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PHOTO-ACOUSTIC STUDY OF ZIRCON-BASED CERAMIC PIGMENTS AND GLASSES CONTAINING HIGH CONCENTRATIONS OF COPPER AND COBALT

S. PARKE, G.P. WARMAN* AND J.H. MELLOR
DEPARTMENT OF CERAMICS, GLASSES AND POLYMERS,
THE UNIVERSITY OF SHEFFIELD

SUMMARY

Zircon stains for the ceramics industry have been produced commercially since 1949. At present the commercial stains are mainly zircon ($ZrO_2.SiO_2$) doped with vanadium praseodymium or iron to produce blue, yellow or pink colours respectively. A research programme is in progress to study the factors controlling the colours of these zircon-based glaze stains and photo-acoustic spectroscopy has been used to monitor the colours of stains prepared by different routes. Spectra of coral pink tiles reveal a broad absorption between 600 nm and 350 nm which is yet to be identified. A blue glaze has a spectrum which suggests the presence of V^{4+} but the yellow glaze has a sharp cut-off near 470 nm which is quite uncharacteristic of the spectrum expected from Pr^{3+}. Single crystal specimens of the doped zircon are being prepared and these too will be examined photo-acoustically. An attempt will also be made to obtain transmission measurements.

Opaque coloured glasses are known to have been produced from a very early date in Egypt and Mesopotamia. Despite the advanced scientific nature of glassmaking today little information is available on how to produce such glasses now or how they were produced more than two thousand years ago. Following enquiries from the British Museum about the reproduction and manufacture of a particular type of opaque red glass it was decided that such glasses were well suited to photo-acoustic examination. Their inhomogeneous nature and opacity makes them difficult to study using more conventional techniques.

Glasses were melted under different conditions to assess how the colour depended on composition, temperature of melting and cooling rate. Both X-ray analysis and electron microprobe analysis were used to study the precipitated crystalline phases and the microstructure was observed directly in the optical microscope.

Only two melts actually reproduced the homogeneous sealing wax red of the British Museum glass and the photo-acoustic spectra of all three samples were almost identical. The heterogenous

* Present address: Forensic Laboratories, Metropolitan Police.

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samples had regions of orange, red and yellow layers and although each showed similar spectral features, in particular, a band edge with structure, the edge progressively broadened as the colour changed from red to yellow. The red glass in fact appeared to have the same PAS spectrum as cuprous oxide.

The primary crystalline phase in all the glasses was cuprous oxide which in many cases grew as very large dendrites, the colours produced varying with dendrite size. Slow cooling from the melt produced large, deep red dendrites whereas fast cooling resulted in small orange or yellow dendrites. The size of the dendrite arms appeared to control the colour.

The majority of spectra were recorded on crushed glass sieved to a size range between 90 μm and 120 μm. However, it was difficult to maintain recording conditions constant since the spectrometer was being continuously modified. In general conditions were adjusted to give the best signal to noise ratio in each case. The inhomogeneous nature of the samples provided an added difficulty in the sense that the cuprous oxide dendrites would be randomly distributed, would be of irregular shape and would have optical and thermal properties different from those of the base glass. The heat flow patterns would therefore be irregular and the frequency response of base glass and crystal phase might well be different. Fortunately it would appear from the results that the signal from the cuprous oxide tended to dominate the overall sample response. A further obvious complication is the change of diffuse reflected component with particle size.

Heavily doped samples of a silicate glass containing 10, 5, 2 and 1 wt.% cobalt were studied at 65 hz using the same volume of material and the same particle size range. Assuming an extinction coefficient of 280 the range of absorption coefficients was estimated to be 120 cm^{-1} to 1140 cm^{-1}. Unfortunately since such large additions of cobalt alter the diffusivity and since data on the latter was not available it was not possible to calculate the response predicted by theory. It is interesting that spectra could be obtained even for the most heavily doped sample indicating that full saturation had not been reached. The signal strengths did in fact increase according to the doping level.

Using a 10 wt.% Co sample spectra were recorded at 80, 240 and 850 hz on a solid disc of material, the relative diffusion lengths being in the ratio 1:0.56:0.31. The spectra became more resolved as the frequency increased. A second experiment using an equivalent volume of glass crushed to a particle size between 38 μm and 53 μm gave an increased signal strength as

expected but surprisingly the resolution was not increased. This can be explained by considering the effect of light scattering and it is well known from reflectance studies that absorption in spectral regions of low absorbance may be anomalously high.