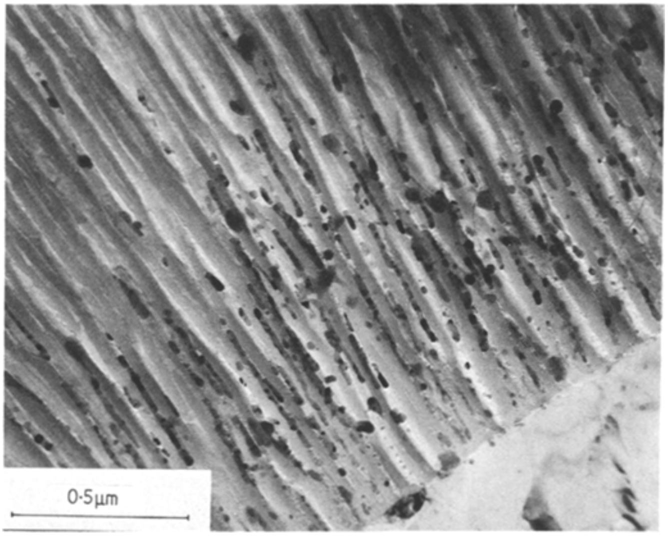

Figure 5 Micrograph of an anodic layer coloured with two different metals for 3 min.

ation, the colouring metal rods having the same diameter as the pores are also sectioned. This is shown in Fig. 1a and b.

If our sections are true vertical sections, the method is suitable for studying the effect of colouring time as shown in Fig. 2a and b. Our method of investigation is able to provide the answers to the following questions: (1) what chemical and physical state of the metal is responsible for the colouring effect as seen in Figs. 3 and 4, and (2) what is the directly presented spatial distribution of the different colouring agents in the layer as shown in Fig. 5?

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Chemical instability of CaO:Y phosphor — a thermoluminescence study

Thermoluminescence (TL) of CaO phosphor doped with various suitable activators has been studied by several research workers, reference to which can be found in the papers of Schwartz and Janin [1] and Khare [2]. It is well known that CaO is relatively unstable in air; reacting with atmospheric moisture it forms $Ca(OH)_2$. Recently, Lehmann [3] has pointed out that because of the problem of chemical stability of CaO in the open atmosphere, although some of the suitably activated CaO phosphors are efficient, their technical utility is questionable. Lehmann's [3] observation is based on cathodoluminescence studies. Incidentally, it is to be noted that in most of TL studies during the excitation/irradiation of the phosphor, in addition to heating the phosphor while recording TL, the sample is invariably exposed to atmospheric moisture. However, in the earlier studies of the TL of CaO

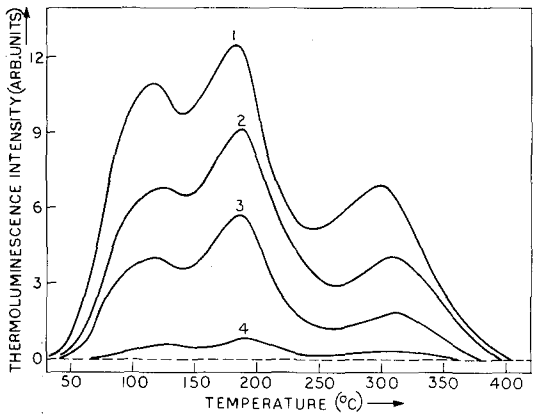

Figure 1 Effect of atmospheric moisture on the TL of CaO:Y phosphor upon exposure to air at room temperature. Curve 1, sample taken straight from the desiccator and X-irradiated for 2 min. Curves 2 to 4, samples exposed to air for 1, 3 and 7 h, respectively, before irradiation.

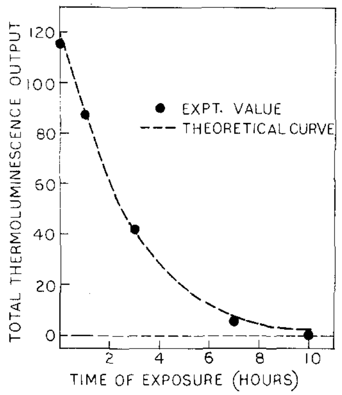

Figure 2 The dependence of total TL output of CaO:Y phosphor on the time of exposure to atmospheric moisture. The theoretical curve is calculated using $I = I_0 e^{-0.386\,t}$ (where t is in h).

phosphor, no attention was paid to this problem. In the present study, we have attempted to study the behaviour of CaO:Y phosphor when exposed to atmospheric moisture by using thermoluminescence. To minimize the unwanted effect of moisture, the irradiation is performed for a short time (2 min in this case) and while recording the TL, the phosphor is heated in a vacuum ($\simeq 10^{-3}$ mm).

The CaO phosphor used in the present study was prepared by heating a fine powder of $CaCO_3$ in air at 1000° C for 4 h. This converts the $CaCO_3$ (with release of CO_2) to CaO. The mixture of CaO + Y_2O_3 (0.2 wt%) was again fired for 4 h at 1000° C to obtain the final phosphor. The phosphor was then exposed to air (relative humidity $\simeq$ 80%) at room temperature for various lengths of time and subsequently irradiated with X-rays, from an Mo target of a Machlett tube operated at 30 kV and 10 mA, for 2 min in all the cases. The TL curves were recorded under identical conditions, the sample being heated in vacuum at a uniform rate of 1.5° C sec^{-1}. The TL emission was detected by an RCA 1P28 photomultiplier tube, the resulting photocurrent being amplified by an electrometer amplifier was fed into a millivolt recorder. The temperature of the sample was recorded on a similar recorder.

The X-irradiated CaO:Y which was taken straight from the desiccator exhibits a bright TL when heated above room temperature. The TL curve shows three TL peaks occurring around 120, 185 and 300° C (curve 1, Fig. 1). The curves of samples exposed to humid air (relative humidity $\simeq$ 80%) for various lengths of time (the sample geometry remaining the same in all cases) are also recorded and are also shown in Fig. 1 (curves 2 to 4). The results show that the intensities of all three peaks decrease rapidly with increasing exposure time of to air. The total TL output (taking the area of the TL curve as a measure) of the phosphor plotted against the time of exposure to air shows that the TL output continues to decrease exponentially with increasing exposure practically reaching zero after about 10 h (Fig. 2). The decay constant was found to be 0.386.

Although no recording of the X-ray luminescence of the CaO:Y phosphor during X-ray excitation was done, visual observation showed that the bright yellow–orange luminescence observed in the unexposed sample decreases in intensity when the phosphor is exposed to air. No luminescence under X-ray excitation was observed visually for the sample exposed to air for more than 10 h. This result qualitatively agrees with that of Lehmann [3].

The above results can be explained in the following way. On exposure of CaO:Y phosphor to humid air at room temperature it reacts with moisture and is converted to non-luminescent $Ca(OH)_2$ as a result of which the total TL output continues to decrease with increase in exposure time. From the present study we tentatively draw the following inferences:

(1) In general, while studying the luminescence properties of CaO phosphors care should be taken to avoid exposure to air as much as possible. Exposure to humid air especially (as in the present study) can deteriorate the quality of the phosphor drastically.

(2) The deterioration of CaO phosphor is due to its reaction with atmospheric moisture, ultimately forming $Ca(OH)_2$ which is non-luminescent. Since TL as a tool is very sensitive [4] it may be a useful a technique to study the reaction kinetics of materials where a luminescent to non-luminescent conversion takes place.

Acknowledgement

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Anisotropic electrochemical reduction of polytetrafluorethylene

New pre-treatments resulting in large increases in adhesion to polytetrafluorethylene were briefly described by Brewis *et al.* [1]. These treatments involved either electrochemically generated intermediates or the direct contact of polytetrafluorethylene with a cathodically polarized lead/antimony electrode. Since then a considerable amount of work has been carried out on the direct contact method.

The object of this communictation is to describe a novel anisotropic effect, i.e. the rate and ultimate degree of electrochemical attack is highly dependent on a skin effect in the polymer surface; this effect could be due to orientation or stress concentrations. Thus large differences are observed between polytetrafluorethylene samples of different processing histories. No similar anisotropic surface treatments have been reported for polytetrafluorethylene, although anisotropic contact angles have been observed after stretching this and other polymers [2].

The electrolyte consisted of a 0.1 M solution of tetrabutylammonium tetrafluoroborate in dimethylformamide which had been superficially dried over molecular sieves. The working electrode was a platinum wire set in glass and this was placed in contact with the polytetrafluoroethylene samples. A black carbonaceous film was formed at the point of contact which grew outwards from the electrode tip. The polarizing voltage used was ~ -2.3 V versus a saturated calomel reference electrode.

A number of polytetrafluoroethylene samples with different processing histories were examined with respect to the rate and extent of electrochemical etching. These materials included pressed sheet (Fig. 1), skived tape, unsintered calendered film and ram extruded rod (Fig.2). In ram extrusion surface layers of the polytetrafluoroethylene are subjected to large shearing forces and much alignment of polymer chains is expected; this has been confirmed by means of birefringence studies. The electrochemical attack of this material was also highly anisotropic (Fig. 2). The unsintered calendered film which also received severe unidirectional processing has been shown, by attenuated total reflectance infra-red analysis, to have a high degree of orientation [3]. When this film was subjected to the electrochemical pre-treatment it showed even more marked anisotropy than the extruded rod. As expected, for pressed sheet, no preferential attack occurred while for skived tape, some orientation induced by the skiving process is probably responsible for the slight anisotropy.