Holographic noise gratings for analyzing and optimizing photochemical processings in bleached silver halide emulsions

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ABSTRACT

Recording noise gratings with single-beam exposures in bleached silver halide emulsions is used as a holographic spectroscopy technique in order to analyze and optimize photochemical processing. In particular, rehalogenating type bleachings are analyzed by measuring the transmittance through the recorded and processed holographic plate as a function of the reconstruction angle, the exposure and the concentration of the rehalogenating agent in the bleach bath. The experimental results obtained show us that the analysis of these spurious gratings provides information about the bleaching action during the processing and allows us to identify the optimal concentration of the bleach bath.

1.- Introduction

With recent advances in holographic technology, many types of holographic optical elements (HOE's) are now being used in different optical systems. HOE's are diffractive optical elements, and therefore work by diffracting light from a generalized grating structure with nonuniform groove spacing [1]. This complex diffraction grating transforms the phase of an incoming wavefront to an output phase. To obtain HOE's with high diffraction efficiency it is necessary to record these elements as volume phase holograms [2]. Bleached silver halide emulsions have long been used as a medium for recording volume phase HOE's. This is due to the relatively high sensitivity and ease of processing of this material, improved processing chemistries, commercial films, and the repeatability of the results. Unfortunately, while the resulting phase holograms have high diffraction efficiency, this is usually accompanied by an increase in the scattering of light and a consequent reduction in image quality. Scattering is due to the granular structure of the silver halide material and takes place both at the recording and at the reconstruction stage.

Noise gratings are an important source of scattering in silver halide emulsions. These gratings are spurious structures recorded at the same time as the desired hologram due to scatter from inhomogeneities in the photosensitive material [3]. The noise gratings reduce diffraction efficiency and signal-to-noise ratio during hologram reconstruction and significantly hamper efforts to obtain high-quality HOE's. Due to the fact that silver halide emulsions consist of fine grain silver halide crystals suspended in a gelatin base, the effect of noise gratings on HOE's recording in photographic emulsions is significant [4, 5]. During HOE formation the scattered field from the photosensitive silver grains interferes with the incident beams and gives rise to noise gratings after processing. The efficiency of these noise gratings depends to a great extent on the chemical processing (if the process introduces very small emulsion

thickness changes, the noise grating efficiency is quite pronounced) [6, 7], the relative polarization between the recording and reconstruction beams [8], the exposure [7], the beams ratio [9] and the reconstruction wavelength [6].

Most papers on noise gratings have explored the properties of these spurious gratings and the methods used to eliminate the negative effect of these gratings. However, it is possible to use the analysis of the characteristics of noise gratings as a technique for studying the mechanism of the chemical processing of the recording material, that is to say, as a holographic spectroscopy technique [13].

In this paper we use noise grating as a method of analysis and optimization of holographic recording materials, basically bleached emulsions. We have considered rehalogenating and reversal bleaches and silver halide sensitized gelatins (SHSG). In Section §2 we describe these chemical processings and we explore some properties of noise gratings recorded with single beam exposures in Agfa 8E75 HD emulsions by performing a set of diagnostic measurements. In Section §3 we analyzed the experimental results obtained. Finally, conclusions are presented in Section §4.

2.-Experiment

Bleached silver halide emulsions have been an important recording medium for obtaining high efficiency holograms and over the last 30 years many papers have been published in which different types of photochemical processing and the experimental results obtained when using them have been presented and analyzed [14]. In this way, holography has served as a technique with which to optimize different types of photochemical processing and it can be said that "if high diffraction efficiencies are obtained, processing is optimized, and, if not, it isn't." Nevertheless, one characteristic of all bleached silver halide holograms, no matter what the processing

used, is the level of noise that degrades the quality of the holographic image. As we said in the Introduction, holographic noise gratings are one important source of noise.

The experimental results that we are familiar with today show that it is possible to obtain HOE's with high diffraction efficiency and low levels of noise given that the photochemical processing in many cases has already been optimized. In order to demonstrate the possibilities that noise gratings offer as a technique for the analysis and optimization of photochemical processing, we have chosen a typical, well-known type of processing in which bleaching takes place after development without a fixation step [15, 16].

The basic bleach used for this evaluation is an R-10 rehalogenating type bleach [15] with a potassium dichromate (10 g) oxidizer, potassium bromide and sulphuric acid (10 mliter) in 1 liter of distilled water. The amount of potassium bromide (the rehalogenating agent) varied between 0 g (standard R-9 mixture) and 35 g (standard R-10 mixture). The reason for this choice was because this bleach bath has a simple variant that converts it into a reversal-bleach (R-9) when there is no rehalogenating agent present. This allows us to analyze rehalogenating bleaches and reversal bleaches at the same time.

In an R-10 rehalogenating bleach, the bleach bath contains a rehalogenating agent (potassium bromide) which converts most of the developed silver back into a silver halide [16, 17]. In this case a phase hologram is obtained mainly by the transfer of silver halide between the unexposed and exposed areas. R-10 bleach has the advantage that changes in the thickness of the emulsion layer are minimized [15], since the overall removal of silver salts from the emulsion is minimal [17]. Therefore holographic gratings can be obtained in which the Bragg angle coincides with the recording angle even though sometimes there is a displacement of the Bragg angle which is caused by shear-type effects [18]. The optimization of this processing depends upon the careful adjustment of the ratio of the concentrations of potassium dichromate

and potassium bromide in its composition.

If we use an R-10 bleach with a high potassium bromide content, there is a clearly rehalogenating response [16], and a great diffusion of material throughout the exposed and unexposed areas takes place. However, the scattering of light increases sharply due to the fact that the particles that remain in the material are larger [19]. If on the other hand, the concentration of the rehalogenating agent (potassium bromide) is reduced, the scattering of the light decreases, but so does the diffraction efficiency [16]. Thus it is possible to reach a level of concentrations in which the potassium bromide of the bleach bath precipitates directly on the emulsion thereby greatly increasing light absorption and the resulting phase modulation and hence the diffraction efficiency are then close to zero.

On the other hand, if potassium bromide is completely eliminated, the bleach bath changes its activity completely and becomes a reversal bleach (R-9), in which the bleach converts the developed silver into Ag^+ which goes into solution leaving a phase hologram made up of the unexposed silver halide grains [16]. Reversal bleaches give high diffraction efficiencies and low values of scattering since the size of the unexposed silver halide grains is not affected significantly by the processing solutions. However, in this case, variations in thickness appear after processing, which clearly affect the geometry of the Bragg planes. This photochemical behavior of the bleaching as a function of the quantity of the rehalogenating agent used in its composition, as shown in this paper, has also been analyzed in studies of holographic gratings and it also coincides with studies that led to the optimization of SHSG [20, 21] in which R-10 is also a very important step in the processing.

It is possible to record noise gratings with a single-beam of coherent light. In this situation, the incident beam interferes with its own scattered radiation field to record the holograms. Syms and Solymar [4] have pointed out that one method of analyzing these gratings is to measure the transmittance of the plate after processing as a function

of the reconstruction angle. The scattered field from noise grating causes a drop in the transmitted intensity when the single-beam hologram is reconstructed under similar conditions to those used for recording.

In our experiments noise gratings were recorded by a single collimated beam polarized perpendicular to the plane of incident, from an He-Ne laser in Agfa-Gevaert 8E75 HD emulsion as we can see in Figure 1 (a). Single beam exposures were made with the illuminating beam entering normal to the surface of the photographic emulsion and with twelve exposures varying between $20 \mu\text{J}/\text{cm}^2$ and $1300 \mu\text{J}/\text{cm}^2$. Spurious reflections were eliminated by placing an index matched absorbing layer against the glass side of the photographic plate. On the other hand, the stability and coherence requirements of the optical beam must be maintained only over the $6 \mu\text{m}$ thickness of the emulsion.

The exposed plates were developed in AAC developer [22]. The developed plates were rinsed briefly and bleached without a fixation step. The developer and bleach formulas, and process schedule the concentrations of potassium bromide used in these experiments are listed in Table I.

After processing, we measured the intensity of the transmitted beam through the plates as a function of the reconstruction angle as we can see in Figure 1 (b), using the same wavelength and polarization that were used during the recording stage. In order to confirm the presence of noise gratings we measured the transmittance with a perpendicular polarized and with a parallel polarized reconstruction beam. In the last case we obtained a considerably smaller dip in transmission as Kostuk and Sincerbox pointed out [8].

The measurements of the angles were taken by using a rotation stage with a precision of 0.02° , also used in recording, which assured sufficient sensitivity. Measurements of the transmittance of the exposed and processed plates were obtained at 0.5° increments around the angle of the recording beam and the error in the transmittance

of these plates is $\sim 4\%$. In all cases the experimental measurements have been corrected by using the Fresnel equations in order to take into account the reflections at the two surfaces of the glass plate and on the surfaces of the emulsion layer. Figure 2 is a typical plot of transmittance as a function of reconstruction angle for an exposed and processed plate showing a pronounced drop in efficiency at the construction angle (0°) due to noise gratings. In this figure the different parameters that were used in this study are shown: I_t is the intensity transmitted by the plate in relation to the incident intensity, ΔI_n is the diffraction efficiency of the recorded noise gratings which responds to the intensity scattered by noise gratings, and the quantity ΔI_{sa} is related to the average absorption of the plate and to the scattering that does not correspond to noise gratings. The combined average absorption and scattering for each plate is determined at an angle $\sim 20^\circ$ (i.e., where the transmittance is maximum).

In the next section we shall see that it is possible to obtain information about the effects of rehalogenating type bleaches on diffraction efficiency and scattering by using plots of the previous parameters I_t , ΔI_n and ΔI_{sa} as a function of exposure and the concentrations of potassium bromide of the bleach bath.

3.-Experimental results and discussion

In Figure 3 we show the parameter associated with diffraction efficiency of the noise gratings, ΔI_n , as a function of exposure for the different concentrations of potassium bromide used. As can be seen in all of the situations analyzed, there exists an exposure value of between $50 \mu\text{J}/\text{cm}^2$ and $200 \mu\text{J}/\text{cm}^2$, with which the efficiency ΔI_n is maximized. When this level of exposure is surpassed, efficiency decreases due to the fact that these high levels of exposure correspond to the non-linear zone of the developer. On the other hand, if the concentration of potassium bromide is increased,

the diffraction efficiencies ΔI_n obtained increase as well, and we find that for a concentration of between 8.75 g/liter and 26.25 g/liter, maximum efficiencies are reached.

When the concentration of potassium bromide is 0 g/liter, which is the case with reversal bleach R-9, the behavior of this bleach is the same as when the concentration is 1.09, 1.65 and 2.18 g/liter. But we should not rely solely upon these graphs when comparing these last four concentrations because even though we obtain same values for ΔI_n , each value is due to a different mechanism. For the 0 g/liter curve, there is almost no noise grating response because in this case we have changed the thickness and therefore Bragg condition is not met for the reconstruction process. However, for concentrations of 1.09, 1.65 and 2.18 g/liter, we have a clear example of potassium bromide precipitation on the emulsion as can be seen in Figure 4 which shows parameter ΔI_{sa} , which gives us information about scattering and absorption as a function of exposure. Note that ΔI_{sa} is higher for these concentrations than for the 0 g/liter concentration.

Figure 4 clearly shows that by increasing the concentration of potassium bromide, scattering and absorption also increase and their behavior in relation to exposure is not uniform. Potassium bromide precipitation and its relation to the concentration of silver and the non-linearity of the developer can be seen in the graphs which correspond to concentrations of between 1.09 and 2.18 g/liter, especially 1.65 and 2.18 g/liter. There isn't a level of concentration that would allow us to carry out the rehalogenating processing and the reordering of silver halide even though we could assume that there would be no appreciable change in thickness. This indicates that modulation is practically zero. Therefore, high levels of absorption and scattering and low diffraction efficiency are achieved because the noise gratings are not stored.

Upon increasing the concentrations of potassium bromide above 3.30 g/liter, there is a clear optimization of the bleaching agent, which then behaves like a true

rehalogenating bleach, producing high efficiencies in the noise gratings. This implies that there is no change in thickness and that modulation is high. Additionally, the levels of absorption and scattering of light are lower than in the three previous cases. If the concentration of potassium bromide is increased even more, above 17.50 g/liter, absorption and scattering increase again due to the increase in the size of the grain, especially at high exposure, in which the metallic silver is more evident and therefore the rehalogenating process is more significant.

Figure 5 shows parameter I_t which corresponds to the transmittance for a reconstruction angle of 0° . The lower the value of I_t and ΔI_{sa} , the clearer it is that the processing has been optimized for that particular concentration of potassium bromide. Thus, we can see that with a concentration of 17.50 g/liter and an exposure between $90 \mu\text{J}/\text{cm}^2$ and $300 \mu\text{J}/\text{cm}^2$, the best results are obtained.

The experimental results shown in Figures 3, 4 and 5 can be summarized in Figures 6, 7 and 8 in which we have shown the values for the parameters ΔI_n , ΔI_{sa} and I_t , respectively, as a function of the concentration of potassium bromide in the bleach bath for four different exposures. If we extend the curves which corresponds to ΔI_n in Figure 6, we can clearly see that once a certain level of potassium bromide (4.37 g/liter) is reached, noise gratings are stored. Figure 7 shows that absorption and scattering also decrease in this zone. In addition, we can observe in these last three graphs that concentrations between 17.50 and 26.25 g/liter give the best results in terms of noise grating efficiency and loss of light due to absorption and scattering and that the best concentrations for the rehalogenating bleach R-10 with 10 g of potassium dichromate and 10 mliter of sulfuric acid in 1 liter of distilled water. As a result we can conclude that the experimental curves lead us to a clear optimization of the processing from the perspective of noise gratings.

4.-Conclusions

For a long time the recording of holographic gratings and the measurement of their diffraction efficiency have led to the analysis and optimization of different photochemical processes which can be used in the production of holograms, diffraction gratings or high quality HOE's with high diffraction efficiencies. In this paper we have shown that it is possible to analyze and optimize the chemical bleaching processes that are produced during the bleach step. This is done by analyzing transmittance as a function of the reconstruction angle and the parameters ΔI_n , ΔI_{sa} and I_t as a function of exposure and the composition of the bleach bath for noise gratings recorded with a beam of light in photographic emulsions. The results obtained are similar to those obtained with diffraction gratings, thereby proving that noise gratings can be used as another technique with which to analyze photochemical processing. Our experimental results clearly confirm the effects of chemical processing on recorded noise gratings in bleached silver halide emulsions. In particular we can see that different behaviours are produced when the amount of the rehalogenating agent is changed.

The simplicity of our experimental set-up and the ease with which measurements can be taken and noise gratings can be detected make this method quite attractive, especially considering the low stability and light coherence that are required for its use.

Finally, it is also very important to point out the applications of this method in optimizing the quality of HOE's since in the case of bleached photographic emulsions, in addition to contributing information about the optimization of processing, it also contributes information about the source of noise and possible ways to eliminate it.

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FIGURE CAPTIONS

- Figure 1: Experimental set-up for (a) recording and (b) reconstruction of the noise gratings.
- Figure 2: The definition of the characteristic parameters of noise gratings: ΔI_n , ΔI_{sa} and I_t .
- Figure 3: ΔI_n as a function of exposure for the different concentrations of potassium bromide in the bleach bath.
- Figure 4: ΔI_{sa} as a function of exposure for the different concentrations of potassium bromide in the bleach bath.
- Figure 5: I_t as a function of exposure for the different concentrations of potassium bromide in the bleach bath.
- Figure 6: ΔI_n as a function of the concentration of potassium bromide in the bleach bath for four different exposures.
- Figure 7: ΔI_{sa} as a function of the concentration of potassium bromide in the bleach bath for four different exposures.
- Figure 8: I_t as a function of the concentration of potassium bromide in the bleach bath for four different exposures.

TABLES

- Table I: Processing schedule, developer and bleach bath formulas and levels of potassium bromide concentration used in the experimental study.

TABLE I

PROCESSING SCHEDULE							
1.- Develop with AAC developer for 5 minutes at 20° C							
2.- Rinse in running water for 1 minute.							
3.- Bleach for 1 minute after the plate has cleared at 50° C.							
4.- Wash in running water for 5 minutes.							
5.- Dry in air.							
FORMULAS							
(a) AAC developer formula							
Ascorbic acid				18 g			
Sodium carbonate				60 g			
Distilled water to make				1 liter			
(b) Bleach formula							
Potassium dichromate				2 g			
Sulfuric acid				1 mliter			
Potassium bromide				As specified			
Distilled water to make				1 liter			
AMOUNTS OF POTASSIUM BROMIDE USED (g)							
0 (standard R-9 bleach)							
1.09	1.65	2.18	3.30	4.37	8.75	17.50	26.25
35 (standard R-10 bleach)

FIGURE 1

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FIGURE 2

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FIGURE 3

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FIGURE 4

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FIGURE 5

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FIGURE 6

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FIGURE 7

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FIGURE 8

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