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.

Semi-physical development of holograms recorded in silver halide emulsions

István Bányász^a, Augusto Beléndez^b, Inmaculada Pascual^c and Antonio Fimia^d

^aResearch Institute for Solid State Physics and Optics
Department of Laser Physics, P.O.B. 49, H-1525 Budapest, Hungary

^b Departamento de Ingeniería de Sistemas y Comunicaciones
Universidad de Alicante, Apdo. 99, E-03080 Alicante, Spain

^c Laboratorio de Óptica, Departamento Interuniversitario de Óptica
Universidad de Alicante, Apdo. 99, E-03080 Alicante, Spain

^d Departamento de Ciencias Experimentales y Tecnología, Universidad Miguel Hernández de Elche
Avda. Ferrocarril, s/n, Edificio La Galia, E-03200 Elche (Alicante), Spain

ABSTRACT

In the course of experiments on measurement of the effects of processing on nonlinear characteristics of silver halide holograms recorded in Agfa-Gevaert 8E75HD emulsions we found that, under certain circumstances, the AAC developer acted as a semi-physical developer instead of the normal chemical developing action. The developed and fixed holograms were of low optical density (<0.5) and of high diffraction efficiency (up to 15 %). Phase contrast microscopy revealed that very clean phase gratings were obtained. This effect of the AAC developer was due to the replacement of one of its components, sodium carbonate of "purest grade" with that of "for analysis grade" of the same company.

Keywords: silver halide materials, semi-physical development, phase contrast microscopy

1. INTRODUCTION

In case of chemical or direct development the silver ions in the vicinity of the latent-image spec are reduced to silver atoms by the developer. There is another type of development, called physical development. In this case the developer contains silver ions, and those ions are transferred to the silver centres in the emulsion (the initial latent-image specs or the silver

centres produced already via chemical development). The silver ions are then reduced to silver atoms by the developer. The semi-physical or solution-physical development differs slightly from the physical one in that the silver ions involved in the process are provided from the silver-halide grains of the emulsion itself. The semi-physical developers contain silver-halide solvents, such as ammonium thiocyanate or high amounts of sodium sulphite. The developer initiates the dissolution of the exposed grains.

Chemical development produces mostly filament-like structures of silver, while physical or semi-physical development yields compact silver plates.

Physical development is particularly useful for processing ultra-fine grain emulsions. Research and development on such materials was done mainly in the Soviet Union in the first decades of laser holography. Good summaries of the principal activities in this field can be found in the books of Syms [1] and Bjelkhagen [2]. The following brief review of some important works in this field is based on these monographs. The first report from the Soviet Union on the production of unbleached phase holograms in very fine-grain emulsions was of Denisyuk and Protas [3]. They increased the very low initial sensitivity of the emulsion via hypersensitization by triethanolamine. (Other methods of sensitization were checked, too, and were compared by measuring the density of the processed emulsion as function of the exposure.) As a solution-physical developer, Lehmann's ammonia-pyrogallol developer was used by them. Andreeva and Sukhanov [4] used a modified version of the pyrogallol developer with the so called 'Valenta' type emulsion that has a grain size of about 30 nm and a thickness of 7 μm . They obtained 20 % diffraction efficiency at and about 15 nm bandwidth at 633 nm. Denisyuk obtained artistic holograms of excellent quality in the experimental fine-grain (<10 nm) emulsion PE-1 [5]. Diffraction efficiencies above 50% were achieved with that emulsion.

According to a paper of Usanov *et al.* [6], solution-physical development gives amplitude holograms when the size of the developed silver particles is quite large, and phase ones when their diameters are 15-20 nm, small enough to alter the index of refraction of the material around them. They found that the average diameter of the developed silver particles decreased with increasing exposure, and the variation around the average grain size decreased with increasing developing time.

Verbovetskiy *et al.* [7] studied the effect of physical development of VRL type photoemulsions on the parameters of phase holograms of binary information. They proved that physical development can be used for the production of low-noise holograms with binary information content.

The first theoretical model for the semi-physical development of silver halide emulsions was developed by Zhang *et al.* in China [8]. They showed that the combination of the Maxwell-Garnett effective-medium theory with the (first order) coupled wave theory can give good predictions on the optical and spectral properties of semi-physically developed holograms, as well as on the dependence of their diffraction efficiency on various parameters. In their experiments they used the Chinese fine-grain holographic plates HEP-RAI, that yielded spherical silver particles of an average diameter between 10 and 30 nm upon semi-physical development. They achieved diffraction efficiencies up to about 55 %, in good agreement with their model.

As for the semi-physical development of Western holographic recording materials, in particular the Agfa HD emulsions, the first reports appeared only in the seventies. Ruzek and Fiala [9] produced reflection holographic portraits in Agfa Gevaert 8E75 emulsions at $\lambda = 633 \text{ nm}$. Actually the reflection holograms were produced from the transmission master holograms recorded with Q-switched ruby laser. They used the well-known solution-physical developer GP-8. They obtained high-quality holograms with efficiencies up to 30%. Optimum exposure proved to be around $300 \mu\text{J}/\text{cm}^2$, i.e. 10 times higher than in case of chemical development.

Aliaga *et al.* [10] used the same holographic recording material as the authors of the present paper, Agfa-Gevaert 8E75HD. They used the so-called CPA-1 processing technique, a slightly modified version of the GP-8 developer. The main difference between the two processing was in the *development time*. Processing in GP-8 lasts for 6 minutes, while in CPA-1 only for 2 minutes. Shortening the development time in case of the Agfa material was indispensable because of its higher sensitivity. Exposure levels between 500 and 1000 $\mu\text{J}/\text{cm}^2$ were used in that work. They obtained reflection holograms with very low noise and diffraction efficiencies of over 40% when the plates were sensitized in triethanolamine. They claimed that the use of deionised water significantly improved their results. The same authors claimed in another report [11] that the solution-physical developer CPA-1 followed by a *fixation step* produced holograms with high archival stability combined with diffraction efficiency up to 26% for Agfa-Gevaert 8E75 HD materials. Another advantage was the improved linearity of the process. These latter results are to be compared with those of the present work.

Bonmati *et al.* [12] investigated four different solution-physical developers for processing reflection holograms on specially made silver-halide emulsions containing various silver-halide concentrations. They found that the Russian developers GP-2 and GP-8 were the best. Leclère *et al.* [13,14] investigated solution-physical development and optimized a developer consisting of pyrogallol, sodium hydroxide and ammonium thiosulphate for the Agfa-Gevaert 8E75 HD emulsion.

In this paper we report on the semi-physical developing effect of the developer AAC that we used for standard processing of bleached holograms in Agfa-Gevaert 8E75 HD plates. We discovered this effect by chance, and found that it was due to one of its constituents, sodium carbonate. In the following detailed description of our experimental results is given.

2. EXPERIMENTS

2.1 Experimental conditions

As mentioned before, we discovered the semi-physical developing effect of the AAC developer accidentally, in the course of our experiments on the characterization of bleached holograms and the quantitative comparison of various processings [15,16].

Plane wave holograms were recorded on Agfa-Gevaert 8E75HD NAH emulsions on rectangular glass substrates with dimensions of 64 mm x 64 mm x 1.5 mm. A helium - neon laser operating at 632.8 nm was used for the recording and the reconstruction. The interbeam angle was 45°, thus the spatial frequency of the gratings was about 1200 line pairs/ mm. Hologram pairs at seven values of fringe visibility, namely at $V=0.2, 0.4, 0.6, 0.8, 0.9, 0.95$ and 1.0 were recorded. Twelve hologram pairs at exposures ranging from 10 $\mu\text{J}/\text{cm}^2$ to 1.6 mJ/cm^2 were recorded at each visibility. The total intensity at recording was maintained constant at 400 $\mu\text{W}/\text{cm}^2 \pm 1\%$ throughout the experiments. The first element of each hologram pair was developed and fixed to obtain an absorption hologram and the second one was developed with the same developer and bleached, without a fixation step.

The beam ratios were set by adjusting a variable beam splitter and inserting appropriate neutral density filters in the unexpanded object beam.

The compositions and the processing conditions of the AAC developer used in the related part of the experiments is shown in Table I. All absorption holograms were fixed in Kodak F24 fixer for 5 minutes. Composition of the bleach is not relevant to the present work, neither is that of the other two developers used in our experiments, but can be found in [16]. All the holograms were processed simultaneously.

Name of the compound	Quantity
Ascorbic acid	18 g
Sodium carbonate	120 g
Distilled water	1 litre
Developing time	3 min.
Temperature	20 °C

Table I Composition and processing conditions of the AAC developer

interference fringes.

2.2 Results

Due to the fact that we measured the before-bleach optical density of each hologram, we could constantly check the proper working of the developer. In the course of our experiments at a certain time our stock of sodium carbonate ran out, and we had to use the "for analysis" grade product of the same manufacturer instead of the "purest" grade one used so far. We found that the plates processed to obtain absorption holograms came out in light brown colour instead of grey, and their optical density was much more lower than expected. Then we performed various checks to find the cause of that anomaly. We repeated the experiments under well controlled conditions, and obtained always "brown" holograms with the new solution of the AAC developer.

It was relatively easy to identify the constituent responsible for the effect, since we knew that the only change in the preparation of the developer solution was the change from "purest" grade sodium carbonate to "for analysis one". So, to check the results we repeated the measurements using a new solution of the developer made this time with "purest" grade sodium carbonate. As expected, this processing gave the correct results, i.e. normal absorption holograms of grey colour.

We measured the optical densities of both the semi-physically developed (brown) holograms and the absorption (grey) holograms. Some representative results can be seen in Figs. 1 and 2. It can be seen that the highest optical density of the semi-physically developed holograms (about 0.4) was less than one tenth of that of the chemically developed ones (about 5.0). The whole experiment was repeated three times and the results reproduced well. So it turned out that the dip in the optical density of the semi-physically developed holograms (in the 200 - 110 $\mu\text{J}/\text{cm}^2$ exposure region) is really a kind of

After all the holograms were processed, optical density of the absorption holograms and diffraction efficiency of the phase holograms were measured. Care was taken to minimise the effects of stray lights. When measuring low intensities (efficiencies below 0.1% and optical densities above 3) the detector was capped by a black box that admitted only light coming directly from the hologram. The intensity of stray light was always checked. Both the optical density and the diffraction efficiency were corrected for reflection losses. In the case of the optical density measurements the intensity of the reflected beam was also measured and subtracted from that of the incident beam. In the case of the diffraction efficiency measurements reflection losses were calculated from the Fresnel-formula instead of measuring the reflected intensity, because the latter proved to be uncertain due to the presence of some

"solarization".

Figure 1 Optical density vs. exposure of semi-physically developed holograms. AAC developer. Visibility is 0.9.

Figure 2 Optical density vs. exposure of chemically developed holograms. AAC developer. Visibility is 0.9.

Diffraction efficiencies of both the semi-physically and chemically developed were also measured. The results, in the case of a fringe visibility of 0.9, are shown in Figs. 3 and 4. It can be seen that the maximum of the diffraction efficiency of the semi-physically developed holograms is well above that of the absorption ones, it attains 14.5 %. The highest diffraction efficiency of the chemically developed holograms was about 4 %. Note the large difference in the sensitivity of the two processes: Peak diffraction efficiency is attained at an exposure of 110 $\mu\text{J}/\text{cm}^2$ in case of semi-physical development and at about 20 $\mu\text{J}/\text{cm}^2$ in case of chemical development. Halfwidth of the diffraction efficiency vs. exposure curve is approximately 500 $\mu\text{J}/\text{cm}^2$ for the semi-physical process and 50 $\mu\text{J}/\text{cm}^2$ for the chemical one.

Figure 3 Diffraction efficiency vs. exposure of semi-physically developed holograms. AAC developer. Visibility is 0.9.

Figure 4 Diffraction efficiency vs. exposure of chemically developed holograms. AAC developer. Visibility is 0.9.

To obtain further verification of our results we studied the holograms with phase contrast microscopy. We used a Labophot-2 type microscope with phase contrast attachment manufactured by Nikon. Both dry (40X) and immersion (100X) objectives were used. All the phase contrast- and normal micrographs presented in the following figures were taken by immersion objective so that the effect of any possible surface structure was cancelled.

One can see a phase contrast micrograph of a semi-physically developed hologram that received the lowest exposure in Fig. 5. Note the relatively noisy appearance of the grating.

The micrograph of the third hologram (in Fig. 6) presents a higher and smoother phase modulation.

Hologram No. 6 is just near the peak of the diffraction efficiency. Its profile is more uniform, with a higher modulation (Fig. 7).

Phase modulation of hologram No. 9 is higher than that of hologram No. 6, but its diffraction efficiency is lower. Noise is still relatively low. (Fig. 8)

A reduced phase modulation and increased noise can be seen in Fig. 9, where phase contrast micrograph and profile of the hologram corresponding to the tenth point in Fig. 3 is presented.

The same series of semi-physically developed holograms was studied with ordinary microscopy, two. Presence of a very weak absorption grating could be detected. So, in fact these holograms can be considered as mixed, phase and absorption gratings, with the phase one being the dominant.

The corresponding series of chemically developed holograms was also studied by phase contrast and ordinary microscopy.

Figure 5 Phase contrast micrograph of a semi-physically developed hologram (first point in Fig. 3) and its profile

Figure 6 Phase contrast micrograph of a semi-physically developed hologram (third point in Fig. 3) and its profile

Figure 7 Phase contrast micrograph of a semi-physically developed hologram (sixth point in Fig. 3) and its profile

No phase grating was found. Even detection of the absorption gratings proved to be difficult especially in the holograms of higher optical density. Two such micrographs can be seen in Figs. 10 and 11. The first one is the micrograph of a hologram with nearly maximum diffraction efficiency, corresponding to the third point in Fig. 4. The second micrograph corresponds to the sixth point of the same diffraction efficiency curve. Drop in the contrast can clearly be seen. Note that the absorption holograms also seem to be of low noise.

Phase contrast and ordinary microscopy provided much more information on the holograms than diffraction efficiency and optical density measurements, in spite of the fact that the spatial frequency of the gratings was rather high, 1200 line pairs/mm. Quantitative analysis of the phase contrast micrograph (ie. determination of the refractive index modulation) is under way. This is not a simple task, since one has to take into account the modulation transfer function of the microscope, too.

Figure 8 Phase contrast micrograph of a semi-physically developed hologram (ninth point in Fig. 3) and its profile

Figure 9 Phase contrast micrograph of a semi-physically developed hologram (tenth point in Fig. 3) and its profile

Figure 10 Ordinary micrograph of a chemically developed hologram (third point in Fig. 4) and its profile

Figure 11 Ordinary micrograph of a chemically developed hologram (sixth point in Fig. 4) and its profile

3. DISCUSSION AND CONCLUSIONS

As mentioned above, the only change between the two series of exposures that gave completely different holograms was the use of "for analysis" grade sodium carbonate instead of the "purest" grade one. So it was clear that this constituent of the developer solution was responsible for the production of semi-physically developed, brownish holograms. To try to reveal the mechanism, we measured the pH of the developers prepared with both types of sodium carbonate. Several measurements were carried out, and the pH of the AAC developer was always between 9.9 and 10.0 when "for analysis" grade sodium carbonate was used, and between 10.8 and 11 when the "purest" grade one was used, ie. a there was a difference of about 1.0 between the two solutions. We checked the developers for any possible pH change during the exposure, but we found that the pH of the developers remained the same at the end of the development. This difference in pH can be attributed to two facts. According to the Panreac company, producer of both types of Na_2CO_3 , there are more impurities in the "for analysis" grade material. Furthermore, the "purest" grade sodium carbonate is richer (acidim.) (99.5 - 100.5%) than the "for analysis" grade.

In the developer of lower pH, made of "for analysis" grade sodium carbonate, chemical development is inhibited, and it is the semi-physical development that dominates. Neither the composition nor the development time have been changed so far, so that this process of producing semi-physically developed holograms is not optimised yet. The relatively high diffraction efficiencies obtained and the low noise in the holographic gratings enable us to hope that this method may become useful in practical holography.

4. ACKNOWLEDGEMENTS

The experimental part of this work was carried out at the University of Alicante in the framework of a guest professorship granted to I.B. who wishes to express his gratitude to the Spanish Ministry of Education and Culture for that scholarship. Helpful discussions with Drs. Ricardo Mallavia and Salvador Blaya of the University of Elche are gratefully acknowledged.

5. REFERENCES

- 1 R. R. A. Syms, "Practical Volume Holography", Clarendon Press, Oxford, 1990
- 2 H. I. Bjelkhagen, "Silver-Halide Recording Materials for Holography and Their Processing", Springer-Verlag, Berlin, Heidelberg, *etc.*, 1993
- 3 Yu. N. Denisyuk i I. R. Protas, " Usovershestvovannue lippmanovskie fotograficheskie plastinki dlya registratsii stoyachish svetovuh voln", *Optika i Spectroscopiya*, 14, 721-725 (1963) (in Russian)
"Improved Lippmann holographic plates for recording stationary light waves", *Opt. Spectrosc.*, 14, 381-3, (1963) (in English)
- 4 O. V. Andreeva and V. I. Suhanov, "Polutchenie neotbelennuh trehmernuh gologramm s vysokoy difrakcionnoy effektivnostyu", *Optika i Spectroscopiya*, 30, 786-787, (1971) (in Russian)
"Production of unbleached volume holograms with high diffraction efficiency", *Opt. Spectrosc.*, 30, 424-5, (1971) (in English)
- 5 Yu. N. Denisyuk, "Hudozhestvennaya golografiya s zapisyu v trehmernuh sredah na osnove lippmannovskih fotoplastinok", *Zhurnal Eksperimental'noy i Tekhnicheskoy Fiziki*, 1683-1687, (1976) (in Russian)
"Holography for artistic purposes with three-dimensional recording and Lippmann plates, *Sov. Phys. Tech. Phys.*, 23, 954-7, (1978) (in English)
- 6 Yu. E. Usanov, N. L. Kosobokova, G. P. Tikhomirov, "Investigation of the dependence of the diffraction efficiency of holograms on the sizes of the developed silver particles", *Sov. J. Opt. Technol.*, 44, 528-530, (1977)
- 7 A. A. Verbovetski, L. P. Vahtanova, E. A. Gruz i K. S. Bogomolov, "Parametri otbelennih gologramm s dvoichnoi informatsiei pri fizicheskom proyavlenii", *Optika i Spectroscopiya*, 43, 135-138, (1976) (in Russian),
"Parameters of bleached holograms with binary data under physical development", *Opt. Spectrosc. (USSR)*, 43, 74-75, (1977) (in English)
- 8 Zhang Chunping, Zhang Guanyin and Cong Hui, " Calculation and measurement of the diffraction efficiency of a dilute developed silver holographic plate", *Optica Acta*, 32, 679-687, (1985)
- 9 Jiri Ruzek and Pavel Fiala, "Reflection hologram portraits", *Optica Acta*, 26, 1257-1264, (1979)
- 10 R. Aliaga, H. Chuaqui and P. Pedraza, " Solution physical development of Agfa-Gevaert emulsions for holography", *Optica Acta*, 30, 1743-1748, (1983)
- 11 R. Aliaga, H. Chuaqui and P. Pedraza, " Archival and wide exposure latitude process for holography", *Appl. Opt.*, 29, 2861-63, (1990)

- 12 A. Bonmati, J. Crespo, M. Pardo, "Factors influencing the colloidal silver formation in reflection holograms", in *Image Detection and Quality, Proc. SPIE*, 702, 101-104, (1986)
- 13 P. Leclère, Y. Renotte, Y. Lion, "Improvement of holographic performances of silver halide emulsions by a solution-physical development", *J. Photogr. Sci.*, 39, 33-37, (1991)
- 14 Yvon Renotte, Yves Lion, Philippe Leclère, "Improvement of recording capabilities of silver halides holographic emulsions by physical and chemical development", *Proc. SPIE*, 1732, 149-158, (1992)
- 15 I. Bányász, A. Beléndez, I. Pascual, and A. Fimia, "Method for the characterisation of hologram processing", *Journal of Modern Optics*, 45, pp. 881-888, (1998)
- 16 I. Bányász, A. Beléndez, I. Pascual, and A. Fimia, "Comparison of nonlinear characteristics of phase holograms processed by various combinations of developers and bleaching agents", *Journal of Modern Optics*, 46, pp. 591 - 605, (1999)