This step-wise elution of bitumen on an anion-exchange column in the acetate form is understood on the grounds that the weakly acidic bitumen is ionized to an appreciable extent in the high *p*H 1 per cent diethylamine in methanol solution, thus ensuring retention of the bitumen on the column. With decreasing *p*H of the eluant from methanol through 25 per cent glacial acetic acid in methanol to glacial acetic acid, there is a decrease in the extent of ionization of the bitumen with its consequent release from the column in stages according to the *p*H of the eluting solvent. The fact that peat bitumens consist of a mixture of acids or acidic groups of differing strength is confirmed by the results of other experiments on humic material, for example, the electrometric titration studies of van Dijk[2] on humic acids which differentiate between the less-weak acid carboxyl groups and the very weak acid (probably) phenolic hydroxyl groups.

Further work is now in progress and the results will be published elsewhere together with details of the present experiments.

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RADIATION CHEMISTRY

Free Radical Formation and Oxygen Effect in Irradiated Polymethylmethacrylate

When plastics, such as polymethylmethacrylate ('Perspex'), are irradiated with large doses (of the order of 1 Mrad) of ionizing radiations, for example, X-rays or electrons, optical changes can be observed[1] and the appearance of electron spin resonance signals[2] indicates the formation of free radicals in the solid. In the case of 'Perspex' the diffusion of oxygen into the irradiated plastic causes changes in the optical absorption spectrum and information regarding the diffusion process may thus be obtained[3]. We have found, however, that in the case of ultra-violet-transmitting plasticizer free 'Perspex' (kindly provided by Imperial Chemical Industries, Ltd.), when the well-known 4 + 5 line electron spin resonance spectrum[2,4,5] due to the methylmethacrylate free radical was produced by large doses, subsequent exposure of the irradiated sample to an atmosphere of air or oxygen for periods up to 12 weeks at ~ 25° C. did not lead to a change in the electron spin resonance spectrum which would have corresponded to the formation of a peroxide radical. The 4 + 5 line spectrum persisted slightly weakened and with the ratio of 4 to 5 line spectrum intensity modified.

On the other hand, using a Varian 100-kc. modulation X-band electron spin resonance spectrometer at its highest sensitivity, we were able to observe detectable signals at doses as low as ~ 1 krad of X-rays. One example obtained in a sample which was saturated with oxygen by diffusion prior to irradiation and then irradiated with ~ 45 krad of X-rays is shown in Fig. 1. It corresponds to that expected from a peroxide radical, O_2^- or RO_2, showing anisotropy, but not HO_2, which is expected to also show some doublet hyperfine splitting.

No trace of the 4 + 5 line spectrum was observable in oxygen-saturated samples until doses higher than

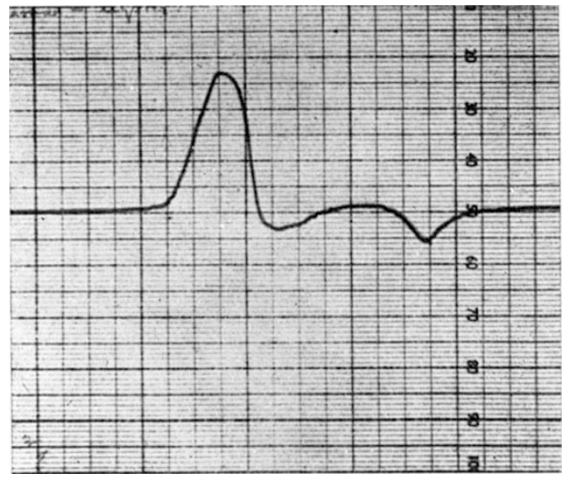

Fig. 1. Electron spin resonance spectrum of oxygen-saturated 'Perspex' irradiated with ~ 45 krads of X-rays at room temperature. Spectrum measured at 77° K.

that used in obtaining Fig. 1 were used. With increasing dose the 4 + 5 line spectrum appeared superimposed on the peroxide spectrum, until at doses of the order of 1 Mrad the peroxide spectrum was swamped by the 4 + 5 line one. Lower doses were sufficient to reach the transition in air-saturated samples, and the lowest ones in evacuated samples.

We conclude that when oxygen is present in the organic polymer during irradiation the peroxide radical is formed to the exclusion of the organic radical giving the 4 + 5 line spectrum.

The peroxide radical shows a *g*-value anisotropy with $g_{\parallel} = 2{\cdot}034$ and $g_{\perp} = 2{\cdot}010$, the separation being 38 gauss.

We hope to publish full details of these and related[3] experiments in the near future.

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Effect of β- or/and γ-rays on Gas Discharge

A chlorine-filled all-glass ozonizer (p_{Cl_2} = 120 mm. mercury at 30°) under alternating-current (50 cycles/sec.) excitation produced a new effect, hitherto unreported, when irradiated with β- or/and γ-rays. Under identical conditions of excitation and detection, β- or/and γ-radiations of fixed activity increased the discharge current i (in darkness) at low applied potentials and as the applied potential is enhanced gradually this increase $+ \Delta i$ in i decreased and reversed sign to $- \Delta i$. While this phenomenon is