Diffraction Efficiency of Bleached, Photographically Recorded Interference Patterns

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An experimental study has been made of techniques that can increase the diffraction efficiency of photographically recorded three-dimensional interference patterns. The efficiency is increased by using bleaching processes that convert the silver image into a dielectric image. Diffraction efficiency vs transmittance curves, chemical formulas of some bleaches, and the bleaching procedures are given. A maximum efficiency of 60% has been achieved. Applications to holography and partitioned zone plates are demonstrated.

Introduction

Recently, the main use of photographically recorded interference patterns has been for recording images as in holography. These patterns also have been used as diffraction gratings[1] and Fresnel zone plates. They can be also used as other optical elements,[2,3] or for producing special waveforms in optical data processing systems.[4] The latter applications are practical only if the diffraction efficiency can be increased above the usual 4% obtained with silver images.

There are several techniques for increasing the diffraction efficiency. One technique is to convert the silver image into a relief image. The relief image is formed by further processing the developed silver image so that the emulsion thickness varies according to the density of the grating.[5–7] This technique produces a maximum diffraction efficiency of 33.9%.[8]

Another technique is to convert the developed silver grains into a transparent compound with refractive index different from that of the gelatin. This technique forms a three-dimensional dielectric grating in a thick emulsion, and the efficiency can reach 100% under proper conditions.[8,9] The developed silver image can be described by $T = 1 - g(I)$, where T is the transmittance and $g(I)$ is a function of exposure. The bleaching process should convert this image into $T = \exp ih[1 - g(I)]$, where $h[1 - g(I)]$ is a function expressing the relation between transmittance of the silver image and the phase of the bleached image.

Photographically recorded three-dimensional interference patterns have been processed in this way and rather high diffraction efficiences have been achieved.[10] However, the published information on bleaches and their characteristics is scarce. We have investigated various bleaches and their effectiveness in converting a silver image into a corresponding dielectric image. In this paper, we report the efficiencies achieved by various bleaches, the contents of bleaching solutions, procedures for using the bleaches, and some demonstrations of the applications.

Experimental Procedures and Results

Diffraction gratings were made by recording the interference pattern between two spherical waves from a He–Ne laser. The gratings were then bleached, reinserted in the original position, illuminated with one of the two beams and the diffracted light intensity was measured. All experiments were made with the plane of polarization perpendicular to the plane of incidence. The angle between the two waves was such that the interference pattern had an average spatial frequency of 2200 lines/mm (included angle of 90°); this ensured that the effect of the surface relief image would be negligible.[7] The intensities of the interfering beams were adjusted to be equal and the patterns were recorded on standard 4 in. × 5 in. × $^1/_8$ in. glass plates with Kodak 649F emulsion.

All plates were developed for 5 min in Kodak D–19 developer at 20°C, rinsed in short-stop bath for 15 sec, fixed for 5 min, and washed for 10 min in running water. Continuous agitation was used in development. The photographic density was measured after the washing step without drying. After this, the plates were bleached according to the procedures given in the appendix.

We define diffraction efficiency as I_d/I_i, where I_i is the incident light intensity and I_d is the diffracted light flux into the first sideorder. The plots of diffraction efficiency vs transmittance before bleaching are shown in Figs. 1–3.

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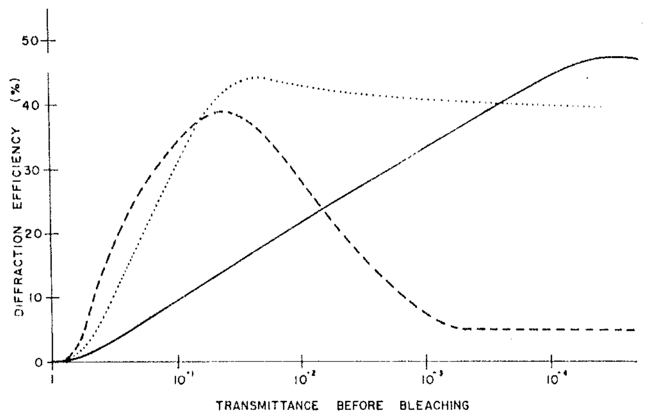

Fig. 1. Diffraction efficiency after bleaching vs transmittance of developed silver image with three bleaches: (2)—Chromium Intensifier Bleach (solid line); (1)—mercuric chloride bleach (dashed line); and (4)—combination R–10 and mercuric chloride bleach (dotted line). The numbers refer to the bleaches listed in the appendix.

Of the bleaches tested, the $HgCl_2$ bleach had the highest efficiency at high transmittance, while the highest diffraction efficiencies of 47% were obtained with the Kodak Chromium Intensifier Bleach* and the R–10 type bleach with potassium bromide in solution B. Figure 3 shows results obtained with several other bleaches. We note that the potassium ferricyanide bleach is very easy to use and the bleached emulsions have good stability.

An important property of the bleaches is to form a stable compound. All bleaches in Figs. 1 and 2 and the copper bromide and hydrogen peroxide bleach form compounds that are unstable and have a tendency to become more opaque with exposure to light. We found that the bleach products could be stabilized by soaking the plates in a solution of the respective cupric halogen (CuO_2, $CuBr_2$, or CuI_2) or mercuric halogen as the final step. Very intense light may cause instability of mercuric halogens. Potassium ferricyanide bleach formed compounds that were stable without further processing. HgCl bleach also forms stable compounds if processed precisely according to the procedure described in the appendix. It should be noted that mercuric compounds present a certain safety hazard, as they may be absorbed through the skin.[11]

Discussion

Ideally, the bleach should convert silver into a transparent compound having refractive index significantly higher than that of the emulsion. The silver can also act as a catalyst: an insoluble compound can be formed in place of the silver and the silver can react to form a soluble compound which is dissolved from the emulsion. In addition, the residual compound should be stable and should not decompose with exposure to light. None of the bleaches tested have all of these desired properties, but they do improve the diffraction efficiency considerably.

We had difficulty in obtaining repeatable results. At the spatial frequency of 2200 lines/mm, any mechanical deformation of the emulsion has a considerable effect on the diffraction efficiency. Frequently, we found that the intensity of the diffracted light varied across the grating area. Since our optical system measured the average diffracted light intensity, such deformation caused occasional low readings. The plotted curves are the maximum points of several trials.

To check the modulation transfer function (MTF) of the bleached emulsion, we measured the diffraction efficiency of plates made with 30° and 50° angles between the two beams that were bleached in modified R–10 bleach with KBr. The efficiencies were the same as those made with a 90° angle between the beams. This indicates that the MTF is approximately flat over this spatial frequency region; a similar result has been obtained with unbleached emulsions.[12]

We did some tests with the two beams entering the emulsion from the opposite sides and forming fringe patterns approximately parallel to the emulsion surface. The maximum diffraction efficiency achieved in this case was only 11%. The measured efficiency as a function of the incident angle of the illuminating beam indicated that the angular sensitivity was lower than predicted by theory.[13] The lower angular sensitivity may be caused by nonuniform processing of the emulsion in depth, or perhaps by nonuniform distribution of silver grains. Any of these nonuniformities would affect the maximum diffraction efficiency and could account for the low measured efficiency.

A difficulty we encountered was that the detrimental effect of the low frequency interference patterns, caused by extraneous reflections and scattering during the exposure was accentuated by the bleaching process. The low frequency patterns, which usually have a

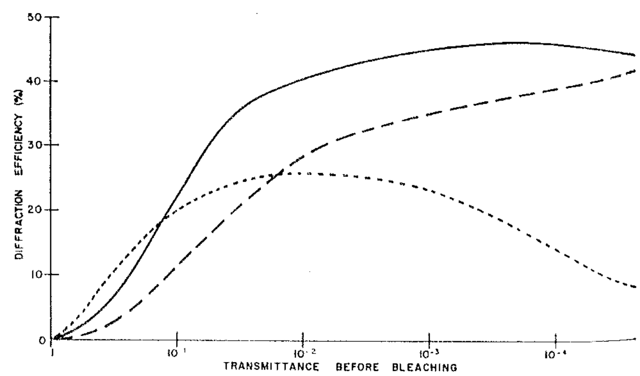

Fig. 2. Diffraction efficiency after bleaching vs transmittance of developed silver image of R–10 type bleaches: (3)—R–10 bleach (long dashed lines), modified R–10 bleach with potassium bromide replacing sodium chloride (solid line), and modified R–10 bleach with potassium iodine replacing sodium chloride (short dashed lines).

* The bleach referred to here is the one produced by Kodak. There are also bleaches called Chromium Intensifier Bleaches with their composition given in the Photo-Lab Index, for example.

negligible effect on the performance of the grating when it is used in the normal manner, produce a strong relief image after bleaching.[7] This relief image acts in a manner similar to a superimposed random scatter plate and thus makes the diffracted beam noisy.

In our experiments, the low frequency pattern was caused by a small amount of light scattered by a pinhole assembly and by the usual reflections from the back surface of the recording plate. We eliminated back reflections by coupling one surface of a prism to the back of the photographic plate with xylene and by placing a black absorbing surface in contact with the other surface of the prism. The absorbing surface attenuated the reflected light, while the prism caused an increase in the average spatial frequency, thus decreasing the diffraction efficiency of the noise pattern.[7]

Distribution of Light

The plots of efficiencies in Figs. 1–3 are lower than can be achieved, since they include losses due to surface reflections. The diffraction efficiency could be increased if an appropriate antireflection coating was placed on the surfaces of the plates. To find the maximum possible diffraction efficiency, the values given by the curves should be multiplied by a factor of 1.23. Thus, the maximum efficiency achieved in our experiments is 60% of the incident light entering the emulsion.

It seemed of some interest to determine the light losses in these plates. In many cases, we observed that the transmitted light intensity was only 1% or 2%, although the diffraction efficiency was not very high. We examined one grating, with 2200 lines/mm average spatial frequency, bleached in modified R-10 bleach, with KBr, and found the following light distribution:

Diffracted light (measured)	44%
Transmitted light (measured)	8%
Surface reflections (estimate based on measurement)	14%
Scattered light (estimate based on measurement)	9%
Absorbed light (estimate of all unaccounted light)	25%

Sometimes lower transmitted light could be achieved by increasing exposure, but due to increased absorption, the diffraction efficiency also decreased.

Chemistry

We were able to convert silver into the following compounds with indicated indexes of refraction: AgCl (n = 2.07), AgBr (n = 2.25), AgI (n = 2.21), copper oxide (n = 2.5 to 2.7), and $Ag_4Fe(CN)_6$ (n unknown). In addition, in some cases, chromium salts were formed that contribute to the refractive index change. The other bleach products are soluble and are removed from the emulsion.

The final chemical reaction for the R-10 type bleaches probably is

$$+ 12NaCl + 7H_2SO_4 + (NH_4)_2Cr_2O_7$$
$$\rightarrow 9AgCl\downarrow + Cr_2Cl_3\downarrow + 7H_2O + 6Na_2SO_4 + (NH_4)_2SO_4.$$

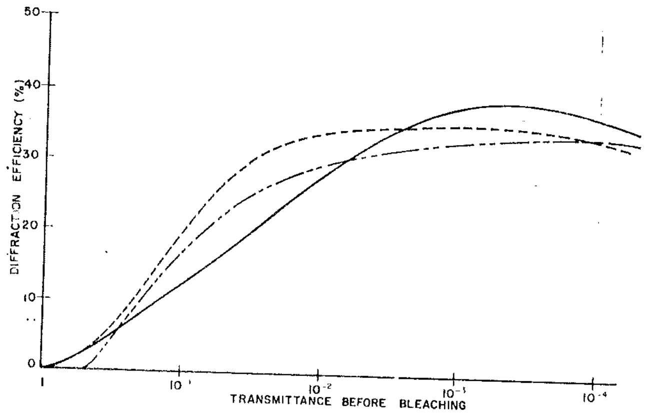

Fig. 3. Diffraction efficiency after bleaching vs transmittance of developed silver image of potassium ferricyanide bleach, (5)—(solid line); potassium bromide and potassium ferricyanide bleach, (6)—(short dashed line); and of copper bromide and hydrogen peroxide bleach, (7)—(alternating long and short dashed line).

In the modified versions, KI or KBr may be substituted for NaCl. The Kodak Chromium Intensifier probably has a similar reaction. These bleaches may be grouped in a class called the chromate base bleaches. They contain Cr_2O_7 with either ammonium $(NH_4)_2$ or some other compound.

The mercuric chloride bleach gives the reaction[14]:

$$Ag + HgCl_2 \rightarrow AgClHgCl\downarrow.$$

The potassium ferricyanide bleach probably reacts with silver to form $Ag_4Fe(CN)_6$:

$$4Ag + 3K_3Fe(CN)_6 \rightarrow Ag_4F(eCN)_6\downarrow + 3K_4Fe(CN)_6.$$

$Ag_4Fe(CN)_6$ apparently has a high index of refraction, since the diffraction efficiency achieved with this bleach is high.

The potassium ferricyanide and potassium bromide form insoluble AgBr, which remains in the emulsion as the refractive compound:

$$Ag + K_3Fe(CN)_6 + KBr \rightarrow AgBr\downarrow + K_4Fe(CN)_6.$$

The copper bromide bleach was tried because the index of refraction of CuO, CuO_2, and Cu_2O is between 2.5 and 2.7; thus, high efficiencies could be expected. The probable reaction is

$$Ag + CuBr_2 + H_2O_2 \rightarrow AgBr\downarrow + H_2O + \text{copper oxide}\downarrow.$$

The copper oxide in the above formula can be either CuO, CuO_2, or Cu_2O. The bleached plates are unstable and darken with exposure to light. High diffraction efficiency was not achieved, and, owing to the difficulties with H_2O_2 forming bubbles in the emulsion, this bleach is not recommended.

Applications

The bleaching techniques were applied to two practical applications: increasing diffraction efficiency of partitioned zone plates[15] and holograms.

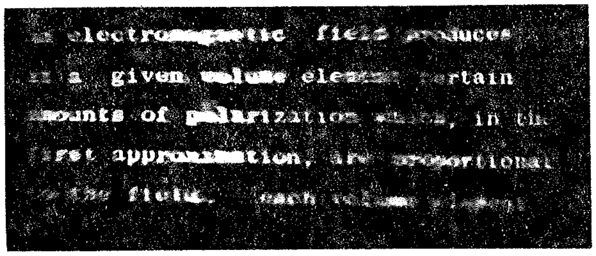

Fig. 4. Imaged transparency by partitioned zone plate consisting of three superimpozed zones. Angular separation between zones was 2° and the angle between the two beams was 90°. Note the three areas where the image is aberration free.

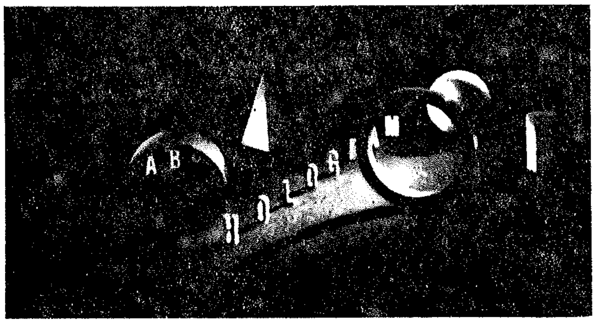

Fig. 5. Reconstructed image from a bleached hologram. The image brightness was increased threefold over a similar unbleached hologram.

Figure 4 shows the image obtained with three superimposed zone plates having 2° separation. The three zone patterns cover a 6° field of view. The areas of best image are clearly visible with some decrease of resolution in regions between each set of zone plates. The efficiency of each zone pattern was approximately 11%.

Figure 5 shows the reconstruction from a bleached hologram. The hologram was exposed to give a threefold increase in diffraction efficiency after bleaching. We can easily achieve higher diffraction efficiencies, but, owing to increased noise from intermodulation terms and nonlinearities in recording, such holograms reconstruct a noisy image.

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Appendix

Note: After the last step in each case, the plates were dried at room temperature.

1. Mercuric Chloride Bleach

Preparation: mix one part saturated solution of mercuric chloride with nine parts of distilled water.

Procedure:
- (a) Bleach for 15 min.
- (b) Wash for 4 min. (Note: HgCl is extremely poisonous.[11])
- (c) Rinse in Kodak Photo-Flo 200 solution.

2. Kodak Chromium Intensifier Bleach (a Product Sold by Kodak)

Preparation: prepare parts A and B as directed on the package. For part C, dissolve 5 g of $CuCl_2$ in 1000 ml of distilled water and add some Photo Flo.

Procedure:
- (a) Bleach for 1 min after the plate has cleared.
- (b) Rinse 30 sec in running water.
- (c) Soak in clearing bath (part B of Kodak Chromium Intensifier) until the emulsion turns white. Agitate occasionally.
- (d) Wash 5–10 min.
- (e) Soak 5 min in part C.

3. R–10 Type Bleaches

Preparation:

Stock Solution A:
- Distilled water—500 ml.
- Ammonium bichromate—20 g.
- Concentrated sulfuric acid—14 ml.
- Distilled water to make—1000 ml.

Stock Solution B:
- Sodium chloride—45 g (or potassium bromide 92 g, or potassium iodate 128 g).
- Distilled water to make—1000 ml.

Solution C (Kodak Clearing Bath CB–6):
- Calgon—0.5 g.
- Sodium bisulfite—15.0 g.
- Water to make—1000 ml.

Solution D:

5 g of respective cupric halogen ($CuCl_2$, $CuBr_2$, or CuI_2) to 1000 ml of distilled water with Photo-Flo.

Just before use, mix one part A and one part B to ten parts distilled water and use this as the bleaching solution.

Procedure:
- (a) Bleach and agitate for 1 min after the plate has cleared—for about 3–5 min.
- (b) Rinse in running water for a few seconds.
- (c) Soak and agitate for 1 min in clearing bath, solution C.
- (d) Rinse for 5 min in running water.
- (e) Soak for 5 min in solution D.

4. Combination R–10 and Mercuric Chloride Bleach

Preparation: just before use, mix one part R–10 bleach solution A, one part R–10 bleach solution B, and two parts saturated solution of mercuric chloride to twenty parts of distilled water. Use this as the bleaching solution.

Procedure:
Same as for R–10 type bleaches, except that the above mixture is used as the bleach.

5. Potassium Ferricyanide Bleach

Preparation: dissolve 15 g of $K_3Fe(CN)_6$ in 1000 ml of distilled water.

Procedure:
(a) Bleach for 4 min; agitate.
(b) Wash for 15 min in running water.
(c) Rinse in Photo-Flo.

6. Potassium Ferricyanide and Potassium Bromide Bleach

Preparation: dissolve 7 g of KBr and 8 g of $K_3Fe(CN)_6$ in 1000 ml of distilled water.

Procedure:
(a) Bleach for 5 min; agitate.
(b) Wash 15 min in running water.
(c) Rinse in Photo-Flo.

7. Copper Bromide Bleach

Not recommended for use since H_2O_2 decomposes in emulsion and tends to remove it from the glass base.

Preparation:

Solution A:
Dissolve 10 g of $CuBr_2$ in 1000 ml of distilled water.

Solution B:
3% solution of H_2O_2.

Mix eight parts of solution A with one part of solution B just before use.

Procedure:
(a) Bleach until the plate turns brown but for not more than 10 min. Continuously brush off bubbles forming on emulsion surface.
(b) Wash for 15 min in running water.
(c) Rinse in Photo-Flo.

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Meeting Reports *continued from page 84*

J.G.A. De Graaf *Netherlands* (left) and K. Vollrath *Germany* photographed at the Stockholm HSP Meeting by R. E. Perkins *CUSP, RAE, Farnborough.*

in this subject whose last public act was to deliver an invited lecture at the last 1965 high speed congress in Zurich, after which he collapsed and subsequently died. This Congress expressed its regard and real affection in silent contemplation and memorialized his name by accepting from Germany their award of the Schardin Medal. This medal was, on this occasion, appropriately given to a collaborator of Schardin's and a fellow-German, Heins Reichenbach. In the future it will be awarded at similar congresses by an international jury to a young scientist for his contributions to the subject and, in particular, his work since the preceding congress. The presentation was supported by the Congress President, E. Ingelstam *Stockholm* and the Session Chairman, Karl Vollrath, a well-known figure from Schardin's old laboratory at St. Louis/Weil-am-Rhein.

Immediately following the presentation, Professor Dubovik, the Russian National Delegate, read a paper by A. A. Sakharov *U.S.S.R.* on International Terminology of High Speed Photography and Cinematography. Terminology has been a subject of discussion for many years but this was no mere discussion as it was supported by a booklet (in limited quantities to national delegates) with 850 entries in 4 languages, English, French, German, and Russian, arranged alphabetically according to the English reference. Sakharov has previously published in the U.S.S.R. an English–Russian, Russian–English Dictionary for Photography and Cinematography. This particular effort is intended as a basis for discussion, correction and addition towards a comprehensive technical dictionary. He is to be congratulated, praised, and thanked for what is really a most considerable *tour de force.*

The congress papers covered the now very wide range of subjects in and around high speed photography. HSP seems, at times, to be a misnomer but it is now too well established to be changed, although I have a personal liking for its German counterpart—*Kurzzeitphysik*, short-time physics or the physics of transients, perhaps. Innovations, improvements, and modifications abound in all branches, too numerous to detail here. The greatest activity and advance in technique occurred in two subjects: image tubes (photoelectronics) and holography (including lasers). The latter are so new that this is the first congress when a half-session was devoted to lasers as light sources and a full session to holography plus references in papers