Holography 2000

Tung H. Jeong
Werner K. Sobotka
Editors

10–14 July 2000
St. Pölten, Austria

Sponsored by
Abteilung für Kultur und Wissenschaft des Amtes der NÖ Landesregierung (Austria)

Cosponsored by
VFG—Vienna Print & Publishing (Austria)

Published by
SPIE—The International Society for Optical Engineering

Volume 4149

SPIE is an international technical society dedicated to advancing engineering and scientific applications of optical, photonic, imaging, electronic, and optoelectronic technologies.

The papers appearing in this book compose the proceedings of the technical conference cited on the cover and title page of this volume. They reflect the authors' opinions and are published as presented, in the interests of timely dissemination. Their inclusion in this publication does not necessarily constitute endorsement by the editors or by SPIE. Papers were selected by the conference program committee to be presented in oral or poster format, and were subject to review by volume editors or program committees.

Please use the following format to cite material from this book:

Author(s), "Title of paper," in *Holography 2000*, Tung H. Jeong, Werner K. Sobotka, Editors, Proceedings of SPIE Vol. 4149, page numbers (2000).

ISSN 0277-786X
ISBN 0-8194-3801-4

Published by
SPIE—The International Society for Optical Engineering
P.O. Box 10, Bellingham, Washington 98227-0010 USA
Telephone 1 360/676-3290 (Pacific Time) • Fax 1 360/647-1445
<http://www.spie.org/>

Copyright©2000, The Society of Photo-Optical Instrumentation Engineers.

Copying of material in this book for internal or personal use, or for the internal or personal use of specific clients, beyond the fair use provisions granted by the U.S. Copyright Law is authorized by SPIE subject to payment of copying fees. The Transactional Reporting Service base fee for this volume is \$15.00 per article (or portion thereof), which should be paid directly to the Copyright Clearance Center (CCC), 222 Rosewood Drive, Danvers, MA 01923 USA. Payment may also be made electronically through CCC Online at <http://www.directory.net/copyright/>. Other copying for republication, resale, advertising or promotion, or any form of systematic or multiple reproduction of any material in this book is prohibited except with permission in writing from the publisher. The CCC fee code is 0277-786X/00/\$15.00.

Printed in the United States of America.

Optimization of fixation-free rehalogenating bleach for BB-640 holographic plates

C. Neipp^{*1}, A. Beléndez¹ and I. Pascual²

¹Departamento de Física, Ingeniería de Sistemas y Teoría de la Señal
Universidad de Alicante, Apartado 99, E-03080 Alicante. SPAIN

²Departamento Interuniversitario de Óptica
Universidad de Alicante, Apartado 99, E-03080 Alicante. SPAIN

ABSTRACT

Fixation-free rehalogenating bleaching is an interesting process for the production of phase holograms. The shrinkage of the emulsion is reduced in comparison with other bleaching methods (reversal bleaching or rehalogenating bleaching with fixation). In this paper we present experimental results for fixation-free rehalogenating bleached holograms derived from the novel BB-640, a red-sensitive ultra-fine grain emulsion from Holographic Recording Technologies. The influence of the Potassium bromide concentration in the bleach solution on the final quality of the holograms is also studied. The concentrations of the different components of the bleach solution are adjusted to obtain the highest values of the diffraction efficiency. We studied transmission and reflection fixation-free bleached holograms. We will show that really high diffraction efficiencies can be obtained, as high as 87% for transmission bleached holograms recorded on BB-640 plates, and 72% for reflection bleached holograms.

Keywords: Holography, Holographic recording material, Photographic emulsion, Photosensitive processing

1. INTRODUCTION

Silver-halide emulsions are one of the most widely used recording materials. Bleaching have proven to be an interesting technique to obtain phase holograms with high diffraction efficiencies from silver halide emulsions. The first advances in bleaching techniques were made by Cathey¹ for laser-recorded holograms. After his work several bleaching processes were studied, like ferricyanide and copper bleaches, introduced by Upatnieks², or the Kodak R-10 bleach, which was improved by McMahon and Franklin³. An important contribution to the bleaching technique was made by Phillips and Porter⁴ by using ferric nitrate in the bleach bath. They also introduced the Para-Benzoquinone (PBQ) bleach, achieving high quality holograms⁵. The main problem linked with working with this bleach is that it is hazardous, this demanding that strict precautions are taken.

In the conventional techniques of bleaching, also called rehalogenating bleaches, the unexposed silver-halide grains are removed from the emulsion in a fixing bath⁶. The rehalogenating bleach contains in addition to an oxidizing agent, an alkali halide, usually potassium bromide, which converts the developed silver back into a silver halide. Thus, in the bleach bath a refractive index modulation is created between the exposed and the unexposed zones. Because this technique is associated with removal of material, the emulsion shrinks after the procedure, so that the geometry of the fringes created in the hologram is altered. This is critical in reflection holograms. This problem can be solved by using rehalogenating techniques, but removing the fixation step from the procedure. The fixation-free method was discovered by Hariharan⁷, and was subsequently improved by Crespo et al⁸ and Kostuk⁹. Kostuk obtained high values of diffraction efficiency, 65 %, for reflection holograms recorded on Agfa 8E75 HD emulsion. The plates were developed with a variant of CW-C1 mixture, and bleached with a modified version of the R-10 bleach. In order to optimize the bleach bath he varied the concentrations of the potassium dichromate (KD), the potassium bromide (KBr) and the sulfuric acid (SA). For Agfa 8E75 HD, Kostuk indicated that the concentration of KBr should be high to maximize efficiency, the concentrations of KD should be low to

* Correspondence: Email: cristian@disc.ua.es; WWW: <http://www.disc.ua.es/>; Telephone: +34-6-5903682; Fax: +34-6-5903464

minimize noise gratings and reduce emulsion swelling and the concentration of SA should also be minimized in order to reduce emulsion shrinkage.

Hariharan and Chidley¹⁰ studied the fixation-free method and showed that the diffusion of material during the bleach bath is the main mechanism under the process. During the bleach bath there is a transference of material from the exposed to the unexposed zones and as a result the silver-halide grains in the non-exposed zones increase their grain size. The refractive index modulation is a consequence of the differences in the grain size of the silver halide grains in the exposed and non-exposed zones. This diffusion process is particularly influenced by the potassium bromide concentration in the bleach solution. The concentration of the potassium bromide must be optimized in order to obtain high values of diffraction efficiency and low values of scattering. Hariharan also studied the influence of the development step in the quality of the hologram¹¹. They showed that the concentration of sodium sulfite influences the quality of the final hologram, this is due to the solvent action of the sodium sulfite. They also show that the action of hardener developers contribute in an opposite direction of the index modulation created by the diffusion process, thus lowering the final achieved diffraction efficiency.

The above mentioned experiments were carried on Agfa 8E75 HD plates. Nevertheless Agfa has ceased production of holographic material. This represents a serious drawback for people who have been using the Agfa material in their work¹². This implies that it is necessary to discover and to study alternative silver-halide materials which could fill the gap created by the withdrawal of the Agfa material, in particular, the currently available silver halide materials such as those of Slavich (Russia), Royal Holographic Art Gallery (Great Britain) and the BB series from Holographic Recording Technologies (Germany). Trials must be carried out with these new silver halide emulsions to find optimum procedures leading to high quality holograms. In this work we adjusted the potassium bromide concentration of an R-10 type bleach in order to obtain high diffraction efficiencies with bleached holograms recorded on the novel BB-640 plates. Also for transmission holograms, the influence of the development step is evaluated.

2. EXPERIMENTAL

The experiments were carried out on red sensitive BB-640 silver halide photographic plates. Unslanted holographic transmission gratings were recorded by using two collimated beams from a 15 mW He-Ne laser (633 nm), with the polarization vector perpendicular to the plane of incidence. The two beams, of equal intensity, impinged on the emulsion, forming an angle (in air), of 45°. With the geometry described, the spatial frequency of the gratings was calculated as ~1200 lines/mm. Also reflection diffraction gratings were recorded. The K ratio, defined as the ratio of the reference beam intensity to the object beam intensity, was taken to be 1 inside the emulsion. One beam impinged perpendicular to the emulsion, whereas the other beam fell on the back side of the plate forming an angle in air of 30° with the perpendicular to the surface of the emulsion. With the geometry described, the spatial frequency of the reflection gratings was calculated as ~5100 lines/mm.

In previous experiments¹³ we have found that the gelatin of the BB-640 plates is hardened to a high degree, so that the products of the developer do not penetrate easily into the emulsion. Therefore, the plates were hypersensitized 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, and the sensitivity of the emulsion is also increased.

After exposure, the plates underwent the schedule procedure illustrated in Table I, so that phase transmission holograms were finally obtained.

Table I
Schedule procedure

- 1.- Development in (20°C) (5 min for D-19, 4 min for AAC, 2 min for CW-C2)
- 2.- Rinse in running water 1 min
- 3.- Bleach for 1 min after the plate has cleared
- 4.- Rinse in running water 5 min
- 5.- Dry at room temperature

The diffraction efficiency η of the recorded phase holograms was calculated as the ratio of the diffracted beam intensity to the incident collimated probe-beam intensity of the He-Ne laser. 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.

The efficiency of the zero-order or transmission τ was similarly calculated as the ratio of the directly transmitted beam intensity to the incident power and was corrected by the same factor.

3. PREVIOUS CONSIDERATIONS

Firstly, unslanted diffraction transmission gratings were developed after the exposure with D-19 developer and bleached in bleach baths optimized for Agfa 8E75 HD plates. Two bleach compositions were used: a version of the R-10 (mod R-10) used by Crespo et al.⁸, and a bleach optimized by Hariharan¹¹. Table II illustrates the compositions of these two bleaches. Figure 1 shows the results of diffraction efficiency versus the exposure for plates bleached in these two different bleach baths. The plates bleached with the mod R-10 bleach were bleached at two different temperatures (50°C and 70°C). It can be seen from the figure that the best results were obtained for plates bleached with the mod R-10 bleach at 50°C, a peak diffraction efficiency of 80% was obtained by using this bleach. The value of the peak diffraction efficiency was lower for plates bleached at a temperature of 70°C, 65% and an even lower value of the peak diffraction efficiency was obtained for plates bleached with the Hariharan bleach, 33%. Although the results of the diffraction efficiency were high when the mod R-10 bleach was used at a temperature of 50°C, the peak diffraction efficiency reached with the Hariharan bleach was quite low. These results indicate that bleaches which could have given good results for Agfa, could give a worse performance for BB-640 plates. Therefore new bleach compositions must be used with these new plates.

Figure 1: Diffraction efficiencies versus exposure, under Bragg condition for transmission gratings recorded on BB-640 plates bleached with R-10 (at 70°C and 50°C) and with the Hariharan bleach.

Table II

Hariharan bleach

potassium dichromate	0.8 g
potassium bromide	4.0 g
sulfuric acid	1.0 ml
distilled water	1 l
Bleach bath temperature	T=50°C

<i>R-10 (Crespo et al. version)</i>	
Potassium dichromate	2 g
Sulfuric acid	10 ml
potassium bromide	35 g
distilled water	1 l

4. OPTIMIZATION OF THE R-10 BLEACH FOR TRANSMISSION DIFFRACTION GRATINGS

The R-10 bleach has been used with Agfa 8E75 HD plates with good results. Table III shows the composition of a modified version of this bleach (mod R-10). The bleach bath solution is composed of two different solutions: A and B. The oxidizer is contained in the solution A, whereas the potassium bromide is contained in the solution B. To obtain the bleach solution 1 part of A is mixed with 10 parts of distilled water and X parts of B. The ratio $X=B/A$ indicates the relation between the potassium bromide concentration and the oxidizer concentration (potassium dichromate). For Agfa 8E75 HD plates, an optimized R-10 type bleach is the one used by Crespo et al.⁸. Nevertheless the differences in the degree of hardening of the gelatin, and the differences in the size and concentration of the silver halide grains between Agfa 8E75 HD and BB-640 plates, make it necessary to find a new optimum B/A ratio for BB-640 plates. The concentration of potassium bromide in the bleach bath determines the rate of the diffusion process. A high rate of the diffusion process favours the refractive index modulation. Nevertheless a high quantity of potassium bromide, tends to increase the amount of light scattered by the final hologram. Therefore it is necessary to adjust the values of the ratio B/A needed to obtain high diffraction efficiencies and low values of scattering. The values of the B/A ratio were varied taking the values: 2, 4, 8, 15, 30, 60, 120, 250, the pH's ranged from 1.57 to 2.51. The studies were carried out by using three different developers: D-19, AAC, CW-C2, because as will be shown the optimum ratio B/A depends on the developer.

Table III
Bleach bath composition (modified version of R-10)

<i>Solution A</i>	
potassium dichromate	20 g
sulfuric acid	15 ml
distilled water	1 l
<i>Solution B</i>	
potassium bromide	100 g
distilled water	1 l

Just before use, mix 1 part of A with 10 parts of distilled water, and add X parts of B, $B/A=X$.

Figure 2 shows the results of the peak diffraction efficiency versus the B/A ratio for transmission diffraction gratings recorded on BB-640 plates and developed with three different developers: D-19, AAC, CW-C2. It can be seen from the figure that the optimum B/A ratio changes depending on the used developer. A peak diffraction efficiency of 86% was obtained for plates developed with D-19 and bleached with a B/A ratio of 8. The value of the transmission efficiency was of 2%, and the absorption and scattering was of 12%. It is also interesting to notice that high values of the peak diffraction efficiency were obtained for a wide range of B/A ratios for D-19: the value of the peak diffraction efficiency was over 80% for the values of the B/A ratio ranging from 4 to 120. Even a higher peak diffraction efficiency was obtained when CW-C2 was used (87%) for a B/A ratio of 15, the value of the transmission efficiency was as low as 1%, and the absorption and scattering was 12%, which means that the diffraction efficiency was almost the maximum obtainable. The value of the peak diffraction achieved with the AAC developer was slightly lower, of 84%, the transmission efficiency 4% and the absorption and scattering 12%. These results, show that the use of tanning developers (D-19 and CW-C2) doesn't prevent from the achievement of high values of diffraction efficiency. The reason is that, the diffusion process in BB-640 plates is efficient enough to produce high refractive index modulations (as will be inferred from figure 3, despite the opposite action of the tanning developers).

Figure 2.- Diffraction efficiencies versus B/A ratio, under Bragg condition for transmission gratings recorded on BB-640 plates developed with three different developers: D-19, AAC, CW-C2: The plates were bleached with R-10 at 50°C at 8 different B/A ratios: 2, 4, 8, 15, 30, 60, 120, 250.

In figure 3 the response of the diffraction efficiency versus the exposure is presented for transmission holograms recorded on BB-640 plates developed with three different developers. The values presented in the figure correspond to transmission diffraction gratings yielding to peak diffraction efficiency. For plates developed with AAC it can be seen that after the first maximum the value of the diffraction efficiency decreases till a minimum and then increases again; the decrease of the diffraction efficiency after the first maximum is due to an excess of modulation. To prove this, the response of the transmission efficiency versus the angle was measured for the hologram which gave the minimum value of diffraction efficiency. By using Kogelnik Coupled¹⁴ Wave Theory, the theoretical function of the transmittance was fitted to the experimental data, and the refractive index modulation for the best fit was of $\Delta n = 0.083$, which is in fact very high. It is clear that, the diffusion process is efficient enough to produce high refractive index modulations in BB-640 plates, thus the maximum achievable diffraction efficiency will be only limited by absorption and scattering.

5. REFLECTION GRATINGS

5.1. Optimization of the R-10 bleach for transmission diffraction gratings

In order to optimize the mod R-10 bleach for reflection gratings, the exposed plates underwent the procedure of Table I and bleached with the mod R-10 of table III. The developer used in this case was the D-19 developer. The ratios B/A were varied taking the values: 2, 4, 8, 15, 30, 60, 120, in a similar manner as was done for transmission holograms. Figure 4 shows diffraction efficiency as a function of the B/A ratio. It can be seen from this figure that the best results were obtained for a B/A ratio of 15. A high peak diffraction efficiency of 72% was obtained. It can also be seen that the peak diffraction efficiency is highly sensitive to the B/A ratio.

5.2. Influence of the B/A ratio on the final thickness of the emulsion.

During the rehalogenating bleaching procedure, the gelatin of the emulsion varies in thickness. This change in the thickness of the emulsion after the procedure alters the fringe spacing, which also affects the wavelength at reconstruction. The relation between the wavelength at reconstruction and the wavelength at the recording can be expressed by the following

relation:

$$\frac{\lambda'}{\lambda} = \frac{\Lambda'}{\Lambda} \quad (1)$$

where Λ, Λ' are the grating periods at the recording and reconstruction respectively and λ, λ' are the wavelengths at the recording and reconstruction respectively.

Figure 3: Diffraction efficiency versus exposure, under Bragg condition for transmission gratings recorded on BB-640 plates developed with three different developers yielding to maximum diffraction efficiency.

Figure 4: Diffraction efficiencies versus the B/A ratio for reflection gratings recorded on BB-640 plates bleached with an R-10 type bleach (at 50°C) with 7 different B/A ratios: 2, 4, 8, 15, 30, 60, 120.

Figure 5: Wavelength at reconstruction versus exposure for reflection gratings recorded on the BB-640 plates bleached with an R-10 type bleach (at 50°C) with 7 different B/A ratios: 2, 4, 8, 15, 30, 60, 120.

The influence of the B/A ratios on the wavelength at reconstruction is clear from figure 5. It can be seen that much care must be taken to minimize the wavelength shift. For instance, when the BB-640 plates are bleached using the B/A ratio which yields maximum diffraction efficiency (B/A=15), the wavelength shift is less than 1% within a range of exposures from 900 to 5000 $\mu\text{J}/\text{cm}^2$. However, for a B/A ratio of 4, the emulsion shrank after the procedure, so that the wavelength at reconstruction remained below 623 nm.

5.3. Angular response of the diffraction efficiency

The efficiency of the diffracted and the transmitted beams, η and τ , respectively, together with the absorption of the material αd (where α is the absorption coefficient and d is the thickness of the photographic emulsion after processing) are three parameters that may be used to characterize holographic transmission gratings recorded on the silver halide sensitized gelatin of BB-640 plates. By means of Kogelnik's coupled wave theory¹⁴, it is possible to obtain an analytical expression for the diffraction efficiency η of volume holograms.

As Kogelnik's theory is limited to the description of two diffracted orders, then:

$$\eta + \tau = \exp(-\alpha d / \cos \theta') \quad (2)$$

and τ can be obtained as follows:

$$\tau = \exp(-\alpha d / \cos \theta') - \eta \quad (3)$$

In equation (3) α takes into account the absorption (and also the scattering; we have no means of differentiating between the two at this point); d is the thickness of the final hologram and θ' is the angle of reconstruction in the medium, which is related to the angle of reconstruction in air θ by Snell's law.

We tested the holograms which yielded peak diffraction efficiency by rotating them, and the variation in transmission with the angle of incidence τ in air was measured. The values of transmission were corrected to take into account Fresnel's reflections and the absorption of the glass substrate. The parameters obtained by fitting the theoretical function to the experimental data were: $\Delta n = 0.034$, $d = 8.1 \mu\text{m}$, $\alpha = 0.0288 \mu\text{m}^{-1}$, Δn is the refractive index modulation of the hologram.

6. CONCLUSIONS

The main process under the rehalogenating bleach technique is material transference from the exposed to the non-exposed zones. This diffusion process is related with the concentration and size of the silver halide grains suspended in the gelatin of the emulsion. Since the amount of light scattered by a small particle is proportional to the sixth power of the radius, the smaller silver halide grains of the BB-640 emulsion in comparison with those of the Agfa 8E75 HD emulsion allow the achievement of higher values of the diffraction efficiency when using BB-640 plates in the rehalogenating bleach technique. We have optimized an R-10 type bleach for this novel BB-640 emulsion for transmission holograms and for three different developers (AAC, D-19, CW-C2) finding that the best results were obtained for CW-C2 at a B/A ratio of 15, with a maximum achieved diffraction efficiency of 87%. The values of the peak diffraction efficiency were also high for the other two developers (86% for D-19 and 84% for AAC). When reflection gratings were recorded on BB-640 plates an also high peak diffraction efficiency was obtained (72%) by developing the plates in D-19 and bleaching them using a B/A ratio of 15. The results presented are some of the best reported for rehalogenating bleaching processing technique at the present time and they confirm the applicability of bleached holograms derived from BB-640 plates for recording high quality transmission holograms.

7. REFERENCES

1. W.T. Cathey, "Three-dimensional wavefront reconstruction using a phase hologram", *J. Opt. Soc. Am.* **55**, 457 (1965).
2. J. Upatnieks, C. Leonard, "Diffraction efficiency of bleached, photographically recorded interference patterns", *Appl. Opt.* **8**, 85-89, 1969.
3. D.H. McMahon, A. R. Franklin, "Efficient, high-quality, R-10 bleached holographic diffraction gratings", *Appl. Opt.* **8**, 1927-1929, 1969.
4. N.J. Phillips, D. Porter, "An advance in the processing of holograms", *J. Phys. E.* **9**, 631-634, 1976.

5. N.J. Phillips, A.A. Ward, R. Cullen, D. Porter, "Advances in holographic bleaches", *Phot. Sci. Eng.* **24**, 120-124, 1980.
6. H. I. Bjelkhagen, *Silver Halide Recording Materials for Holography and Their Processing* (Springer-Verlag, Berlin, 1993).
7. P. Hariharan, C.S. Ramanathan, G.S. Kaushik, "Simplified processing technique for photographic phase holograms", *Opt Commun.* **3**, 246-247, 1971.
8. J. Crespo, A. Fimia, J.A. Quintana, "Fixation-free methods in bleached reflection holography", *Appl. Opt.* **25**, 1642-1645, 1986.
9. R. Kostuk, "Factorial optimization of bleach constituents for silver halide holograms", *Appl. Optics*, **30**, 1611-1616, 1991.
10. P. Hariharan, "Rehalogenating bleaches for photographic phase holograms. 3: Mechanism of material transfer", *Appl. Opt.* **29**, 2983-2985, 1990.
11. P. Hariharan and C. M. Chidley, "Photographic phase holograms: the influence of developer composition on scattering and diffraction efficiency", *Appl. Opt.* **26**, 1230-1234, 1987.
12. N.J. Phillips, "Agfa-Gevaert departure problem, or a new dawn for holography", *Holography Newsletter* **8** (1), 12, 1997.
13. A. Beléndez, C. Neipp, M. Flores and I. Pascual, "High-efficiency silver-halide sensitized gelatin holograms with low absorption and scatter", *J. Mod. Opt.* **45**, 1985-1992, 1998.
14. H. Kogelnik, "Coupled wave theory for thick hologram gratings", *Bell Systems Technology Journal*, **48**, 2909-2947 (1969).