

We believe that, in general, the assumption is not justified, and that measurements on samples exposed to discharge between large plane electrodes can be misleading. Indeed, we suggest that the mechanisms leading to gross changes in measured conductivity are not the same as those leading to breakdown; the following experiment demonstrates this.

Films of low density polythene (MFL.7) 0.01 cm thick were subjected to discharges in a hemisphere/plane electrode system<sup>2</sup>. The gap between the hemisphere and upper film surface was 0.03 cm. Discharge was produced by applying 4 kV root mean square 500 c/s to the electrodes. On removing the film from the exposure rig after about 1 h and measuring the loss tangent at 500 c/s using plane/plane electrodes 1.75 cm in diameter, we found that the loss angle had indeed increased from its original value. The increase depended on the time of exposure, and at times just less than the time to breakdown (5–6 h) reached values in the range 0.04–0.5. During exposure to discharge an opaque white ring, 1.5 cm in diameter and 0.1 cm wide, was formed and by scanning the surface with a flat-ended rod electrode 0.3 cm in diameter, the high loss tangent was found to be confined to the material under the ring. Here the loss tangent reached 0.56; elsewhere, including the region immediately under the sphere, where breakdown invariably occurs, the loss tangent was less than 0.001 which was the limit of sensitivity. The ring was a surface deposit and could be wiped off with a dry cloth or better with ether, reducing the loss tangent to the original value. The deposit was not analysed, but oxalic acid and oxalates have been reported in similar deposits by other workers<sup>3</sup>.

Interrupting the tests to wipe off the ring of deposit did not materially affect the time to breakdown. Breakdown frequently occurred soon after wiping when the loss tangent was low.

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<sup>1</sup> Boeck, W., *Elektrotech. Z.*, A, **85** (22), 730 (1964).

<sup>2</sup> Meats, R. J., and Stannett, A. W., *I.E.E.E. Trans. on Power Apps. and Systems*, **49** (1964).

<sup>3</sup> Grossman, R. F., and Beasley, W. A., *J. App. Polymer Sci.*, **11**, 163 (1959).

## CHEMISTRY

### A Lower Transition Point for Polymethyl Methacrylate at 30°–32° C

IN view of the use of polymethyl methacrylate (PMMA) for the production of surgical and dental prostheses, its properties at body temperature and those encountered in the mouth are of particular importance. Furthermore, the necessity for the incorporation of metal inserts and porcelain teeth makes its thermal properties of unusual interest. The thermal expansion of both commercial PMMA ('Perspex') and samples prepared by dental techniques was examined by means of a specially constructed dilatometer. Increase in length was recorded by means of a dial gauge reading to 0.0005 mm, and temperatures were measured at three points along 70 mm specimens by means of a Leeds and Northrup potentiometer. Specimens were arranged in a silica vessel which in later experiments was filled with water to determine the effect of water absorption on the thermal properties of PMMA. Increase in length was plotted against rise in temperature between 20° and 40° C. The resulting graphs showed a change in upward slope between 30°–32° C. The thermal properties were studied daily for periods up to 35 days with the specimens immersed in water and for similar periods with the same specimen drying out. Graphs

prepared as before showed no alteration in the position at which an upward change in slope occurred, although the thermal expansion was greater for saturated specimens than for dry ones. Several second-order phase transition points have been recorded<sup>1</sup> for PMMA, but so far as we can ascertain, no reference to one in the temperature range of 30°–32° C has previously been reported.

It is considered that this observation is important in relation to the testing of the material for compliance with the appropriate standards, and it is suggested that the temperatures at which testing is now done may require review.

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<sup>1</sup> Strella, S., *J. App. Polymer Sci.*, **7**, 569 (1963).

### Molecular and Crystal Structure of a 5-Covalent Iron (III) Complex with Spin, $S=3/2$

THE magnetic properties of mononuclear compounds of trivalent iron (configuration  $3d^5$ ) conform to the predictions of ligand field theory. Both high-spin  ${}^6A_1$  ( $\mu_{\text{eff}} = 5.9$  Bohr magnetons (B.M.)) and low-spin  ${}^2T_2$  ( $\mu_{\text{eff}} = 2.3$  B.M.) ground states are observed for complexes with octahedral microsymmetry. Quartet ground states ( $S = 3/2$ ) are specifically excluded by the theory, so that the successful isolation of a new class of such compounds is of special interest.

We find that treatment with concentrated hydrohalic acids of a benzene solution of *tris*(dialkyldithiocarbamate)-iron (III) results in the immediate separation of crystalline compounds of the general type  $(\text{Fe}(\text{S}_2\text{CNR}_2)_2\text{X})$ , where  $\text{X} = \text{Cl}, \text{Br}, \text{I}$  and  $\text{R} = \text{Me}, \text{Et}, \text{Pr}^i$ , and  $\text{Bu}^{\text{sec}}$ . Typical of the series is the dark green crystalline compound,  $(\text{Fe}(\text{S}_2\text{CNET}_2)_2\text{Cl})$ , which melts at 250°–255° C with decomposition and is monomeric in freezing nitrobenzene (at  $1.5 \times 10^{-2}$  M, molecular weight =  $386 \pm 10$ ; calculated 388). The magnetic susceptibility of the powdered solid follows Curie's law between 130°–300° K with  $\mu_{\text{eff}} = 3.98$  B.M., close to the spin-only value of 3.88 B.M. for  $S = 3/2$ . In chloroform solution ( $3.1 \times 10^{-2}$  M) at room temperature, the value 3.88 B.M. is obtained. The infra-red spectrum resembles that found for dithiocarbamates which are chelated to iron by way of two sulphur atoms. The iron-chlorine and iron-sulphur stretching modes occur at 309 and 353  $\text{cm}^{-1}$ , and the high carbon-nitrogen stretching frequency in the region of 1,500  $\text{cm}^{-1}$  suggests that delocalization of the  $\pi$ -cloud about the  $\text{CS}_2$ -group includes the adjoining nitrogen atom.

This evidence for a quartet ground state of an iron (III) compound is unambiguous, and to our knowledge is paralleled only by that for iron (III) phthalocyanine chloride as reported by Griffith<sup>1</sup>. A stereochemistry based on five-co-ordinated iron is suggested, but the data do not differentiate between the square pyramidal ( $d_{x^2-y^2} sp^3$ ) and the trigonal bipyramidal ( $d_{z^2} sp^3$ ) geometries. However, this ambiguity is resolved by X-ray methods using single crystals of the diethyl derivative.

The crystal data for the ethyl compound are as follows:  $\text{C}_{10}\text{H}_{20}\text{N}_2\text{S}_4\text{ClFe}$ ,  $M = 387.8$ , monoclinic,  $a = 16.43$ ,  $b = 9.42$ ,  $c = 12.85$  Å,  $\beta = 120.5^\circ$ ,  $U = 1713$  Å<sup>3</sup>,  $D_m = 1.52$  (by flotation),  $Z = 4$ ,  $D_c = 1.50$  g  $\text{cm}^{-3}$ , space group  $P2_1/c$ , ( $C_{2h}^2$ ; No. 14); co-radiation (unfiltered), single crystal oscillation and equi-inclination Weissenberg photographs,  $\mu = 107$   $\text{cm}^{-1}$ .