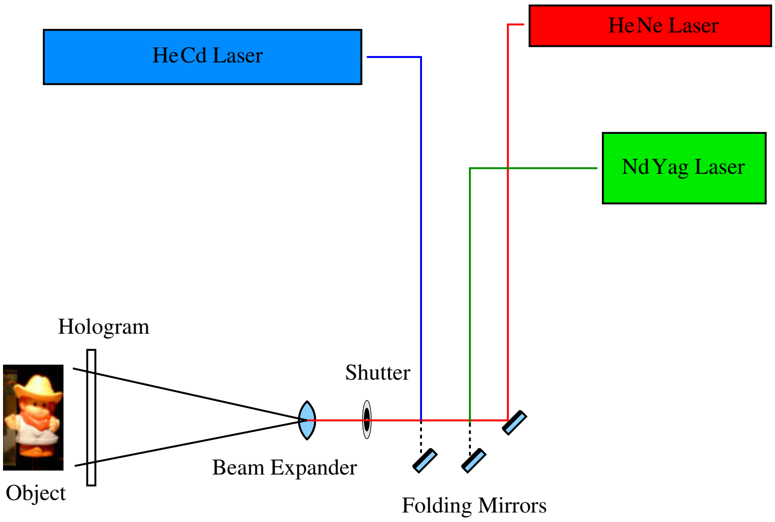

Figure 2. Recording setup used for the diffuse object color hologram study of the BBPan emulsions.

The diffuse object color hologram study was performed with a holographic setup in a Denisyuk configuration shown in figure 2. The folding mirrors were sequentially placed in order to multiplex the three holograms, starting with the blue, then the green and finally the red laser. Plate size for this study was 2″ × 2.5″, except for the last one that was 4″ × 2.5″.

Exposed plates were developed with AAC developer (Ascorbic Acid 18 g/l + Sodium Carbonate 60 g/l) [15]. After washing they were bleached

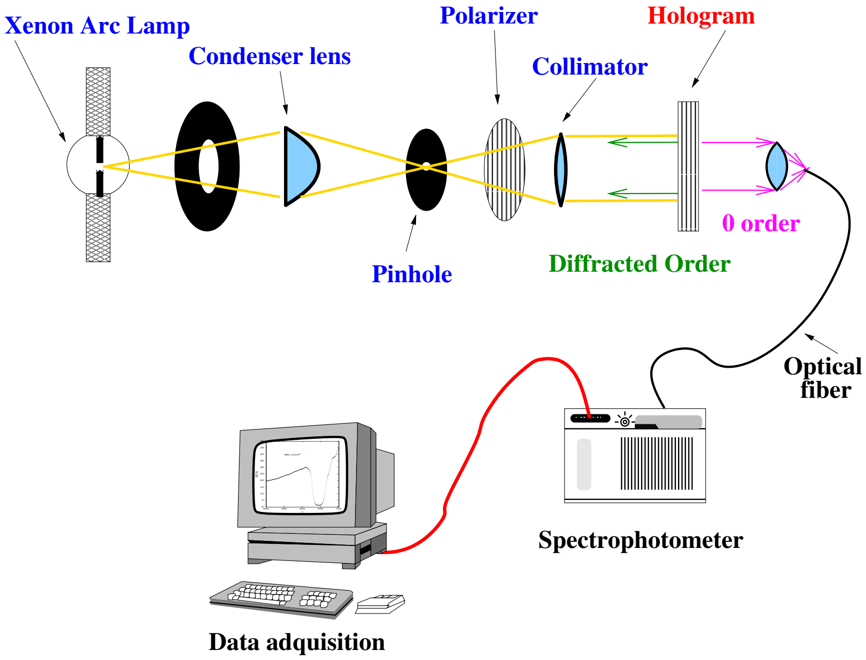

Figure 3. Analysis setup.

with fixation-free rehalogenating bleach R-10 (Potassium Dichromate 2 g/l+ Sulphuric Acid 10 cc/l + Potassium Bromide 35 g/l). After bleaching, the plates were washed and soaked in deionized water with a few drops of Photoflo and Acetic Acid to prevent printout, and dried in the normal laboratory conditions mentioned above.

After drying, the plates recorded in both the characterization setup and the diffuse object setup were analysed using a fibre fed spectroradiometer. With this device we measured the zero order of the grating with a replay angle of 0°, matching the recording geometry. A short arc xenon lamp was used as the light source, collimated and polarized perpendicular to the plane of incidence to match the recording conditions. Light was collected by an optical fibre that fed the spectrophotometer and data were transferred to a computer for storage and analysis. Reflection losses were experimentally evaluated and found to have a value of 6.7%. The schematic of this setup is shown in figure 3.

Two different studies were performed: a preliminary spectral sensitivity characterization of the plates, followed by a study of multiplexed gratings on a single plate with plane gratings and a diffusing object.

Characterization of the Plates

The plates were first tested for single wavelength recordings with each of the laser beams used in order to check their spectral sensitivity and the response of the material when recording holographic reflection gratings.

Three sets of tests, one for each wavelength, were carried out, including presensitizing, exposing, processing and analysis as explained above. Exposure energies ranged from 30 to 2400 μJ/cm^2 for the He–Cd laser and from 150 to 2400 μJ/cm^2 for the frequency-doubled Nd–YAG and He–Ne lasers.

Multiplexed Holograms

In this case, the exposure of the reflection gratings was made sequentially on the same area of the plate, starting with the blue wavelength, followed by green and then red. We obtained a set of multiplexed reflection gratings with different exposure energy combinations for each wavelength, ranging from 120 to 225 μJ/cm^2 for the He–Cd laser, 150 to 250 μJ/cm^2 for the frequency-doubled Nd–YAG laser and 800 to 1200 μJ/cm^2 for the He–Ne laser.

Results

Single sensitivities of BBVPan plates for each of the three recording wavelengths are presented in figure 4, and the most relevant results are summarized in table 1. From these results it is clear that the exposure energy for maximum Diffraction Efficiency (DE) of this emulsion is the highest for the blue wavelength (320 μJ/cm^2), followed by the green (1200 μJ/cm^2) and with the lowest sensitivity for the red (2400 μJ/cm^2). Replay wavelengths match very closely with those used at recording, with an error of less than 2%. This wavelength shift can be modified by changing the soaking bath times in the presensitizing process.

Table 1. Relevant results obtained for single-wavelength recording of holographic reflection gratings on BBVPan plates

Recording λ (nm)	Max DE (%)	Energy for max. DE (μJ/cm^2)	Replay λ (nm)	$\Delta\lambda$ (nm)
442	73.7	320	448.6	25.2
532	82.8	1200	536.7	29.0
632.8	74.1	2400	645.9	26.0

One of the key characteristics of this new material is its even response to all the wavelengths we used. Former western emulsions suffered from high absorption in the blue region of the spectrum. This limited their use for recording multiplexed color reflection holograms on a single plate. With the experimental setup described above, we worked not only with three well-separated wavelengths, but with the highest spatial frequencies holographically achievable in each case. The results obtained show that the maximum diffraction efficiency with each of these spatial frequencies is almost constant, with a small drop in the case of the blue wavelength due to the proximity of the absorption band of the silver halide grains, located

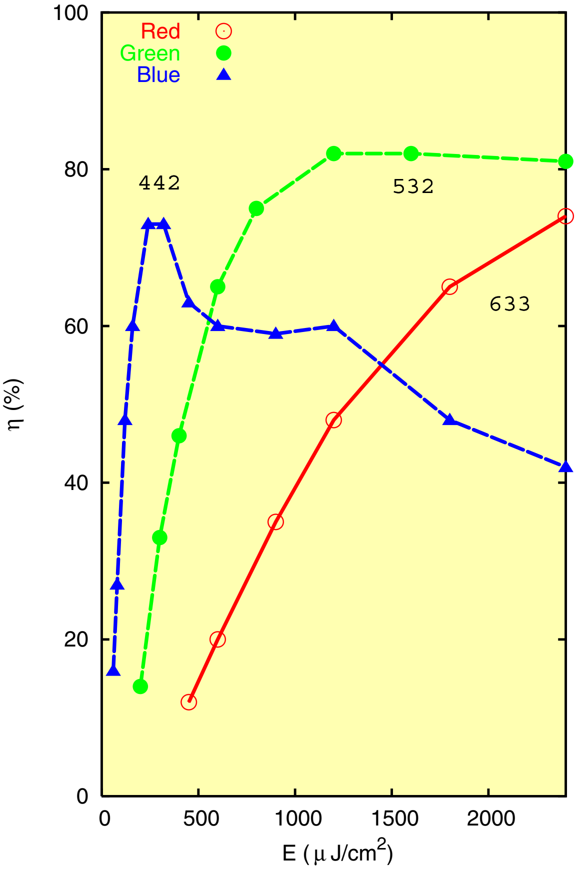

Figure 4. Dependence of the diffraction efficiency of BBVPan plates on exposure energy for each of the recording wavelengths.

at about 400 nm, and the absorption band of the supporting glass plate and the gelatin emulsion. For the red wavelength there is another small drop in diffraction efficiency, but this time due only to the low sensitivity of the plate in this region of the spectrum. Nevertheless, all maximum DE values for single wavelength are well above 70%.

The transmission spectra of the recordings corresponding to the three diffraction efficiency maxima are shown in figure 5. The blue band is affected by the absorption of the ultra fine grain emulsion referred to above, thus reducing the diffraction efficiency of this recording, although the zero order is of the same magnitude as that obtained with the green wavelength.

With all the information obtained after this preliminary study, we multiplexed three reflection gratings, each with a different wavelength, onto a single plate, following the procedure described in section . The best result was obtained with a sequence of exposures with energies of 150 (442 nm) + 250 (532 nm) + 1200 (632.8 nm) μJ/cm^2, at which the diffraction efficiencies of each band are balanced, as shown in table 2, with the corresponding spectral transmission curve shown in figure 6. The DE for all

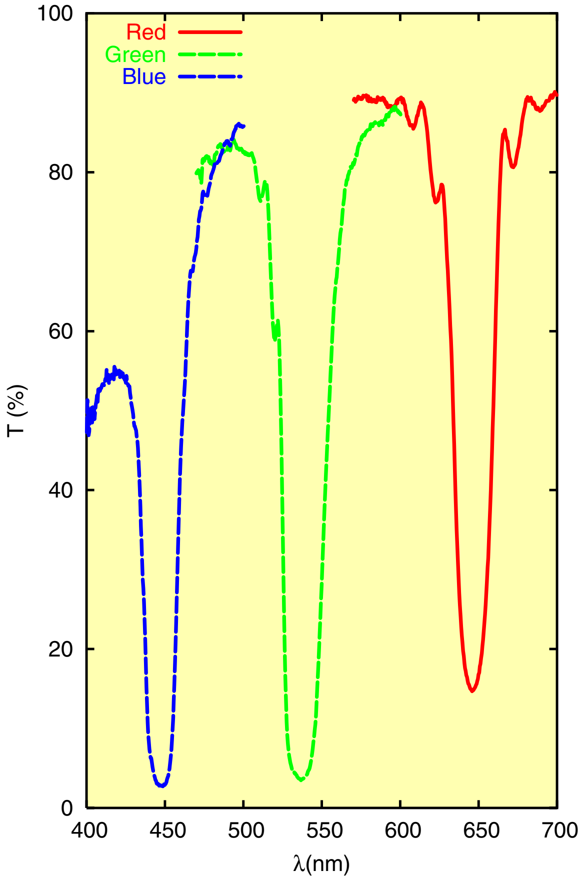

Figure 5. Transmission spectra corresponding to the three single wavelength holographic reflection gratings with maximum DE recorded on three BBVPan plates.

the recordings is higher than 52%, which indicates a high index modulation capacity for this material. Other exposure energy sets were tested, and small changes in one of the exposures were seen to substantially affect the DE of all three bands.

Table 2. Relevant results obtained for multiplexed holographic reflection gratings recorded with three wavelengths on BBVPan plates

Recording λ (nm)	Exposure (μJ/cm^2)	DE (%)	Replay λ (nm)	$\Delta\lambda$ (nm)
442	150	57.1	452.5	19.4
532	250	62.1	546.3	17.2
632.8	1200	52.6	650.8	19.4

In order to check that the effect of crosstalk between diffraction bands was negligible, we applied a model based on Kogelnik's theory with three bands [16]. With this model we obtained the index modulation and effective

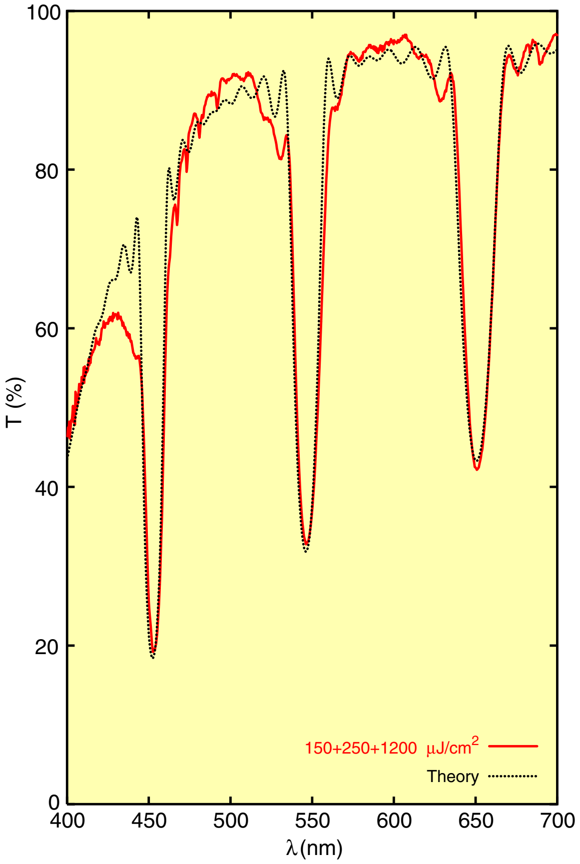

Figure 6. Transmission spectrum of the multiplexed holographic reflection grating recorded on a single BBVPan plate. The dashed line shows the result obtained with the theoretical simulation.

thickness of the multiple band recordings with great accuracy. Experimental data were fitted and a good match was obtained, as can be seen in figure 6, in which the dashed curve corresponds to the theoretical approach. The best result was obtained for an effective thickness d of 7.3 μm. Approaches with three different values of the index modulation n_1, one for each wavelength, were tried, but the best result was obtained when each one had the same value, namely 0.027.

After looking at the results obtained in this study with reflection diffraction gratings, several of the points raised in the introduction may now be discussed. The high diffraction efficiencies obtained with the multiplexed holograms contradicts what has been said about a reduction in diffraction efficiency of multiplexed holograms (although those studies were done with angular multiplexing). In fact, results obtained with this material show that its modulation capacity is greater than that needed to record a unique holographic grating, since if we consider such a case, we can obtain a maximum index modulation of 0.054, while if we use the sum of the three individual

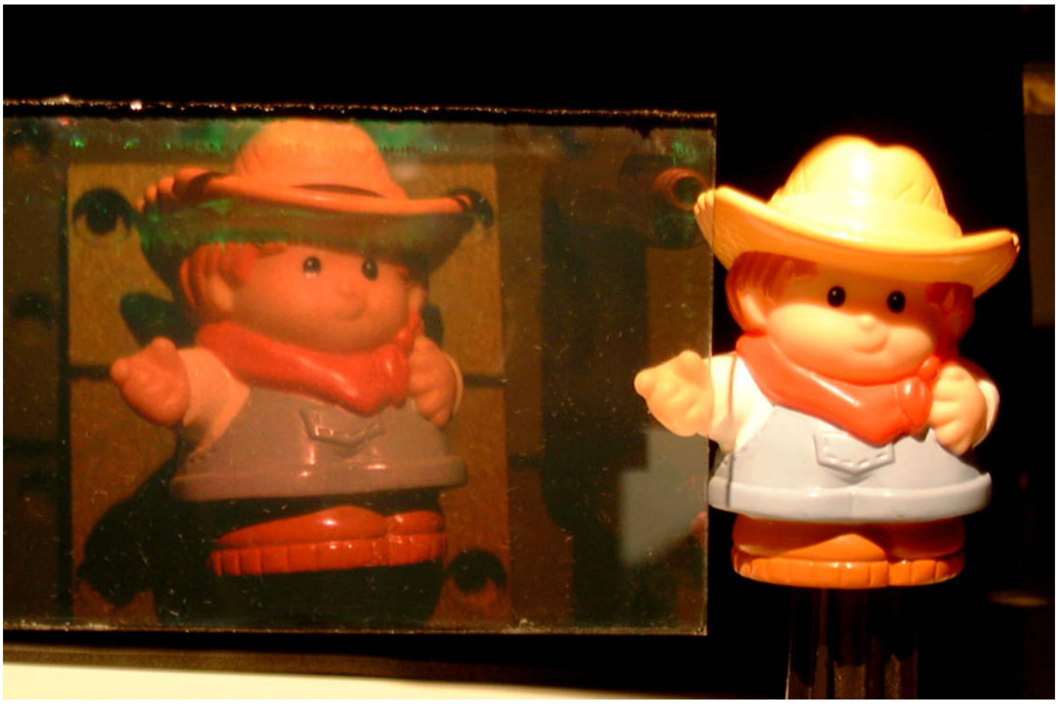

Figure 7. Color reproduction of the final diffuse object hologram compared with the real object under the same reconstruction/illumination source.

index modulations as the storage capacity of the material, a value of 0.081 is obtained. This is much higher than any other reported value for a silver halide emulsion. Therefore, the total DE is not reduced by multiplexing several gratings, but is increased to another value that corresponds to the real storage capacity of this emulsion.

After completing this study with gratings, and considering the sensitivity values obtained, we continued with a study with diffuse object holograms. We chose an object containing tones which were hard to reproduce, such as skin color, yellow-orange, and blue. The best result, one with high brightness and good color reproduction, was obtained with exposure energies of: 225 μJ/cm^2 (He–Cd), 350 μJ/cm^2 (Nd:YAG) and 1.5 mJ/cm^2 (He–Ne), values which are not very far form the optimal values obtained for diffraction gratings. A color reproduction of the final hologram, replayed with an halogen lamp, and with the real object under the same illumination, is shown in figure 7.

Replay wavelengths with an angle of reconstruction of 45° are 445 nm, 538 nm and 639 nm, which are very close to the recording wavelengths. A sample of the transmittance spectrum obtained with the analysis device with the probe beam incident at an arbitrary location of the hologram is shown in figure 8. Estimated diffraction efficiencies for each of the bands are around 20% for the blue and green bands and around 40% for the red, which are

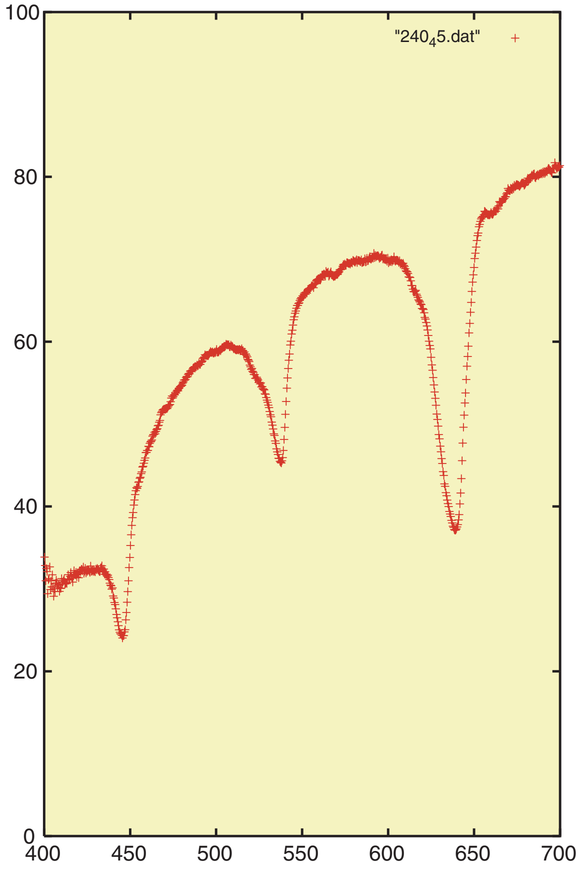

Figure 8. Transmission spectrum of the diffuse object hologram recorded on a single BBVPan plate.

not bad values for a diffuse object. It must be noted that the transmittance spectrum depends on the area of the hologram sampled.

Conclusions

We tested the new BBVPan panchromatic holographic emulsions for reflection holography. The material was first evaluated using single recordings with three different wavelengths, and a DE higher than 72% was reached in all cases. After characterization, the plates were used to record a three-band holographic reflection grating with spatial frequencies from 5000 l/mm to more than 7000 l/mm, all with high diffraction efficiencies, namely over 52% for each of the three bands. The study with diffuse objects rendered good color images with good diffraction efficiencies. With the properties mentioned, this material can be used to manufacture holographic combiners for projection display systems, as well as for color display holograms.

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