PROCEEDINGS OF SPIE REPRINT

SPIE—The International Society for Optical Engineering

Reprinted from

Holographic Materials V

26 January 1999
San Jose, California

Volume 3638

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Box 10, Bellingham, Washington 98227 USA. Telephone 360/676-3290.

Silver halide sensitized gelatin holograms from BB-640 plates

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ABSTRACT

In this paper we present the results of our research on the recording of SHSG holographic transmission gratings using the new BB-640 photographic emulsion, a red sensitive ultra-fine-grained emulsion from Holographic Recording Technologies. The exposed plates were processed following a process similar to that optimized by Fimia et al. for Agfa 8E75 HD plates but with the temperature of the bleaching bath modified to 70°C. This increase in temperature improves the diffraction efficiency but does not produce an increase in absorption and scattering, as opposed to what happens in the case of the Agfa 8E75 HD emulsion. The influence of the developer on various holographic parameters is analyzed and discussed.

Keywords: Holographic Recording Materials, Silver Halide Emulsions, Volume Holograms.

1. INTRODUCTION

Silver halide sensitized gelatin (SHSG) is an interesting technique for recording phase holograms which has some advantages over other procedures. It can be considered as an hybrid technique between dichromated gelatin and silver halide emulsion so it combines the relatively high sensitivity of photographic emulsions with the well known low scattering and high diffraction efficiency corresponding to dichromated gelatin. The main success of SHSG processing consists in the conversion of the variations in optical density between the exposed and non-exposed zones of the emulsion into a variation in the degree of hardening of the emulsion gelatin¹, so that a phase hologram is obtained with an advance over bleached holograms, namely the removal of silver halide grains after fixing which increases the diffraction efficiency and lowers the scattering. The difference of the degree of hardening of the gelatin is a consequence of cross-links created by Cr^{3+} ions between the gelatin chains. This action takes place in the vicinity of the oxidized silver grains where the developed silver is oxidized to Ag^+ and the Cr^{6+} ions are reduced to Cr^{3+} during the bleaching process. An amplification of the latent image occurs during the dehydrating step by sequential baths in isopropanol and water at different concentrations. Agfa 8E75 HD and 8E56 HD emulsions have proven to be suitable materials to be used in the SHSG process^{2,3}. But these emulsions will no longer be produced. New materials have sprung up in the market like Slavich material from Russia, Red Star plates from Great Britain and BB plates from Germany. We show here that the BB-640 material is not only a substitution, but may offer better results than Agfa 8E75 HD. By modifying some steps of the SHSG optimized procedure from reference 2 we will also show the influence of some parameters in the final quality of the holograms obtained from BB-640 and Agfa 8E75 HD plates.

2. EXPERIMENTAL

2.1. Initial experimental considerations

In order to increase the sensitivity of the plates, these were pretreated by immersing them in a solution of distilled water with a sodium sulphite concentration of 1% and urea concentration of 5% (by weight) for 10 min at 20°C, after a rinse in running water for 1 min at 20°C the plates were dried for 24 h at 20°C and 60% RH. The urea of this solution softens the gelatin, which is hardened to a high degree for BB-640 plates.

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2.2. D -log E curves

Experiments were carried out with BB-640 plates. Unslanted holographic gratings were recorded on BB-640 emulsion by the interference of two collimated beams from a He-Ne laser (633 nm). The beam ratio was 1:1, and the polarization plane was normal to the plane of incidence. The angle between the normal of the plate and each of the incidence beams was $\theta = 22.5^\circ$, therefore the interbeam angle was $2\theta = 45^\circ$. With this arrangement the spatial frequency of the diffraction gratings came to be ~ 1200 lines/mm.

The exposed plates were developed rinsed in running water for 1 min and fixed in F-24 fixer for 2 min, all solutions were at 20°C and amplitude holograms were obtained using this procedure. To show the influence of development in the sensitivity of holograms, four different developers were used and also different times of development were chosen: 5 min when D-19 is used, 4 min for AAC⁴, 3 min for MAAC⁵ (a metol-ascorbic developer) and 2 min for CW-C2⁶.

The transmitted I_t and incident I_i beam intensities were measured to obtain the transmittance of the plates as the ratio $T = I_t/I_i$. The optical density D was calculated as $D = \log_{10}(1/T)$ and the D -log E curves were obtained.

The results of the optical density are plotted as a function of exposure in Figure 1, where the influence of development in D -log E curves is shown. The slope of the linear zone of the D -log E curves is greater for D-19 developer, implying that D-19 gives a greater contrast, while holograms developed in CW-C2 give the lowest. The lowest maximum density is obtained when CW-C2 developer is used, being the maximum density for D-19 slightly higher than that for AAC. Holograms developed with MAAC present real high values of the optical density (maximum density near 8), even though the solarization region is not reached in the range of exposures studied.

Figure 1.- Density as a function of exposure for hypersensitized BB-640 plates and various developers.

2.3.-Trials to soften the gelatin

An important characteristic of BB-640 emulsion is that the gelatin of this emulsion is hardened to a high degree, so that distortion of the planes of interference during processing is avoided. However, it is necessary to soften the gelatin in order for high diffraction efficiencies to be obtained for holograms recorded in silver halide sensitized gelatin. We tried to soften the gelatin by other ways in addition to pretreatment. In this direction the temperature of the bleach bath included in the schedule procedure of Table I was increased from 50°C to 70°C and another experiment was made by immersing the plates in distilled water at 70°C after the bleach bath.

Unslanted holographic gratings were recorded on BB-640 and Agfa 8E75 HD using the same geometry used in recording the amplitude holograms. The exposed plates were processed according to SHSG processing of Table I, using D-19 developer, so that phase holograms were obtained. The diffraction efficiency of the phase holograms is calculated as the ratio of the diffracted beam intensity to the incident power, and in order to take into account Fresnel losses and absorption due to the

glass substrate this expression was corrected by multiplying by an appropriated factor.

In Figure 2 diffraction efficiency as a function of exposure is shown for BB-640 and Agfa 8E75 HD plates with and without pretreatment, and bleached at 50°C (a), and when the bleach bath temperature was increased to 70°C (b). The curves of Agfa plates are displaced to the left of the exposure axis, suggesting that Agfa plates have a higher sensitivity than BB-640 plates, due to the lower silver-halide grain size of BB-640 emulsion⁷.

Table I.- Processing schedule.

A. Hyper sensitization (included, not included)	
B. Exposure	
C. Development	
1. Development.	
2. Rinse in running water for 2 min.	
3. Bleach for 30 s after the plate has cleared at 50°C or 70°C.	
4. Rinse in running water for 2 min.	
5. Soak in nontanning fixer F-24 for 2 min.	
6. Wash in running water for 10 min.	
8. Dehydrate in 50% isopropanol for 3 min.	
9. Dehydrate in 90% isopropanol for 3 min.	
10. Dehydrate in 100% isopropanol for 3 min.	
11. Dry in desiccator for 24 h at 20° C and RH < 20%.	
<i>All solutions are at 20° C except the bleaching step.</i>	
Bleach formula	
<i>Solution A:</i>	
Ammonium dichromate	20 g
Sulfuric acid	14 mL
Distilled water	1 L
<i>Solution B:</i>	
Potassium bromide	92 g
Distilled water	1 L
<i>Just before use, mix one part A with ten parts distilled water, then add 30 parts B.</i>	

As can be seen from Figure 2, pretreatment increases the diffraction efficiency of the plates, being a more influential step for BB-640 plates, because the gelatin of BB-640 plates is harder than that of Agfa^{7,8}, so that developer products can hardly penetrate into the gelatin because of the harder BB-640 emulsion, unless it is softened. Holograms recorded on Agfa and bleached at 70°C also show high diffraction efficiencies, but pretreatment slightly increases these results. The best results achieved are for pretreated plates and a bleach bath temperature of 70°C for both Agfa 8E75 HD and BB-640 plates. The effect of an increase in the temperature of the bath after the fixing step was also studied⁹. The plates were immersed in distilled water at 70°C for 10 min after the fixing bath. In Figure 3 diffraction efficiency as a function of exposure is presented, showing that this modification doesn't increase the diffraction efficiency, but lowers it.

2.4. Influence of the developer

Development is crucial, since at this step the latent image is formed as a combination of zones with metallic silver and zones with silver halide grains. After exposition the latent image is formed as a distribution of silver specks. When the developer penetrates into the gelatin, the developer is oxidized in the vicinities of these specks whereas silver ion is reduced to silver¹.

Figure 2.- Diffraction efficiency, η , as a function of exposure for Agfa 8E75 HD and BB-640 plates and for bleach bath temperatures of (a) 50°C and (b) 70°C.

Figure 3.- Diffraction efficiency, η , as a function of exposure for hypersensitized BB-640 plates and for different temperatures of the bath of water used after the fixing step.

The influence of the development solution in the quality of the final hologram takes place through factors such as pH (influencing the speed of the reduction reaction), concentration of KBr which avoids the development of unexposed grains, concentration of sulfite (its tendency to react with the oxidation products of the developer must be taken into account), or oxidation products (some oxidation products absorb light affecting the final diffraction efficiency).

Phase holograms were obtained from BB-640 emulsion. Unslanted holographic gratings were recorded at two interbeam angles: $2\theta = 32.5^\circ$, $2\theta = 45^\circ$ yielding spatial frequencies of 850 and 1200 lines/mm respectively, and the exposed plates were processed according to the SHSG processing schedule shown in Table I including pretreatment and bleaching at 70°C. The development step was modified in order to find the influence of different developers in SHSG processing.

In Figure 4 diffraction efficiency is shown as a function of exposure for BB-640 plates pretreated and bleached at 70°C. Comparison is made with two non tanning ascorbic acid developers, AAC and MAAC and another two developers: D-19 and CW-C2. Diffraction efficiency (after allowing for reflections) as a function of exposure is shown in Figure 4 (a) for diffraction gratings with a spatial frequency of 850 lines/mm. Diffraction efficiency of holograms developed in D-19 developer is the highest achieved. Due to the high content of sulfite, tanning action of D-19 developer¹⁰ occurs in the bleach bath, oxidation products from the developer crosslink the gelatin in the exposed zones, which could enhance the effect of the chromium ion resulting in higher efficiency. CW-C2 gives worse results. Now tanning action takes place during development. This action could be opposite to the trials of softening the gelatin by means of a pretreatment and an increase in the bleach bath temperature, so bleach products couldn't easily penetrate into the gelatin. Also holograms developed in MAAC give lower values of diffraction efficiency in comparison with D-19 and AAC developers, showing very low values at high exposures.

When holograms with spatial frequency of 1200 lines/mm are recorded, the maximum achieved diffraction efficiency is obtained when the holograms are developed in AAC, 96%, whereas for D-19 developed holograms a slightly lower diffraction efficiency is obtained, 90%. Because AAC is a non tanning developer these results show that chromium is efficient enough to promote local hardening of the gelatin¹¹, so that tanning development could not only be an advantage, but as in the case of D-19 could lead to grain growth increasing absorption and scattering and, thus, lowering diffraction efficiency. Again lower peak diffraction efficiencies are obtained when CW-C2 and MAAC developers are used: 66%, 73%, respectively (after allowing for reflections), but at a spatial frequency of 1200 lines/mm an increase in diffraction efficiency from that of 850 lines/mm is observed for both developers, being more substantial for the non- hardening metol-ascorbic developer. Again, low efficiencies are obtained for MAAC developer at high exposures.

Figure 4.- Diffraction efficiency, η , as a function of exposure for hypersensitized BB-640 plates and different developers. Two spatial frequencies are considered.

In order to evaluate the absorption and scatter losses, a percentage as a function of exposure was calculated as $A\&S = 100 - \eta - \tau$ where η is the diffraction efficiency and τ is the efficiency of zero-order, calculated as the ratio of the transmitted beam intensity to the incident power, taking into account Fresnel losses. Figure 5 shows the results for absorption and scatter losses for hypersensitized plates developed in four different developers, the diffraction gratings were recorded at a spatial frequency of 1200 lines/mm. High values of absorption and scatter are obtained for CW-C2 and MAAC developers, as can also be inferred from visual inspection of the processed plates which are stained to a high degree. Absorption and scatter of holograms developed in D-19 is lower, but the best results at this spatial frequency are obtained when AAC developer is used. Colorless oxidation products from ascorbic acid after development allows low absorbing holograms to be obtained when using a developer containing this agent.

Figure 5.- Absorption and scattering, A&S, as a function of exposure for hypersensitized BB-640 plates and different developers. Spatial frequency equal to 1200 l/mm.

A comparison of the absorption and scattering between BB-640 and Agfa 8E75 HD plates is made in reference 12 for plates developed in D-19 developer with a spatial frequency of 1200 lines/mm. The plates followed the SHSG procedure of Table I. For Agfa 8E75 HD plates pretreated and bleached at 70°C the total losses caused by absorption and scatter took values from 15 to 22%, whereas for BB-640 plates total losses were as low as 3-7%.

2.5. Comparison of BB-640 results

After watching the benefits of pretreatment and a bleach bath temperature of 70°C we processed holograms recorded on BB-640 plates according to the schedule procedure of Table I including development in D-19 and bleaching at a temperature of 70°C. Diffraction efficiency versus exposure is shown in Figure 6 for BB-640 plates including the best results obtained for the SHSG process when D-19 developer is used and for diffraction gratings recorded on different plates at a spatial frequency of 1200 lines/mm^{2,11,13}. In order to achieve a meaningful comparison, all results were corrected so that Fresnel losses were taken into account. The maximum achieved diffraction efficiency of 90.3% (after allowing for Fresnel losses) for BB-640 plates is the highest ever obtained for transmission holograms following SHSG processing with developer D-19 at 1200 lines/mm.

3. CONCLUSIONS

The influence of hypersensitization in the SHSG procedure is studied in this work showing that this influence is more important for BB-640 plates than for Agfa 8E75 HD plates due to the high degree of hardening of the emulsion gelatin of these plates. Also the increase of the bleach bath temperature from 50°C to 70°C is beneficial for phase holograms recorded on BB-640 and on Agfa 8E75 HD. Our research into development reveals that D-19 and AAC developers are more suitable for the optimized SHSG processing of Table I than CW-C2 and MAAC at spatial frequencies of 850 lines/mm and 1200 lines/mm. The results presented in this work for holograms derived from BB-640 plates are some of the best reported for the SHSG technique. The very high diffraction efficiency and low absorption and scatter obtained breaks new ground with regard to results obtained with experiments with SHSG holograms. This confirms that BB-640 plates are a potential replacement for Agfa 8E75 HD emulsion.

ACKNOWLEDGMENTS

This work was financially supported by the Comisión Interministerial de Ciencia y Tecnología (CICYT) of Spain (project MAT97-0705-C02-02).

Figure 5.- Comparison with the results obtained by other authors. Developer: D-19.

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