Influence of R-10 bleaching on latent image formation in silver halide-sensitized gelatin

A. Fimia, A. Beléndez, and I. Pascual

The authors are with the Departamento Interuniversitario de Optica, Laboratorio de Optica, Universidad de Alicante, Apartado 99, Alicante E 03080, Spain. Received 17 June 1991. 0003-6935/92/173203-03\$05.00/0. © 1992 Optical Society of America.

The optimization of the silver halide-sensitized gelatin process is analyzed by considering the bleaching action, the influences of the developer, and the hardening modulation process.

Key words: Holography, holographic recording materials.

Silver halide-sensitized gelatin (SHSG) is a hybrid processing method that combines the energetic and spectral sensitivity of photographic emulsion with the high diffraction efficiency and low noise of dichromated gelatin (DCG).¹ In SHSG processing the developed Ag of the photographic emulsion is converted through bleaching, fixing, washing, and dehydrating in isopropanol baths into a refractive index modulation of the gelatin, forming a phase hologram. Nevertheless, the latent image-formation mechanism in SHSG processing has not been fully investigated. Hariharan² has pointed out that the tanning action of the oxidation products of the developer plays a significant part in the formation of the latent image in the holograms. On the other hand, Angell³ has optimized the processing to increase the diffraction efficiency and the signal-to-noise ratio by providing a method for controlling emulsion shrinkage by chemically modifying the gelatin matrix.

Basically, once the photographic emulsion has been exposed it is developed and bleached. Because of this bleaching action the developed Ag is oxidized to Ag^+ whereas the Cr^{6+} ion is reduced to Cr^{3+} during the same bleaching wash. In this way the Cr^{3+} ion is linked to the gelatin chains in the vicinity of the Ag⁺ grains, achieving variation in hardening between the exposed and nonexposed zones of the emulsion. In this Note we point out the influence of the R-10 bleach bath composition on the latent image formation of SHSG holograms from the point of view of Chang and Leonard's model of differential hardening in DCG (see Ref. 4). According to this model, water developing creates an initial refractive-index modulation by swelling, which forms a strong volume hologram. This initial refractive-index modulation is amplified further by the final alcohol developing. There is a proportional relationship between these index modulations just as there is between the diffraction efficiency measurements before and after the dehydration steps. By knowing these diffraction efficiency measurements it is possible to optimize the photochemical process.

Experiments were carried out with Agfa-Gevaert 8E56 HD plates. Unslated holographic transmission-diffraction gratings with a spatial frequency of 1000 lines/mm were recorded on each plate with exposures ranging from 40 to 400 μ J/cm² by using two collimated beams of equal intensity from an Ar⁺ laser ($\lambda = 514$ nm). The exposed plates were processed according to the processing schedule shown in Table I. Two developers were used in these experiments. One was a developer obtained with ascorbic acid and sodium carbonate (we call this developer AAC),⁵ which avoids the influence of the oxidation products during developing. The other was Kodak D-19, a nontanning developer. (However it is important to note that oxidation products of this developer produce an important tanning action.) The bleaching used is a modified R-10 bleach bath in which we substituted ammonium dichromate for potassium dichromate (typical of R-10 bleaching). These salts have the same chemical properties and their behavior is similar. On the other hand, an R-10 bleach bath produces a tanning action comparable with that of a tanning developer. This action can be varied by changing the dilution with water or by changing the composition of the solution.⁶

The experiments were carried out by the following steps:

- 1. Develop for 4 min (D-19, AAC).
- 2. Rinse in running water for 1 min.

3. Bleach in a modified R-10 solution for 30 s after the plate has cleared at 50° C (for formula, see Table I).

- 4. Rinse in running water for 30 s.
- 5. Soak in fixer F-24 for 2 min.
- 6. Wash in running water for 20 min.
- 7. Dehydrate in 50% isopropanol for 3 min.
- 8. Dehydrate in 90% isopropanol for 3 min.
- 9. Dehydrate in 100% isopropanol for 3 min.
- 10. Dry in a vacuum chamber.

(*Note:* All solutions are at 20°C except in the bleaching step.)

In our experiments the measurements of diffraction efficiency were made in steps 6 and 10 of the processing to control the refractive-index modulation during processing.

Table I. Developer and Bleach Bath Formulas

Formula		Amounts
AAC Develope	er	
1-Ascorbic acid		18 g
Sodium carbonate		60 g
Distilled water to make		1 liter
Modified R-10	Bleacha	
Solution A	Distilled water	500 mL
	Ammonium dichromate	20 g
	Sulfuric acid	14 mL
	Distilled water to make	1000 mL
Solution B	Potassium bromide	92 g
	Distilled water to make	1000 mL

Just before use, mix one part A with ten parts distilled water, then add x parts B, according to the text.

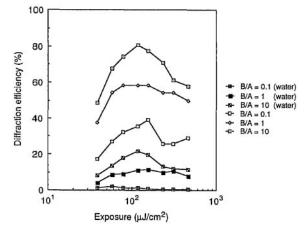


Fig. 1. Maximum diffraction efficiency measured inside a water tank before final alcohol development and after processing, as a function of exposure for unslated holographic transmission gratings at a spatial frequency of 1000 lines/mm developed with AAC and bleached with modified R-10, for different values of ratio B/A.

The diffraction efficiency was defined as the ratio between the power in the first diffracted order and the incident power. The composition of the R-10 bleach bath was modified, which changed the ratio between the A and B baths in order to analyze the effect of the relation between the Cr⁺³ and Br⁻ ions of the bleach bath on its tanning action. The rehalogenating bleach mechanism⁷ shows that the refractive-index modulation is formed by transferring AgBr from the exposed areas to the neighboring unexposed areas and by decreasing the Br⁻ concentration, which gives us a decrease in diffraction efficiency. At the same time the life span of the chromium ion Cr^{3+} is controlled by adjusting the ratio of solution A to B, as we can see in Fig. 1. In this figure we have represented the influence of ratio B/A on diffraction efficiency measurements in water (i.e., when the plate is situated inside a water tank before the final alcohol development) and the final diffraction efficiency after processing. When we increase the Br concentration (the ratio B/A) the diffraction efficiency increases in the water from 2% (B/A = 0.1) to 23% (B/A = 10), and after processing increases from 39% (B/A = 0.1) to 80% (B/A = 10).

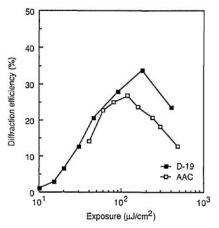


Fig. 2. Diffraction efficiency measurements inside a water tank before the final alcohol development as a function of exposure for unslated holographic transmission gratings at a spatial frequency of 1000 lines/mm developed with AAC and with D-19.

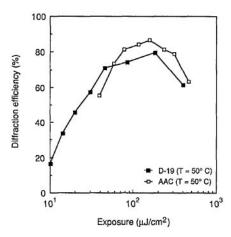


Fig. 3. Final diffraction efficiency as a function of exposure for unslated holographic transmission gratings at a spatial frequency of 1000 lines/mm developed with AAC and with D-19.

In Figs. 2 and 3 we can see the diffraction efficiency measurements of plates placed inside a water tank and the diffraction efficiency after the final alcohol development (after processing) for the AAC and D-19 developers used. As we can see from these figures, the oxidation products of the developer modified the values of the diffraction efficiency in water, and this diffraction efficiency is better for D-19 than for AAC. However, after processing, the diffraction efficiency is better for AAC than for D-19. It is possible that this is due to the fact that, at the same time the differential hardening is increased by the oxidation products of the bleach bath, the growth of the emulsion grain is modified so that there is a decrease in the refractive index modulation. This was pointed out previously for PAAP and D-19 developers.⁸

In conclusion, it is possible to obtain and to control the hardening bias level in SHSG by analyzing either the

Recoded signed-digit binary addition-subtraction using opto-electronic symbolic substitution

Abdul Ahad S. Awwal

The author is with the Department of Computer Science & Engineering, Wright State University, Dayton, Ohio 45435. Received 10 April 1991.

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Two opto-electronic implementations of carry-free addition and borrow-free subtraction of recoded signed-digit binary numbers that use optical symbolic substitution are proposed.

Key words: Symbolic substitution, modified signeddigit number, optical computing.

Carry-free addition using modified signed-digit (MSD) numbers¹ is well suited for optics since it eliminates the need for propagating the carry. Since the addition can be performed at all digit positions in parallel, it provides an elegant mapping of the powerful computing algorithm to the parallel cellular computing architecture² of optical symbolic substitution (OSS).³ N-step,⁴ three-step,⁵ two-step,^{6,7} and developer-oxidizing products or the tanning action of the bleach bath. In order to optimize the process it is necessary to take into account the relationship between the diffraction efficiency measurements in the water tank (before dehydration) and those taken after the final alcohol developing, according to the method proposed by Chang and Leonard⁴ for DCG. An adequate balance of the two photochemical processes (developer-oxidizing products and tanning action of the bleaching) can lead to an optimum processing schedule with high diffraction efficiency, high energetic sensitivity, and low noise levels.

References

- B. J. Chang and K. Winick, "Silver-halide gelatin holograms," in *Recent Advances in Halography III*, T.-C. Lee and P. N. Tamura, eds., Proc. Soc. Photo-Opt. Instrum. Eng. **215**, 172– 177 (1980).
- 2. P. Hariharan, "Silver halide sensitized gelatin holograms: mechanism of hologram formation," Appl. Opt. **25**, 2040–2042 (1986).
- D. K. Angell, "Improved diffraction efficiency of silver halide (sensitized) gelatin," Appl. Opt. 26, 4692–4702 (1987).
- 4. B. J. Chang and C. D. Leonard, "Dichromated gelatin for the fabrication of holographic optical elements," Appl. Opt. 18, 2407–2417 (1979).
- 5. J. Crespo, A. Fimia, and J. A. Quintana, "Fixation-free methods in bleached reflection holography," Appl. Opt. **25**, 1642–1645 (1986).
- 6. R. L. Lamberts, "Characterization of a bleached photographic material," Appl. Opt. **11**, 33-41 (1972).
- P. Hariharan, "Rehalogenating bleaches for photographic phase holograms. 3: Mechanism of material transfer," Appl. Opt. 29, 2983–2985 (1990).
- A. Fimia, I. Pascual, and A. Beléndez, "Silver halide sensitized gelatin as a holographic storage medium," in *Laser Technologies in Industry*, S. P. Almeida, L. M. Bernardo, and O. D. Soares, eds., Proc. Soc. Photo-Opt. Instrum. Eng. **952**, 288–291 (1988).

single-step⁸ carry-free addition based on an OSS scheme have already been proposed.

Careful investigation into all MSD schemes reveals that at least 6 bits (N-step requires more) of information needs to be inspected in order to generate 1 bit of substitution result. For example, in the three-step implementation,⁵ 2-bits/step are inspected to result in a 1-bit substitution. In the two-step approach, 4 bits are inspected in the first step and 2 bits in the second, which requires 6 bits of information in total. Single-step processes⁸ require a large number of rules while multiple-step processes require optic-toelectronic-to-optic conversion. The search for algorithms such that the total number of rules as well as the number of steps is optimized is the goal of OSS. To achieve these goals without sacrificing the parallelism of optics, two carry-free addition schemes are proposed. First, a hybrid symbolic substitution scheme based on a recoding of input numbers is investigated such that the optical addition process can be carried out in a single step. In this scheme, the to-be-added numbers are encoded, independently, into MSD numbers such that they result in limited carry-free addition.⁹ The optic overhead of the process is reduced by encoding the input numbers electronically in parallel beforehand unlike other single-step processes, and the addition step is then