INTRODUCTION

Thomas and King\(^1\) reported in 1975 that the presence in poly­
ethylene of certain antioxidants of the substituted phenol type
caused a dielectric relaxation at 4.2 K. Although peak loss factor
occurred at several kHz, the loss enhancement at 50-60 Hz was
significant in view of the possible use of polyethylene tapes for
the insulation of a superconducting power transmission line. It
has now been found that all antioxidants that are derivatives of 2,6
di-tert-butyl phenol ("DBP" - see figure 1) cause such a relaxation,
but that any other phenol or non-phenol antioxidant may be used
without causing significant loss enhancement at cryogenic tempera­
tures.\(^2\) DBP and its derivatives cause similar relaxations when
added to polyethylene, polypropylene or other polyolefins, or
dissolved in paraffin or decalin.\(^3\) By an appropriate isotopic
substitution it has been demonstrated that the effect is due to the
hindered rotation of the hydroxyl groups of the molecules,\(^4\) so in
fact it is now clear that Thomas and King rediscovered at cryogenic
temperatures a dielectric relaxation which had been known since
1957. Davies and Meakins\(^5\) then reported that a solution of 2, 4,
6 tri-tert-butyl phenol in decalin had two resolved relaxations,
and were able to identify the faster one (30 GHz loss peak at
ambient temperature) with hydroxyl group rotations and the slower
one with rotations of entire molecules. There are strong grounds
for supposing that at cryogenic temperatures and in solid matrices,
rotation of entire molecules will be negligible, but that the
hydroxyl groups will continue to rotate by quantum mechanical
tunneling. The tunneling hypothesis was made by Thomas and King\(^1\)
and was confirmed by the deuteration experiments\(^3,4\) when it was
found that a DBP derivative with a deuteroxy group relaxed 10^4
times more slowly than a DBP derivative with a (proton) hydroxy group - the biggest isotope shift of a dielectric relaxation that we know.

Figure 1 shows the structural formula of 2,6 di-tert-butyl phenol ("DBP"), and its antioxidant derivatives. DBP is the molecule illustrated with R an H atom. The simplest commercial antioxidant, BHT, has R a methyl group. The molecule studied by Davies and Meakins had R a tert-butyl group. Other antioxidants have R a long chain (example: Irganox 1076) or else a methylene or other group which serves to join two or more DBP molecules together "tail to tail" (examples: Ionox 220, Ionox 330 or ethyl 330, Irganox 1010).

Studies of a wide variety of phenol derivatives diluted in various matrices or solvents have revealed that the relaxations are never so well developed as in the case of DBP and its derivatives in polyolefins. It seems that these are the best systems that can be devised to study this remarkable physical phenomenon.

Our present purpose is firstly to restate briefly the basic finding of electrical engineering interest, and in doing so to set the record straight in view of some erroneous conclusions in the recent literature; secondly to suggest how the effects may be used in sub-Kelvin thermometry.

ANTIOXIDANTS IN POLYOLEFINS

Polyolefins are generally stabilised against oxidative degradation by the addition of a milli-molar concentration (100-1000 ppm by weight) of an antioxidant which is usually a phenol derivative, but may also be an amine. We recently reported that a low-density polyethylene sample containing an amine antioxidant showed no sign of extra loss, nor did two other such samples containing other anti-oxidants that were neither phenols nor amines. Two samples containing DBP derivatives (Irganox 1010 and Irganox 1035) exhibited the relaxation, but so did three samples containing the non-DBP phenols illustrated in figure 2. It was later discovered however, that this series of samples had been prepared by adding the Nonox WSP etc to a polyethylene which already contained an antioxidant, so the conclusions were invalid. New polyethylene samples containing Topanol CA, Nonox WSP and Santonox R were examined and