The fabrication of wavelength shifting lightguides from clear acrylic sheet by disperse dyeing

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Abstract. Wavelength shifting lightguides have found extensive use as a means of collecting scintillation or cherenkov light from large areas onto a smaller area photodetector and for matching the emitted spectrum to the spectral response of the photodetector. Conventionally, such lightguides are fabricated by casting acrylic polymer with the fluorescent dye incorporated in the bulk. A technique has been developed in which plain cast acrylic sheet is disperse dyed in an aqueous bath. The resulting lightguide has the fluorescent dye held in a thin layer at the surface of the material. A number of different fluorescent dyes are demonstrated.

1. Introduction and inspirations
Wavelength shifting lightguides are extensively used as a means of collecting scintillation or cherenkov light from large areas onto a smaller area photodetector and for matching the emitted spectrum to the spectral response of the photodetector. Their operation is reviewed by Keil [1]. Conventionally, such lightguides are fabricated by casting polymethylmethacrylate (or polyvinyltoluene) with the fluorescent dye incorporated in the bulk. This inevitably requires tonne scale production. The technique suggested here is useful for small scale or bespoke production with experimental dyes.

Viehmann and Frost [2, 3] identified that the fluorescent dye does not need to be uniformly distributed through the bulk of the lightguide, but instead can be applied to the surface as a thin film of lacquer without loss of efficiency. However, it has been found impossible to reliably and repeatably produce optically perfect lacquer layers on large area acrylic sheets.

Mufson and Baptista [4] successfully dyed the surface layer of cast acrylic sheet with the wavelength shifter TPB by spraying with a solution in methylene chloride, followed by surface heating to melt the acrylic. This was done without degrading the optical quality of the surface.

This information inspired a search for other acrylic dyeing techniques. A domestic industry was discovered in which acrylic jewellery and similar items were being produced by surface dyeing using dyes intended for fabrics [5]. This dyeing was performed in hot water using the “disperse dyeing” technique.

Further investigation revealed that this technique was developed and published by ICI in the 1940’s [6, 7, 8, 9]. The technique is also described in a recent technical brochure [10] from Evonik, the current German manufacturer of Plexiglas. It is perhaps surprising that it has not previously been used with fluorescent dyes for lightguide production.
2. Disperse dyeing
Disperse dyeing [11] is a technique extensively used in the textile industry for the colouration of fibres which are hydrophobic, such as polyester, nylon and cellulose acetate. The dyes used are insoluble in water at room temperature and are only sparingly soluble at higher temperatures, however, they have high solubility in the textile fibres. They are present in the dyebath as a fine aqueous suspension in the presence of a dispersing agent. The water dissolves individual molecules of the dye and the fibres then absorb the dye molecules from the solution.

When applied to acrylic sheet, a dyestuff is required which is largely insoluble in the aqueous phase but readily soluble in polymethylmethacrylate acrylic. In addition to water, the dyebath contains finely divided powdered dye and ingredients known in the dyeing industry as “auxiliaries”. These are a surfactant which forms micelles, which carry the dye molecules from the powder grains to the surface of the acrylic. A “carrier” which causes the surface layer of the acrylic to swell and open sufficiently for the dye to penetrate. Finally, a “levelling agent” which produces a spatially even distribution of dye. The exact method of operation of this last ingredient appears unknown. The dyebath is operated at as high a temperature as possible, close to boiling point. After the dyeing process the acrylic must be washed, then baked to remove residual water and carrier.

3. Results to date
Experiments were performed on blue-green emitting wavelength shifters with the intention of fabricating low cost panels for collecting light from large area zinc sulfide sheets. Some initial experiments have been performed with TPB and bis-MSB in an attempt to produce a deep UV wavelength shifter.

The dyebath recipes were developed by examining previous work [5, 6, 7, 8, 10] and substituting materials with currently available equivalents, then performing experiments on small test samples.

The choice of carrier is important. If a carrier is chosen which is too aggressive, the surface of the acrylic melts and becomes sticky, thus permanently degrading the optical finish. If the carrier is not aggressive enough the dye will not penetrate the acrylic. Suggested carriers included benzyl alcohol (phenylmethanol) and acetone (propanone). It was found that isopropyl alcohol (2-propanol) was adequate and preferable to some others when volatility was considered.

A number of different surfactants were tried but best results were obtained with Triton X-100. Many of the earlier recipes suggested acidifying the bath with acetic acid. Experiments were tried at various values of pH, with little change in result, so acidifying was discontinued.

The last ingredient, the levelling agent, was chosen to be lecithin. The literature contained various suggested materials with wildly different costs and availability. Lecithin was one of these and its availability as a food ingredient at low cost made it attractive. Sufficient was added to the bath to make it resemble a thin broth. The result was a very even dyeing of the samples, rather than patchy or speckled colouration.

By polishing one edge of the acrylic, illuminating the face and viewing the edge with a microscope, it was determined that the depth of the dyed layer was around 40 µm.

4. Experimental procedure
Experiments were performed with test strips of polymethacrylate acrylic. It was discovered that not all acrylic is of identical composition. Material which is extruded is affected much more by the carrier and takes up dye much more readily than cast material. It is thought that this reflects the fact that the average molecular mass of cast material is much higher than that of the extruded material. Since the long term intention was to dye large optically perfect cast sheets, the test strips had to be cut from this material. It is possible that samples from different manufacturers will perform differently, but this has not yet been investigated.
The test strips used were 190mm × 40mm × 10mm. These were treated in a volume of dyebath held in a re-sealable polyethylene bag suspended in a bain marie. A typical successful bath contained 300g water, 7g BBQ dye, 10g lecithin, 8g isopropanol and 2g triton X-100. It is not thought that any of these quantities were critical.

The samples were held in the dyebath for 30 minutes at a temperature of 95°C. By that point, further immersion did not result in greater uptake of dye. The samples were then taken from the bath, allowed to cool and washed in clean water for some minutes. They were then dried in an oven at 40°C for at least six hours.

Success has been achieved with BBQ (CAS 23749-58-8), Solvent Green 5 (CAS 2744-50-5), TPB (CAS 1450-63-1) and Bis-MSB (CAS 13280-61-0). Dyes which have high solubility in water, e.g. Fluorescein (CAS 518-47-8) and Solvent Green 7 (CAS 6358-69-6) were complete failures.

5. Initial optical measurements

In the initial stages, the dyeing process was optimized by altering the procedure and examining the test sample visually, deeper colouration being considered better. While this was a workable procedure for blue-green emitting dyes, it is completely unworkable with UV absorbing violet emitting dyes. Further, it is extremely subjective and objective measurements are clearly required.

Absolute optical measurements are notoriously difficult, however, much can be learnt from comparative measurements. A special purpose experimental fluorometer has been constructed, which is shown in figure 1. On the right hand side, a beam of light enters from an Optronic Laboratories OL750 spectrophotometer. The wavelength can be controlled from 200nm through...
to 1000nm. This light falls on the sample and produces fluorescence. A fraction of the fluorescent light passes down the sample and falls on a photomultiplier, which is operated in photon counting mode. Since the OL750 spectrophotometer does not produce equal intensities at all wavelengths, a calibration run against a Lambda UV/VIS radiometer is required.

As the wavelength of the incoming light is swept through the absorption band of the fluorescent dye, the photon count rate from the photomultiplier rises and falls. The output measures the integral of the emission spectrum of the dye convoluted with the spectral response of the photomultiplier. Better samples produce a higher rate, while worse samples produce a lower rate. Initial measurements have been performed which suggest that the surface dyed materials are comparable with commercially available waveshifter materials.

As the dye is not uniformly distributed throughout the matrix of the material, it is expected that the attenuation length will be long. An additional system is being planned which will measure the attenuation length of large samples.

6. Future work
When the optical measurements are completed, a more complete paper will be published. It is also intended to extend to other dyes, particularly those that fluoresce when exposed to deep UV light. There is also the possibility of using the technique to transport scintillating molecules such as p-terphenyl or naphthalene into the surface of acrylic to produce alpha particle sensitive detectors which are largely insensitive to beta or gamma radiation.

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