

We find that the most effective activators contain one or more aromatic rings with substituent groups capable of reacting to form part of the resin molecule. Generally, —OH or —NH₂ groups are present but condensed ring hydrocarbons having active positions also give phosphors, though of lower activity. In all cases, the presence of —SO₃H groups augments the luminescence and shifts both the peak excitation and luminescence towards longer wave-lengths. Some of the phosphors exhibit luminescence which is visually detectable (in the dark) for up to 40 sec after ultra-violet irradiation. The greatly enhanced intensities and durations suggested that these systems might be qualitatively different from those previously reported. No detailed study has been made of the chemical or radiative processes involved, but some activators were structurally modified in an effort to establish if chemical linkage with the resin matrix were essential. The results indicate that this is so. Thus, cyanuric acid containing 1 per cent of *p*-hydroxy-diphenyl yields a formaldehyde-condensation product showing luminescence, in the range 4300–6300 Å, which is visually detectable for about 20 sec after irradiation at 2537 Å. If the *p*-hydroxy-diphenyl is replaced by di-*p*-diphenyl ether or methyl-*p*-diphenyl ether there is no visually detectable delayed luminescence after irradiation with long- or short-wave ultra-violet light. Also, the phosphorescence imparted by *p*-phenylene diamine is slightly exceeded by that of the (nuclear substituted) 2,3,5,6-tetra-methyl derivative but no phosphorescence is observed if *N,N,N',N'*-tetra methyl *p*-phenylene diamine is used. The blockage of the —OH and —NH₂ groups has in each case resulted in a drastic reduction of the phosphorescent properties, with no obvious change in the fluorescence.

The work is insufficient to justify firm conclusions, but it does seem probable that these materials differ qualitatively from the solutions which have been generally studied. Oster *et al.*¹ give some evidence for specific interactions between activating molecules and the polymeric matrix. It may be that the amino-resins provide an environment specially favourable to high phosphor efficiencies, even for dissolved species, but it also appears that the purely physical effects of a rigid matrix are here augmented by chemical bonding of the activating centres to the main network of the amino-resins.

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¹ Oster, G., Geacintov, N., and Khan, A. U., *Nature*, **196**, 1089 (1962).

² Forster, C. F., *Post Off. Elect. Eng. J.*, **54** (3), 180 (1961).

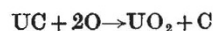
³ British Patent No. 870,504 (1961).

Acid Leaching of Uranium and Thorium Carbides

In a recent communication by Sasaki *et al.*¹ attention is directed to the use of the carbides of uranium, plutonium and thorium as nuclear fuels and to the problems associated with processing and recovery of the irradiated fuel. It is revealed that in the acid leaching of thorium carbide (ThC₂) with nitric acid of concentrations below 4 N gaseous hydrocarbons are evolved, whereas at concentrations above 4 N organic material is produced, and evidence is presented that this organic matter does not have a C—H bond as indicated by the results of infra-red analysis. The formation of organic material during the

acid leaching of uranium monocarbide has also been observed by Simpson *et al.*² and the presence of this could constitute a hazard in the uranium recovery process, although its formation may be avoided by prior hydrolysis of the carbide in water and subsequent dissolution of the resulting oxides in nitric acid³.

We have examined the reaction of uranium monocarbide with nitric acid (6 N) and after removal of uranium from the resulting solution with tributyl phosphate in benzene⁴ the aqueous raffinate was evaporated and the residue esterified with diazomethane. Chromatography of the mixed esters on alumina from benzene solution gave hexamethyl mellitate, which was identified by analysis and by comparison with an authentic specimen. Further elution of the column gave intractable resins. In one experiment involving the dissolution of uranium carbide in nitric acid (6 N) the solution was left for six weeks before processing and oxalic acid separated from the reaction mixture. An X-ray analysis of the uranium monocarbide utilized in the leaching process did not reveal the presence of free graphite and we suggest that the reaction proceeds by a breakdown of uranium carbide with formation of graphitic carbon which is then oxidized to oxalic and mellitic acids.



Mellitic acid was also isolated (as the hexamethyl ester) from the reaction of nitric acid (6 N) with uranium dicarbide (UC₂), uranium sesquicarbide (U₂C₃) and the carbides of thorium (ThC, ThC₂ and Th₂C₃).

In a typical experiment uranium monocarbide (519 g) and nitric acid (6 N; 4 litres) were allowed to react for twenty-six days and filtered from insoluble material. The aqueous filtrate was extracted until free of uranium with a 20 per cent solution of tributyl phosphate in benzene which had been equilibrated with nitric acid (6 N). Evaporation of the aqueous raffinate under reduced pressure gave a residue (12.7 g) which was suspended in ether and treated with an excess of ethereal diazomethane. Filtration from insoluble matter (24 g, containing 13.5 per cent of the initial carbon) and evaporation of the filtrate gave a mixture of esters (13 g) which was chromatographed on alumina from benzene solution. Elution with benzene furnished hexamethyl mellitate (5.1 g). Further elution of the column with ether, ether-methanol and methanol gave intractable mixtures. Approximately 30 per cent of the initial carbon was evolved as carbon dioxide during dissolution in nitric acid. Together with a 4.3 per cent yield of oxalic acid isolated in one case, the foregoing products account for 83 per cent of the carbon present initially. The optimum material balance (95 per cent) was secured in the case of uranium sesquicarbide, which afforded 38 per cent carbon dioxide, 10 per cent mellitic acid and 46 per cent other acids (unidentified: yield estimated as 'mellitic acid'). The corresponding yields for the other carbides were approximately: UC₂: 29, 8, 25; ThC: 47, 5, 23; ThC₂: 33, 3, 8 and Th₂C₃: 27, 1, 15 per cent.

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² Simpson, A. M., and Heath, B. A., *U.K. Atomic Energy Auth.* (private communication).

³ Hartley, K., and MacLennan, G., *British Pat.* 5682/58 (April 1958).

⁴ Healy, T. V., and McKay, H. A. C., *Rec. Trav. Chim.*, **75**, 730 (1956).