New Emulsions for Holography

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Abstract

The paper describes a new technology to manufacture holographic materials based on ultra-fine grained silver bromide emulsions. The thickness of the dried layer layer is 5 µm, and the mean grain size is by about 15 nm. During manufacturing, emulsion precipitation and coating are separated strictly from spectral and chemical sensitization. Thus, a material of high performance with respect to sensitivity, resolution, contrast and diffraction efficiency could be obtained.

Introduction

From all light sensitive materials with extremely high resolution, ultra-fine grained silver bromide emulsions show the highest sensitivity[1]. Because of such an excellent perfomance, this system has been turned out to be the most favorized one for display holography. In recent years however, many traditional manufacturers discontinued the production. In this situation, the authors succeeded in developing do-it-yourself materials named as DESA emulsions, refering to the names of the four inventors **D**ünkel, **E**ichler, **S**chneeweiss, **A**ckermann. The new technology has been filed as well as by German and by International Patent Application PCT, in 2002 and 2003, respectively[2]. The process should be available to any experienced holographer with normal darkroom conditions. Improvements are made especially during precipitation of emulsion and desaltation, sensitization and hypersensitization processes, respectively. The new concepts are based on a better understanding of process details. Thus, a material of high performance has been obtained considering resolution, sensitivity, contrast and diffraction efficiency, respectively[3]. The new material has been applied successfully in research and student courses. This holds for all holographic geometries, i.e., for recording Denisyuk single beam reflection and split beam transmission holograms[4].

Manufacturing

There are two major problems which have to be solved in order to produce ultra-fine grained silver bromide emulsions in top quality for holography. *First*, any crystal growth should be prevented in all consecutive steps following the first nucleation step after precipitation. *Second*, due to the very high resolution of such an emulsion, a very sophisticated technology has to be developed in order to exploit the whole potential of the silver halide emulsion system to reach maximum sensitivity. Sensitivity is correlated inversely with resolution, i.e., with grain size. But furthermore, maximum sensitivity is the second important factor for maximum contrast which influences substantially the diffraction efficiency, i.e., the brightness of the display hologram in reconstruction.

For precipitation of the ultra-fine grained silver bromide emulsion, the recipe of *Thiry*[5] has been used, as published in 1987. The technology is the traditional double-jet method for preparation of Lippmann's emulsions by a contineous procedure, i.e., by pouring aqueous silver nitrate and potassium bromide solutions into a vigorously stirred gelatin solution at 37^o C. Silver nitrate is applied in stoechiometric excess. Thus, complexation of silver bromide by formation of silver dibromid ions is suppressed which normally promotes crystal growth due to Ostwald ripening. According to the recipe of Thiry, precipitation takes place in the presence of small amount of iodide ions. Their incorporation into the silver bromide crystal lattice provides a retarding action to further crystal growth, too.

The final grain size is about 15 nm, as determined by TEM. According to our technology, there is neither a need for a sophisticated mixing device to exclude atmospheric contact and to remove the emulsion from the reaction zone immediately after nucleation nor special grain growth restrainers have been applied during precipitation which are adsorbed onto the emulsion grains, as reported elsewere in 1990[6]. Such molecules have normally a desensitizing action which should be avoided because of reasons explained above.

Desaltation is carried out before the layer is dried. This is different compared with procedure of *Thiry*[5]. However, the gelatin content of the liquid emulsion system is very low and amounts to about 1,5 weight percent. Thus the emulsion is deposited on a refrigerator table and cooled down and washed in deionized water. After desaltation, the jelly system is warmed up again, and chrome alum is added on the basis of 0,25 % of the mass of gelatin before drying. This substance improves not only the rheologic performance of the emulsion. It works also as hardening agent by subsequent tempering of the dried layer at 60^o C. In contrast to the reported formerly state of the art, spectral and chemical sensitization are carried out by diffusion processes onto the emulsion layer after drying and hardening have been completed. In doing so, two advantages should be mentioned. First, adequate process regulation should be better in case of a dried layer system than in case of a liquid emulsion. Second, embedding the emulsion grains into the rigid layer provides an efficient kinetic barrier against further crystal growth which should be otherwise promoted considerably by the proportionally crude sensitizing conditions, such as tempering and complexation.

Spectral sensitization is the key step in this procedure. We used 3-Carboxymethyl-3', 9-diethyl-5,5'-dimethyl thiacarbocyanine betaine as sensitizing dye for cw-HeNe-laser radiation at 632,8 nm which has been customized by ORGANICA Wolfen under the name Bch 3032. But we have to consider a theoretical problem related to the electrical charge distribution within the dye molecule. The above betaine designation indicates a double ion. The positive surplus charge is localized at the photolytically active polymethine system. Conseqently, a charge barrier must be surmounted by adeaqate dye adsorption onto the emulsions grains. Due to the excess of silver ions during precipitation the grain surface has a positive charge, too, which is compensated correspondingly by the polyelectrolytical behavior of the gelatin. By considering this situation, we applied the diffusion method for holographic emulsion layer preparation, as published by *Blyth et al.*[7] in 1999. We used aqueous methanol dye solutions containing lithium bromide for reloading the grain surface by bromide adsorption with the positve result that sensitivity has been immediately raised up by many orders of magnitude compared with former values by direct dye input into the liquid emulsion.

Manufacturing is completed by different steps for chemical sensitization and hypersensitization. The immersion in CWC2 developer solution[8] has led to very good results concerning the improvement of sensitivity and diffraction efficiency. However, any subsequent step of sensitization and hypersensitization remains rather ineffective, if spectral sensitization has not been optimized before.

Layer Processing and Application

Figures 1. and 2. show two display holograms obtained for Denisyuk reflection and for Benton rainbow transmission geometries, respectively. The most astonishing result is the high diffraction efficiency of the white light reflection hologram in Figure 1 which has been determined for the diffusely scattering white snail shell in the middle of the hologram to be higher than 50 % allowing sufficiently clear reconstruction under moderate day light conditions. However, the dried emulsion layer has a thickness of 5 µm, only. This means that not more than roughly ten semitransparent mirror planes could be recorded for HeNe-laser radiation at 632,8 nm. Theoretically, a greater layer thickness would be advantageous to obtain high diffraction efficiencies due to the enlarged number of mirror planes after exposure and rehalo bleach. In this context, the developer CWC2 and PBU rehalo bleach have been used very successfully, as recommended by *Bjelkhagen et al.*[8] for Slavish materials.

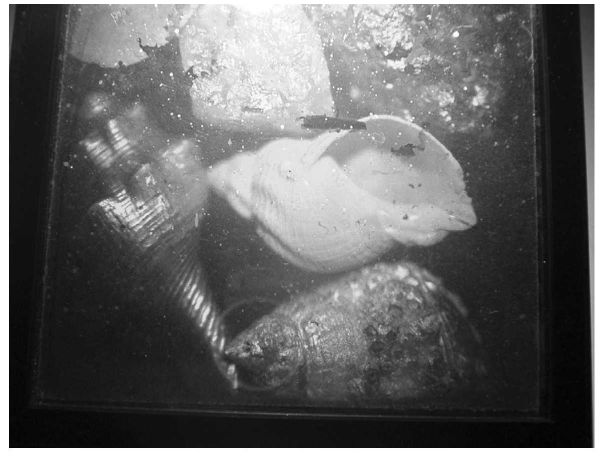

Figure 1. White-Light-Reflection Hologram recorded on DESA silver bromide emulsion (grain size: 15 nm) in Denisyuk single beam geometry with a HeNe-laser (20 mJoules) at 632,8 nm: crystallized rose quartz, pyrit, snail shells

Figure 2. Rain Bow Transmission Hologram recorded on DESA silver bromide emulsion (grain size: 15 nm) in Benton split beam geometry with a HeNe-laser (20 mJoules) at 632,8 nm: faucet

But evidently, optimization of holographic emulsion layers has its own philosophy. Quite naturally, the sensitivity for maximum diffraction efficiency in Denisyuk single beam geometries is manufacture charge dependent. Corresponding values have been determined to be between 80 and 120 µJoules/cm^2. These are very excellent results and should provide the high diffraction efficiency together with the small grain size of 15 nm, the high silver density and the excellent opto-mechanical layer performance due to efficient desaltation as well as rheologic behaviour during coating and hardening processes.

Compared with the results of Thiry[5], DESA emulsions have an unequivocally higher sensitivity. But with respect to the diffusion procedure of Blyth and al.[7], an other advantage should be mentioned: the high transparancy and clarity of the glass plates supporting DESA holograms, after exposure and final processing. Undoubtedly, this determines the high image quality, too, together with the extremely high resolution, as evaluated to be greater than 8000 lp/mm^2 in accordance with the small grain size to be found.

Why Do-It-Yourself Materials?

Our efforts to manufacture do-it-yourself materials are well in accord with the deficient market situation for getting holographic plates. For the photographer however, do-it-yourself materials were the state of the art in the middle of the XIXth, but not of the just beginning XXIth century. Should be the present-day holographer not protected from manufacturing the recording material by his own, too? Our clear answer is: No!

Today, any progress in Holography is restricted mainly due to limitations in recording material performance. Holographic silver bromide emulsions, for example, are in strong competition with dichromate gelatin providing a far smaller sensitivity but an unsurpassed high diffraction efficiency. However, relating to ultra-fine grained silver bromide emulsions, there is no comprehensive theory for getting highest diffraction efficiencies. Important details are industrial secrets. By contrary, the holographer must start his investigations with a profound understanding of the interconnected network of very different processes during manufacturing which have an crucial influence on his final results. What is true for the digital revolution is true for holography, too. Further holographic progress must be application driven considering that most of the possible applications are unknown yet.

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Biography

Lothar Duenkel received his diplom degree in Chemistry from the University at Jena in 1966 and Dr.rer.nat. as well as Dr.sc.nat. titles in Physical Chemistry from the Academy of Sciences of the GDR in 1977 and 1989, respectively. Since 1993 he has worked at the Technische Fachhochschule Berlin University of Applied Sciences. His work has primarily focused on protein research, X-ray crystallography, photochemistry and holography including modelling and preparation. He is a member of the IS&T and of the German Society of Crystallography.