materials

Smart holograms

Jeff Blyth
jeff@biotech.cam.ac.uk

About the author

After graduating in 1973 in Applied Chemistry he worked in a company with dichromated gelatin, unrelated to holography. In '77, he was amazed to see a holographic pendant made using the very material he was researching. His life 'changed for ever'. He subsequently worked on photopolymer materials for Ilford, which became the subject for an MPhil at Wolverhampton Polytechnic. Since '91 he has been involved in 'blue sky' research at the Institute of Biotechnology in Cambridge, UK. Jeff is the recipient of the Royal Photographic Society's Saxby award for 2003 (http://www.holography.co.uk/events/saxbyaward/jeffblyth/jeff.htm).

It is always impressive to see how a green reflection hologram temporarily changes to red when you let breath-moisture condense on the gelatin surface. (This effect is due to the gelatin swelling and the inter-fringe distance in the gelatin film increasing so that it reflects red instead of green light.) Apart from the obvious use of this effect in measuring the relative humidity of gases or liquids [1] our team at the Institute of Biotechnology wanted to use this effect to make many other types of measurements.

It was at the end of August 1995 that I tried an experiment which was to cause a revolution in our Institute and beyond! For over three years I had been experimenting on making so called "Lippmann" silver halide emulsions using basically the traditional method of squirting, alternately, solutions of silver nitrate and potassium bromide into a hot solution of gelatin [2]. The precipitated grains of silver bromide (AgBr) are very much finer in Lippmann emulsions than in emulsions used for normal photography. To be able to record holographic fringes satisfactorily the photosensitive grains need to have diameters at least a factor of 10 smaller than the width of a hologram fringe (around 200 nm, i.e. half the laser wavelength divided by the refractive index of the gelatin layer.) Conventional fine-grained photographic emulsions have grain sizes around 1000 nm or more. The experiment which changed everything for us was to take a just a **precoated** and hardened gelatin layer and to try and produce those vitally small AgBr grains inside the layer just by using a silver ion diffusion process, while still achieving a sufficient degree of photosensitivity [3]. The moment of success came when I glimpsed a holographic image on a coated microscope slide of a polished penny.—One of those all-too-rare eureka moments!

So the success had come by sequentially diffusing into the layer, a solution of silver nitrate and following it up by diffusing in a solution of lithium bromide . (I chose lithium rather than the common potassium salt because I thought I might need the extra leeway of its very large solubility in both water and alcohol [3].)

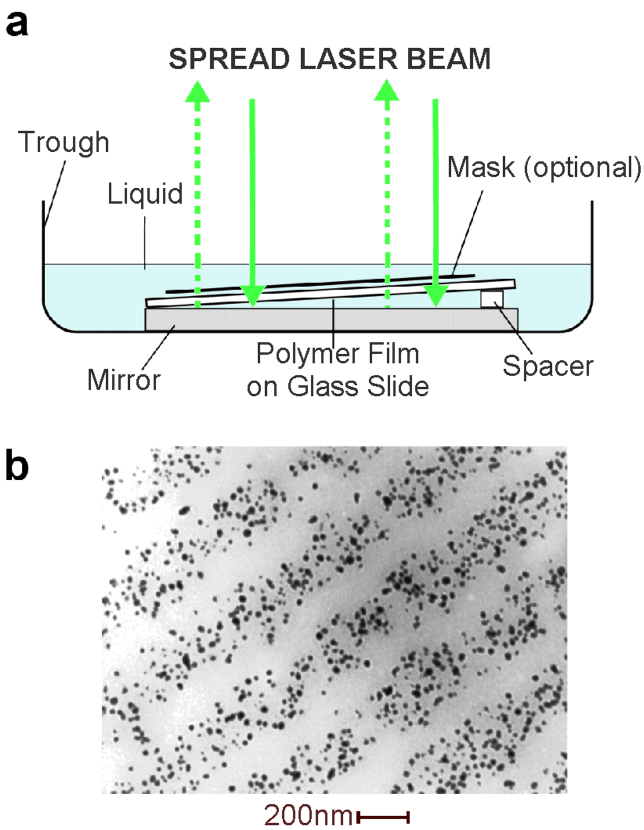

Figure 1. a. The diagram of a microscope slide coated with a smart polymer layer, which has been impregnated with photosensitive silver bromide, being exposed in a trough of aqueous liquid. b. An actual transmission electron micrograph showing the very fine grain size achieved to make the fringe structure.

The reason this was such a breakthrough was that we could then use the principle on a whole range of pre-coated hydrophilic polymers which responded to various specific factors in the environment.

The vast majority of tests required in biotechnology are made in physiologically based aqueous liquids, so polymers need to be hydrophilic from this standpoint apart from the fact that the precipitation of AgBr is an ion exchange process which does not lend itself to taking place in a hydrophobic polymer. So an early question was just to see how far the scope of this diffusion process could be taken towards the hydrophobic end between the typical extremes of say polyacrylamide and polypropylene. Using as reactants the two most soluble salts of silver and bromine in organic liquids, namely silver perchlorate and lithium bromide, I tested out the sequential diffusion system on a few different polymers that were to hand. I found I could get reflection holograms in the cellulose based wrappers commonly on so many of our consumer products. But I did not manage to get any result on the backside of a piece of old Agfa holographic film . This meant that cellulose triacetate was too hydrophobic but with the help of a proportion of acetone I did manage to get an 'OK' result in cellulose diacetate polymer film.

I also managed to get a hologram in nylon (polyamide) but it was not brilliant. I must say at once for those who instantly jump as I did, to the idea of putting holographic gratings **inside** the fabric of say nylon tights, I had used nylon film and not mesh. I did, however, carry out a few experiments trying it with nylon mesh where the first requirement was to "index out" the mesh i.e. make it invisible by a suitable liquid to actually record the hologram. Although I managed to make the pure mesh almost disappear in an organic liquid (DMSO), the act of putting the AgBr salt inside the nylon mesh caused some unavoidable refractive index variation and therefore bad light scatter so I only got *photographic* images in silver, not *holographic*. A pulsed 532 nm YAG laser was used so movement did not cause the failure.

As for other common plastics, I found "Perspex" or PMMA (polymethylmethacrylate) to be too hydrophobic whereas poly(hydroxy)methylmethacrylate or poly-HEMA is excellent at forming bright holograms. A nice piece of work carried out in 1998 by my colleague Andrew Mayes (now at the University of East Anglia) used a small polyHEMA hologram to make very effective measurements of the alcohol content of various drinks [4]. I show the table of his results in table 1 . Strong spirits are not included in the table because they shift the hologram replay wavelength into the infrared—beyond the range of the small reflection spectrometer available for us at the time.

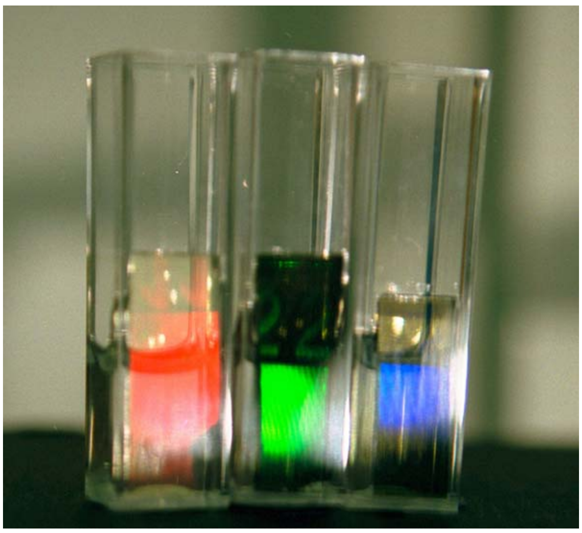

Figure 2. The slide is sliced up and placed in a sample liquid in a cuvette. As the substance in the liquid alters then the replay colour of the hologram may change. In the 3 cuvettes shown, the same polymer material is contracting from left to right.

Table 1. Stated alcohol content of 17 drinks compared with the alcohol content measured with the holographic sensor, together with the pH and conductivity data for each drink

Beverage	Alcohol (vol %)	pH	Conductivity (mS/cm)	Wavelength (nm)	Calc alcohol (vol %)	Error (vol %)
Kaliber lager (Guiness)	0.03	4.10	0.91	503.6	−0.32	−0.35
Swan Light lager	1	3.70	0.84	514.2	1.21	0.21
Steinbrau lager	3	3.95	0.79	524.9	2.67	−0.33
Heiniken lager	5	4.26	1.16	542.3	4.88	−0.12
Carlsberg Special Brew	9	4.11	0.96	575.6	8.72	−0.28
Weihenstephaner Hefe Weissbier	5.4	4.31	1.05	547.1	5.47	0.07
Woodpecker cider (Bulmers)	3.5	3.19	0.76	534.4	3.90	0.40
"Katy" strong cider (Thatchers)	7.4	3.46	0.91	563.6	7.39	−0.01
White Label Bitter (Whitbread)	1	4.01	0.66	513.5	1.11	0.11
Exmoor Gold Bitter	5	4.07	1.17	543.4	5.02	0.02
Newcastle Brown Ale	4.7	3.88	0.87	541.3	4.76	0.06
Guiness	4.3	3.91	0.99	539.2	4.50	0.20
Hoopers Hooch	4.7	2.77	0.81	536.5	4.16	−0.54
Liebfraumilch white wine	9.5	3.36	1.00	582.4	9.45	−0.05
French red wine	11.5	3.56	1.40	600.9	11.36	−0.14
French white wine	11	3.29	0.97	603.3	11.60	0.60
Ruby port	20	3.55	0.69	683.2	18.85	−1.15

I remember we had a bit of trouble reclaiming the petty cash from the accounts department for this lot and had to convince them that it really was for a new scientific breakthrough. (Actually we only needed about 5 ml out of each bottle and as for the rest of each bottle. . . . Well, we did not want to bother them with the finer details of the experiment!)

For several years we have been making polymers with certain chemical groups able to respond specifically to specific ions, enzymes and other analytes by swelling or contracting in saline solution, so when we make a reflection hologram of a mirror in these "smart" polymers we obtain a "smart hologram"mirror. (see: the OE magazine report – http://www.oemagazine.com/fromTheMagazine/mar03/diagnostics.html)

In a future article in the Holographer I hope to reveal more about the amazing possibilities opened up by this new holographic ball game.

References

[1] J. Blyth *et al.* 1996 *Anal. Chem.* **68** 1089–94
[2] H. Thiry 1987 *J. Phot. Sci.* **35** 150–4
[3] J. Blyth *et al.* 1999 *Imaging Sci. J.* **47** 87–91
[4] A. Mayes *et al.* 1999 *Anal. Chem.* **71** 3390–6