New silver halide materials for the mass production of holograms

Glenn P Wood

Ilford Limited, Mobberley, Knutsford, Cheshire WA16 7HA, England.

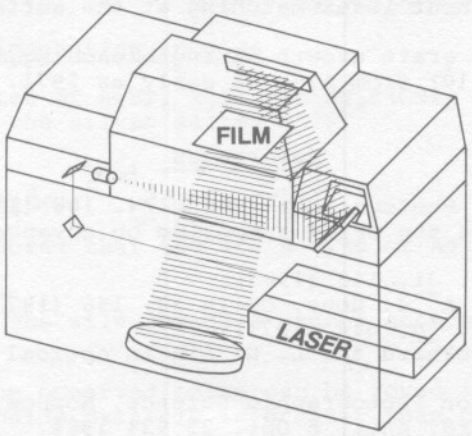
Abstract

A low scatter silver halide based film has been developed for the mass production of copy holograms on the AHS1 Holocopier system. Machine-compatible replenishable chemistry was devised to be used in conjunction with the film. The primary emulsion has now been sensitised to produce both blue/green and red sensitive film. The holography programme at Ilford has included the development of special red shifting chemistry and light stabilisation techniques.

Introduction

The traditional methods of exposing and processing original holograms offer little incentive to the manufacturer of silver halide based media to improve his products and fully support the business. The techniques of exposure and subsequent processing are time consuming and labour intensive and therefore result in holograms that are small in number and high in price thus appealing to a limited market. The decision by Applied Holographics PLC (of Braxted in England) to develop an exposure and processing system which would automate the production of silver based holograms offered an attractive and challenging opportunity to Ilford Limited to look afresh at the needs of holographic consumables for mass production techniques. A detailed description of the overall process and its subsequent embodiment in the AHS1 Holocopier are given in a separate paper at this symposium. Suffice it to state here that the system is based on the contact copying of a master hologram using the light of a pulse ruby laser (694nm) see Figure 1.

Figure 1
Schematic diagram of AHS1 holocopier



The master hologram remains stationary but a transport mechanism advances the copy film frame by frame and synchronises it with successive 50ns pulses from the laser. The advance mechanism would therefore transport the film from a stock roll to an uptake spool which when full, is removed from the machine and loaded into a roller transport processor for development and bleaching. The task facing Ilford Limited was to develop a suitable emulsion for this process, to coat it onto the required base and to provide the resulting film on spools suitable for the exposure and processing mechanisms. The format chosen was 240mm wide lengths of film 400ft long. Appropriate processing chemicals also had to be devised which would both be compatible with the automatic processor and lead to bright holograms principally of the Lippmann-Bragg reflection type.

Emulsion specification

The three principal requirements for the emulsion were that it should have minimal scatter, maximum sensitivity at 694nm and reciprocity characteristics optimised for pulse exposures of very short duration. Scatter in a holographic emulsion is due to the

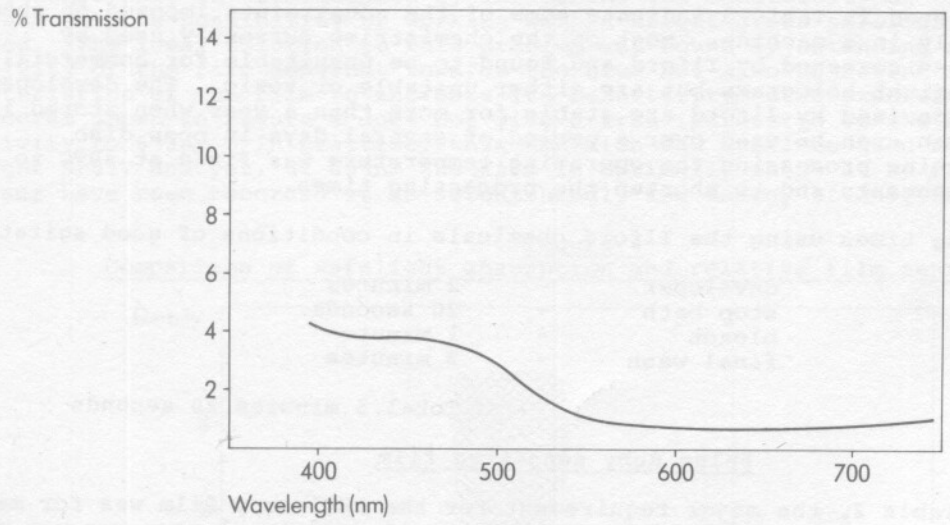
presence of particles larger than the wavelength of light. If all the particles present in a coated layer are significantly smaller than the wavelength of light, (approximately 0.5μm) then the layer will appear optically transparent. The presence of only a few hundred particles per square centimetre which exceed 0.5μm in diameter, give the layer an opalescent haziness. Such scattering layers are not good for holography since the light which is being internally scattered is reducing the contrast of the interference fringes being recorded. It is undesireable to reduce this scatter by the additional of antiscatter dyes since this increases the optical density of the layer and reduces the object to reference beam ratio in contact copying. By use of its ultrafine grain (UFG) emulsion technology, Ilford has been able to create an emulsion in which the silver halide crystals are remarkably uniform in size and free from scattering centres. This emulsion is very stable and is able to survive long periods of storage before, during and after the coating process without suffering Ostwald ripening effects. The scatter is sufficiently low to enable holographic optical elements to be made from the film.

The principal specifications for this emulsion are given in Table 1 and the scatter characteristics, measured by recording the ratio of specularly transmitted to forward scattered light, are shown in Figure 2.

Table 1
Emulsion characteristics

Very low scatter	Good stability
Better fringe integrity	Reproducible manufacture
Brighter highlights	Long shelf life
Low noise	Good for automated systems
No anti-scatter dyes	
High optical transmission	
Record in blue region	

Figure 2
Scatter characteristics of holographic emulsion



Holofilm 250 PAR description

For use in the AHSl Holocopier the coated film had to be maximally sensitised to 694nm (see below for data) and had to retain its latent image for a minimum of 24 hours to enable a roll of film to be exposed one day and processed the next without noticeable deterioration in image quality. Since the processing sequence employed makes use of a solvent bleach step following development, the effect of latent image regression is to cause less wavelength shifting on reconstruction. The ideal reflection copy hologram should be yellow-gold in colour corresponding to maximum reflection at 580nm. This is achieved by removal of the developed silver in the bleach bath. In order to achieve a layer thickness reduction corresponding to a replay wavelength shift of 114nm (694-580nm) the layer thickness should reduce, during processing, by the ratio 580:694. The emulsion layer is 7μm thick.

To ensure the maximum area of film on a roll of convenient size and weight, the emulsion is coated on polyester substrate only 63μm thick. At this thickness, birefringence in the polyester is minimised.

The stock rolls are on standard aerial spools 240mm wide (9½ inches) and the film length is 400 feet giving approximately 480 exposures per roll on the Holocopier.

The principal specification for the film are given in Table 2.

Table 2
Product description of Holofilm 250 PAR

Sensitivity at 694nm	-	20μJ cm^{-2} (for density 1)
Latent image stability	-	24 hours minimum
Substrate	-	63μm polyester
Film length	-	400 feet
Film width	-	240mm
Optical transmission at 694nm	-	70%
Scatter	-	<1%

Specification for processing chemistry

The major requirements of the processing chemicals used in the AHS1 Holocopier are listed in Table 3.

Table 3

Developer and bleach in form of liquid concentrates
Shelf-life of concentrates, 1 year minimum
Machine compatible (non-corrosive and replenishable)
Solvent bleach
Rapid processing
Safe-handling
Bright holograms

The parameters listed in Table 3 indicate some of the constraints imposed on chemistry when used commercially in a machine. Most of the chemistries currently used by holographers have been screened by Ilford and found to be unsuitable for commercial use. They often produce bright holograms but are either unstable or toxic. The developer and bleach concentrates devised by Ilford are stable for more than a year when stored in filled bottles and can even be used over a period of several days in open dish processing. For machine processing the operating temperature was fixed at 30°C to allow for use in hot environments and to shorten the processing times.

Typical processing times using the Ilford chemicals in conditions of good agitation are:

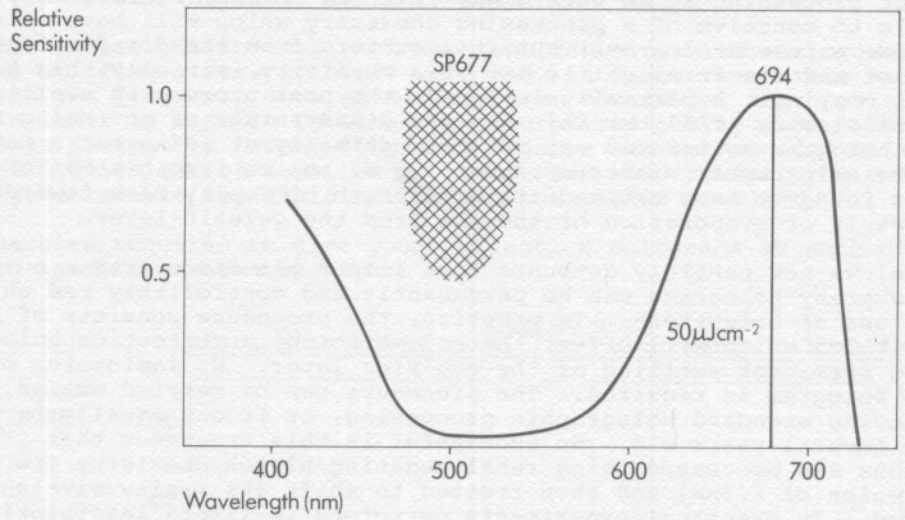
developer	-	2 minutes
stop bath	-	20 seconds
bleach	-	1 minute
final wash	-	2 minutes
		Total 5 minutes 20 seconds

Pulse Ruby sensitive film

As indicated in Table 2, the major requirement for the AHS1 copy film was for maximum sensitivity at 694nm. Since compatibility with other red emitting lasers was not part of the specification, the Holofilm 250 PAR was sensitised only to a narrow bandwidth in the vicinity of 694nm. This had the advantage of leaving a wide window of insensitivity between the blue and red spectral regions thus enabling a bright green safelight to be used in conjunction with this film.

The spectrum shown in Figure 3, demonstrates the sensitivity of the film obtained by a flash white light exposure (10^{-4} seconds) followed by standard development. Superimposed upon the spectrogram is the transmission curve for the Ilford bright green safelight filter SP677. It can readily be seen that the film is perfectly safe to use with this filter and, in practice, the safelight level that can be used is bright and comfortable.

Figure 3
Spectrogram of ruby sensitive film

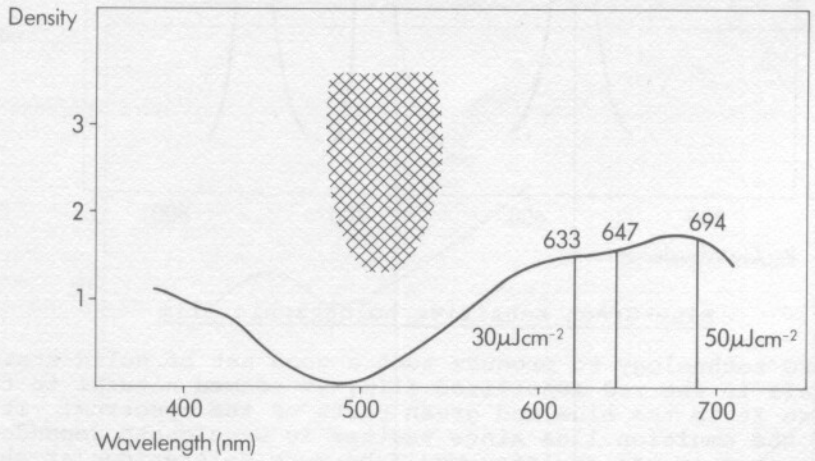


Relative spectral sensitivity of SP673 to white light flash exposure (10^{-4}s)

General Red sensitive mastering film SP673

As the AHS1 project developed it became clear that the majority of masters used in the system would be made using HeNe lasers. Indeed it was desireable that this should be the case since it would enable all those creative holographers who already possessed and worked with HeNe lasers to originate artwork and exposures which could be replicated on the AHS1 system. The need for a mastering film sensitive to HeNe (and possibly Kr laser lines), could only be accommodated by increasing the sensitivity of the film down towards 600nm and yet the possibility of working with a bright green safelight should be retained. The ideal solution to this problem was found by extending the spectral sensitivity of the film somewhat towards the blue but also adjusting the reciprocity characteristics of the film to increase its sensitivity to CW exposures. The new wedge spectrogram shown in Figure 4 does not give a true indication of the new emulsion's sensitivity to 633nm. In practice, this emulsion can still be used with the bright green safelight SP677 and yet, at 633nm the film is optimally rated at 30 $\mu J\ cm^{-2}$ and holograms have been recorded at an astonishingly low energy of only 5$\mu J\ cm^{-2}$.

Figure 4
Comparison of safelight absorption and relative film sensitivity



Red shifting procedure

At this point we should recall that for a master hologram to copy successfully in the AHS1 it should have high reflectivity at 694nm since that is the wavelength of the copying light. Holograms which have little or no reflectivity at 694nm are effectively invisible

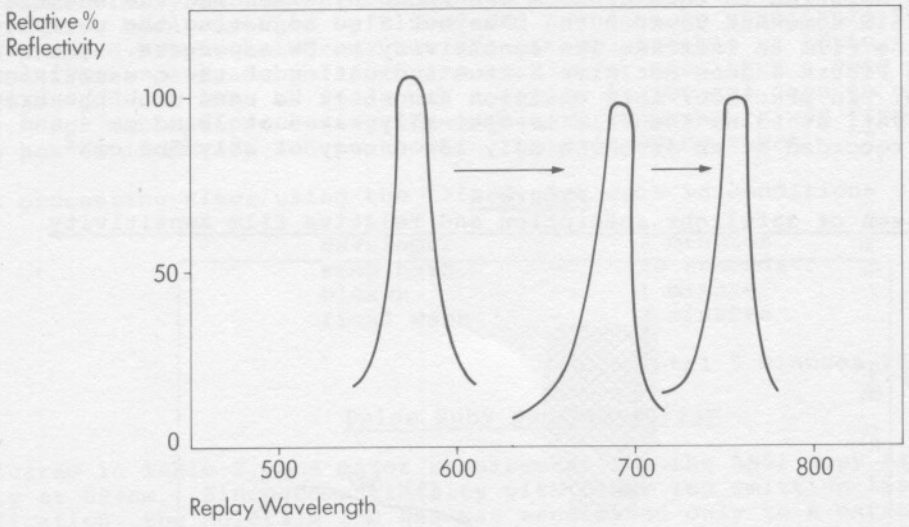
to the copying device. An immediate problem facing the holographer wishing to create a master hologram, can now be seen. The problem consists in exposing the hologram with a HeNe laser (633nm) but processing it in such a way that its maximum reflectivity is at 694nm. It is possible to conceive of a processing chemistry which will have this red shifting effect on HeNe exposed holograms, but this suffers from the disadvantage that if the holographer has not had the foresight to use this chemistry initially, his hologram is not suitable for AHS1 copying. A partial solution is the post processing swelling of the hologram using Triethanolamine (TEA) but this has the disadvantage of not being completely stable. One day the hologram so treated may reflect optimally at 694nm but a few weeks or months later (when the holographer wishes a repeat run of copies from his master to be made) the hologram is found to have shifted its wavelength of replay back towards the blue. This is the result of evaporation of the TEA from the gelatin layer.

For the first time, we now publicly announce that Ilford has discovered a novel, and proprietary system, whereby holograms can be permanently and controllably red shifted without significant loss of brightness. In practice, the procedure consists of bathing the hologram in a solution which will effect the red shifting in reflection holograms by producing uniform and permanent swelling of the emulsion layer. No lamination or encapsulation of the hologram is required. The procedure can be carried out as part of the final rinse following standard holographic processing, or it can equally be performed on holograms already several years old. So successful is this treatment that a hologram can be exposed at 633nm and processed using rehalogenating bleach chemistry (to give replay also in the region of 633nm) and then treated to shift its replay wavelength even as far as the infrared. In practical experiments performed in Ilford laboratories holograms have been shifted up to 850nm. They could probably be shifted even further but 850nm is the recording limit of our spectrophotometers!

The procedure works irrespective of the processing used originally or the recording wavelength and so we now possess beautiful gold and red holograms which were recorded with an Argon laser (514nm), processed in pyrogallol developer and appeared green before the red shifting treatment.

Figure 5 shows some typical reflection spectra of red shifted holograms originally exposed with a HeNe laser.

Figure 5
The effect of shift procedure on replay wavelength



Blue-Green sensitive holographic film

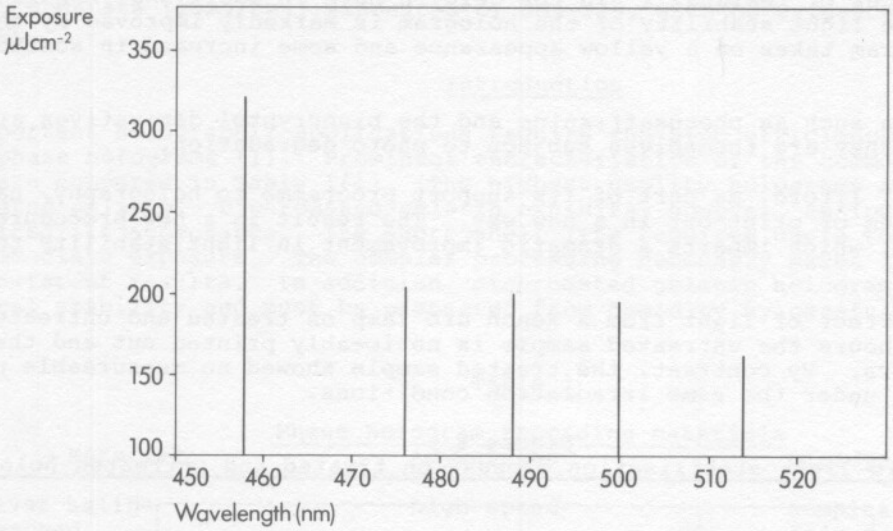
Having used the UFG technology to produce such a good set of solid-state photo detector devices as the crystals in the red sensitised film, it seemed natural to take the same emulsion and sensitise it to the blue and green parts of the spectrum. It is here that the real strength of the emulsion lies since scatter is wavelength dependent and any scattering centres present in the emulsion would be more deleterious at shorter wavelengths and indeed can be seen as a blue opalescence in inferior emulsions. The high optical clarity of the present emulsion should enable it to be formulated with a blue/green sensitiser without the need for an additional anti-scatter dye. This indeed turned out to be the case and a blue/green sensitised emulsion has been produced with a sensitivity so high, and a scatter so low that Denisyuk recordings have been made

employing the 457.9nm line of the Argon ion laser. Holographic optical elements with diffraction efficiencies of 97% in both reflection and transmission have been reported for this material with negligible scatter.*

Although at present there is no mass replication system analogous to the AHS1 and based on a green emitting laser, if there were one, it seems reasonable to suppose that it would be based on the frequency doubled Nd:YAG laser because of the high repetition rate of which this laser is capable (greater than 30 pulses per second). This repetition rate is so high that successive frames of moving objects can be recorded in a flicker-free holographic equivalent of a motion picture. For this reason, the sensitivity maximum of the blue-green sensitised emulsion lies in the region of 530nm.

The energies required to give good reflection holograms at each of the major lines of the Ar ion laser are shown in Figure 6

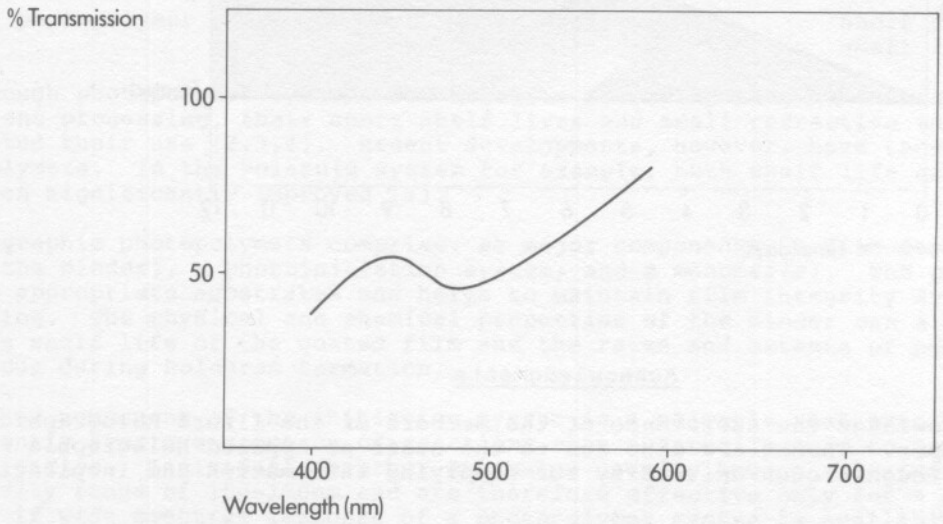
Figure 6
Ilford blue/green sensitive holographic film SP672



It will be noted that the sensitivity of the film is linear throughout the green region of the spectrum, decreasing only as the middle region of the blue is approached.

The optical transmission characteristics of the unexposed film are shown in Figure 7 where it can be seen that 50% of the light is transmitted at 514nm and 457.9nm.

Figure 7
Optical transmission characteristics of SP672



*N.J. Phillips, University of Loughborough, Private Communication

Light stability

Phase holograms, consisting of silver halide, are inherently susceptible to photo reduction (print-out). This is a photochemical phenomenon whereby the transparent grains of silver halide are progressively converted to darker grains of metallic silver by the action of light. The halides of silver are inherently sensitive to this reaction in the order,

$$AgI < Ag\,Br < Ag\,Cl$$

Thus holograms processed in such a way that the image is comprised primarily of silver bromide, can be rendered more light stable by an iodide treatment which converts the bromide either partially or totally to the iodide.

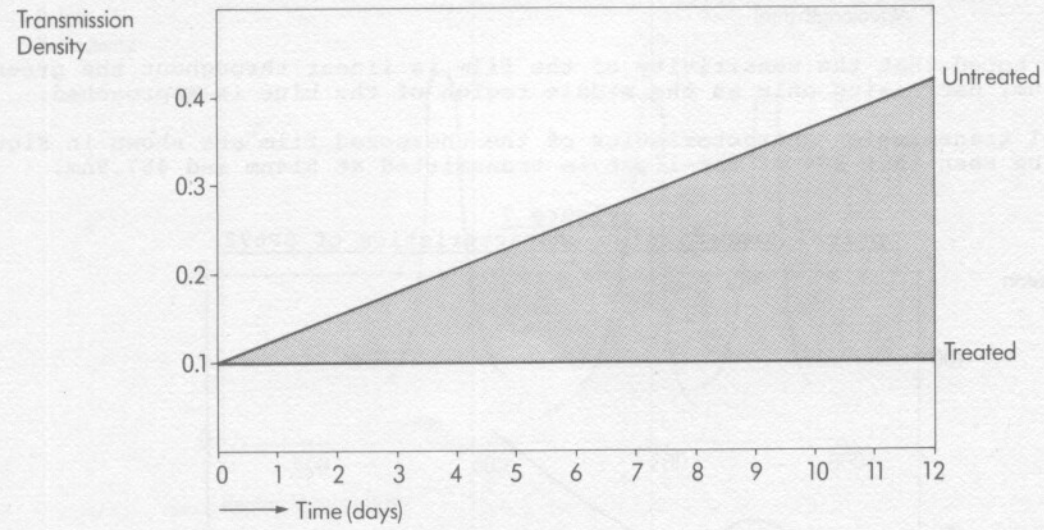
This can be achieved practically by washing the hologram in a solution of 2.5g/l of potassium iodide in water for two minutes. Thorough washing after this procedure should be avoided since traces of residual I^- in the gelatin have an additional beneficial effect. Although the light stability of the hologram is markedly improved by this technique, the hologram takes on a yellow appearance and some increase in scatter will be noticed.

Desensitising dyes such as phenosaffranine and the pinocryptol derivatives are of limited use because they are themselves subject to photo degradation.

For these reasons, Ilford, as part of its support programme to holography, has approached the problem of print-out in a new way. The result is a new procedure, using colourless compounds, which imparts a dramatic improvement in light stability to bleached holograms.

Figure 8 shows the effect of light from a Xenon arc lamp on treated and untreated holograms. After 8 hours the untreated sample is noticeably printed out and the hologram useless after 24 hours. By contrast, the treated sample showed no measureable print-out even after 300 hours under the same irradiation conditions.

Figure 8
Effect of Ilford light stabilisation process on treated and untreated holograms



Acknowledgments

I would like to acknowledge the assistance of the members of the Ilford holographic team in preparing this paper. Thanks are also due to the staff at Applied Holographis PLC and to N.J. Phillips at Loughborough University for supplying information and inspiration.