Reflection-hologram processing for high efficiency in silver-halide emulsions

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The results are described of experiments carried out to develop improved processing methods for reflection holograms in bleached silver halide emulsions, as a result of which overall efficiencies of nearly 66% (75% after allowing for specular reflections) have been achieved for gratings recorded by two plane waves at 514.5 nm in an index-matching tank. These figures are limited almost solely by scatter and may approach the limits obtainable with the recording material, Agfa 8E56HD. Close agreement has been reached between experimental measurements of the off-Bragg response of the gratings and theoretical predictions based on coupled-wave analyses, allowing determination of the principal grating parameters and revealing maximum efficiency to correspond to a permittivity modulation of ~8.7%.

I. Introduction

Silver halide materials are generally the most convenient for phase holographic recording due to their high sensitivity and ease of handling, and, while the results that can be achieved using existing emulsions certainly will not approach the quality obtainable with dichromated gelatin, it has until recently been the shortcomings of the processing rather than of the materials which only too clearly have proved the limiting factor. During the seventeen years since Cathey's resurrection[1] of an original idea by Rogers,[2] it is apparent that most research has been preoccupied with the bleach as the major stumbling block, a problem which has been eased significantly with the introduction by Phillips *et al.* first of a ferric nitrate bleach[3] and then of *p*-benzoquinone,[4] a reagent now widely recommended (e.g., [Ref. 5]). However, subsequent success in producing high-efficiency phase holograms in bleached photographic emulsions has, if one is to judge from the published literature, been markedly greater in the case of transmission, rather than reflection, gratings. The purpose of the present paper is to describe and discuss the results of trial experiments on the processing of reflection holograms recorded in the Agfa 8E56HD emulsion leading to the achievement of nearly 75% efficiency, after allowing for losses due to specular reflection, for planar gratings.

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II. Background

A processing scheme which is suitable for reflection holograms should work equally well with transmission ones; but the reverse is not the case, there being several reasons the processing requirements for reflection holograms are more stringent.

In the first place, emulsion shrinkage is less of a problem with transmission holograms since it has little effect on the fringe spacing—or none at all, in the case of an unslanted grating—and hence it is appropriate to carry out fixing after development, to remove undeveloped silver halide before bleaching. It is apparent that this will facilitate the achievement of high permittivity modulation in the final grating by maximizing the variation in the silver bromide distribution which can be obtained after bleaching. At the same time, it helps greatly to reduce absorption and scatter losses at reconstruction, the final plate being colorless and almost transparent to the eye. With this type of process, where the variable distribution of silver bromide is the principal modulation mechanism, the choice of developer will be less than crucial provided that the development process is adequately selective, nonstaining, and leads to compact grains after bleaching.

Use of the GP61 developer, followed by fixing and bleaching in ferric nitrate as recommended by Agfa,[5] will allow an efficiency of at least 75% (after allowing for reflections) to be obtained for unslanted planar transmission gratings recorded in Agfa 8E56HD emulsions.[6]

With reflection holograms, by contrast, where the fringe planes are approximately parallel to the emulsion layer, shrinkage can be a major problem, causing a significant reduction in fringe spacing and producing fringe rotation as well in slanted gratings. There will

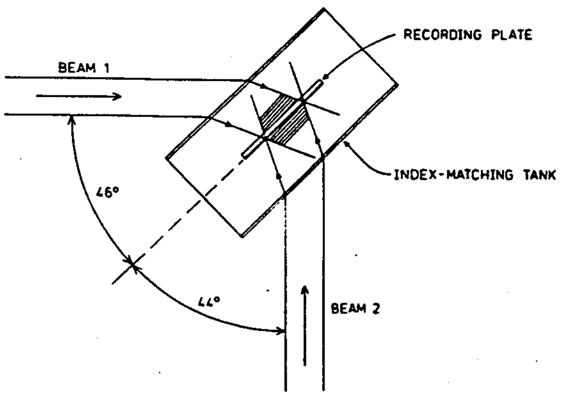

Fig. 1. Schematic diagram of the hologram recording geometry in an index-matching tank.

be a corresponding decrease in the optimum wavelength for reconstruction, and the diffracted beam will, in general, be distorted. Shrinkage may also be nonuniform across and/or through the hologram, further degrading performance.

Although reswelling is possible, for example, by using triethanolamine, it is likewise difficult to obtain a uniform result, and, in addition, we have observed an unpleasant mottled effect in reswollen gratings corresponding to highly localized variations in thickness caused by surface contamination of the emulsion. Other possibilities which have been suggested also have their disadvantages.

For these reasons it is desirable to minimize shrinkage of reflection holograms during processing, and on present experience this requirement precludes fixing, a restriction which is particularly ironical since the achievement of a given efficiency requires a considerably higher modulation in a reflection grating than in a transmission grating for a hologram of given thickness. This can be seen directly from Kogelnik's solutions for the intensities of the transmitted beams in simple lossless planar gratings,[7] respectively, $\cos^2\nu$ and $\mathrm{sech}^2\nu$ for transmission and reflection gratings, where $\nu = \kappa d(\cos\theta_1 \cos\theta_2)^{-1/2}$, κ being Kogelnik's coupling constant and proportional to the modulation, d the grating thickness, and θ_1 and θ_2 the angles of refraction of the recording beams inside the material. While for the transmission grating total depletion is obtained for $\nu = \pi/2$, in the reflection case, 96% depletion corresponds to $\nu \approx 3\pi/4$. The level of modulation necessary to achieve this value is a lot to ask of the thin Agfa emulsions (5–6 μm), and the difficulty is compounded too by the higher spatial frequency of the reflection gratings, taking present materials to limits at which decay of the modulation transfer function is likely to affect the results adversely.

With these problems in view, it is interesting to note from the published literature surveyed, for example, in Ref. 8, that reports of efficiencies achieved in reflection gratings are rather sparse, the outstanding result being that of Graube[9] in Kodak 649F. In our own initial experiments using a pyrogallol-metol developer essentially similar to GP62, followed by bleaching with GP432 (a p-benzoquinone bleach) as recommended again by Agfa[5] (without fixing), we were able to obtain just 33% efficiency after correcting for specular reflection losses for planar reflection gratings recorded in Agfa 8E56HD at 514.5 nm.

III. Experimental Setup

The recordings were made in a parallel-sided index-matching tank (to minimize the problems of boundary reflections giving rise to spurious gratings[10]) using an Ar laser at 514.5 nm with the geometry shown in Fig. 1. Di-n butyl phthalate, or alternatively xylene, was used as the index-matching liquid. The recording beams polarized perpendicular to the plane of incidence were collimated with an external interbeam angle of 90°; and the plate positioned parallel to the tank walls was angled to produce a grating slant of ~0.5°, sufficient to ensure separation of the various beams at reconstruction. The beams were also masked to prevent light entering the edge of the plate and to prevent reflections from the tank walls interfering with the recording of the gratings.

The replay geometry is illustrated in Fig. 2, the hologram being illuminated with a narrow collimated beam of ~5-mm diam, again at 514.5 nm, at a variable angle of incidence Θ. The relative intensities of the output beams were measured by means of a 1-cm^2 photodiode, the output of which was normalized against that of a similar diode measuring a split-off portion of the incident beam using an analog divider. All measurements of efficiency were made in air, the overall efficiency being defined as the ratio of the intensity of the diffracted beam to that of the incident beam. In air, however, the performance of the grating is substantially reduced by specular reflections, and a better measure of the quality of the grating, which we have termed the intrinsic efficiency, may be calculated from the overall figure by allowing for the reflection losses, first of the incident beam and then of the diffracted beam, at the air–gelatin or air–glass interface, these losses being determined from the Fresnel coefficients. (Reflection of the incident beam at the input surface reduces the amount of light entering the emulsion. Reflection of the diffracted beam at the same surface also represents light irrevocably lost for a slanted grating, most of it appearing as a secondary transmitted beam.) We shall

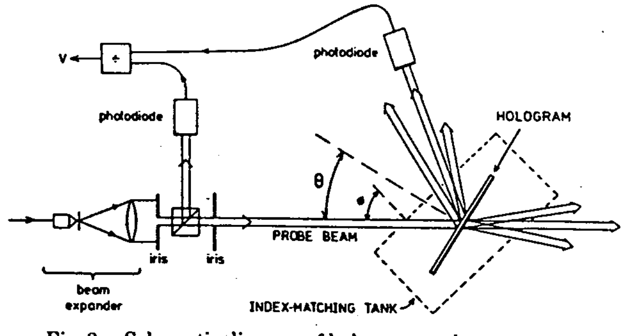

Fig. 2. Schematic diagram of hologram replay geometry.

Table I. Results for Various Developers; Holograms Recorded and Replayed in Air; PBQ-1 Bleach

Developer	Time (min)	Description	Transmission depletion (%)	Overall diffraction efficiency (%)	Ref.
PAAP	2	Phenidone/ascorbic acid	89	31	13
GP61	2	Metol/hydroquinone/ phenidone	86	19	5
Neofin blue	1	Used concentrated	Causes major shrinkage		3
Pyrogallol-metol (CW-P1) (similar to GP62)	1	1 pyro + 5 metol + 10 sulfite + 30 carbonate	78	24	5
Catechol (CW-C1)	2	10 catechol + 10 sulfite + 30 carbonate	90	32.5	

Table II. Bleach Formulas

	(g/liter)
Bleach PBQ-1	
p-benzoquinone	2.0
Boric acid	1.5
Potassium bromide	30
Bleach PBQ-2	
p-benzoquinone	2.0
Citric acid	15
Potassium bromide	50
Bleach 1½ × clearing time at ~20°C (45 sec–2 min) continuous agitation	

refer to the two values for efficiency as η_0 and η_i, respectively, and all figures quoted are for reconstruction from the emulsion side of the plate unless otherwise indicated.

The recordings were made, with a few specific exceptions, on Agfa 8E56HD 6.3- × 6.3-cm (2.5-in. square) silver halide photographic plates marketed as Millimask HD, batch 591525, with an emulsion thickness of ~5.1 μm. Recording beams of nearly equal intensity were used, and the recording energies found to produce optimal results were in the 0.6–0.8-mJ/cm^2 range (corresponding to a developed density of ~2.5). With the geometry described, the spatial frequency of the gratings was calculated as 5700 mm^{-1} (before shrinkage).

IV. Processing Trials

All processes described, development, washing, and bleaching, were carried out at 20°C, although, in fact, no difference could be detected after bleaching at 15°C or even lower. Removal of the antihalation dye from the emulsion by preliminary washing was not found to give any improvement in results. After the final washing, the plates were rinsed in water containing a wetting agent and left to dry in a vertical position. For each combination of reagents, several exposures were made (the plates being processed simultaneously) with the aim of bracketing the optimum, enabling us to predict closely the corresponding maximum efficiency from measurements of the recorded gratings. In each case, the angle of incidence of the reconstructing beam yielding optimum efficiency was also recorded. The deviation from the original recording angle of 44° offers a measure of the change in thickness of the emulsion, a smaller angle corresponding to shrinkage.

Given to the paucity of information available on processing reflection holograms in silver halide materials, we could find no basis for our experimental scheme save that of trial and error, and with so many variable factors in play we could not expect our results to be entirely conclusive. Looking first at the developer, we elected after initial tests to concentrate on one particular reagent, which proved advantageous in respect of achievable efficiency, visible scatter, and shrinkage: this was catechol, which we now find to have been used by Lamberts and Kurtz[11] and recommended by Kodak.[12] Some results of a series of experiments using different developers are given in Table I for recordings made in air, development being followed in each case after thorough washing by bleaching with *p*-benzoquinone using the formula PBQ-1 given in Table II.[4,5] Such developers as GP61 or Neofin Blue, intended for transmission holograms, unsurprisingly turned out to be quite unsuitable for reflection gratings. The formulation termed PAAP proved the closest rival to catechol overall, while pyrogallol remains of particular interest on account of its ability to swell the gelatin, an advantage for display holograms not shared by catechol. In the case of pyrogallol, unfortunately, the achievable efficiency is reduced by the heavy stain characteristic of this reagent; but this stain is again beneficial in display holograms, as it gives an improvement in contrast. In subsequent experiments we also tried using pyrogallol monomethyl ether (1-methoxy 2,3-dihydroxybenzene), introduced as a developer by Schultes,[14] but obtained slightly less efficiency than with catechol, probably as a result of slightly increased stain.

Focusing attention next on the bleach, we were able virtually to eliminate the modest stain ensuring from using the above formula for the pbq bleach by increasing the acidity using citric acid instead of boric acid, although this also reduced the final emulsion thickness slightly. A marked improvement in efficiency was obtained regardless of developer: the simple catechol formulation, CW-C1 now yielding 56% overall efficiency. The efficiency could also, we found, be further boosted by increasing the KBr content of the bleach to 50 g/liter or even 100 g/liter, in the latter case at the cost of a drastic increase in visible scatter, seen as an opacity when the grating was viewed in white light away from the Bragg angle.

As a possible means of combating shrinkage and increasing modulation, attempts were made to bleach to iodide or ferricyanide, but results were highly unsatisfactory: scatter dramatically increased, and swelling of the emulsion was accompanied by severe exaggeration of surface relief due to the presence of low-frequency fringes caused by reflections at the emulsion–glass and emulsion–liquid interfaces during recording.

Although the basic developer CW-C1 was constituted almost by guesswork, we were subsequently unable to achieve any significant and consistent improvement by varying the developer concentration and development time, sulfite content, or pH. Trying the effects of various additives, we found almost all to be deleterious, many of them disastrously so: thus, to take examples, addition of 0.5-g/liter phenidone, or of 2-g/liter KBr, or of 0.2 g/liter benzotriazole, reduced the efficiency from 56% (η_0) to 41, or 49, or 16%, respectively. Certain additives did, however, allow us consistently to squeeze an extra few percent efficiency out of the recorded gratings, and our highest values were achieved using the formula given in Table III, termed CW-C2 for reference, in conjunction with the bleach formula given in Table II, PBQ-2. The use of urea, which softens gelatin, possibly serves to increase penetration by the developer by combating hardening of the emulsion due to tanning.

It also proved advantageous in some respects to choose ascorbic acid instead of sulfite as a preservative with pyrogallol, the resulting stain being noticeably less dense: using 5-g/liter pyrogallol, 5-g/liter ascorbic acid, and 30-g/liter sodium carbonate (formula CW-P2) followed by the PBQ-2 bleach, we were able to achieve an overall efficiency of 43% with the emulsion still slightly swollen. This figure can be further increased by soaking the grating after bleaching in a freshly acidified 20-volume solution of hydrogen peroxide, which does slowly reduce the stain but with the accompanying problems of shrinkage and oxygen bubbles. Addition of a little hydrogen peroxide to the developer will also reduce the stain.

All values of efficiency which are quoted were measured after bleaching and drying the gratings but before exposing them to bromine vapour for ~15 min in a glass container. The increased resistance to printout of gratings bleached using bromine vapor was pointed out by Graube.[9] We found gratings bleached in this way rather than with pbq to be of inferior efficiency, but we found also that a postbleach treatment was likewise effective in inhibiting printout—this is not surprising, since gelatin is a halogen acceptor. In some cases, bromination was found to reduce scatter or absorption losses and also to increase efficiency slightly, a change which might be attributable merely to concomitant changes in emulsion thickness (see Sec. V), which tended to prove permanent if the process were prolonged.

Table III. Developer CW-C2 Formula

	(g)
Catechol	10
L-Ascorbic acid	5
Sodium sulfite (anhydrous)	5
Urea	50
Sodium carbonate (anhydrous)	30
Distilled water	to make 1.0 liter
Develop for 2 min at 20°C continuous agitation	

All the experiments which have been described were carried out using 8E56HD plates from batch 591525, which was fortunate, for when we came to use plates from batch 591520, we found maximum efficiencies achievable using the same processes to be lower by ~10%. Plates from batch 591520 processed using CW-C2 followed by PBQ-2 were discernibly pink in color, while those from batch 591525 were virtually colorless. Attempts to discover the difference from the manufacturer have met with no success, but we suspect the sensitizing dye. However, removal of most of the dye by soaking plates before development in a solution of 2-g/liter sodium thiosulfate, the efficacity of which was increased by addition of isopropanol, did not improve matters. (Such treatment would serve to dissolve away the outer parts of the grains to which the dye is firmly bound.)

V. Theoretical Comparison

After one process had emerged from the trials as being of particular interest for simple gratings, more detailed measurements were made to determine grating parameters. The most important source for these is the off-Bragg curve, showing the response of the grating as the angle of incidence of the reconstructing beam is varied. An independent value is needed of either refractive index or emulsion thickness, however, and both of these, together with the loss parameter, can be obtained from measurements made at glancing incidence, where diffraction is negligible. The whole scheme has been described by Owen *et al.*[10]

The glancing incidence measurements are made with the grating in an index-matching tank (with the beam incident on the emulsion side of the plate). The variation of both transmitted and reflected beams is found to be rapidly oscillatory as the angle of incidence of the reconstructing beam is changed owing to interference between reflections from the liquid–emulsion and emulsion–glass interfaces, these boundaries being unmatched to about the same degree; the results for a typical grating are shown in Fig. 3. Also shown are theoretical curves for a uniform dielectric slab calculated from the Fresnel coefficients with values for the refractive index, thickness, and loss coefficient chosen to obtain as close as possible a fit with the experimental

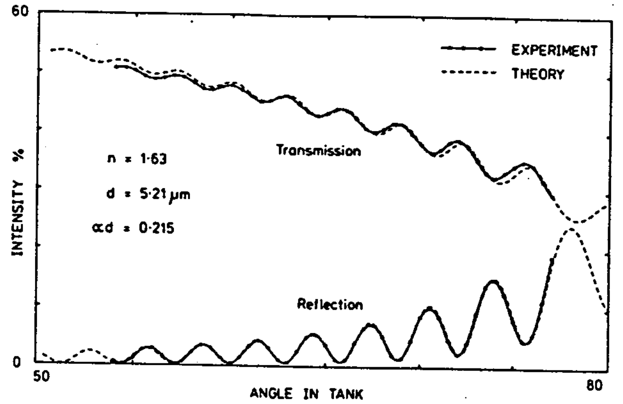

Fig. 3. Emulsion characterization: theoretical matching of grazing incidence measurements in the tank.

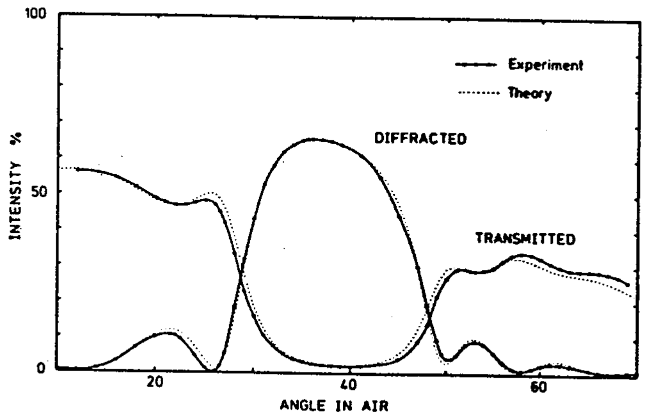

Fig. 4. Off-Bragg curve: measured diffracted and transmitted beam intensities and theoretical match.

Table IV. Grating Parameters Used for Theoretical Fitting of Off-Bragg Curve in Fig. 4

Grating period	Λ	170 nm
Emulsion thickness	d	5.10 μm
Loss coefficient	αd	0.23
Average refractive index of emulsion	n_e	1.63
Absorption modulation	$\epsilon''_{r1}/\epsilon''_{r0}$	-0.08^a
Permittivity modulation	$\epsilon_{r1}/\epsilon_{r0}$	8.7%
Replay wavelength	λ_0	514.5 nm

[a] Minus sign indicates the absorption modulation to be out of phase with the permittivity modulation.

results, the refractive indices of the liquid and the glass being known independently. Although the matching process was found to be quite critical, there remains a noticeable discrepancy. Variations in the hologram thickness over the area of incidence of the probe beam, which varies with angle, seem a likely source of error. Also, since the theoretical curves were calculated on the assumption that the presence of the grating could be neglected—the emulsion being considered as a uniform dielectric—another possible source of slight error would be removed by solving the wave equation for the problem, with the second-order derivatives retained as described by Moharam and Gaylord.[15] However, the vagaries of scatter cast something of a veil of uncertainty at this level of accuracy.

The results of the subsequent attempt to match theoretical to experimental curves for the off-Bragg behavior of both transmitted and diffracted beams of the hologram measured in air are shown in Fig. 4, and the values of parameters thereby established are shown in Table IV. Only the refractive-index value has actually been retained from the grazing-incidence measurement, since a much improved match for the transmitted and diffracted beams was obtained by using slightly different values of d and αd. Such a change in thickness could easily have occurred between the two experiments, as the hologram was not sealed. The discrepancy in losses might be taken as an indication that these are nonuniform through the thickness of the emulsion. The theoretical curves were calculated from Kogelnik's solutions, very slightly modified in respect of the wave vector assumed for the diffracted wave, with boundary reflections being accounted for by means of the Fresnel coefficients. Allowance could be made for nonuniformities (with depth) in the grating by dividing into uniform layers and matching individual solutions at the boundaries. The program used was that of Owen *et al.*,[14] modified to make improved provision for boundary reflections. Attempts to improve the fit by introducing nonuniformities were not conclusive, although the observed asymmetry of the first sidelobes could be better fitted by introducing a slight linear chirp in the grating period. A discrepancy remaining between efficiencies measured for reconstruction, respectively, on the glass and on the emulsion side of the plate after allowing for differing reflections might be attributable to nonuniform modulation, higher at the gelatin surface and decaying with depth, or possibly to nonuniform losses—again, a conclusive fit was not obtained.

Possible sources of error in the theoretical curves might include the need to take into account the +1 diffracted order at the lower angles of incidence and again to retain the second-order derivatives in the wave equation to allow for the effect of the grating modulation on reflections at high angles of incidence. However, the heavy losses due to scatter are themselves a major source of uncertainty, and in particular the influence of noise gratings formed by scatter at recording is not clear. The occurrence of such gratings has been reported by Syms and Solymar.[16] In our own measurements conducted on a plate which had been exposed to the two recording beams sequentially instead of simultaneously, noise gratings were found to produce up to ~12% depletion of the transmitted beam. The situation will, however, be entirely altered by the presence of a strong planar grating. The behavior of the noise gratings will also be affected by changes in emulsion thickness, offering a likely explanation for some observed small changes in grating efficiencies, for example, resulting from bromination. A change in emulsion thickness from recording will probably have the effect of diluting the influence of the noise gratings (by preventing satisfaction of the Bragg condition for them) and so actually producing an increase in efficiency of the primary grating.

VI. Discussion

From the values of parameters given in Table IV, for a typical grating processed in CW-C2 and PBQ-2, it can be established first that the effective shrinkage of the emulsion used is ~2.6% if the measured value for the grating period normal to the plane of the plate is compared with a calculated value at recording of 175 nm. The figure for the absorption modulation is determined from the asymmetry of the peak of the diffracted beam (Fig. 4), which can also be affected by nonuniformities, so the comparatively high figure given cannot be taken as wholly reliable. Most interesting is the very high figure for the permittivity modulation, which is probably close to the saturation level for the given process and material, with the proviso that the actual maximum value might be higher, if the modulation is not uniform through the grating. The value which emerges for ν (as defined in Sec. II) is 0.77π.

In Fig. 5, the variation is shown of peak efficiency with exposure for plates processed simultaneously for development of CW-C2 and also CW-P2. In both cases, the optimum efficiency is obtained for ~97% depletion of the transmitted beam, at which level the theoretical rate of increase of efficiency with modulation is small. The subsequent decay in efficiency with increasing exposure, despite a measured slight increase in depletion, can be explained broadly by supposing the rate of increase of noise with exposure to be faster than the corresponding rate of increase of efficiency. (The more rapid decay with CW-P2 is due to the increasing density of developer stain.) It is, however, quite possible that the increase in depletion is itself due to an increase in the strength of noise gratings, the primary modulation being on the point of saturation. The presence of any second-harmonic modulation after saturation should not be significant for a reflection hologram since the waves to which it can give rise will be very far from

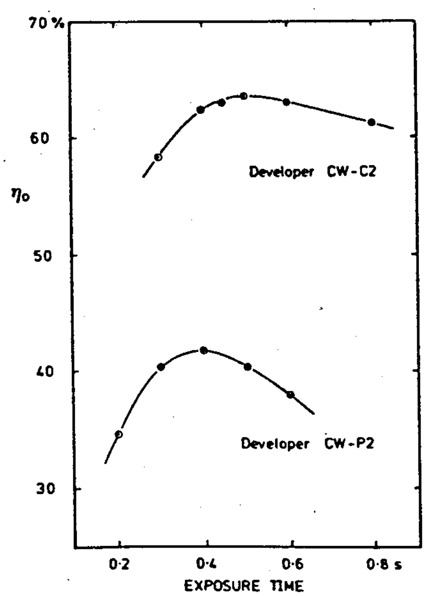

Fig. 5. Peak efficiency vs exposure curves for holograms developed in CW-C2 and CW-P2 and bleached in PBQ-2.

Table V. Light Distribution at Reconstruction in Air

	LH minimum	On-Bragg	RH minimum
Incident light (%)	100	100	100
Zero-order reflections	7.9	7.3	12.1
Diffracted beam	0.4	65.6	4.1
Transmitted beam	47.0	2.5	28.9
Higher-order transmitted beams	0.5	0.3	0.4
Higher-order reflected beams	0	3.5	0.06
Totals	55.8	79.2	45.6
Unaccounted for (absorption and scatter)	44.2	20.7	54.4

satisfying a Bragg condition. As *prima facie* evidence for saturation may be cited the observed boost to the achievable efficiency given by increasing the KBr content of the bleach, despite the evident worsening of scatter, which suggests that an increase has been obtained in the degree of modulation achievable—the saturation level. It is likely that addition of urea to the developer has a similar effect through improving the uniformity of development.

That such a high level of modulation can actually be achieved without fixing is really rather remarkable and encourages speculation that tanning of the gelatin by the developer is operating as an important supplementary modulation mechanism in addition to expected redistribution of silver bromide.[17] This is strongly indicated in view of the fact that the two developers found to produce much the highest modulation, pyrogallol and catechol, are recognized among common reagents as those which produce the most localized tanning. It is possible also that the *p*-benzoquinone, itself a tanning reagent, contributes to the modulation since it has been found always to produce higher efficiency than other bleaches. The joint contribution of developer and bleach to tanning modulation has been discussed by Tull for processes designed to produce relief images.[18]

With both catechol and pyrogallol enabling 97% depletion of the transmitted beam to be achieved, the advantage of the former lies in the virtual absence of stain resulting from its use with the citric acid–pbq bleach, so that losses must be attributed very largely to scatter rather than absorption. In Table V a breakdown is shown of the measured distribution of light resulting from reconstruction of a grating at three angles of incidence (on the glass side). Of the light incident on the emulsion, 20.7% remains unaccounted for, lost through scatter and absorption. (No attempt was made to measure the scattered light.) However, the losses are minimized for replay on Bragg, because in this case, most of the power in the incident beam is diffracted out of the grating over the first few fringes and so travels a shorter distance through the emulsion. A more realistic measure of the losses from the grating is obtained at the angles corresponding to the first minima of the diffracted beam, either side of the peak, for which the figures of light unaccounted for turn out to be 44.2 and 54.4%. By comparison, the scatter losses from an un-

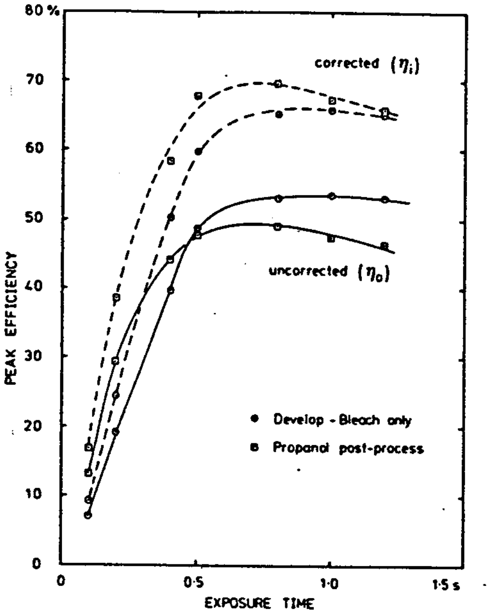

Fig. 6. Effect of postprocessing in propanol: corrected and uncorrected curves of peak efficiency vs exposure.

developed plate whose antihalation dye had been washed out were found to be ~19%.

Of this enormous increase in losses from unexposed plate to hologram, some part must be regarded as inevitably associated with the formation of the grating due to modulation of scattering centre size. An indication that the figure does not reveal serious shortcomings in the processing scheme is provided by preliminary tests of the same process on a very fine grain emulsion: the Russian LOI-2. While efficiencies obtained were low (due to low modulation, the material being sensitized primarily for use in red light), gratings produced at 514.5 nm were remarkable for a total absence of visible scatter—away from the Bragg angle, the gratings were indistinguishable to the eye from virgin plates (the sensitizing dye apparently being unaffected by the processing). Direct evidence, in fact, that another factor is at play in the Agfa emulsion is provided by the observed 10% difference between efficiencies achievable with plates from two different batches (processed together), which represents an increase in losses at peak efficiency from 20.7% to ~30%. We suggest that this increase may be at least partly due to reaction of the processing reagents with the sensitizing dye; but whatever the cause, it raises the question of how much of the original 20.7% loss is similarly unnecessary.

Heavy losses due to scatter are particularly undesirable in display holograms because of the resulting poor contrast, and the countervailing advantage of brown stain in this respect has been pointed out by Phillips *et al.*[4] Quite good contrast was obtained for displays by following the catechol developer with the boric acid–pbq bleach, but images were disappointingly dim, replay occurring at ~500 nm as a consequence of shrinkage. For recording at 514.5 nm, the advantage is overwhelming of producing holograms which are swollen, so that replay occurs in the part of the spectrum to which the human eye is most sensitive—~550 nm—and this is achieved by using pyrogallol alone (without sulfite or ascorbic acid) to maximize tanning. Brightness is increased a little by using the more acidic PBQ-2 bleach, while excellent contrast is obtained because of the brown stain.

The problem of shrinkage remains the one obvious drawback of the catechol developer, and it would clearly be advantageous if a reagent could be found which combines the better features both of catechol and of pyrogallol—producing highly localized tanning, able to swell the emulsion, and causing very little stain. Such a developer might conceivably be found among less readily available reagents: for example, higher molecular weight hydroquinones, for which diffusion is reduced as a result of the molecular size,[19] or daphnetins,[20] or even a reagent such as 2-amino-5-diethylamino-toluene, found to be an effective tanning agent and producing little stain for relief images.[18] In any event, however, exploratory tests have suggested that a solution to the problem might be closer to hand.

VII. Further Experiment

The speculation that tanning of the gelatin is operating as an important modulation mechanism prompted an experiment to attempt to enhance this effect by soaking the emulsion after developing and bleaching in propanol in a manner similar to that used to achieve modulation in dichromated gelatin. A set of holograms was exposed over a suitable exposure range and processed in CW-C2 and PBQ-2. The plates were then cut in two, and one half of each was soaked in 50% propan-2-ol (IPA) for 1 min, then 100% propanol for 2 min, before being allowed to dry.

It was found that the propanol-processed holograms replayed at an angle larger than the recording angle and the control holograms at a smaller angle, corresponding to swelling of ~4.3% and shrinkage of ~1.5%, respectively, for the more heavily exposed plates. Due to the large difference in replay angle, the boundary reflection losses for the two sets of holograms will be substantially different, and so an appropriate correction factor should be applied to achieve a useful comparison. Both corrected and uncorrected results for efficiency vs exposure are shown in Fig. 6, corresponding, respectively, to values of η_i and of η_0 as defined in Sec. III.

It is seen that the propanol treatment certainly increases the intrinsic efficiency for the lower exposures. It also appears to do so right up to the highest exposure level, but this result depends critically on the accuracy of the correction factor applied. It should be noted, moreover, that the mere fact the grating is swollen and on-Bragg at a much larger angle may be responsible for an increase in efficiency depending on the modulation level and absorption constant, an effect which will ultimately disappear with increasing modulation. The peak corrected efficiency is below the 75% previously measured, as the propanol experiment was performed with the later batch of 8E56 which consistently gave poorer results.

The results do seem to indicate that the propanol treatment serves to boost the modulation achievable for a given exposure, apparently with a less than proportionate associated increase in noise. The analogy with the processing of dichromated gelatin holograms is clear. In the latter case, differential tanning is believed to be translated into differential density by the propanol.[21]

VIII. Conclusions

It has been suggested by van Renesse, from a model put forward to describe scattering in fine-grained emulsions, that low tanning developers should be chosen to reduce scatter[22]; but the analysis neglects to consider that any contribution of tanning to the holographic modulation would correspondingly ease the problem of scatter due to variation in grain size (where this is the alternative source of modulation). At present, a clear advantage has been established for tanning developers in producing the high modulation required to achieve high efficiency for reflection holograms in thin emulsions. The maximum achieved efficiency of nearly 75%, after allowing for reflections, is limited almost solely by scatter, but the indications are that there is much more scope for improvement of the emulsion than of the processing scheme. The crucial requirement is for a consistently fine grain emulsion comparable with those long available in the Soviet Union, but it is also most important that dyes used in the emulsion do not produce severe losses through reaction with the processing reagents, or else can be removed prior to processing. A slightly thicker emulsion is certainly needed to reduce the modulation requirement: with the present grain size, an increase of as little as 2 μm would probably suffice for the simple catechol developer (CW-C1). It would be advantageous, also, if the refractive index of the substrate were matched to that of the emulsion.

Further experiment and analysis are required to clarify the effects of treatment with propanol as an additional processing stage. This promises, however, to be an effective method of controlling emulsion thickness as well as a potential source of additional modulation leading to the achievement of slightly higher efficiency.

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ANNOUNCEMENT

The 2nd International Symposium on Diffuse Reflectance Spectroscopy will be held at Wilson College, Chambersburg, PA, from August 12–17, 1984. Sessions (3–4 hrs.) will be conducted on Data reduction; Instrumentation; Spectroscopy; Chemistry and Surface Effects; Industrial applications in near- and mid-infrared in the petrochemical, pharmaceutical, textile, paint, food, feed, agricultural, dairying, and other fields, and a special session on Definitions and Terminology.

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