COMPOUNDS OF TLDs AND HIGH-MELTING ORGANICS FOR FAST NEUTRON PERSONNEL DOSIMETRY*)

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ABSTRACT

The search for a replacement of the NTA film in fast neutron personnel dosimetry has not yet produced a completely satisfactory result. Various investigators have attempted to increase the low fast neutron sensitivity of inorganic thermoluminescent materials by mixing them with liquid or solid organic recoil proton radiators, but most of the systems described so far either exhibited a very pronounced energy response, or they required the separation of the constituents prior to evaluation, because almost all hydrogen-rich organic compounds evaporate and/or disintegrate at temperatures below those which are required for the read-out and annealing of the more stable TLD materials.

In this feasibility study, a finely powdered, highly sensitive and fading-resistant phosphor ($CaSO_4$:Dy) has been hot-pressed into pellets with p-sexiphenyl (melting point $\sim$ 450°C) as a high-melting and stable hydrogenous radiator. Outgassing of the pellets in a vacuum furnace at 150°C removed residual volatile impurities. The response of detector pairs, consisting of such pellets and of Teflon-embedded phosphors, has been investigated.

The sexiphenyl-embedded phosphor is sensitive to UV light. An efficiency of about 50 % of the gamma radiation response was observed for recoil protons produced by fission and also for 14 MeV neutrons. The response is a linear function of dose. Desirable follow-up studies are outlined.

In recent years, the discussion about various possible replacements of the NTA film as a fast neutron personnel dosimeter has intensified (1-3). Among the more promising approaches are:

1. track etching techniques, either based on recoil nuclei or on fission fragment registration (for a review, see ref. 4);

2. recoil proton registration with detectors based on stimulated exoelectron emission (5,6); and

3. recoil proton registration with TLD, which is the subject of this paper.

It was first shown almost ten years ago that the low inherent fast neutron response of inorganic TLD detectors can be increased by intimately mixing them with hydrogenous materials. This principle was first used (7) by mixing LiF:Mg,Ti during irradiation with alcohol, which can easily be evaporated prior to the reading. Further studies of the energy response of the system (8) were only partially encouraging, because the system required continuous stirring or shaking during exposure, and its response decreased rather rapidly with neutron energy (0.17 per 100 erg/g neutron kerma in tissue at 2.9 MeV, 0.66 at 14.9 MeV). A better response at low neutron energies could be expected with extremely fine-grained LiF, but this introduces other problems such as a drop in inherent radiation sensitivity. Naturally, mixing of LiF with alcohol or other liquids also affects its photon energy dependence (9). Mixing of fine LiF powder with water is not recommended because this induces a rapid fading (10).

Other investigators have, therefore combined TL phosphors with solid organic materials, either by just covering a solid TL phosphor layer with radiator foils (11, 12), or by intimately mixing a phosphor such as $CaSO_4$:Tm with a water-soluble radiator such as glucose (13). This mixture is exposed in a Teflon tube together with another tube containing $CaSO_4$:Tm only; the glucose is washed out prior to evaluation; and the difference in the reading of the two detectors is related to the fast neutron dose.

Obviously, it would be much more convenient in routine applications if compounds of the TL phosphor and a high-melting radiator could be made which are capable of undergoing multiple readout and annealing cycles without the need for separating the constituents. Some work along this line was carried out in the Soviet Union (14), but no details are known and attempts to reproduce the reported results have met with limited success. As there are several fairly easily available hydrogenous compounds with melting points above 300°C, a search for a material with desirable properties was carried out. Lithium hydride (M.P. $\sim$ 690°C), ammonium aluminum chloride (M.P. 304°C) and some other inorganic compounds had to be ruled out due to poor stability in humid air and/or low hydrogen content.

There are several organics which are not intensily colored and would not, therefore, absorb too much of the TL light. Some of them are: adenine (365°C); 1-alanine (318°C); 1, 5 - dinitro-anthroquinone (384°C); 2-hydroxy-anthraquinone (302°C); m-azoxybenzoic acid (345°C); benzidine sulfone (327°C); p-carboxy-cinnaminic acid (358°C); dinocotinic acid (323°C); guanine (360°C); isonicotinic acid (317°C); isophthalic acid (330°C); dl-isovaline (307°C); dl-leucine (332°C); d- or dl-norleucine (< 300°C); quercetin (310°C); 5-quinolinecarboxylic acid (339°C); taurine (328°C); theobromine (337°C); trimesic acid ($\sim$ 350°C); dl or d-tyrosine (316°C); uracil (338°C); methyl uric acids (360-400°C); l-valine (315°C); and dicoumarin (> 330°C).

Unfortunately, many of these materials undergo rapid deterioration (discoloration, sublimation, "outgassing" of volatile impurities, etc.) when heated repeatedly to temperatures close to their melting point. We concentrated, therefore, on high-melting polyphenyls such as p-quaterphenyl ($\sim$ 320°C), which is commercially available (Pilot Chemicals Div., Watertown, Mass. 02172), and p-sexiphenyl ($\sim$ 450°C) wich has been prepared at ORNL (15). Polyphenyls are known to be stable compounds with a relatively high hydrogen content (5.9 % in quaterphenyl, 5.68 % in sexiphenyl) and interesting luminescence properties. Even the carefully purified material, however, exhibited some sublimation of impurities at high temperatures which led to a white condensate at the interference filter of the TL reader. After keeping the samples in a vacuum furnace at 150°C overnight, this disturbing effect disappeared.

Small pellets of about 20 mg weight, 6 mm diameter and less than 1 mm thick, have been produced by hot-pressing a mixture of very finely powdered (average grain diameter $\sim$ 4 µm) TL phosphor with the powdered polyphenyl or Teflon at about 200°C and a pressure of about 2000 kg/cm^2. As a phosphor, $CaSO_4$:Dy, which has been prepared as previously described (16), was used. Some thermal neutron sensitivity of this material due to its Dy content was of no concern in these tests because it affects both the Teflon- and the sexiphenyl-embedded material to the same extent. Several mixing ratios have been tried, but a 1:1 ratio was chosen as a compromise between sensitivity and mechanical stability requirements. The detectors were annealed at 280°C (Teflon) and 350°C (p-sexiphenyl), respectively, for about two hours prior to re-use. No residual TL signal could be detected after this treatment, and there was no change in sensitivity during multiple use.

The response of both the Teflon and the p-sexiphenyl embedded detectors is a linear function of the gamma radiation dose between at least 1 and 1000 rad. The response of the Teflon-embedded detectors was 75 % higher due to a larger quantity of phosphor per detector. The standard deviation of the dose readings, both during multiple reading of the same and of different detectors, amounted to less than ten percent but could undoubtedly be reduced to 1-2 % for mass-produced detectors which are produced under more carefully controlled conditions.

For exposure, the Teflon-embedded detectors were placed in a Teflon shield, and the sexiphenyl-embedded detectors in a polyethylene shield of about 2 mm thickness in order to establish recoil particle equilibrium. The results of various exposures of the detectors to mixed neutron and gamma radiation fields are summarized in Table I.

Table I. Fast Neutron Response of $CaSO_4$:Dy Embedded in p-Sexiphenyl

Radiation Source	Sexiphenyl/Teflon response ratio *)	neutron/γ dose ratio (rad/rad)	recoil proton efficiency
HPRR reactor	3	7	$\sim$ 0.4
14 MeV (d,T)	10	25	$\sim$ 0.4

*) Normalized for equal gamma radiation sensitivity

As can be seen, the relative efficiency of the phosphor to recoil protons amounts to about 40 % for both fission and 14 MeV neutrons, which is more than what one would expect from the known LET response of TL phosphors. Perhaps some of this response is due to an "indirect" response of the phosphor to light which is produced by the protons traversing the highly luminescent sexiphenyl. Indeed, a relatively high sensitivity of the sexiphenyl-embedded material to UV light was observed, which made it necessary to handle the detectors in red light instead of the standard laboratory fluorescent light illumination. It is not known whether this UV sensitivity is due to an optical or an electronic energy transfer between the sexiphenyl and the phosphor.

In further studies, it is intended to employ some other constituents, with low-Z phosphors with good sensitivity and stability, but low thermal neutron response (Mg_2SiO_4:Tb, BeO etc.) replacing the $CaSO_4$:Dy, and other organic compounds including some hydrogenous, temperature-resistant polymers (polyimides, Dexsil, polyaryl sulfone etc.) replacing the p-sexiphenyl. Also, the phosphor to radiator ratio has to be varied within wider limits, and the effect of protective coatings of the detector pellets be studied. The practical threshold of the system for lower neutron energies (estimated to be presently around 0.1 MeV) has to be established, and the photon energy response of the optimized detector must be measured.

It is hoped to arrive, after these studies have been completed, on a system for fast neutron dosimetry which is as simple to employ as the presently used ^{6}LiF/^{7}LiF pairs for thermal neutron dosimetry.

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