

NOVEL METHODS FOR THE CREATION OF SILVER FREE IMAGES IN HOLOGRAPHY USING CONVENTIONAL SILVER-HALIDE EMULSIONS

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Abstract

In this paper, we revisit the area of silver halide process technology associated with the formation of voided gelatin — conventionally known as silver halide sensitized gelatin (SHSG). Comparative studies have shown that this method is capable of creating master holograms (in transmission mode) that are virtually free of the grain scattering noise that besets conventional silver halide gelatin (SHG) holograms. Despite intuitive conclusions that such noise reduction must be associated with a proportional reduction of diffraction efficiency, it is found that holograms of high efficiency and simultaneous low noise are achieved. Such methods are ideally suited to mastering for embossing or recording onto the substantially noiseless Du Pont photopolymers.

1. Introduction

Substantial published work exists to show that the removal of silver halide crystals from the gelatin structure of conventional halide hologram can leave a residue of voids that endow the holograms with a moderately high diffraction efficiency not unlike that apparent in regular dichromated gelatin structures. The reader is referred to the bibliography at the end of the paper to provide some of the relevant historical information. It is evident that the use of tanning bleaches based on the dichromates is essential to the process since the voided gelatin layer will collapse into a state of spatial homogeneity in the absence of tanning.

Much of our work at Loughborough over a period of many years has been developed with the aim of understanding the physico-chemical mechanisms that underlie the process of development and bleaching in silver halide holography. With this experience in mind and a basic desire to at least understand the process of optimization of the SHSG technique, the contents of this paper were created.

In the literature, it has become clear [1] that transmission holograms with their relatively low spatial frequencies

are somewhat easier to structure in the SHSG mode than reflection holograms. Careful studies, by for example Fimia and colleagues [2], suggest that a spatial frequency limit of some 1500 lines/mm roughly defines bandwidths of simplistic SHSG holograms that are endowed with acceptable diffraction efficiency.

In our approach to the problem, we have scanned a large number of chemical routes so as to gain at least an understanding of the chemical barriers to success. At the outset, we shall make it clear that we too have found difficulty with the reflection hologram case but at least we have a view of what the major chemical problems are and we shall offer a working solution to this mode of problem in forthcoming publications.

It is timely to take a serious view of the SHSG methods because mastering for the recording of copy holograms in Du Pont's photopolymer is now limited by the indifferent, if not totally inadequate quality of the silver halide materials. We must remember the wide differences of sensitivity of the silver halides and the Du Pont materials. We must expect to record holograms in the faster of the Du Pont materials at a sensitivity of approximately $8000 \mu\text{J}/\text{cm}^2$, whereas we can easily demonstrate good diffraction efficiency of silver halide holograms at a level of some $25 \mu\text{J}/\text{cm}^2$. The difference is profound and means that only the most stable of objects can be recorded in the Du Pont material for the purposes of display holography. Very stable objects are of course suitable for direct mastering in the photopolymer but the technology of the recording apparatus for such ultra-stable recordings is high and the casual worker will find it beyond his grasp.

When we began our work, it was with the fear that either SHSG would be impractical and highly complex, or that it would result in holograms of low efficiency due to the removal of the highly refractive halide. That neither of these problems is of importance creates a helpful scenario and it is the purpose of this paper to provide some usable recipes for the chemistry that inspire

confidence in the method so that the general worker will be encouraged to use it.

2. The SHSG Process — Some Historical Approaches

Historically, two routes appear to have a place of prominence; these can be outlined as follows:

The method of Graver et al [3].

- Develop the hologram to a density $D \geq 2$.
- Solvent bleach the hologram to remove the developed silver — using a tanning solvent bleach.
- Fix out the remaining unexposed (undeveloped) silver.

NB In this method, the inherent effects of high gamma leading to holographic non-linearity are endemic. Results reported by Graver and co-workers indicated diffraction efficiencies for gratings of the order of 35%.

The method of Chang and Winnick [4].

- Develop the layer.
- Rehalogenate in a tanning rehalogenating bleach.
- Fix out the remaining halide.

This method has received much attention since efficiencies as high as 75% have been reported. The reader is referred to the recent and detailed studies of Fimia and co-workers for an update.

The ideas embodied in these two methods cover many of the tricks that can be played with the method of SHSG but the chemical formulations appear in either case to be either flawed or a trifle primitive. What we shall do here is to show how to construct optimized chemical baths for the process from which further developments can be constructed.

3. Optimized Chemical Baths for the Silver Halides and the SHSG Method

Developers

Our experience here is that the optimal developing chemistry is still somewhat empirical but some clear winners have emerged.

Fimia and co-workers claim that for the correct manifestation of the SHSG method then tanning effects in development should be avoided. As a result, detailed studies of developers based on ascorbic acid (a developer known not to tan) have been conducted by his group. Some novel advances in this area are to be published (Phillips, Fimia, et al [5]) in the near future.

For the moment, we can give workers a comfortable prediction of success (in the transmission mode of recording) by the use of the developer CWC2 (below):

Distilled water 800 ml.

Ascorbic acid	5 g.
Sodium sulphite (anhydrous)	5 g.
Catechol	10 g.
Urea	50 g.
Sodium carbonate (anhydrous)	30 g.
Make up to 1 l.	

Bleaches

These we have optimized and the formulae are given with relevant comments on rationale.

Non-tanning rehalogenating bleaches

NTB1

Distilled water	800 ml.
Copper sulphate	10 g.
Potassium Bromide	17 g.
Glacial acetic acid	10 ml.
Potassium persulphate	10 g.
Make up to 1 l.	

NTB2

Distilled water	800 ml.
Ferric nitrate	50 g.
Potassium bromide	17 g.
Potassium persulphate	20 g.
Make up to 1 l.	

At this point it is timely to ask how such formulations are arrived at.

Firstly, we note the use of the agent potassium persulphate. This is used to regenerate the oxidizing agent (e.g. cupric sulphate or ferric nitrate) after its reduction as a result of attacking the silver of the image. The merit of this regeneration process has been discussed at length [6].

The halide (KBr) level is set so as to avoid the formation of coarse crystallites of silver bromide without too much loss of efficiency.

The overall rate of bleaching is also important and has been found to be optimized somewhere around a clearance time of 5 minutes. Overall dilution exerts the necessary control of rate.

Tanning bleaches

Despite a detailed search by the authors [6], we concluded that only the dichromates have the effect of hardening the gelatin in the correct mode for use with SHSG. We evolved the tanning bleaches below as follows:

(i) Solvent tanning bleach (STB)

Distilled water	800 ml.
Potassium dichromate	8 g.
Glacial acetic acid	40 ml.
Potassium persulphate	10 g.

Potassium hydrogen sulphate 1.5 g.
Make up to 1 l.

Here, the tanning is influenced by the pH of the solution. As the pH is raised, the rate of silver solvent action diminishes. A five minute clearance time has been found to be a minimum for serious gelatin hardening to take place.

The basic level of dichromate determines the overall rate of clearance together with the following constraints:

- It is found that the glacial acetic acid exerts control over pH and enhances the hardening reaction.
- Potassium persulphate regenerates the reduced Cr^{6+} ions (from their Cr^{3+} state).
- Potassium hydrogen sulphate exerts a crude but effective control over the overall level of acidity.

It is clearly observed that tanning action is enhanced by slowing the rate of clearance. Such observations are related to the clear indication of chromium attachment to the gelatin made observable by yellowing of the layer. Since potassium persulphate is capable of reoxidizing the Cr^{3+} ion back to the Cr^{6+} state (a consequence of its large Redox potential), this agent has a rôle to play in resolution enhancement of the overall process. Thus the uncontrolled diffusion of the Cr^{3+} ion, which might lead to uniform tanning, can be inhibited.

(ii) Rehalogenating tanning bleach (RTB)

In this form the bleach must be subject to a degree of internal conflict. It must tan or harden the gelatin layer and yet must also promote the physical transfer of halide that leads to the modulation of the image. With these features in mind, we evolved the following bleach.

Part A.
Distilled water 400 ml.
Potassium bromide 17 g.
Di-sodium EDTA 10 g.
Make up to 500 ml.

Part B.
Distilled water 400 ml.
Ammonium dichromate 4 g.
Glacial acetic acid 40 ml.
Potassium hydrogen sulphate 2.5 g.
Potassium persulphate 10 g.
Make up to 500 ml.

Equal parts are mixed immediately prior to use and the mixture diluted 1 + 4 with distilled water.

With either the solvent or rehalogenating tanning bleaches, powerful agitation is needed during the bleach process. For the reasons outlined above, failure to agitate will create stagnation due to the inhibition of physical transfer in the bleached layer and into the bath. When solvent bleaches are applied, an insoluble precipitate is formed. Such precipitation must be washed away (cleared) in an appropriate solution. We have found that a

suitable clearing solution may be prepared as follows:

Distilled water 900 ml.
Sodium metasilicate 2 g.
Sodium sulphite (anhydrous) 50 g.
Make up to 1 l.

The subtlety of the need for a clearing bath lies in the fact that the precipitation takes place external to the recording layer and also within the voids of the gelatin. Thus in fact, lack of clearing also leads to a loss of index modulation of the bleached layer.

4. Experimental Strategies

For the average worker, effective results can be obtained using the following procedure in transmission mode:

- Develop in CWC2 to a density $D \approx 2.5$.
- Rehalogenate in RTB with agitation.
- Fix for 2 mins.
- Dry (see later).

An examination of the bleached but unfixed hologram layer clearly points out the undesirable scattering consequences of large and imperfectly formed silver-halide grains. In fact, the Agfa materials 8E75HD and 8E56HD, both exhibit poor control of improbable but large grains in the tail of their statistical distribution.

The removal of the halide grains at the fix stage still leaves a bright and clear void image that can be further amplified at the drying stage. The net result is a remarkable reduction of image noise but with little or no reduction of the signal if proper drying procedures are adopted.

The solvent bleach route is outlined below:

- Develop in CWC2 to a density $D \approx 2.0$.
- Solvent bleach in STB with agitation.
- Clear.
- Fix.
- Dry (see later).

Using the solvent bleach also produces results of importance, but because of the precipitation problem mentioned earlier, it is best just to rehalogenate with the bleach RTB when no such precipitation occurs.

5. A New Experimental Strategy that Combines the Best of All Approaches

In this case the image modulation is first established by diffusion transfer in a non-tanning bleach (e.g. NTB1 or NTB2). The layer is then reactivated and totally redeveloped prior to final tanning, rehalogenation, and fixing:

- Develop in CWC2 to a density $D \approx 2.0-2.5$.
- Wash.
- Bleach (NTB1 or NTB2).

- Wash.
- Reactivate and expose to strong white or UV light.
- Redevelop to completion.
- Wash.
- Rehalogenate using RTB.
- Wash.
- Fix.
- Wash.
- Dry (see later).

The novelty of this approach lies in the hardening levels achievable for the layer. Since *all* the initial silver population is rehalogenated, the hardening level is now at its maximum for such a layer.

This method has been found to be very effective in creating holograms of very low noise and simultaneous high efficiencies. For this method we introduce two new stages of processing. These are formulated as follows:

Reactivator bath.

Distilled water	900 ml.
Sodium sulphite (anhydrous)	50 g.
Calgon (sodium hexametaphosphate)	0.5 g.
Make up to 1 l.	

Immerse bleached hologram in bath for 2 minutes under safelighting. Wash and transfer to second developer.

Redeveloper bath.

An effective redeveloper has been constructed from a modified D19 solution as follows:

Distilled water	800 ml.
Sodium sulphite (anhydrous)	10 g.
Metol	2 g.
Quinol	14 g.
Sodium carbonate (anhydrous)	50 g.
Urea	50 g.
Few drops of wetting agent.	
Make up to 1 l.	

The hologram is inserted into the developer after reactivation in safelighting and then placed under an intense white or UV lamp. The effect of the lighting is to create almost instant high silver density. Immersion in the redeveloper can be extended to approximately 30 seconds – 1 minute.

Though this method may seem tedious in the number of steps necessary, it produces outstanding results.

6. Drying and Packaging of the Finished SHSG Hologram

If rapid drying of the layer is invoked, say by the use of hot propanol, then the voids created during the processing of the holographic layer can be 'propped up' so as to remain as the modulation mechanism of the hologram [7]. Because these voids are subject to collapse if moisture is allowed to permeate the layer, specialized

packaging of the finished result is imperative.

The drying process can be as follows:

Immerse the plate in a warm bath (48–55°C) of propanol-water mixture at a specific gravity of 0.86. Then immerse, with agitation, in at least two baths of warm dry propanol. Remove slowly to avoid drying marks.

We have also evolved the following method for drying which has yielded outstanding results.

First immerse the wet layer in methanol (at room temperature) to remove excess water and droplets etc. Second, immerse in ethyl methyl ketone (at room temperature). Both these steps can be for say 2 minutes with agitation. Finally, immerse in a bath of either ethyl methyl ketone or methyl methacrylate at an elevated temperature (65°C) for a few minutes and then lift out carefully to avoid drying marks or streaks.

The dried layer is, of course, moisture sensitive but in fact considerable use can be made of an uncovered master made by this method so long as the relative humidity of the working environment is low enough. It is preferable to cover the hologram quickly using a UV curable cement and glass cover.

7. Conclusions

In this paper, we have outlined our experience and rationale behind the manufacture of SHSG holograms. The results offer noise levels not attainable by grainy silver halide holograms. The reflection hologram case is not so simple and will be the topic of further publications.

With the increasing demands of mastering for embossing and exposures into photoresist or photopolymers, these exotic methods take on a pragmatic and important rôle.

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