Improving the visual quality of photographically recorded holograms

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IMPROVING THE VISUAL QUALITY OF
PHOTOGRAPHICALLY RECORDED HOLOGRAMS

by

DAVID PORTER

Supervisor: N. J. PHILLIPS

Submitted for the Degree of Doctor of Philosophy
of the Loughborough University of Technology

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Improving the Visual Quality of Photographically Recorded Holograms

The aim of this project has been to improve the visual quality of holograms by improving the quality of commercially available photographic recording materials and their associated photochemical processing. This aim has been achieved by carefully considering all aspects of processing stages and applying them to the very high resolution images encountered in holography.

The first chapter gives a brief summary of experimental techniques used for the exposure of holograms in the course of this work, and the apparatus needed to ensure minimal vibration and maximal optical quality in the exposures.

Chapter 2 details all the components of photographic emulsions for use in holography, and the improvements made in the course of this project. All processing stages except development and bleaching are considered at the end of Chapter 2.

Chapter 3 presents a general model for the optimization of developer action in all modes of holographic imaging, together with the experimental observations which led to the formulation of this model.

Chapter 4 shows how bleach action has been optimized, over the duration of this project, to the stage where high quality phase reflection images can be consistently produced, to be viewed in a dry state at the colour of recording the image.

Chapter 5 explains why relief-image master holograms cannot be produced successfully by photographic etching or tanning techniques. The etching of relief holograms by a novel enzyme-etching technique has been experimentally shown to be of no practical use. A processing method for the production of relief images with a resolution of up to 3000 lines per m.m. is given to conclude the chapter.

Chapter 6 considers the application of colour processing to holography.
A processing technique for the production of high quality and efficiency diffraction gratings has been formulated, which is explained and discussed with reference to the electronic polarizability properties of dyes.

Acknowledgements

I would like to thank and acknowledge my supervisor, Mr. N.J. Phillips, for his complete co-operation in the work of this project. Also special thanks to Mr. Cullen for his experimental work, with particular reference to relief imaging.

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Chapter 1  Holographic Techniques

A hologram is the reconstruction of an object or scene as a "complete" three-dimensional image. The purpose of this project was to improve the visual quality of optical holograms to the extent that holograms would appear merely as a window, through which a perfect replication of a three-dimensional subject is viewed.

The aims of the project have been fulfilled by optimising conventional photographic processing techniques in the special case of high resolution holographic recording emulsions. The subjective comparison of holographic images has been used as the basic test procedure in this optimisation operation. It is hoped that the results of this project will speak for themselves about the extensive investigations which led to their creation.

The text and references of the monograph on optical holography by Collier, Burckhardt and Lin (1) can be taken as the starting point for the work of this project.
1.1 Transmission Holograms

1.1a. Diffraction Gratings

Figure 1.1 shows the practical arrangement used for the exposure of sinusoidally modulated line diffraction gratings, to which the holographic theory of Kogelnik (2), Burckhardt (3,4) and van Renesse (5) can be applied. Holographic lenses were exposed by replacing planar beams by the corresponding converging or diverging beams.

1.1b. Virtual Images

Figure 1.2 shows the standard off-axis arrangement used for exposing virtual images. The holograms have poor wavelength selectivity, and all tests have been viewed with a laser reconstructing light source.

"Image Quality" has been loosely defined as the subjective brightness and signal to noise ratio of a holographic image, and was used as the basic test parameter for all processing techniques. Image quality was always compared with the best available holographic image at that time to ensure that image quality was never reduced.
Exposure of Transmission Gratings

Exposure of Virtual Image Transmission Holograms
The main types of holographic image noise were found to be:

(i) In-image fog; which is an ambient scattered light level in the whole of the image volume.

(ii) In-plate scatter; which originates from crystals or damage points within the recording medium.

(iii) In-image flare; which is seen as a diffuse halo around each object in the image, and is usually corrected by increasing the intensity beam ratio of reference beam to subject beam.

1.1c. Semi-real Projection Images (6)

A pseudoscopic projection image from a virtual image master hologram is created by its time-reversed reference beam. The pseudoscopic projection is then recorded on a second holographic plate, as shown in figure 1.3. The pseudoscopic projection of this second image is seen as an orthoscopic semi-real image, when viewed with its own time reversed reference beam.
Figure 1.3

Recording a Semi-Real Projection Image

- Time reversed reference beam
- Master plate in pseudoscopic projection mode
- Recording plate
- Master image
The proximity of semi-real images to the holographic plate allows the use of discharge lamps for viewing, by virtue of their greater achromatic condition. This property is enhanced by the greater diffraction efficiency of semi-real projection images over virtual images. The increased efficiency is a result of the use of lower beam ratios during exposure. Low beam ratios, of almost 1:1, can be used since cross-modulation within the subject beam is significantly reduced by the aperturing of the field of view of the master plate in the second recording.

The low angular selectivity of the "thin" recording emulsions used in this project allowed the approximation of the time-reversed reference beam, for viewing the semi-real projection image, by a diverging source. The resulting aberrations in the field of view are not objectionable.

A modification of the projection image apparatus has been used to expose the "Rainbow" images of Benton (7,8). The horizontal slit illumination of the master holographic plate was derived from a cylindrical lens, which replaced the spatial filter assembly of the standard projection arrangement.

Little use has been made of "Rainbow" images because of their restricted field of view.
1.2 Reflection Holography (1,2)

The processing of reflection holograms was investigated towards the end of this project in order to satisfy the need for colour-selective, white-light holograms. The modified apparatus for virtual and projection images in reflection mode is shown in Figure 1.4. The use of a non-time-reversed reconstruction beam for the orthoscopic projection images caused no problems, due to the low angular selectivity of the image processing system devised. The poor angular reference beam selectivity has not been accompanied by a correspondingly poor wavelength selectivity.

The need for high vibrational stability of optical components during exposure is particularly strict for reflection holography.

1.3 Equipment

1.3a. Lasers

A Spectra-Physics 171 argon-ion laser has been used on a flat, polished optical bench of reinforced concrete, mounted upon inflated tyre inner-tubes, for continuous-wave exposures. A power of up to 6 Watt at 511 nm with a rated coherence length of about 100m removed the need for accurate path-length matching during exposure.

Pulsed exposures have been made with an 800mJ. pulsed ruby laser, which gave a useful depth of field of about 3.50m with correct path-length matching during exposure (9,10,11,12,13).
Figure 1.4a

Subject reflection beam

Virtual Image
Reflection Hologram

Figure 1.4b

Master plate

Recording plate

Semi-real Reflection Hologram
1.3b. Beam Splitters and Lenses

Pulsed systems used only fixed-ratio, dielectric coated, thick glass beam splitters, which diverted the beams into concave meniscus lenses to be diverged.

C.W. beam splitting for exposure commenced with a variable beam splitter composed of a Wallaston prism and half-wave plates. Variable beam ratio and beam polarization were thus available at the point where reference and subject beams were separated. Further splitting of the subject beam was done with fixed-ratio, thick glass beam-splitters with an anti-reflection back-face coating. A beam power threshold has been found to exist for metallized film beam-splitters, above which the beam was self-focussed by thermally induced refractive index gradients. This power threshold is accompanied by an apparent reduction of coherence length. If the narrow, self focussed beams are then fed into cemented-lens microscope objectives to be diverged, the cement melts and the lenses become "burnt-out".

1.3c. Subject and Reference Beams in C.W. Exposures

Spatially filtered expanding beams have been used exclusively for subject illumination. Diffuse illumination reduces the resolution of holographic image by speckle noise and also reduce image brightness (14). If a diffusely lit subject image is used as a projection image master, the final semi-real image contains much in-plate scatter due to the random scatter from localized, high intensity, focussed speckle points.
The Lighting-point support pillar design was finalized after many problems of instability. A 2" diameter "Tufnol" column is bolted to a 9" diameter steel base, 2" in thickness. The base stands upon 3 ball-bearings, embedded in the base. The spatial filter assemblies are mounted upon a sliding sleeve around the tuflon pillar, which is secured by bolts onto the pillar. Vibrational stability can be tested by tapping a component, and then watching the damping-down of the movement of the speckle pattern upon a stable object. Only heavily damped oscillations in optical components can be tolerated.

The overhead reference beam support for a height of 5'6" was made with 2" diameter aluminium scaffold posts, filled with dry sand for damping, in the form of a tripod with two cross-linking members between each leg. Damper bars were attached to each leg and cross-linkage to add greater stability.

1.3d. Plate Holders

Aluminium posts, 2" in diameter with a suitable slot cut along their length, have been found to be stable enough for holding plates of up to 1 m² when the posts were bolted to steel bases of up to 12" in diameter and 2" in thickness. Plastic, double-glazing, edging strips are used with 3 and 5mm. thickness plates to provide damping between the metal pillars and glass plates. The damped packing of the plates into their holders is essential for plate stability.
1.4 Recording Materials

The need for high efficiency and quality volume holograms in this work narrowed the choice of recording material down to photopolymers and silver halide photographic emulsions.

Experimental results with photopolymer emulsions (1,15,16,17,18,19) throughout the world indicate that they are not sensitive enough for use in display holography with commercially available lasers. Trials to compare the sensitivity of dichromated gelatin and silver halide emulsions for a given diffraction efficiency show the extent of their differences:

\[ \eta = 10\% ; \] \begin{align*}
\text{dichromated gelatin at } 450\text{nm} & = 200\text{mJ/cm}^2 \\
8\text{E56 emulsion at } 511\text{nm} & = 2\text{mJ/cm}^2
\end{align*}

\[ \eta = 50\% ; \] \begin{align*}
\text{dichromated gelatin at } 450\text{nm} & = 2\text{J/cm}^2 \\
8\text{E56 emulsion at } 511\text{nm} & = 10\text{mJ/cm}^2
\end{align*}

A quoted sensitivity of 7mJ/cm² for Agfa 8E emulsions (20) at D = 0.5 would allow the exposure of 1m² plates with the Spectra-Physics 171 laser operating at a conservative 1W, for with a typical image recording configuration (1) of figure 1.2 under 2 seconds. Silver halide emulsions were, thus, chosen as the basis for this project; the problem then being to improve the quality of image processing by refining well established photographic processing techniques.
Chapter 2 The use of Silver Halide Emulsions in Holography

Silver halide emulsions have often been called "the holographer's only friend" because of their high sensitivity, high resolution capabilities, reliability, and versatility. Photographically developed images in silver halide emulsions form high quality amplitudem images, which are then readily bleached to produce high efficiency dielectric phase holograms.

In spite of all these virtues, silver halide emulsions have never consistently produced the noise-free, high efficiency phase image of which they were thought capable. The high noise levels were due to a combination of unsuitable base emulsions and inappropriate photographic processing methods. The bulk of the work in this project has been applied to the production of a good commercial holographic emulsion, in co-operation with Agfa-Gevaert in Belgium, and to refining the processing of the emulsion to produce totally noise-free images. The texts of Mees (21,22) and Clerc (23) present a good introduction to the photographic operations.
2.1 Components of 8E Photographic Emulsions

Emulsions discussed in this work will be only Agfa-Gevaert 8E emulsions. No Kodak emulsion has ever been able to compare with 8E products, in terms of noise-free imaging. Kodak materials, such as 649F, are fast but have a large grain size, which results in intolerable scatter levels in the processed emulsions.

2.1a. The Complete Emulsion (24,25)

Figure 2.1 shows a cross-section of an 8E emulsion. Silver halide micro-crystals are suspended in a gelatin layer, which is coated upon a transparent glass or plastic support medium.

Ag⁺ and Br⁻ ions are first mixed in a dilute gelatin solution and allowed to ripen under carefully controlled environmental conditions to the correct size distribution. More gelatin is then added, together with additives such as sensitizing dyes, hardeners, stabilizers, anti-halation dyes, and image restrainers. The emulsion is then coated upon a surface adhesive layer on the support medium substrate.
Cross-section of an 8E Emulsion

Table 2.1
Minimum Thickness of Glass Plates

<table>
<thead>
<tr>
<th>Plate Size</th>
<th>Min. Thickness</th>
</tr>
</thead>
<tbody>
<tr>
<td>10' x 8'</td>
<td>2.2 mm.</td>
</tr>
<tr>
<td>30 x 40 cm.</td>
<td></td>
</tr>
<tr>
<td>50 x 60 cm.</td>
<td>5 mm.</td>
</tr>
<tr>
<td>95 x 100 cm.</td>
<td></td>
</tr>
</tbody>
</table>

(Commercially available sizes are given.)
2.1b. Support Medium

Glass is the best support medium for holographic emulsions. Glass combines rigidity, resistance to scratch, and the highest clarity, but is expensive, difficult to handle, and is limited in size during coating to only 1 m\(^2\). The alternative for 8E emulsions is a polyester support medium, since the harder, more resistant polycarbonate sheets are prohibitively difficult to coat on a large scale, due to poor adhesion of the emulsion to the less porous polycarbonate surface.

The polyesters are coated with a maximum thickness of only 0.9 mm, and are not rigid enough for continuous wave exposures, but are convenient for pulsed work. Scratch resistance and clarity in polyester coatings is not as good as with glass.

The rigidity due to thickness of glass holographic plates has been extensively tested after 8E56HD Millimask plates, at 32 x 42cm. size, were found to have insufficient rigidity across the plate with a thickness of only 1.5mm. Movement at the plate centre is shown by a gradual loss of image from the plate edge to the centre. Table 2.1 shows the minimum thickness of glass plate needed for reliable rigidity at a given plate size.
Before the emulsion is coated upon the support medium, the support is coated with an adhesive layer to prevent peeling-off of the emulsion. The adhesive properties of this coating have been shown to be dependent upon gelatin hardness. A soft emulsion is seen to peel-off glass much more easily than a harder emulsion. This problem does not arise on polyester coatings since their production lines have much better emulsion hardness controls.

2.1c. Gelatin

The generalized structure and properties of photographic gelatin are well catalogued (26 — 33 for example), and need not be detailed here. It is sufficient to note that the diffusion coefficient of salts in a gelatin gel is increased by increases in temperature, such that the diffusion coefficient at 20°C is approximately twice that at 0°C (26), and that both swelling and diffusion coefficient are reduced by increased inorganic salt concentration in the gelatin.

Any chemical reaction between gelatin and silver salts will be assumed to be negligible (32,33), except for a chemisorption bonding between the gelatin and silver halide grain, which can take place also through an intermediate dye layer (34,35). It has been reported (36) that the ionic mobility of silver ions can be modified by a gelatin ionic double layer around each Ag⁺ ion, and that this is pH dependent.
2.1d. Silver Halide Crystals \( (1,22,23,37,88,39) \)

The size and the spatial distribution of the halide grains within 8E emulsions is determined by the ability of Agfa-Gevaert to consistently produce the smallest grains possible, in a large scale production environment. High quality emulsions with 300 Å grain size are currently available with 8EHD emulsions, with assurances that a 100 Å material will soon be available for test.

8E emulsions use a silver halide concentration of 5 g.m.\(^{-2}\) for an emulsion thickness of 7 μm. The mean grain size for 8E emulsions is 0.050 μm with a spread of 0.0074, and the mean grain size for 8EHD emulsions is 0.035 μm with a spread of 0.0063 \( (40) \).

If the silver halide grains are assumed to be spherical and distributed uniformly through the emulsion, then Table 2.2 shows how the average minimum separation of adjacent grains is related to average grain size. It is essential that grain separation for the proposed 0.015 and 0.01 μm grain size emulsions is optimized, by varying the silver halide concentration, before coating procedures are finalized. Since a molecular length of 0.002 μm for a sensitizing dye \( (34) \) is comparable to the grain separation of 0.014 μm for 0.01 μm grains, sensitization links may be induced between adjacent grains which would randomly distribute a high spatial frequency, holographic latent image through the emulsion, thus eliminating the image.
<table>
<thead>
<tr>
<th>Grain Size</th>
<th>Average Grain Size</th>
<th>Minimum Separation</th>
</tr>
</thead>
<tbody>
<tr>
<td>8E</td>
<td>0.05 µm.</td>
<td>0.07 µm.</td>
</tr>
<tr>
<td>8EHD</td>
<td>0.03 µm.</td>
<td>0.04 µm.</td>
</tr>
<tr>
<td></td>
<td>0.015 µm.</td>
<td>0.02 µm.</td>
</tr>
<tr>
<td></td>
<td>0.01 µm.</td>
<td>0.014 µm.</td>
</tr>
</tbody>
</table>

Table 2.2
The probability of developer fogging is also increased by decreased grain separation, due to contaminant diffusion from developed grain sites, and the lower limit of grain separation for negligible developer fogging will probably be controlled totally by this effect (see section 3.2f).

2.1e. Chemical Additives

With the generous help of Agfa-Gevaert, the suitability of chemical additives to the 8E emulsions for application to holography has been examined. All tests were made relative to a standard emulsion made to the published commercial specifications (20).

(i) Hardener:

The integrity of the emulsion during processing and adhesion of the emulsion to the support medium are controlled by gelatin hardness, which is itself determined by the extent of inter-molecular cross-linkages within the body of the gelatin.

Agfa-Gevaert measure hardness on a relative scale with the numerical limits of 0 and 1000. A hardness of below 300 is too soft for "normal" processing, and most commercial 8E emulsion coatings have a hardness of between 300 and 600.

The standard hardening agent, used in all 8E emulsions, produced the best plate sensitometry and highest absolute diffraction efficiencies in trials with various hardening agents. The worst hardening agent under test reduced the diffraction efficiency of trial gratings by a factor of 10.
Unless the correct type and amount of hardener are added under precise conditions at the point of mixing the ripened emulsion with more gelatin and additives, then the gelatin cannot be artificially hardened by heat curing or chemical baths. It appears that the gelatin in the ripened solution and the added gelatin become incompatible, and prevent the formation of molecular cross-links between the two gelatin states, which cannot be artificially induced at a later stage. "Aging" of the emulsions over many months allows the gelatin to revert to a consistent form in the emulsion, and natural hardening can then occur.

(ii) Anti-Halation Incorporated (A.H.I.) Dyes:

Anti-halation layers for most photographic emulsions are usually applied as a coloured absorbing layer to the back of the support medium or at the gelatin/glass interface (22). Anti-halation of this kind cannot be used in holography because it prevents the recording of reflection holograms and does not eliminate the scatter from silver halide grains in the emulsion, which could cause fogging of adjacent grains.

It has been shown (41) that by incorporating a uniform suspension of anti-halation/anti-scatter, absorbing screening dye in the emulsion, then the resulting improvement of line contrast within the holographic image gives improved diffraction efficiency. Agfa-Gevaert use a red A.H.I. dye for the SE56 emulsions, which gives an attenuation of about 75% for transmitted light at 511nm.
This level of optical attenuation is undesirable for holography since it distorts the beam ratio and exposure level through the depth of the emulsion. Figure 2.2 shows this effect in the case of reflection holography, where a beam ratio gradient exists between the two faces of the emulsion. Thus, beam ratio can never be truly optimized in an absorbing A.H.I. emulsion. It has, therefore, been suggested to Agfa-Gevaert that the possibility of non-absorbing screening dyes be investigated until the advent of 0.01μm grains, which will need no screening dye due to minimal granular scatter in the emulsion, which has a sixth power dependence upon grain size.

A non-absorbing screening compound would be a layer of organic material adsorbed around each grain to "blush" the silver halide and the gelatin at their interface on each grain. This would probably be applicable to 8E and 8EH D materials, where colourless developer oxidation products and substances such as triethanolamine have shown that such a reduction of scatter level is possible.

(iii) Image Retention Substance:

The incorporation of an image retention substance into 8E75 emulsions gave the most significant improvement of their holographic images, during the course of this project, by effectively reducing the probability of developer fogging in the emulsion during processing. This is achieved by reducing the ionic migration of fogging ions from a developed silver site to adjacent grains.
Figure 2.2

Absorbing A.H.I. in Emulsion

Subject Beam

\[ \frac{R}{4} \]

Ref. Beam

\[ \frac{S}{4} \]

Variation in beam ratio due to A.H.I.
The need for an image retention substance was indicated by the low diffraction efficiency of holograms recorded on 8E75 emulsions from before April 1977, as compared with 8E56 emulsions which incorporated an image retention substance. This difference between the 8E75 and 8E56 emulsions was accentuated at that time by uncertain developer action.

The diffraction efficiency in images recorded on 8E75 material has been improved by a factor of 2 by the incorporation of an image retention substance into 8E75 emulsions under identical processing conditions.

(iv) Sensitizing Dyes (29);

The sensitometry of a silver halide emulsion is controlled by the interaction between the halide grains and a light absorbing dye which is adsorbed to them. Section 2.2 details the sensitometry of the various 8E emulsions.

Requests for an 8E emulsion without sensitizing dye being automatically incorporated have been ignored by Agfa. Emulsions to which sensitizing dyes could be added before use, at any desired wavelength, would be economically disadvantageous for Agfa, even though Russian workers have reported success with applications of dilute dye solutions to unsensitized plates (41).
2.2 Recording Parameters of SE Emulsions

2.2a Wavelength Sensitivity

The "official" wavelength sensitivity of SE56 and SE75 emulsions is shown in Figure 2.3 (20). These curves are misleading for practical exposure purposes, since SE56 emulsions can be used only on the 511nm. argon line, and SE75 emulsions only in the truly red spectral regions. Outside these wavelengths there is a dramatic loss of line resolution, even if an image density can be developed after an exposure.

Pan 300 emulsions are sensitized over all the visible spectrum (42). In practice, Pan 300 is at least a factor of 20 times less sensitive than SE56 or SE75 emulsions at any given wavelength, and has a very poor relative imaging capability once a density has been developed. The only relevant difference between SE56D and Pan 300 emulsions is the use of different sensitizing dyes on the same basic emulsion.
Figure 2.3  Wavelength Sensitivity in 8E emulsions

a. 8E75

b. 8E56

(Agfa - Gevaert)
The poor imaging qualities of 3E emulsions with blue laser lines is easily explained by the increased grain scatter in light with a smaller wavelength (39,1). The antisensitizer action of sensitizing dye mixtures is very unpredictable (43) and would explain the low photic sensitivity of Pan 300, but the poor resolution of all the 3E emulsions in the low scatter spectral regions removed from their dye sensitization peaks has not yet been explained.

Poor line resolution in the emulsion is associated with false sensitization of grains adjacent to the truly exposed grains. It appears that the sensitizing dyes are acting with a wavelength dependent refractive index, which causes either increased scatter cross-section or electronic coupling between grains at wavelengths other than their dye/silver halide maximum sensitizing wavelength. No records have been found of any investigation into the optical refractive index and electronic properties of sensitizing dyes in the case of grain sizes and spacings far below the wavelength of light. The solution of this problem may involve a detailed study of the wavelength dependence of the refractive index of dyes, the charge transfer properties of sensitizing dyes, and the effect of dye molecular dipole orientations upon a silver halide grain; this is beyond the scope of this project.
It is essential that an experimental solution be found to the problem of broad-band sensitization of 8E emulsions, since multicolour reflection holography needs a 100 Å grain material sensitized over all the visible spectrum for further progress to be made.

2.2b Exposure Sensitometry of 8E Emulsions

An example of Hurter and Driffield curves for 8E56 emulsions with different developers is shown in Figure 2.4. A curve for Pan 300 is shown for comparison.

The curve for concentrated Neofin Blue shows the important ability to develop a non-fog density at lower exposure levels than the published data for the G3P developer; this prevents the loss of low level detail on large, extended scene display plates.

8EHD emulsions have shown an unexpectedly high speed for their grain size. It appears that the sensitivity/grain size curve flattens in the low grain size regions such that the speed of 300 Å 8EHD emulsions is half that of 500 Å 8E emulsions, rather than the expected loss of speed by a factor of about 10 (44). It is hoped that this "flat" sensitivity curve continues for the 100 Å materials.
Figure 2.4
Sensitometry of 8E56 at 511 nm.
2.2c Emulsion Thickness

8E materials can have a thickness of 7µm or 15µm (8E56B or 8E75B). The 15µm thickness has offered no advantages at any time during this project. Developer fogging and surface micro-reticulation are increased in the thicker emulsion, and no increase of diffraction efficiency with increased thickness has been observed.

A slight increase in angular selectivity with 8E56B emulsions relative to 8E56 was disadvantageous for laser viewing in a non-perfect viewing environment. No improvement in wavelength selectivity in reflection mode has been seen with 15µm emulsions over 7µm emulsions, probably due to the high index modulation of the top Bragg layers, which prevent the participation of the lower Bragg layers in the image reconstruction.

Trials with 45µm thickness 8E75B emulsions have never produced a holographic image due to a total degrading of the swollen emulsion during processing, which distorted the emulsion irreversibly.
2.3d Image Resolution and Emulsion Granularity

High quality reflection images, which require an image resolution of between 4500 and 6000 lines per mm, have been recorded on 8E56 HD materials. The official resolving power of an 8E emulsion is 3000 lines per mm, but this is a conservative estimate based upon conventional Modulation Transfer Function theory and average granularity tests. Modulation Transfer Function theory (45,46,47,48) is of little more than academic interest in holography, since resolutions greater than the wavelength of visible radiation are needed.

Since the granularity of the 8E emulsions has been very variable during this project, it has been suggested to Agfa-Gevaert that the white-light scatter from an emulsion should be compared to that of a standard emulsion of known grain size. Since optical scattering by the grains is proportional to the sixth power of grain radius, this test would have a high accuracy. Subjective evaluation of emulsion scatter levels varies between total transparency for 200 Å grains and great opacity at 1000 Å. Between these limits the comparative ability of subjective evaluation is capable of detecting an average grain size difference of about 50 Å in two emulsions. It is important to remove A.H.I. screening dye before this test is used. Electron micrographs would provide accurate grain size data for the reference emulsions.
2.3 Processing Photographically Recorded Holograms

All stages in the photographic processing of holograms have been investigated. The following processing procedure has been adopted:

Hardening or Pre-washing of the emulsion
Development
Fix/Rehalogenate or Solvent Bleaching
Desensitization
Drying
Index Matching

The development and bleaching stages are discussed in chapters 3 and 4 respectively.

2.3a Water Washing Between Stages

Removal of all processing chemicals from the emulsion between stages is essential, to prevent contamination of the holographic image by unwanted inter-stage reaction products. Washing with flowing distilled water would be ideal, but is impractical on a large scale. The Cl⁻ ionic concentration in local tap water has been very unpredictable, with large surges of high Cl⁻ concentration after periods of low or high rainfall; at these times a tap water wash should be followed by a short (30 second) soak in a distilled water bath.
High Cl− ion concentration gives either high solvent action during bleaching or a highly opaque, white precipitate in the emulsion during development or bleaching (see Chapter 4).

The washing temperature should, ideally, be the same as that of all the processing solutions to prevent reticulation by thermal expansion stresses. In practice, a soft emulsion may require a cool (10°C or lower) wash to reduce the damage risk, by further softening of the emulsion, during vigorous washing.

A washing duration of 5 minutes is adequate in most cases, but a post-bleach wash of up to 15 minutes has been seen to remove slightly soluble, scattery reaction products, such as ferrous salts.

2.3b Pre-development Processing

(i) Washing and Hardening:

It has been observed that dyes in the photographic emulsion can degrade during processing to leave a fine, white, scattering precipitate around the processed grains. Methanol, alkali solution, and benzotriazole solution have all been seen to remove A.H.I. dye completely, and remove most of all types of sensitizing dyes from the grains.

Methanol is recommended as a pre-developer wash bath, since it acts as a mild hardening agent on the gelatin over a period of about 10 minutes, which reduces the risk of reticulation in the following processing stages.
The risk of damage in an alkaline formalin hardening bath has been seen to be greater than the risk of damage to a soft emulsion in the handling during processing. Alkaline formalin is not therefore recommended for bleached silver holography.

(ii) Supersensitization:

Pre-exposure treatments of the emulsion have been found to introduce dirt and grain scatter noise into holographic recordings. Supersensitization, with substances such as triethanolamine, has been found unnecessary with the formulation of high power, low fog developers.

2.3c Fixation

Initial processing trials used a hardening fixer, but this has been found to introduce severe reticulation into the emulsion before rehalogenation bleaching. The reticulation is induced by the competitive actions of the silver halide solvation and gelatin hardening; the hardener strives to maintain gelatin rigidity, whereas fixation necessitates elastic contraction of the gelatin.

The problem has been solved by using a non-hardening fixer (such as Agfa G33h) for a processing time of only 30 seconds, since the small grain size of 8E emulsions allows rapid solvation of all the silver halide.
2.3d Desensitization

Desensitization prevents print-out of a bleached silver image. The best print-out stability for silver bromide images has been achieved with bromine vapour and bromine water after bleaching, but these induce degrading of the gelatin (see chapter 4).

A modified Agfa-Gevaert desensitizer has been found to provide sufficient print-out stability for displays in normal room lighting conditions, without inducing any detectable reticulation:

- 500 ml Iso-propyl alcohol
- 500 ml Distilled Water
- 5 g Potassium Bromide
- 200 mg Phenosafranine
- 10 g Ferric Nitrate
- 10 ml Glycerol

As much non-effective, coloured phenosafranine as possible should be water-washed from the emulsion after processing.
2.3e Drying

Since commercial "Drysonal" is expensive, and leaves a scattering dirt residue on the holographic emulsion, a "home-brew" drying bath has been formulated:

900 ml Methanol
100 ml Distilled Water
Wetting agent as instructed by manufacturer.

The fraction of water in the drying agent is important in reducing drying stresses at the wet/dry emulsion interface.

2.3f Index Matching

Where a density modulation has been introduced into a photographic emulsion, surface relief modulation is unavoidable because of local volumetric changes in the emulsion, caused by loss or gain of granular material. Relief modulation or surface micro-reticulation introduces noise into a holographic image and has to be eliminated by coating the surface of the emulsion with smooth layer of the same refractive index as the photographic gelatin (49). This process is known as "Index Matching".

Initial trials with small, 3" x 3", test plates were index-matched with "super-glue" to great effect, but at great expense. Clear resin has been used successfully, in the same way, to bond holograms to a piece of clean glass. Above a size of 30cm x 40cm it is difficult to remove small bubbles which become embedded in the resin as the hologram and glass plate are brought together. Beetle (B.I.P. Chemicals) and Crystic (Scott-Bader) resins are both suitable for index-matching.
The highest quality index-matching has been achieved by covering the wet holographic emulsion with a second wet, clear gelatin emulsion from which all silver halide had been removed (50). The problem of reference angle distortion by swelling of the emulsion can be minimized by first drying the emulsion completely and then wetting both the emulsions with alcohol for the matching. The edges of the plates can then be sealed with a resin adhesive for a permanent bond.

Holographic plates of 50cm x 60cm size, and larger, have not yet been successfully index matched.

2.3c Swelling Correction for Volume Holograms

Where contraction of the emulsion of a volume hologram has occurred during processing, due to removal of material from the emulsion, the Bragg optimum reconstruction wavelength shifts towards the blue end of the visible spectrum. Correction must then be applied by swelling the emulsion.

Wet plate index-matching can be applied with the correct alcohol/water mixture for the desired degree of swelling; more water gives greater swelling.

A humidity cabinet can be used to swell the emulsion, and a cover glass is sealed round the hologram to retain the correct humidity. This method is temperature sensitive.
Established triethanolamine swelling techniques (1) gave non-uniform swelling and colour gradients across the emulsion, due to concentration redistribution of the swelling agent during drying.

Non-fixed rehalogenation bleaching techniques have eliminated the need for swelling correction, and have also eliminated colour gradients across the emulsion due to corresponding density gradients before bleaching.
Chapter 3  Developing the Silver Image

1.1 Introduction (21,22)

An extensive investigation has been carried out to find the optimum photographic developer for holographic images. Many hundreds of permutations and combinations of commercial developers and individual developing agents have been tested upon transmission diffraction gratings and transmission holograms as an initial study. Table 3.1 shows the results of this preliminary study. All developers were tried under various conditions of pH, temperature, preservative content, and concentration to ensure that no possible mode of use had been missed.

Initial trials were bleached with a Ferric/Bromide post-fixation bleach (see chapter 4), and recorded upon 7µm 8E56 emulsions at 511nm.

1.2 The Action of Selected Developers in Further Trials

1.2a Grain Structure

Electron microscope studies of developed silver grains were made using conventional enzyme techniques (see chapter 5). Plates 3.1 to 3.10 show examples of studies with some of the developers from initial trials, which were made in Loughborough and at Agfa-Gevaert in Antwerp.
<table>
<thead>
<tr>
<th>Developer</th>
<th>Transmission Gratings ($\theta=15$)</th>
<th>Virtual Images</th>
<th>Comment</th>
</tr>
</thead>
<tbody>
<tr>
<td>G3P, G201, G170, D19</td>
<td>Reasonable</td>
<td>Poor</td>
<td>Typical Commercial Developer</td>
</tr>
<tr>
<td>Studional</td>
<td>Good $\eta = 60%$</td>
<td>Poor</td>
<td>Grey Silver</td>
</tr>
<tr>
<td>Dokumol</td>
<td>Good $\eta = 63%$</td>
<td>Bright but Ill-defined</td>
<td>Powerful Developer</td>
</tr>
<tr>
<td>Rodinal, Amidol</td>
<td>Reasonable</td>
<td>Poor</td>
<td>Use Concentrated</td>
</tr>
<tr>
<td>Emofin, Ultrafin</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Neofin</td>
<td>Poor $\eta = 25%$</td>
<td>Very Good</td>
<td></td>
</tr>
<tr>
<td>Metol</td>
<td>Poor</td>
<td>Poor</td>
<td></td>
</tr>
<tr>
<td>Hydroquinone</td>
<td>Poor $\eta = 50%$</td>
<td>Poor</td>
<td></td>
</tr>
<tr>
<td>p-Phenylenediamine</td>
<td>Poor</td>
<td>Poor</td>
<td></td>
</tr>
<tr>
<td>Phenidone</td>
<td>Poor</td>
<td>Poor</td>
<td></td>
</tr>
<tr>
<td>Cathecol</td>
<td>Reasonable</td>
<td>Poor</td>
<td></td>
</tr>
<tr>
<td>Pyrogallol</td>
<td>Good</td>
<td>Good</td>
<td></td>
</tr>
<tr>
<td>Glycin, 4-aminoph.</td>
<td>Excellent $\eta = 75%$</td>
<td>Reasonable</td>
<td></td>
</tr>
<tr>
<td>Multitoner I</td>
<td>Reasonable</td>
<td>Sometimes Good</td>
<td></td>
</tr>
<tr>
<td>Multitoner II</td>
<td>Poor</td>
<td>Poor</td>
<td></td>
</tr>
</tbody>
</table>

Comment:
- Small Developed Grains
- Reticulation Stains
- Large Grains
- Unpredictable
Plates 3.1—3.
Developed Silver Grains of 8E Plates

3.1
Refinal M = 50k.

3.2
G3P M = 120k.

3.3
G3P M = 50k.
3.4
GF (Agfa) \( M = 40k \)

3.5
GF \( M = 60k \)
3.6

Neofin  M = 60k

3.7

Neofin  M = 90k

3.8

Neofin  M = 50k

(induced depth development)
3.9
Studional M = 8
(top layer)

3.10
Studional M = 80
(lower layers)
Most of the developers produce a filamentary silver grain structure, which is typical of "chemical" development. The small scale non-localization of these grains during development would have a small effect upon the relatively low resolution grating trials (\( \theta = 15^\circ \)), but the higher spatial frequency 3-D transmission images would show reduced efficiency and image contrast.

Concentrated Neofin, which is exceptionally good in the development of virtual transmission images, produced the only compact, spherical developed silver grains, which are typical of "physical" development. The poor diffraction grating efficiency of Neofin was later shown to be caused by it's surface development nature. When greater depth of development was induced by alkaline pre-washes of the emulsion, and greater developer pH by alkali buffering, the Neofin developed grains became filamentary and image quality was reduced (plate 3.8).

Studional showed dichroic fogging at the back of the emulsion (plate 3.10), but standard chemical development at the top of the emulsion (plate 3.9) where initial development took place.
1.2b Depth of Development

All developers, except Neofin, have been seen to be capable of developing all the way through to the back of a 7μm emulsion by observations under a high power microscope. The best diffraction grating efficiencies have been achieved with developers (glycin and 4-aminophenol) which gave very black silver completely to the back of the emulsion.

3.2c Preservative Level

Neofin has the lowest preservative level of all the commercial developers tested, and must be used within about 4 hours of exposure to the atmosphere. Formation of a brown oxidation product indicates that Neofin has "gone-off", and should not be used. Fresh Neofin produced the best virtual transmission images.

The most successful holographic image developers have been found to be concentrated Neofin, pyrogallol, glycin, and 4-aminophenol, but all have to be used with zero, or very low, preservative levels. A sulphite level of 5g per litre would be typical. All the developers have to be used fresh, as soon as possible after mixing, before the build-up of any oxidation product in solution.
2.2d Induction Period and Developer Power

The best images with Neofin, pyrogallol, glycin, and 4-aminophenol have been obtained with short induction periods in development. The induction period depends upon pH level, exposure, and concentration. Figure 3.1 shows how the relative reconstructed image brightness of a virtual transmission image is reduced by dilution of Neofin Blue developer.

Pyrogallol shows the most striking example of the effect of induction power. A low exposure level with a pyrogallol developer gives a long induction period and develops a grey silver, which gives a very noisy, low efficiency image. High exposures, of up to 10 times the recommended level, gave black silver grains all through the emulsion and produced good 1-D holographic images with a short induction period.

Poor holographic images are produced by developers with symptoms typical of dichroic fogging.

3.2e Temperature

Concentrated Neofin has an optimum developer temperature of 18°C. Up to 18°C developer power increased, with good image quality, but the beam ratio of the hologram exposure had to be increased to eliminate increased in-image flare with temperature rise. Above 18°C, developer power continued to increase with increased temperature, but image quality deteriorated. Neofin has been seen to develop high quality holographic images at 0°C. Neofin has been used at temperatures of between 14°C and 19°C in normal practice.
The effect of Neofin concentration upon image brightness.

\[ \eta_i \] - brightness with undiluted Neofin.
Glycin has a large temperature dependence. A
diffraction efficiency of 40% was achieved at 15°C, but the
efficiency jumped up to 86% as temperature was increased to
25°C with the same grating exposure. This indicates
increased developer fogging at lower temperatures, or
increased depth of development at higher temperatures.

3.2f Oxidation Product Retention

Developer oxidation products are known to increase the
probability of development of both sensitized and unsensitized
silver halide grains (21). Remembering that inter-grain
distances in holographic emulsions are very small, the risk
of developer fogging by migration of developer oxidation
product from a developed grain to surrounding grains is
great; oxidation product migration to unsensitized grains
reduces line contrast and image resolution in this way.

The risk of oxidation product fogging in the thin
surface developed layer of powerful concentrated Neofin is
minimal, but, as ambient oxidation product concentration
increases or the developer is depleted by diffusion into
the thickness of the emulsion, the probability of oxidation
product contamination increases.

The high diffraction efficiencies of glycin developed
transmission gratings were made more predictable and
consistent by adding a trace of pyrogallol to the glycin.
Pyrogallol has a strong oxidation product interaction with
gelatin, and appears to form an envelope of immobile
oxidation product around each developed grain, which reduces
the migration of fogging developer reaction products.
Some colour developers have strong oxidation product retention around a developed silver grain which allows dye forming reactions with colour couplers (see chapter 6). Multitoner I colour developer has produced very bright "Rainbow" images, but retention of the oxidation product quickly forms a barrier layer around each developed grain, which prevents further progress of the development reaction. The resultant small grains give a low index modulation of the image with post-fixation bleaching, and the diffraction efficiencies of gratings is relatively low (up to 40%).

The retained oxidation products of Multitoner I and pyrogallol appear to contribute to the modulation in a holographic image. Fixed silver amplitude gratings which Multitoner I have been made with transmission diffraction efficiencies of up to 12%, at an optical density of 0.45. The efficiencies of phase gratings on 8E emulsions show "volume" hologram characteristics, which should give a maximum predicted diffraction efficiency of 3.7% in amplitude mode(1). The difference between predicted and observed values of amplitude diffraction efficiency indicates that the oxidation product forms a phase image around the amplitude image, which is similar in form to the dye images of chapter 6.
3.2g Grain Size

For a given grain distribution in a holographic emulsion, the developed grain size determines the final index modulation in the image after rehalogenation bleaching. Larger grains give a higher index modulation, due to higher local silver halide concentration.

Rehalogenated glycin-developed grains are larger than the silver halide grains before development; Comparison of pre- and post-processing silver halide grain optical scatter levels in SE56 HD emulsions make this clear. The increased post-processing scatter levels are not those due to silver salt migration during bleaching, which produce a greater opacity in the processed emulsion. An increase in grain size during development is caused by solvation of silver from undeveloped grains, which is then deposited upon the developed grains. Non-fixed rehalogenated gratings confirm that silver transfer has occurred to create index modulation.

Silver solvation and redeposition explains the "physical" nature of some developed grains and also the dichroic fog at the back of a studional developed emulsion, which is caused by random precipitation of a supersaturated silver solution in a very weak depleted developer solution. The solvent nature of a developer is brought-out by the very small grain size of the emulsion, whose large surface area per unit mass increases the rate of solution of the silver halide.
With solvation/redeposition during development it is essential that the latent image sites are quickly established by a short induction time to provide accurate seeds for the growth of silver grains (see section 3.2d).

Very small colour shifts in reflection images developed in pyrogallol, and rehalogenated without fixing, indicate very little loss of silver from the emulsion during solvation/redeposition, and very bright images confirm that heavy index modulation has been created (see section 3.6).

3.3 A Model for Successful Developer Action in Holography

The low preservative level of successful holographic developers makes them applicable to the early, simplistic theories of photographic developers (21). All the observations of section 3.2 are in agreement with Ostwald's (1893) original "Supersaturation Theory" of development, where a developer solvates the outer layers of the silver bromide grains and reduces the silver ions in solution to silver. The supersaturated silver solution is then preferentially precipitated around photolytically induced silver sites, which creates the distinction between sensitized and non-sensitized silver halide grains.
Work by Staude (1939) showed that developer oxidation product can act as a catalyst in the development reaction\(^{(2)}\) in the emulsion. Low ambient developer oxidation product concentrations and localization of the oxidation products near to developed grains are, therefore, essential for low developer fogging in the close grain spacing environment of holographic emulsions.

Based upon this simple model of developer action, it has become clear that each mode of holographic recording (i.e. diffraction gratings and virtual images in transmission mode and reflection images) have a different optimum developer action. Each mode shall now be discussed in turn.

3.4 Developers for Virtual Image Transmission Holograms

2.4a Introduction

Concentrated Neofin stands alone in its ability to develop high quality virtual image transmission holographic images. The most important characteristic of Neofin is that it is a surface developer. All other developers have developed to a greater depth in the emulsion. The extra depth of development has invariably introduced in-image flare to the hologram. The intensity beam ratio had, then, to be increased during exposure to eliminate the flare, thereby negating the potentially higher diffraction efficiency of greater development depths and also introducing more redundant information noise into the holographic emulsion.
In the exposure of a virtual image transmission hologram, two images are created: firstly a reference beam/average subject beam interference pattern, and secondly a cross-modulated image within the subject beam alone. As the image is reconstructed by the original reference beam, the subject beam is created by the first interference pattern in the photographic emulsion. The subject beam then acts as the "reference" for the second cross-modulation pattern, which causes a distribution of faint images to be created around the main holographic image. This distribution of images is the "in-image flare", which increases as more subject beam is created from the original reference beam at greater emulsion thicknesses. Thus a planar holographic recording medium does not allow the in-image flare to be created by the subject cross-modulation. Hence the success of Neofin surface developer, since flare is created in the thickness of a holographic emulsion.

The cross-modulation interference pattern consists of a continuum distribution of low intensity, self-referenced holographic images, which integrate over all the image space to form flare noise. If the exposure level of these low intensity images is taken below the recording threshold of the emulsion/developer combination, but the exposure of the main interference pattern (recorded between the whole subject beam and the reference beam) remains within the recording range of the emulsion, then only the main image would be recorded. This effect depends upon a sharp recording threshold of the developer on the emulsion, such as with G3P on SE56 (see Figure 2.4), where a high ambient reference beam exposure can "swamp" the cross-modulation in an
exaggerated manner. With developers which induce a low recording threshold in an emulsion, such as some pyrogallol developers (see Figure 3.4), the cross-modulation cannot be totally eliminated, even by a beam ratio of over 30:1.

3.4b Optimizing Neofin Development

Figure 3.2 shows how the diffraction efficiency of Neofin developed diffraction gratings varies with pre-bleach optical density. The maximum diffraction efficiency of 33% on these symmetric, sinusoidal phase gratings shows the "planar" nature of the Neofin developed image. The slight increase in diffraction efficiency with a pre-development wash in alkali appears to be due to an increase in development depth. This pre-wash is not useful with 3-D images, since it increases image noise and introduces in-image flare.

Figure 3.3 shows how image brightness changes with pre-bleach optical density for virtual image transmission holograms. "Image brightness" is measured as the brightness of the holographic image relative to the original subject brightness at the beam ratio used in the exposure. A beam ratio of 6:1 and a post-fixation Ferric/Bromide rehalogenation bleach was used with the images in Figure 3.3.
Figure 3.2

Neofin Developed Gratings, $\theta=15^\circ$

- • amplitude mode
- ▲ post-fixation bleach
- ▼ alkali pre-bathe

Pre-bleach Density vs. $\eta\%$
Figure 3.3
Neofin Developed Transmission Images

Relative Image Brightness (%) — see text
A clear maximum image brightness is shown at $D=2.3$ for both Neofin Red and Neofin Blue. Neofin Blue has been chosen as the standard developer because of its less density-selective maximum brightness. With less - solvating rehalogenating bleaches than Ferric/Bromide (such as Benzoquinone/Bromide: see chapter 4) the maximum is even less precisely located, and little change in image brightness is seen between $D=1.5$ and $D=2.5$. A lower density within this range is preferable, since greater pre-bleach densities give greater granular noise in a rehalogenated image; a density of $D=1.8$ has been used for the highest quality images.

3.4c Developer "Home Brews"

All the attempts to formulate a rival developer to Neofin have failed. All the formulations by Agfa-Gevaert have given lower image brightnesses and higher noise levels than Neofin, probably due to development fogging by their very concentrated contents.

Agfa-Gevaert suggested that glycin and phenidone were probably the two major Neofin components; phenidone for fast induction and glycin for the compact, spherical grains. Many formulations of this type have been tried, but none have been considered suitable.
The green oxidation product of Neofin suggested the use of 4-aminophenol, which is a very low fog, high contrast developer. 4-aminophenol gave the best of all "home-brew" results. A basic solution of:

\[
\begin{align*}
5g & \quad 4\text{-aminophenol} \\
10g & \quad \text{Sodium Sulphite} \\
500ml & \quad \text{Distilled Water}
\end{align*}
\]

is raised to pH12 by adding sodium hydroxide pellets to the point where a clear, purple solution is formed. This developer has a short usable lifetime (about 5 minutes) and needs a beam ratio of about 16:1 to combat development depth. The high exposure/development threshold of this low fog developer may help to control cross-modulation with a manageable beam ratio of only 16:1.
3.5 Transmission Diffraction Gratings

Line diffraction gratings, holographic transmission optics, "Rainbow" holograms, and semi-real, projection holograms all fall into the same class of holograms by virtue of their lack of subject beam cross-modulation, which is eliminated by limiting the image field-of-view. The theory of volume transmission holograms applies, therefore. The hologram thickness is fixed at 7μm by the 8E emulsions, and phase modulation is controlled by the depth of optical density modulation in the case of post-fixation, rehalogenated images (5).

The best developer for transmission line gratings and holographic optics has been found to be:

\[
\begin{align*}
5g & \text{ Glycin } \\
0.5g & \text{ Pyrogallol } \\
30g & \text{ Sodium Carbonate } \\
1 \text{ litre} & \text{ Distilled Water }
\end{align*}
\]

Post-fixation, rehalogenated have given a maximum efficiency of up to 86% with this developer, at a pre-bleach density of 1.5. Subjective optical scatter noise is negligible, due to the pyrogallol component which appears to index-match each grain to the gelatin by a layer of light-brown oxidation product, giving a "glassy" feel to the images.
The main virtue of the glycin based developer is its ability to develop large silver grains. These produce a very high index modulation when rehalogenated (see section 3.2g). The large grain size of the glycin developed emulsions limits the use of this developer to regular line structures of the image in the emulsion, since more random image distributions in the emulsion cause stresses which degrade the gelatin.

A more suitable developer for projection images is a pure pyrogallol developer, which produces a more controlled grain growth:

- 5g Pyrogallol
- 10g Sodium Sulphite
- 30g Sodium Carbonate
- 1 litre Distilled Water

With all the powerful, low preservative developers, sulphite must be mixed with the developing agent before the alkali is added; this reduces the risk of aerial oxidation as the alkali is mixed into solution.

The maximum diffraction efficiency of gratings developed in commercial developers was 60%, with Dokumol, but images were noisy. Multitoner I has been found to produce very good "Rainbow" images.
3.6 Developers for Reflection Holography

3.6a Introduction

The structure of the modulation in a reflection image is well documented (1, 2, for example) as needing an accurate recording resolution of 4500 lines per mm. SEHD emulsions have this resolution capability, but only just.

Reflection images are recorded on the glass side of a photographic emulsion, such that relief distortion of the emulsion does not introduce noise into the image. This increases the demands upon the photographic developer to avoid depletion as it progresses through the emulsion, and to not introduce developer fogging at the back of the emulsion by oxidation product contamination of unsensitized grains.

3.6b Initial Trials

The first reflection image trials in this project were made by solvent bleaching or post-fixation bleaching of the silver image. After bleaching, the emulsion is swollen to select the correct wavelength of image reconstruction (see section 2.3c). The most successful developing agents for reflection images were established as pyrogallol, glycin and 4-aminophenol. Almost any combination of these agents has been found to give reasonable results with a single-step development stage, but results could not compete with those of Russian workers.
Pyrogallol was chosen as the most promising developer for reflection holography, since the large grain sizes of glycine and 4-aminophenol introduced greater noise levels into the emulsion. The brown oxidation product stain of pyrogallol itself reduced the subjective noise levels in the processed emulsion. Much of the brown stain is removed during rehalogenation in a Benzoquinone/Bromide bleach, but sufficient remains around each grain to reduce noise (see section 3.2f).

3.6c Non-solvating Processing

Solvation/redeposition of silver in the development of a holographic image was first established by rehalogenating a reflection image without fixation, which did not introduce a colour shift into the image reconstruction (see section 3.2g). This unexpected result allows reflection images to be viewed without messy swelling correction of the emulsion, and also eliminates colour shifts across the emulsion due to corresponding density variations, particularly in semi-real projection images.

Pyrogallol, glycine and 4-aminophenol have all been shown to exhibit solvation/redeposition during development.
3.6d Reducing Developer Fogging

With the introduction of high quality benzoquinone rehalogenation bleaches and non-solvating processing, the blame for inconsistent diffraction efficiency and noise levels in reflection images was finally laid upon incorrect development at the back of the emulsion, due to developer fogging.

Developer fogging has been reduced by introducing inactive developing agent into the whole of the emulsion, and then inducing activity by adding alkali to the solution. Developer depletion and oxidation product build-up at the back of the emulsion is thereby reduced. By using the low mobility of the pyrogallol oxidation product, in combination with a pre-bath of inactive developer, very high efficiency, consistent results have been achieved. A typical developer stage would be:

(i) Pre-bathe in 5 g/l pyrogallol at pH7 for 2 minutes.
(ii) Add an equal volume of 30 g/l carbonate solution, mix thoroughly, replace the hologram, and develop for 2 minutes.

The developer must be used only once, and is automatically fresh by using this technique. Borate alkalis should not be used, since they form chemical complexes with the developers, which reduce image quality.
Figure 3.4 shows a typical Hurter and Driffield curve for the development of an 8E56 emulsion by pyrogallol. The optical density of pyrogallol oxidation product has not been subtracted in this curve.

Work with reflection images has been continued by Mr. Ward, who has established a pre-bleach density of anywhere between 1 and 2 as producing good bleached-silver phase images. Pre-bleach optical densities have been found to be non-critical in this project; a density tolerance of 0.25 would be typical of all recording modes, due to the liberal Bragg-Angle conditions of the 7μm 8E56 emulsions.

A beam ratio of between unity and 2:1 has given best reflection image results, with the reference beam incident upon the glass side of the emulsion.

Further work upon developers suitable for holographic images must continue with an investigation into the properties of developers with photographically inert oxidation products, which would reduce the constraint of having to localise the development reaction products (76).
Figure 3.4

Hurter-Driffield curve for Pyrogallol on 8E56

D
3
2
1
o

Pyrogallol
Neofin

E (erg/cm²)

10⁰  10¹  10²  10³
Chapter 4 The Bleaching of Silver Images

4.1 Introduction

After a high quality silver amplitude holographic image has been developed in a photographic emulsion, the silver can be bleached to form a phase image of refracting grains of a silver compound. Bleaching can take the form of either solvent bleaching, where the silver image is dissolved out of the emulsion to leave a complementary image of unexposed silver halide grains, or post-fixation bleaching, where unexposed grains are fixed out of the emulsion and the silver image is transformed into an insoluble silver salt.

At the start of this project, two extremes of photographic bleaching for holography were available. High quality, low noise images could be made with the Agfa solvent bleach, with it's dubious virtue of using a mild silver halide solvent "clearing bath" (51). This process is unpredictable and has given a maximum diffraction efficiency of 30%. The alternative was to use the dangerous bromine vapour bleach, originally proposed by Thiry (52) and later reincarnated by Graube (53). A high diffraction efficiency of 70% is the virtue of vapour bleaching, since no solution of index modulation can occur, but the high noise level of the bleached emulsion is intolerable.
An unhappy medium between the two extremes was offered by the Kodak EB-2 (54) or the bromine water (55) rehalogenation bleaches. Surface reticulation and volume degrading of the gelatin emulsion was again inappropriate for the display of 3-D images.

Van Hennesse and Bouts (5) offered the choice of deadly mercuric chloride or very noisy ferricyanide bleaches to support their electrical polarizability theory of dielectric modulation.

Other techniques (57,58,59,60,61) offered no advantages over the above mentioned bleaches. No bleach, therefore, could offer both high diffraction efficiency and low noise imaging capabilities.

4.2 The Chemical Action of Bleaches (21,22,23)

A silver bleach is an oxidizing agent which converts silver to its ionic form;

$$Ag = Ag^+ + e^-$$

The silver ions are then available for solvation from the emulsion, or for reaction with an anion to form an insoluble, refracting silver salt;

$$Ag^+ + X^- = AgX$$
The requirements for noisless bleaching action are:

(i) The product $\text{AgX}$ should be the only insoluble component in a bleach reaction.

(ii) The compound $\text{AgX}$ should not migrate from its reaction site.

(iii) No degrading of the gelatin substrate should occur.

(iv) No solvation of the modulating compound should occur during bleaching; this would reduce diffraction efficiency.

4.3 Bleaching Agents

All common photographic bleach reagents have been tested under varied reaction conditions of concentration, pH, and anionic species for their application to holographic imaging. Subjective evaluation of the quality of virtual image transmission holograms was used as the basic test of a bleaching agent in these initial trials.

4.3a Free Halides

(i) Bromine:

Bromine vapour, aqueous solution, and alcoholic solution all degrade the gelatin substrate by oxidative cleavage of peptide molecular chains. Holograms are efficient and have excellent print-out stability, but are very noisy.

(ii) Chlorine:

No chloride or chlorine bleaches have been found to give good holographic images.
(iii) Iodine:

Iodide bleaches give a greater refractive index modulation in holographic images than either bromide or chloride, but iodide bleaches are invariably noisy due to large grain growth. Free iodine degrades gelatin in the same way as bromine.

The most successful iodine bleach has been formulated by controlling the liberation of free iodine in a low power solution of the oxidizing agents potassium persulphate and cupric sulphate;

- 20g Cupric Sulphate
- 10g Potassium Persulphate
- 5g Potassium Iodide
- 1 litre Distilled Water

the iodide is dissolved in 100ml of the water and added very slowly to the bulk of the solution. Persulphate is the only agent which would control the liberation of iodine in the cupric solution and prevent the precipitation of a dark brown substance from solution.

4.3b Cupric Bleaches

\[ \text{Ag} + \text{Cu}^{3+} = \text{Ag}^+ + \text{Cu}^{2+} \]

Cupric salts are caustic and caused severe reticulation of gelatin in all tests, which is exaggerated by the use of hydrogen peroxide accelerator (recommended by both Agfa and Kodak).
The best cupric bleach formulation was non-acidic, and relied upon the presence of bromide to neutralize the charge barrier layer at the silver grain surface in post-fixation mode:

100g Cupric Nitrate
20g Potassium Bromide
1 litre Distilled Water

No suitable cupric solvent bleach has been formulated.

4.3c Ferricyanide

\[ 4\text{Ag} + 4\text{K}^+\text{Fe(CN)}_6^- \rightarrow \text{Ag}_4\text{Fe(CN)}_6^- + 3\text{K}^+\text{Fe(CN)}_6^- \]

Ferricyanide

Ferrocyanide

Van Renesse postulated (5) that ferrocyanide modulation would be ideal for high efficiency holographic images, because of it's very high electrical polarizability and molecular size, but all tests with ferricyanide bleaches produced very high in-plate optical scattering.

4.3d Mercuric Chloride

This bleach produced very noisy images under all conditions.

4.3e Potassium Permanganate

Produced stains and heavy reticulation under all conditions, both as a solvent or rehalogenation bleach.
4.3f Ceric Sulphate

\[ \text{Ce}^{4+} + \text{Ag}^+ = \text{Ag}^+ + \text{Ce}^{3+} \]

Acidified ceric sulphate was found to be very unpredictable as a solvent, or rehalogenation bleach, and extensive reticulation damage discouraged further investigations.

4.3g Persulphate

\[ 2\text{Ag} + \text{K}_2 \text{S}_2 \text{O}_8 = \text{Ag}_2 \text{SO}_4 + \text{K}_2 \text{SO}_4 \]

Ammonium persulphate gave very noisy images, but potassium persulphate proved to be useful as a bleach reaction moderator (see section 4.3a and section 4.5b) and as a novel bleach reagent in collaboration with Bindschedler's Green dye. The persulphate oxidation reactions are not fully understood, but Appendix I gives some suggestions for further work with this promising reagent.

4.3h Potassium Dichromate

Dichromate was chosen for further investigation as a solvent bleach, in the form of a modified Bl formula of Buschmann (51), because of its very low solvent action on the silver halide complementary image. Diffraction gratings with dichromate/bromide rehalogenation bleaches have produced very high diffraction efficiencies, which were considered as being promising for holographic optics (see section 4.6b).
4.3j Ferric

\[ \text{Fe}^{3+} + \text{Ag}^+ = \text{Fe}^{2+} + \text{Ag} \]

The near equality of the redox potentials of the ferric/ferrous reaction and the silver/silver ion reaction (62) promoted the suspicion that ferric ions would oxidize silver without the liberation of free energy, which could cause damage to the gelatin structure. This naive view led to the rapid formulation of a simple ferric rehalogenation bleach, which gave the best results of all the initial trials;

- 60g Ferric Nitrate
- 10g Potassium Bromide
- 1 litre Distilled Water

Ferric was chosen as the basis of further bleach trials in rehalogenation mode. No ferric solvent bleaches were considered suitable for holography.

4.4 The Bleaching Environment

4.4a Water Purity

The use of tap-water in the preparation of bleach solutions created much confusion about the suitability of bleach formulations for holography. The chloride content of tap-water causes the solvation of silver compounds from the holographic emulsion (23), particularly silver bromide, which reduces index modulation.
As the solvated silver meets the bulk of the bleach solution at the surface of the emulsion, a layer of silver chloride is often precipitated. Thus efficiency is reduced and noise levels are increased.

Distilled water must be used in bleach solutions.

4.4b Stresses in the Emulsion

Localized volumetric changes in a holographic emulsion induce stresses in the gelatin substrate during processing. Stresses are minimized by solvent bleaching, since volume changes within the emulsion are unidirectional; Contraction occurs in both development and bleaching. Post-fixation bleaching, however, induces stress reversal; Contraction occurs during development and fixing, but the silver grains expand during rehalogenation.

If the emulsion has been hardened or degraded during processing, the induced stresses break the inter-molecular bonds in the gelatin to form optical scatter centres around each grain. It is the combination of stresses and chemical interaction with the gelatin which can induce optical scatter noise into a holographic plate.

Plates 4.1 and 4.2 show surface relief pictures of a processed emulsion. Plate 4.1 shows damage to the emulsion in a post-fixation hologram containing high local index modulation, due to the use of a unity beam ratio during exposure. Plate 4.2 shows a portion of the same plate with low surface damage in a low local index modulation region. Solvent bleached plates show little damage, even at high index modulation.
Plate 4.1
High Index Modulation Region

Plate 4.2
Low Index Modulation
4.4c Index Modulation

(i) Origin:

The refractive index modulation in a bleached silver phase hologram is achieved by modulating the concentration of bleached silver compound in the emulsion, which is itself controlled by the original distribution of grains and the final size of the bleached-silver grains in the emulsion.

Figure 4.1 shows how the diffraction efficiency of Neofin developed diffraction gratings varies with pre-bleach optical density for both solvent and post-fixation rehalogenation bleaches. The two cases are very different, showing that the index modulation achieved by solvent bleaching is very much less than by post-fixation rehalogenation bleaching (5). This lower index modulation has two main sources; firstly the solvation/redeposition effect during development (see section 3.2g) reduces the size of the complementary image silver halide grains and increases the size of the rehalogenated grains, and secondly the solvent bleach action of that time tended to solvate the silver halide complementary image together with the silver image.

For a given grain distribution, a compromise must always be reached between high index modulation and the optical scatter associated with the larger grains.
Figure 4.1

Bleached Grating Efficiencies (Neofin Developer)

△ post-fixation rehalogenated
□ solvent bleached
(11) Optical Density:

At the very high spatial frequencies of holographic imaging, no relationship has been established which would relate spatial waveform to the average optical density. The redistribution of silver during development probably "squares-off" the profile of a sinusoidally modulated grating exposure.

With no redistribution of silver during development, the original $5 \text{ g. m}^{-2}$ distribution of silver bromide in an 8E emulsion would give a maximum peak index modulation of 0.08 at an optical density of half the saturation density (5). For 8E emulsions the saturation density lies between 4.5 and 5, depending upon the developer used. With silver redistribution in development, the optical density/index modulation relation changes slightly, such that a maximum index modulation is achieved in rehalogenation bleaching mode at an optical density greater than $D_{oc}/2$ (see Figure 4.7, for example).

4.5 Solvent Bleaching

Although solvent bleaches have never allowed the same high values of diffraction efficiency as rehalogenation bleaches, their gentle action upon the gelatin of the holographic emulsion has allowed the improvement of developer techniques in situations where rehalogenation bleaches were too caustic.
Earlly trials with reflection imaging are a good example of this; rehalogenation bleaches at that time degraded the gelatin to such an extent that the effect of different developers was masked by bleaching damage, whereas solvent bleaches had minimal effect upon the integrity of the emulsion.

Acidified potassium dichromate was chosen as the bleach reagent for further studies into solvent bleaching, since it had the lowest solvent action upon the silver halide grains of the complementary image during solvation of the silver image.

4.5a Eliminating Ag Br Solvation

Solvent bleaches had been seen to solvate almost all the modulation of the silver bromide complementary image. A pre-bleach bath of 500 mg per litre of Benzotriazol was introduced to act as a blanket protective around each silver bromide grain by an adsorbed layer of Benzotriazol. The "anti-fogging" action of the Benzotriazol did decrease the rate of solvation of silver halide relative to that of the silver.

4.5b Evolution of the Bleach Formula

The Agfa-Gevaert solvent bleach formulae are very powerful and degrade the gelatin of the emulsion by the oxidative cleavage of the swollen acidified gelatin molecular chains.
Both surface relief damage and volume damage in the emulsion have been greatly reduced by diluting the bleach to the form:

1g Potassium Dichromate
2ml Conc. Sulphuric Acid
1 litre Distilled Water

Any further reduction of acid level resulted in the precipitation of a fine, scattery layer of chromic oxides in the emulsion.

The bleach was still too rapid and damaging at this stage. Persulphate was added to the above bleach in the hope that it would moderate the bleach action. The concentration of dichromate was also reduced until a bleach with undetectable emulsion damage was formulated:

5g Potassium Persulphate
100mg Potassium Dichromate
2ml Conc. Sulphuric Acid
1 litre Distilled Water

The dichromate appears to produce the initial bleaching, which provides catalytic silver ions (21) for the persulphate to continue the bleaching action. Solvation of the complementary image has not been a problem with this bleach, and the Benzotriazol pre-bath has not been necessary.

It is important to use a fresh bleach solution for each hologram. The build-up of halide and silver ions in the bleach solution introduces random precipitation and grain solvation into an emulsion.
11.6 Rehalogenation Bleaches

Investigations to improve the quality of rehalogenation bleaches were started by optimizing the very successful early trials with Ferric based bleaches. Almost all the trials with the ferric bleaches have been conducted with the very reliable developing action of concentrated Neofin Blue upon transmission holograms. By isolating the causes of emulsion damage in Ferric bleach solutions, rules have been established which allow the consistent reproduction of very low noise bleached-silver holograms.

4.6a Ferric Based Bleaches

(i) Ferric Concentration:

The use of acid buffers has been avoided in all rehalogenating bleaches, to prevent the acid hydrolysis of gelatin during processing. The pH level of ferric nitrate solution is shown in Figure 4.2. The pH level appears to become constant at about 5g per litre of ferric nitrate, but Figure 4.3 shows that the remaining hydroxide ion concentration in the ferric solution can cause the precipitation of silver hydroxide, which leaves a scattering opacity in the emulsion. The opacity can be reduced by adding a small amount of bromide into the solvent bleach solution to cause the preferential crystalization of silver bromide, once the ferric concentration has reached a level where hydroxide ion concentration is not dominant over the bromide concentration.
Figure 4.2

pH of Ferric Nitrate Solution

Figure 4.3

The Scatter Opacity of Ferric Solvent Bleaches

Ferric alone

Ferric + 5g/l KBr
Figure 4.4 demonstrates how much silver is precipitated as silver hydroxide by showing the redeveloped transmissivity of a fixed ferric solvent bleached emulsion with a pre-bleach transmissivity of 0.1. At low ferric concentrations almost all the silver is left in the emulsion to create in-plate scatter noise. The silver hydroxide precipitate can be eliminated by adding sulphuric acid to the ferric, but this induced silver migration in later rehalogenation trials and was not incorporated into bleach formulations.

Any brown residue left in a ferric bleached emulsion appears to be due to the precipitation of ferrous salts, which can usually be washed out of the emulsion by dilute (1/100) HCl.

Ferric solutions have been seen to solvate silver halide from the emulsion over long periods of time (2 hours approximately). Attempts to avoid this solvation, by dissolving the ferric in an alcohol/water mixture, proved fruitless. The ferric appears to form a chemical complex with iso-propyl alcohol over a period of days, which reduces bleach activity and increases the noise in bleached images.

(ii) Bromide Concentration:

Figure 4.5 shows how bromide concentration affects the speed of a ferric bleach at a constant ferric concentration of 30g per litre. It shows how a concentration of only 1g per litre of bromide can completely break down the charge barrier layer at the surface of an oxidized silver grain.
Figure 4.4  Redevelopment Density of Ferric Solvent Bleached Plates

Dokumol developer.
fixed, pre-bleach D=1
Figure 4.6

The Effect of Bromide Concentration on the Speed of a Ferric Bleach (30g/l).

Figure 4.6

The Effect of Bromide Concentration on Post-Bleaching Scatter Opacity (Ferric = 30g/l, D = 3.5).

Graph 1:
- Time to bleach for different KBr concentrations (g/l).
- D = 2 (min).

Graph 2:
- Scatter opacity for different KBr concentrations (g/l).
- KBr concentration range from 0 to 35 g/l.
Figure 4.6 shows how the scatter opacity in the emulsion increases with increased bromide concentration. The scatter has two origins; diffuse grain scatter and degrading of the gelatin. This can be demonstrated by fixing the bleached emulsion to separate the effects.

The excess bromide ions appear to adsorb to the molecules of silver bromide formed in the bleach reaction. The charged molecules diffuse away from the reaction site, where the concentration of charged molecules is greatest. The silver bromide eventually precipitates in a non-crystalline form in the emulsion, which causes increased optical scattering.

The diffuse precipitation has been reduced by limiting the diffusion of the silver bromide molecules and silver ions. A large dye molecule is introduced into the bleach, which adsorbs preferentially to the bleached silver and limits diffusion. This effect was found accidentally when phenosafranine was introduced to a ferric bleach to incorporate desensitization. Bleaches with phenosafranine concentrations of up to 300 mg per litre are subjectively much less noisy than their non-dyed equivalents.

The gelatin damage due to increased bromide concentrations was unexplained at that time, but was reduced by the addition of phenosafranine to the bleach.
Increased concentrations of potassium bromide in a ferric bleach give a deeper red/orange colour to the solution. This is caused by a liberation of free bromine, which was seen to cause degrading of gelatin in early bleach trials with bromine water (see section 4.6).

(iii) The Final Ferric Formulation;

A concentrated bleach stock solution of:

- 100g Ferric Nitrate
- 33g Potassium Bromide
- 300mg Phenosafranine in 20ml Methanol
- 1 litre Distilled Water

is diluted by 4 parts distilled water to 1 part bleach stock solution. This bleach gave excellent results with both diffraction gratings and virtual image transmission holograms, but created too much emulsion damage for use in reflection image trials.

Figure 4.7 shows how the efficiency of diffraction gratings is related to pre-bleach density for different developers with the above ferric bleach in post-fixation mode. Figure 3.3 (page 56) shows a similar curve for the relative brightness of virtual image transmission holograms.
Figure 4.7

Diffraction Efficiency of Ferric Bleached Gratings

\[ \eta \%
\]

\[ \text{G3P} \quad \& \quad \text{Dokumol} \]

\[ \text{Neofin} \]

\[ D \]

0 1 2 3 4 5
4.6 Rehalogenation with Organic Reagents

(i) Protecting the Emulsion:

Interest in the use of organic reagents in bleach formulations started with phenosafranine in the ferric bleach, which appeared to control grain growth, protect the emulsion, and desensitize. The use of organic dyes as accelerating agents in bleaching is discussed in Appendix I.

The protective action of phenosafranine on the emulsion is effected by its reduction potential, which mops-up the free bromide ions in a bleach solution before they harm the gelatin. The free bromine can break the hydrogen bonds in gelatin, as shown in Figure 4.8, or it can liberate a free electron into the peptide molecular chain of the gelatin and cause direct bond breakages.

\[ \text{i.e. } \quad \text{Br}^- \rightarrow \text{Br} + e^- \]

These degrading reactions upon the gelatin occur at the bleach reaction sites. The phenosafranine reduction potential of $\text{Ea}^{\frac{1}{2}} = +1.21 \text{ V}$ is sufficient to preferentially accept the bromine oxidation reactions and prevent damage to the gelatin. A search was started at that time for a colourless organic, with a similar or more powerful reducing action in acidic solution, to replace phenosafranine.
Figure 4.8
Degradation of Gelatin by Bromide

 Hydrogen bonds between free gelatin radicals.

\[ \text{HO-C=O} \quad \text{HO-C=O} \quad \text{Br} \]
(ii) Benzoquinone Bleaching Agent (23,64):

An organic bleaching reagent was eventually found which is powerful enough to bleach silver in mildly acidic solution; this is p-benzoquinone. After many trials with different acidic buffering agents and reagent concentrations, the following formula produced very good post-fixation rehalogenation images:

- 2g p-Benzoquinone
- 20g Boric Acid
- 20g Potassium Bromide
- 200mg Phenosafranine
- 1 litre Distilled Water

Virtual image transmission holograms with this bleach are very bright and have low scatter levels, but damage is not low enough for it to be used in reflection imaging.

Mild developing agents have been tried within the above bleach to find a suitable protective agent for the emulsion. Glycine, resorcinal, phenidone, hydroquinone and 2-aminophenol were unsuitable, but quinhydrone was immediately successful in reducing damage to the emulsion.

A very good bleach formulation using quinhydrone is:

- 2g p-Benzoquinone
- 0.5g Quinhydrone
- 20g Potassium Bromide
- 15g Boric Acid
- 1 litre Distilled Water
It is interesting to note the formula of quinhydrone;

\[ \text{OH} \quad \text{O} \]

\[ \text{OH} \quad \text{O} \]

Quinhydrone is composed of hydrogen-bonded Benzoquinone and hydroquinone. It can act, therefore, as either an oxidizing or reducing agent. The latent reduction potential of the hydroquinone protects the gelatin from the free bromine. The oxidizing properties can be shown in the bleach formulation:

- 2g Quinhydrone
- 20g Potassium Bromide
- 15g Boric Acid
- 1 litre Distilled Water

It is only when the quinhydrone acts in a subservient role to the benzoquinone, or other oxidizing agent, that it protects the gelatin. Quinhydrone alone is a very poor bleaching agent. The protective action of quinhydrone is best demonstrated by a modification to the R-10 dichromate rehalogenation bleach, which gives very efficient grating results due to low modulation solvation and the quinhydrone protective action;
The above bleach is suitable only for images with a regular line-structure, such as holographic optics, and has given a diffraction efficiency of 86% in post-fixation rehalogenation mode with a glycine/pyrogallol developer.

The disadvantages of quinhydrone are short bleach lifetimes, due to decomposition of the quinhydrone during bleaching, and toxic powder clouds which "hang" in the air after mixing the bleach. A well ventilated room or fume cupboard should be used when mixing quinhydrone solutions.

An extra protective reagent has been found in the use of benzotriazol (see section 4.5a), which appears to reduce the migration of silver during bleaching. The resultant bleach formulation has produced very bright images with subjectively acceptable noise levels;

- 2g p-Benzquinone
- 0.5g Quinhydrone
- 1g Benzotriazol
- 20g Potassium Bromide
- 10g Boric Acid
- 1 litre Distilled Water

The above bleach formulation has produced the best bleached-silver transmission images during the course of this project, and has been applied to the non-fixed rehalogenation bleaching of reflection images, with excellent results.
Chapter 5  Relief Imaging for Holography

5.1 Introduction

A convenient way of mass-producing holographic images would be to press a relief image into a plastic film with a metal mould. The metal mould would be a replica of a master surface-relief image, formed on a silver halide photographic emulsion.

Modern surface relief processing of photographic emulsions depends upon either tanning the gelatin of the emulsion during development, or by etching away the gelatin with an inorganic etching bleach (23) after normal development. A novel etching bath was proposed as an alternative, which depended upon the retardation of the hydrolysis of gelatin in proteolytic enzyme solution by heavy metal ions (77) (78).

5.2 Depth of Modulation

In transmission mode for a relief grating, it can be shown that maximal efficiency is attained at a thickness modulation, $\Delta T$, of (1);

$$\Delta T_{\text{peak}} = \frac{\lambda}{(n_o - 1)}$$

which gives $\Delta T = 0.5 \mu m$ for argon green upon a modulated gelatin substrate of $n_o = 1.5$. This value of $n_o$ would also be typical of most common plastics upon which the grating replicas would be pressed.
5.1 Enzyme Etching

5.3a. Introduction

The etching of protein substrates by enzymes is a well-catalogued process, which is frequently used by photochemists to isolate silver grains from the gelatin for electron microscopy investigations. If the rate of etching in the gelatin could be controlled by the modulating component in a holographic image, high resolution relief images would be produced by the unhydrated gelatin.

Inhibition of hydrolysis by proteolytic enzymes is effected by heavy metal ions in low concentrations; silver, copper, mercury and lead at concentrations of less than $10^{-3}$M. This is probably due to the influence of these metal ions upon the affinity between enzyme and substrate, and thus have an indirect effect upon reaction rate. It was thought that inhibition could be effected by the developed silver lines in a holographic diffraction grating. The gelatin between the silver lines would then be preferentially etched away to form the troughs of the relief image.
Enzymes act as a catalyst for the hydrolysis of a protein substrate, at the surface or in the volume of the substrate (77). Collagenase and Gelatinase are the specific enzymes for use with a gelatin substrate, but are prohibitively expensive. The following enzymes have been found to be suitable for investigation (79):

- Rapidase (pH 7 at 40°C)
- Trypsin (pH 7-9 at over 25°C)
- Pepsin (pH 2-4 at over 25°C)
- Bromelain (pH 4-7 at over 35°C)

All these are inhibited by silver ions. The mechanism of their inhibition is that of catalyst poisoning by the formation of a metallo-enzyme complex (80).

The enzymes are dissolved in water, buffered to the operational pH, and maintained at a temperature above their minimum activity temperature. An incubation period of enzyme activity precedes any observable reaction in the substrate, which is followed by hydrolysis of the protein according to the reaction rate:

\[ x = K t \sqrt{E} \] at fixed temperature

where x is percentage digestion, K is a constant and E is percentage enzyme concentration (80).

Temperature dependence in the above reaction is very complicated, but increases very rapidly between 20 and 80°C.
The extent of the hydrolysis reaction on the gelatin substrate can be viewed by optical density reduction of a dyed substrate layer:

\[ D = - \log_{10} (\exp - 2\alpha T) \quad \text{where} \quad \alpha = \text{absorption coeff.} \]

\[ \therefore D = 2\alpha T \cdot \log_{10} (e) = 0.869\alpha T \]

i.e. D proportional to T

Average silver density could also be used as a measure of substrate thickness in an etching-rate test, if development of all the emulsion thickness is assumed. Figure 5.1 shows the ideal characteristics of a gelatin substrate containing a developed silver density.

5.3c. Experimental Procedure and Results

(i) Test Solutions:

Most experiments have been conducted with a 1% Rapidase or Trypsin solution at 40°C in un-buffered distilled water. Temperatures above 40°C produced inconsistent results, due to melting of the gelatin. Enzyme concentrations of over 20% gave too fast a reaction rate for accurate measurement. An incubation period of 10 minutes was allowed before each test.

Silver deposits from solvated gelatin layers must be regularly removed by a light wipe of the finger across the emulsion surface.
Figure 5.1

The ideal etching of a developed emulsion.
(ii) Preliminary Trials:

A uniform optical density was developed on 8E56 plates with Pyrogallol, G3P and concentrated Neofin Blue. Figures 5.2 and 5.3 show the rate of density change during etching for pyrogallol and G3P developed plates respectively. Both these curves show an ideal etching-rate reaction system. The curves for the Neofin surface developer were totally unpredictable, as was expected, since all the developed density is located in the first layers of gelatin (1μm) to be etched (see chapter 3).

(iii) Blanket Inhibition;

Half of an 8E56 plate was developed to saturation density in pyrogallol (D=4). The plate was fixed and washed for 10 minutes.

The plate was immersed in enzyme solution for 20 minutes, with frequent washes to remove deposited surface silver which could contaminate the emulsion. After 20 minutes, all the undeveloped half of the emulsion had been etched away from the plate, leaving the silver-containing half of the emulsion as a soft layer on the glass plate.

Differential etching rate of developed and undeveloped emulsion was indicated by this result. Maximum differential of etching rate was given by Trypsin and Rapidase, with bromelain being negligibly inhibited by developed silver.
Figure 5.2  
Etching by Rapidase (1\%) at 40°C  
Pyrogallol developer.

Figure 5.3  
G3P developer.
(iv) Coarse Modulation of Density;

A contact print of a Fresnel zone plate was made on an 8E75 plate. The plate was developed, fixed and washed to give a square wave amplitude modulation varying between 1 and 10 lines per cm.

The etching process was repeated, with different immersion times of plates in the enzyme solution. The plates were washed, hardened, and solvent bleached in acidified dichromate solution to ensure that any relief modulation was not caused by the volume of developed silver in the emulsion. A filtered, expanded laser beam was passed through the emulsion to observe any modulation.

Sharp lines of emulsion discontinuity were projected by the beam which corresponded to the original developed silver pattern. The discontinuities could be felt by lightly drawing a fingernail across the emulsion, indicating a relief modulation.

(v) Narrow Angle Diffraction Gratings;

Amplitude diffraction gratings were made on 8E56 emulsion with $\phi = 5^0$ and an average density of $D = 1.5$. Enzyme etching was repeated with immersion times of samples separated by 5 minutes.

The gratings were washed, hardened, solvent bleached, and dried using a final alcohol wash to aid uniform drying of the very soft emulsions.
Clear phase gratings of low efficiency ($\xi \approx 1\%$) were produced by this technique. Surface relief imaging was confirmed by index-matching half of the grating with "Crystic" resin, which largely eliminated the grating effect. Gratings were always of low efficiency, inconsistent, and too soft to be used as masters for a metallic mould. No hologram of a three dimensional object was ever successfully recorded by enzyme etching.

It has been shown that any process which degrades the gelatin of a photographic emulsion can never successfully record a high frequency relief image because the integrity of the image lines is automatically destroyed. It is the volumetric degrading of the gelatin which prevents the creation of etched relief images, rather than an unsuitable surface removal action of the enzyme on the gelatin substrate.

Further research into the production of relief image master holograms has been pursued on more conventional photochemical lines, with an accent on non-interaction between processing chemicals and the gelatin substrate.
5.4 Photochemical Relief Processing

5.4a. Introduction

If chemical interaction with the emulsion is to be avoided in relief processing, then tanning developers cannot be considered. Tanning occurs in a swollen, wet, state of the emulsion. Induced stresses in the hardened gelatin, as the emulsion contracts during drying, could cause bond breakages in the gelatin, which would degrade the image line integrity.

The relief image must, therefore, be created by the volumetric occupation in the emulsion of the modulating silver or silver halide grains. The processing procedure finally adopted was; develop, fix and rehalogenate with a non-damaging bleach.

5.4b. Volumetric Changes in the Emulsion

An 8E56 emulsion contains 5g/m² silver bromide. Thus, 0.85μm of the 7μm emulsion thickness is composed of silver bromide grains. Since expansion in the plane of the emulsion is not possible, the emulsion thickness is related to the volume of grains in the emulsion.

Optical density can be shown (5) to be proportional to the volume of grains at a particular point in the emulsion. So if thickness modulation ΔT, is considered to be based upon a gelatin layer of constant thickness, 6.15μm;

\[
\frac{D}{D_\infty} = \frac{\Delta T}{\Delta T_{\text{max}}}
\]
where: \( D \) is the pre-rehalogenation density.
\[ \Delta T \] is the post-rehalogenation thickness due to grains.

For most developers, Agfa quote a saturation density, \( D_{\infty} \), of 4.5 for SE56 emulsions. This density should give a maximum thickness, \( \Delta T_{\text{max}} \), of 0.85\( \mu \)m. Thus:

\[ D = 5.3 \Delta T \]

If maximum diffraction efficiency occurs at \( \Delta T = 0.5\mu \)m for a sinusoidally modulated relief grating, and average pre-bleach density is half the peak density, then:

\[ D = \frac{5.3 \Delta T_{\text{peak}}}{2} = 1.33 \text{ for maximum efficiency.} \]

This value for density ignores fog density and solvation/redeposition effects during development (see chapter 3).

5.4c. Processing Details

(i) Fixing:

Fixing in Agfa G334 rapid fixer for 30 seconds was found to introduce no observable loss of line integrity. No hardener should be included in the fixer solution.
(ii) Rehalogenation Bleach:

The bleach, detailed below, was non-damaging to the developed silver relief image, and is known to have low solvent action (see chapter 4, page 32).

- 1g p-Benzquinone
- 0.5g Quinhydrone
- 1g Benzotriazol
- 20g Potassium Bromide
- 10g Boric Acid
- 1 litre distilled water

(iii) Development:

Minimal reaction of a developer with gelatin should occur at the isoelectric point of gelatin, pH5. Organic developing agents act in alkaline solution usually, and so a pH5 organic developer was impractical. A neutral, pH7, developer was accepted as a compromise.

After many developer tests (see section 3.1) a 4-aminophenol developer at pH7 has been shown to give best relief image results, with very little loss of line integrity at densities below D=2. 4-aminophenol is a low fog developer and develops all the emulsion thickness. No significant interaction between developer oxidation product and gelatin has been observed; interaction would be indicated by very small grain size and retention of the green/blue oxidation product in the emulsion after bleaching.
Additional protection of the gelatin was incorporated by including Benzotriozol into the developer, which forms an adsorbed layer between grain and gelatin. The final developer formula was:

\[
\begin{align*}
5g &\quad 4 - \text{aminophenol} \\
300mg &\quad \text{Benzotriozol} \\
1 \text{ litre} &\quad \text{Distilled water.}
\end{align*}
\]

A surprising alternative to this developer at the higher spatial frequencies and more "random" line distribution of the Benton "Rainbow" Images was found to be Tetenal's Multitoner I. The strong retention of the developer oxidation product round the grain was not accompanied by interaction with the gelatin, and the oxidation product seemed to offer protection to the gelatin without any interaction. Trials were viewed in reflection mode by coating the samples with a vapour deposited aluminium film.

5.4d. Results

Scan electronmicrographs of relief gratings with line frequencies of 900 L/mm. and 2800 L/mm. are shown in plates 5.1 and 5.2. These gratings were developed in the neutral 4 - aminophenol developer, detailed above.

The optimum pre-bleach density was found by Mr. Cullen to be very precisely fixed at \( D=1.3 \) at 633nm for SE56 emulsions developed in 4 - aminophenol. The limit of line frequency resolution under the above conditions was 3000 L/mm., but further optimization of processing may lead to an improvement of this figure.
Plate 5.1
Electronmicrograph of relief grating of frequency 900 L/mm.

Plate 5.2
Electronmicrograph of relief grating of frequency 2800 L/mm.
5.5 Conclusions

High quality relief-image mould master-gratings were made with a line frequency of up to 3000 lines/mm. by standard photographic processing techniques.

Enzymes appear to have their greatest worth in the study of developed silver grains under an electron microscope. The action of enzymes does not comply with the need for maintenance of gelatin integrity for high quality relief imaging.
6.1 Introduction

Before the advent of 300 Å halide grains and very mild processing reagents, it was thought that photographically recorded bleached-silver phase holograms would automatically incorporate in-plate scatter to a subjectively unacceptable level for display holography. A recording method was sought which would allow the replacement of a silver grain by a localized aggregate of organic material in a photographic emulsion. In this way it was hoped that a closer approximation to a non-scattering, "continuum" recording medium would be achieved.

Photographic colour processing provides a method for replacing silver by dye aggregates. Molecular diffusion in emulsion had limited colour processing resolutions to about 500 lines per m.m. (75, 77). Agfa-Gevaert had abandoned attempts to produce blue coloured photo-masks for micro-electronic circuit printing because of insufficient recording resolution, even upon 8E emulsions with a "black and white" processing resolution of 3000 lines per m.m. A programme of work was undertaken to improve colour processing resolution, for application to holography, as the first stage in the evolution of a generalized, colourless-organic replacement technique.

Colour toning of 8E emulsions was the only convenient way in which the viability of the technique could be tested. In colour toning, the oxidation product of a photographic developer is reacted with a colour coupler, at the site of a developed grain, to form a dye which is localized in the emulsion by its lack of mobility, due to its large molecular size. All silver compounds are then removed from the emulsion by bleaching and fixing (69, 74).

6.2 Preliminary Work

The origin of the idea for dye-replacement techniques in holography came in the work on organically accelerated bleaches (see page 161), where coloured images in phenosafranine and methyl blue were obtained in bleaches such as (65):

| 50 g  | Ferric Nitrate |
| 1 g   | Phenosafranine |
| 1000 ml | Distilled Water |

The coloured images could be fixed or redeveloped. This showed that they were composed of silver chloride, with dye molecules strongly adsorbed to the chlorided grains.
The chloride ions are provided by the dye anions. Phenosafranine, for example, has the structure:

![Chemical structure of Phenosafranine]

Although low in diffraction efficiency, these dye/grain images were of high image quality, with a low granularity appearance to the images. No suitable bleach dye-replacement processing techniques could be found in photographic literature to warrant further investigation of dye-bleaching techniques.

6.3 Colour Toning

Indirect toning (72) of a "black and white" developed holographic image was avoided to eliminate one development stage and one rehalogenation stage of processing. The direct colour development processing adopted was:

- Colour development
- Solvent bleaching
- Fixation of undeveloped silver bromide
- Image stabilization and emulsion hardening
- Image presentation

Since image localization and resolution is controlled almost exclusively by the colour development processing stage, the post-development processing was first optimized, so that developers and colour couplers could be compared with minimal risk of the image being degraded at a later processing stage. The aim of the project was then to maximize the localization of the dye image round each developed grain centre on 8E56 photographic emulsions. Figure 6.1 shows the difference between suitable and unsuitable processing with the direct colour development sequence adopted.
Figure 6.1

6.1a
Correct Colour Processing

6.1b
Unsuitable Colour Processing
The processing of holographic diffraction gratings and virtual image transmission images was used as the basic test for processing applicability to holography; this necessitates a resolution capability of only 2000 L/m.m. in the recording medium.

6.4 Post-development Processing

a. Bleaching the Developed Silver

The gentle rehalogenation bleaches of conventional bleached-silver holography were found to not be powerful enough to penetrate the dye envelope of a colour-developed silver grain (see chapter 4). Rehalogenation bleaches were, thus, avoided because of the risk of damage to both dyes and gelatin in the emulsion if more powerful agents were used.

An unmodified acidified dichromate solvent bleach was found to have a suitable power and lack of damage in the form:

\[ \text{2 g Potassium Dichromate} \\
\text{4 ml Conc. Sulphuric Acid} \\
\text{1 litre Distilled Water} \]

Gelatin damage was observed by solvating to dye from a processed emulsion with methanol.

The use of combined bleaching and fixing stages was avoided for the sake of simplicity, since the action of these solutions in holography was unknown.

The bleach has a function besides that of silver solvation; it inactivates any developer, or developer oxidation product, remaining in the emulsion. This secondary function facilitates the coupler-to-dye reaction.

b. Fixation

Non-hardening fixers, such as Agfa G334, were found to introduce no observable damage to the emulsion in a fixing time of 2 minutes.

c. Image-Stabilization and Emulsion Hardening

Both image-stabilization and emulsion hardening can be effected by the same processing solution of alkaline formalin. Image-stabilization reduces the tendency of the dye to revert back to an uncoloured form (74 in the presence of any colour coupler left in the emulsion.
Hardening the gelatin of the emulsion reduces the mobility of dye in the emulsion. This was found to greatly increase the storage lifetime of a dye image in the wet state from about 2 days to many months.

The processing solutions of the Tetenal Multitoner I toning kit were found to be suitable in all trials.

d. Image Presentation

Successful dye holographic images were found to degrade reversibly, when dried, to a very noisy, low efficiency state (see section 6.7b). Best image quality was seen in plates viewed in a water-wet state. Viewing and storage are best done by covering the wet emulsion with a glass plate, and sealing the perimeter of the two plates with a resin adhesive to prevent evaporation of the water (50).

Organic solvents cannot be used, since they solvate the dyes from the emulsion.

6.5 Colour Development

Colour development is effected by the reaction of colour developer oxidation product and a colour coupler, which is introduced into the developer solution immediately before use. The developer and coupler are freely mobile in the emulsion, but their dye reaction product must be totally immobile in the gelatin matrix. A simple example of this reaction is the formation of a yellow azomethine dye from an open chain methylene group coupler and diethyl p-phenylenediamine colour developer:

\[
\text{X} \rightarrow \text{CH} + \text{NH}_2 \rightarrow \text{N(C}_2\text{H}_5)_2 + 4\text{AgBr} \rightarrow \\
\text{Y}
\]

\[
\text{C} \equiv \text{N} \rightarrow \text{N(C}_2\text{H}_5)_2 + 4\text{Ag} + 4\text{H}^+ + 4\text{Br}^-
\]
The dye must be formed and localized as close to the developed silver grain as possible for holography. The localization of the dye reaction is controlled mainly by the mobility of the developer oxidation product before it reacts with the colour coupler. Good oxidation product retention is often indicated by low granularity of a plate developed without the presence of colour coupler; retention of the oxidation product can retard the complete development of a grain by forming a barrier layer round the grain to prevent further developer penetration. A very low oxidation product mobility is needed for dye localization within the 400 Å grain spacing limit of SEHD emulsions (see section 2.1d).

A high mobility of the colour coupler would be a secondary localization control for the dye reaction, by increasing the reaction probability with the outward diffusing oxidation product. An alternative to this would be a colour coupler which adsorbs to the silver halide grains during development, and is thereby well localized ready for a dye forming reaction.

Since the properties of colour couplers would be difficult to quantify or compare with the limited equipment available, it was decided to determine a good colour developer by granularity considerations and then to compare colour couplers on a trial-and-error basis with this good developer as a constant reaction component. It was hoped that rules for good development of a holographic dye image could then be formulated for use in further work.

6.6 Results

a. Colour Developers

P-phenylenediamine and its derivatives were rejected on the grounds of poor monochrome development results, which were of low efficiency and noisy.

Agfa recommended the use of Kodak CD-3 and CD-4 developing agents, but the recommended developer formulations were impractically complicated, with too many variable components for easy study purposes.

The Tetenal Multitoner kits were directly applicable. Multitoner II. was caustic, with poor monochrome grains and images; it appeared to be a simple p-phenylenediamine derivative from its violet colour and image characteristics.

Multitoner I colour developer was an immediate monochrome success. It has the lowest granularity of all the commercial developers tested, and bleached-silver images were very bright and clear.
Rehalogenation bleaches often had great difficulty in penetrating the oxidation product barrier around Multitoner I developer grains. The colourless constituents of Multitoner I developer have not been determined, but the developer was used exactly as directed in the literature.

Multitoner I has a long induction time, which ensures that colour coupler has a good chance to diffuse onto the reaction sites. The speed of emulsions developed in Multitoner I is about 5 times less than for concentrated Neofin Blue. Exposures of 200 erg/cm² were found adequate for 8E56 plates at 511 nm. The only successful dye-holograms have been made with Multitoner I to date, and it was chosen as the standard developer for all colour coupler trials.

b. Colour Couplers

All available Tetenal commercial colour couplers were tried in diffraction grating trials, and only the cyan coupler of the Multitoner I kit produced a positive result under any circumstances; this was a very low efficiency grating at \( \theta = 15^\circ \).

Agfa-Gevaert provided samples of two Kodacolour couplers which were known to give a well localized dye layer round developed grains of 2 mm diameter; probably due to a strong adsorption tendency of the coupler to the silver halide grains. Trials were quickly successful in producing diffraction efficiencies of up to 20%. These two couplers are known as CCl6 and CM38, and their typical development reactions are shown in figure 6.2.

These colour couplers were, eventually, found to be best prepared for solution in the developer by dissolving their powders in a mixture of methanol and aqueous sodium hydroxide solution;

\[
\begin{align*}
5 \text{ ml} & \quad \text{coulper} \\
5 \text{ ml} & \quad \text{methanol} \\
3 & \quad \text{distilled water} \\
3 & \quad \text{pellets of sodium hydroxide}
\end{align*}
\]

for 200 ml Multitoner I developer.

Aeriel oxidation quickly degrades the coupler/developer mixture, and the developer must, therefore, be used immediately after mixing.

The concentration of CCl6 or CM38 colour coupler in the developer solution must be investigated at a later time, when more practical experience of the processing chemistry has been obtained. A concentration of 2 g per 200 ml of developer gave the most efficient, noise-free images, but some of the coupler would often precipitate out of solution during mixing, even under apparently identical conditions of temperature, concentration and pH. Lower concentrations gave a lower dye density in the plate, and a lower final diffraction efficiency. Higher concentrations than 2 g per 200 ml were unpredictable and often produced very noisy images or precipitated out of the developer solution.
Figure 6.2
Typical Development Reactions of CM38 and CC16

CM38:

\[ \text{NH}_2 - \text{NH} - \text{C} - \text{CH}_2 + \text{NH}_2 - \text{N} \left( \text{C}_2 \text{H}_5 \right)_2 + 4 \text{AgBr} \]

\[ \Rightarrow \text{NH}_2 - \text{NH} - \text{C} - \text{C} = \text{N} - \text{N} \left( \text{C}_2 \text{H}_5 \right)_2 + 4 \text{Ag} + 4 \text{H}^+ + 4 \text{Br}^- \]

CC16:

\[ \text{C} - \text{NH} - \text{CH}_2 - \text{CH}_2 - \text{N} - \text{C} - \text{CH}_3 + \text{NH}_2 - \text{N} \left( \text{C}_2 \text{H}_5 \right)_2 + 4 \text{AgBr} \]

\[ \Rightarrow \text{C} - \text{NH} - \text{CH}_2 - \text{CH}_2 - \text{N} - \text{C} - \text{CH}_3 + 4 \text{Ag} + 4 \text{H}^+ + 4 \text{Br}^- \]
A maximum diffraction efficiency of 30% was achieved with the CM38 coupler, viewed as a wet plate diffraction grating with a He-Ne laser.

The next advance came when a yellow coupler CY54 was tried. Identical conditions were employed as with CM38. A diffraction efficiency of 65% was achieved with CY54 as a wet plate diffraction grating, viewed in yellow light filtered from a tungsten-halogen lamp by a mercury-yellow filter. At the 633nm He-Ne wavelength, the diffraction efficiency was reduced to 50% by the greater dye absorption of light at this wavelength. Gratings with all values of $\theta$ have been successfully produced.

CC16, CM38 and CY54 were all seen to give good virtual image transmission holograms. CC16 and CM38 gave holograms with very low noise, but not so bright as images in CY54, which were subjectively noisier. The wet-plate viewing of the larger dye holograms, on 10" x 8" plates, had the problem of limited field of view, which was manifested as the image only appearing as a narrow band across the plate, due to the swollen state of the emulsion relative to it's exposure condition.

6.7 Discussion of the Results

a. Nature of the Dye Image

A dye image can be formed in an amorphous state, or be deposited in a microcrystalline form (29). Both these forms of dye image were seen with CC16, CM38 and CY54 couplers. The amorphous state of the dye was very scattery in it's holographic images and was avoided at all costs.

The microcrystalline form of the dyes appears with a low scatter density in the emulsion. In this case the dye is formed in parallel plane aggregates, adsorbed edge-on to the silver/silver halide grains during development. Adsorption of this kind is usually strongly polarized, and is started by the adsorption of the positively charged coupler ions to the surface of the silver bromide grains being developed. The dye microcrystals are then built-up in a strongly polarized form, with the direction of their polar axes being dictated by the orientation of the initially adsorbed, charged dye layer. At low coupler concentrations, however, van der Waals forces usually predominate, and result in a more random, amorphous structure of the deposited dye.

The unpredictable nature of the scatter in dye images, under identical processing conditions, is apparently due to the variable extent of amorphous dye deposition at the start of development.
Overexposure gives a short development induction time, which does not allow sufficient coupler to diffuse to the grain sites to start a microcrystalline deposition of dye. Gelatin Hardness, which affects the relative diffusion rates of dye and coupler in the emulsion, was another very variable parameter which gave unpredictable dye-image results for the same reason.

b. The Optical Properties of Dyes (68)

The colour selective properties of dyes are a result of a resonance hybrid condition of two dye structures of similar stability, but different charge distribution. The oscillation between the two charge distributions corresponds to an energy difference between the two dye structures. Quantum Theory has been applied to the relation between colour and chemical structure in dyes (68), but insufficient data was available on the successful colour couplers to make calculations useful. A simple physical model was used to understand the results.

Figure 6.3 shows a possible set of resonance states for the dyes formed with the Agfa colour couplers in a simplified form. These resonance conditions can be further simplified to:

\[ X \ldots Y = X^+ \ldots Y^- \]

or

\[ X^+ \ldots Y = X \ldots Y^+ \]

These resonances have an electronic polarizability associated with them, but since these dyes are highly unsymetric, the energy difference between the two energy states is large and the interaction takes place via a number of intermediate charge distributions. The transition through the intermediate charge distributions is made easier if a polar solvent fills the space between the unfavourable separation of charges. A larger solvent dielectric constant will, thus, increase the electronic polarizability of the dye. An example of the effect of solvent dielectric constant upon the extinction coefficient of a basic dye is shown in Figure 6.4, which is adapted from a recent Ph.D Thesis (70).

Van Renesse and Bouts (5) have shown that phase modulation is determined by the electronic polarizability of the modulating medium. The greater polarizability of "wet" dye molecules will, thus, give a higher diffraction efficiency because of the greater phase modulation than in the "dry" state of the dye. The lower diffraction efficiencies of CC16 and CM38 dyes, as compared with CY58, indicates that a solvent with a higher dielectric constant would bring the efficiencies of all the dye-gratings to a higher level; methanol for example. Unfortunately, all organic solvents dissolve the dyes out of the emulsion. The use of aqueous solutions of inorganic salts had no effect upon diffraction efficiency.
Figure 6.3 Possible Dye Resonance Systems

CC16

CY54

CM38
Figure 6.4
Absorbivity of Safranine o-Tetrachloraurate in Various Solvents (Ref. 70)

Molar Absorptivity ($\times 10^3$)

Dielectric constant of the solvent.
The observation of dye holographic diffraction gratings has effectively demonstrated the validity of the van Renesse and Bouts theory, without recourse to the highly scattering inorganic silver salt images of $\text{Ag}_4\text{Fe(CN)}_6$ and $\text{Ag Hg Cl}_2$.

6.8 Conclusion

High quality and high efficiency coloured dye holographic images have been made by improving the resolution capabilities of conventional photographic colour toning processing. A resolution of up to 3000 lines per m.m. has been achieved, which could be applied to other micro-imaging uses, such as photo-masks for microelectronic circuits in a single blue dye.

The viability of the organic replacement of silver salts in a photographic emulsion has been established for use in holography. Future work could be applied to removing the colour dependence of the images, and decreasing the probability of scatter in the recording plane.
By critically investigating all aspects of the processing chemistry of photographically recorded holograms it has been possible to improve their visual quality to a very great extent. By further application of the methods employed in this thesis, it should be possible to make further gains in image quality.
Appendix

Organically Accelerated Bleaches (65)

It has been noted, in desensitisation trials, that organic dyes have the effect of accelerating the action of cupric and ferric bleaches. This effect has been explained by Willems (66), who considered that electrostatic double layer of dye molecules around the silver atoms, which permits greater penetration of oxidizing agent ions. Figure I shows the acceleration of a ferric bleach by methyl blue.

The first reaction to this observation was that it might be possible to replace the silver image by an organic dye. This conclusion has been found to be erroneous, but was arrived at because regions of high silver density were observed to be highly coloured after the conversion of silver to silver halide. Colouring of images in this way was a very early method of producing quasi-colour photographs.

Methyl blue thionine, and phenosafranine accelerated bleaches produced observably finer crystal structure than undyed bleaches, indicating that the adsorbed dye on the silver ions reduces the mobility of the silver ions in the gelatin. This would decrease the diffusion path length before a bromide ion combined with the silver to precipitate silver bromide.
Figure I

- Ferric alone
- 50mg/l Methyl Blue
- 100mg/l Methyl Blue
- 150mg/l Methyl Blue

Time taken to bleach a density D = 2.
An alternative to this theory is that the dyes adsorb to the silver grain and automatically introduce a very localized Cl\textsuperscript{-} ion concentration which will result in the precipitation of AgCl, rather than AgBr from the bromide ions in the rehalogenation bleach. The answer to this dilemma is probably that both precipitation reactions take place in proportion to the ratio of Br\textsuperscript{-} to Cl\textsuperscript{-} ionic concentrations at the silver surface, and thus in indirect proportion to bleach solution ionic concentrations. The observation that colour dye density is very high at zero, or very low (1 g.L\textsuperscript{-1}), bromide concentration but decreases with increased bromide concentration in the bleach to almost zero final colour density at 30 g.L\textsuperscript{-1} potassium bromide supports the proportional precipitation hypothesis.

Attempts have been made to replace the chloride anions of methyl blue and phenosafranine, shown in Figure II, by bromide anions, such that pure bromide precipitation would be ensured. Amberlite resin IRA-93 was used for this purpose. Images obtained with this bromided dye form were not observably different from chlorided dye images, and so further work was abandoned.

The acceleration of persulphate by dyes was an interesting case. Attempts at bleaching with persulphate had either been very slow in solvent bleaching mode, or very noisy in rehalogenation mode. With Bindschedler's Green, however, persulphate produced some very clear, low noise images in solvent mode which were not unacceptably slow.
Figure II

Methyl Blue

Phenosafranine

Thionine

Bindschedlers Green
Bindschedler's Green also accelerated rehalogenation bleaching with persulphate. During trials with Bindschedler's Green it was noted that only low bromide concentrations would give low noise rehalogenated images with persulphate bleaches. An example of a successful persulphate rehalogenation bleach would be:

- \(5g\) Potassium Persulphate
- \(300mg\) Bindschedler's Green
- \(4g\) Potassium Bromide
- \(4ml\) Conc. Sulphuric Acid
- 1 litre Distilled Water

Willems (66) suggests that the quinone component of certain organics, in the adsorbed state, has a redox potential greater than that of the \(Ag/Ag^+\) system. The dye thereby starts the oxidation reaction in the adsorbed state and is itself reduced. The adsorbed dye reaction product can then be regenerated by persulphate to reform an oxidizing agent dye, which will continue the reaction.

\[
e.g. \quad Q^{\text{++}} + Ag \rightarrow Ag^{\text{+}} + S^{-}
\]

then \[
2S^{\text{+}} + S_2O_8^{-} \rightarrow 2Q^{\text{++}} + 2SO_4^{-}
\]

This very gentle, localized bleach reaction warrants further investigation for optimization to the rehalogenation mode of bleaching. A useful direction for further work may be an investigation into the silver-dye bleach reaction (67), which is based upon Redox Intermediate Catalysts as oxidizing agents. These agents depend upon the high localization of the organic reagents to the silver (i.e., adsorption).
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