

# Investigations of Stabilizing Additives. IV. PEPQ as a Primary Radical Scavenger

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## Synopsis

Studies of PEPQ in a model antioxidant activity system have demonstrated that this material behaves not only as a hydroperoxide decomposer but as a primary radical scavenger. The temperature dependence of the antioxidant activity also indicates that PEPQ is more effective at higher temperatures than at ambient conditions. The relationship between the model antioxidant activity system and melt stability measurements in polypropylene is in good agreement and implies that PEPQ is an effective melt stabilizer even in the absence of conventional phenolic stabilizers such as BHT.

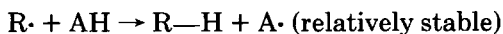
## INTRODUCTION

Polymer stabilization is best achieved by the incorporation of a primary radical scavenger, which is generally a phenolic derivative.<sup>1-3</sup> The radical scavenger has to compete with absorbed oxygen for the radical site; thus, a considerable amount of polymer oxidation takes place even with the best radical scavengers. The growing importance and increasing demands for better stabilization of polymers has resulted in the synthesis of numerous hydroperoxide decomposers to be used in conjunction with known phenolic radical scavengers. The peroxide decomposer further improves the polymer stability by stopping the auto-oxidative chain through the decomposition of peroxides into stable oxidative groups.<sup>4-6</sup> Typical hydroperoxide decomposers are thioesters such as diallyl-thio-dipropionate and phosphites such as tris(nonylphenyl) phosphite. When the hydroperoxide decomposers are used in conjunction with phenols, improved polymer stability is generally reported.<sup>7</sup> In the case of thioesters, antagonistic effects have been found with selected radical scavengers.<sup>8</sup>

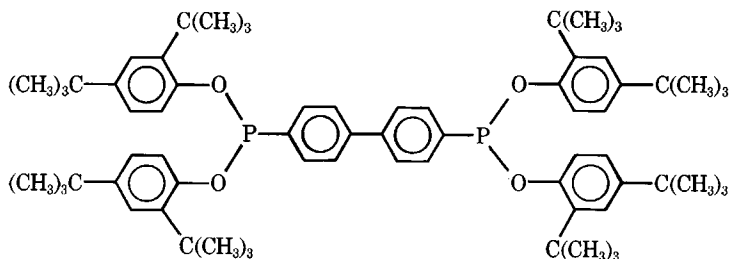
In recent years a phosphonite, tetrakis (2,4-di-tert-butylphenyl) 4,4'-biphenylene diphosphonite, has received considerable attention as a hydroperoxide decomposer that confers good polymer processing stability. In the current study this material, generally referred to as PEPQ, has been examined in polypropylene and in a model antioxidant activity system.

## EXPERIMENTAL METHODS AND MATERIALS

The details of the model antioxidant activity measurement technique are given in Ref. 9. Briefly, the measurement consists of subjecting a 2% concentration of the antioxidant in benzene with a 2% solution of benzoyl peroxide for 50 hs at a given temperature and determining the antioxidant radical concentration by electron spin resonance (ESR). The more effective antioxidant (AH) will be the one which scavenges the most radicals (R·) during the experiment, i.e.,



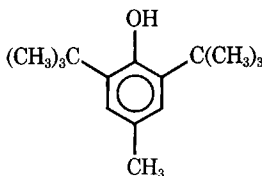
The phosphonite, PEPQ, was obtained commercially from Sandoz and has the following structure:



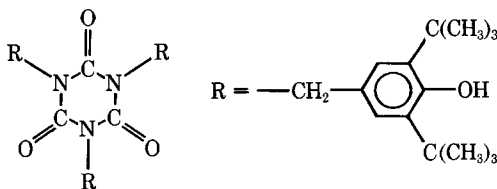
tetrakis (2,4-tert-butylphenyl) 4,4'-biphenylene diphosphonite

## RESULTS AND DISCUSSION

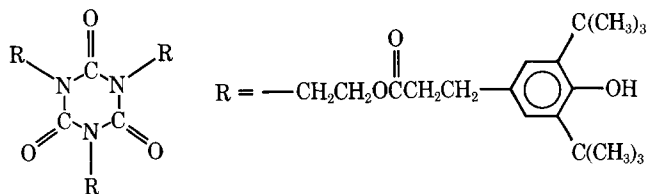
Literature results<sup>10</sup> on melt stability measurements made on polypropylene with and without PEPQ indicate dramatic improvements in process stability in the presence of phenolic radical scavengers. Although PEPQ is reported to be a hydroperoxide decomposer, the extent of melt stabilization brought about by PEPQ is hard to explain based only on hydroperoxide decomposition.<sup>7</sup> In view of the aromatic structure of the molecule, it was suspected that the PEPQ might also be working as a radical scavenger in much the same fashion as hindered phenols such as BHT:



In order to check this hypothesis, the PEPQ was subjected to a model antioxidant activity measurement developed for the purpose of measuring the relative efficiency of antioxidants to scavenge radicals.<sup>9</sup> In the model system, if radicals are observed then the additive must be behaving as a radical scavenger; otherwise, the primary radical population will decay in less time than that required for the ESR measurement. It is apparent from the radical spectrum in Figure 1 that, indeed, the PEPQ is behaving mechanistically as a radical scavenger. The actual concentration of radicals observed under these conditions was  $7.3 \times 10^{14}$  at  $65^\circ\text{C}$  as shown in Figure 2. Also shown in Figure 2 are comparative results for Goodrite 3114 and Goodrite 3125, which are well-known phenolic radical scavengers:



Goodrite 3114



Goodrite 3125

At a lower temperature, 25°C, the spin concentration of PEPQ decreased to  $1.5 \times 10^{14}$ .

The melt stability measurements for PEPQ, Goodrite 3125, and Goodrite 3114 are summarized in Figure 3. Clearly, PEPQ works as well as Goodrite 3125, although it is reported to be a hydroperoxide decomposer. At this point, it seems reasonable to conclude in view of the ESR data in Figure 2 and the melt stability data in Figure 3 that the PEPQ is behaving mainly as a primary radical scavenger and should not require a phenolic to confer polymer melt stability.

In a separate set of experiments, the irradiation stability of PEPQ was compared to Goodrite 3125 and Goodrite 3114 in polypropylene. The melt flow rates after various doses of irradiation were measured and the results are summarized in Figure 4. It is apparent that the PEPQ in the absence of a phenolic offers as much protection as a standard phenolic system such as Goodrite 3125.

Finally, the exact assignment of the radical structure for the PEPQ radical species is not clear and additional work is underway to understand the nature of the radical.

## CONCLUSIONS

In summary, PEPQ has been found to be an effective radical scavenger as measured directly by ESR techniques, although this material has been reported to be a hydroperoxide decomposer. In view of these findings, it has been shown by melt stability studies that PEPQ can be used effectively by itself without the

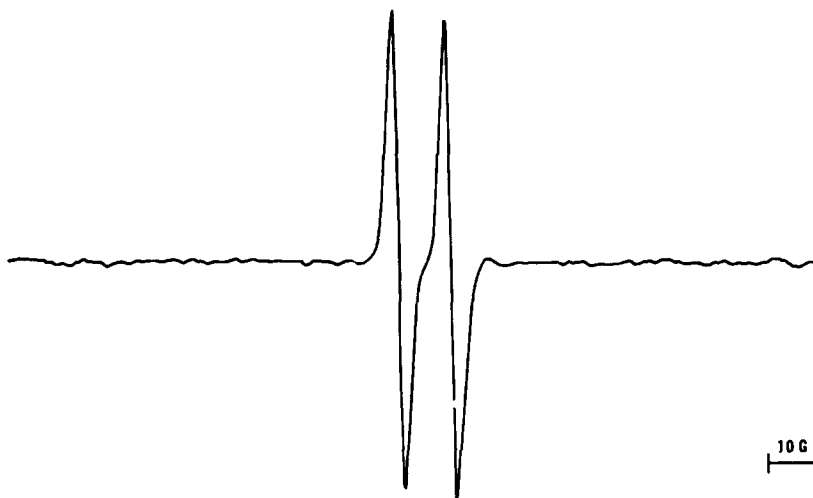


Fig. 1. PEPQ radical spectrum (9.25 GHz, 3304.0G, 200G sweep, 2.0 mW power, 4.0 modulation, 0/5-s t.c., 2-min scan).

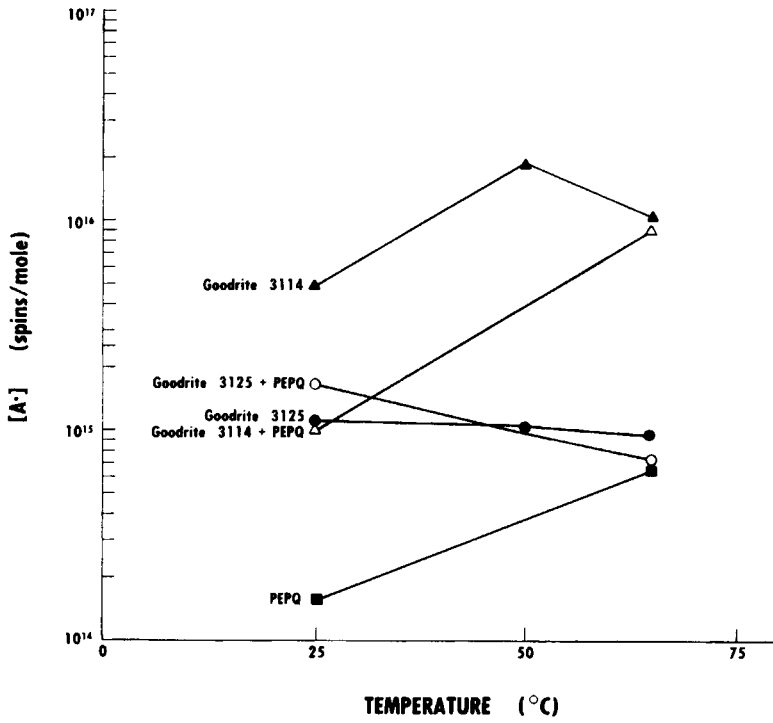


Fig. 2. Concentration of antioxidant radicals as a function of temperature.

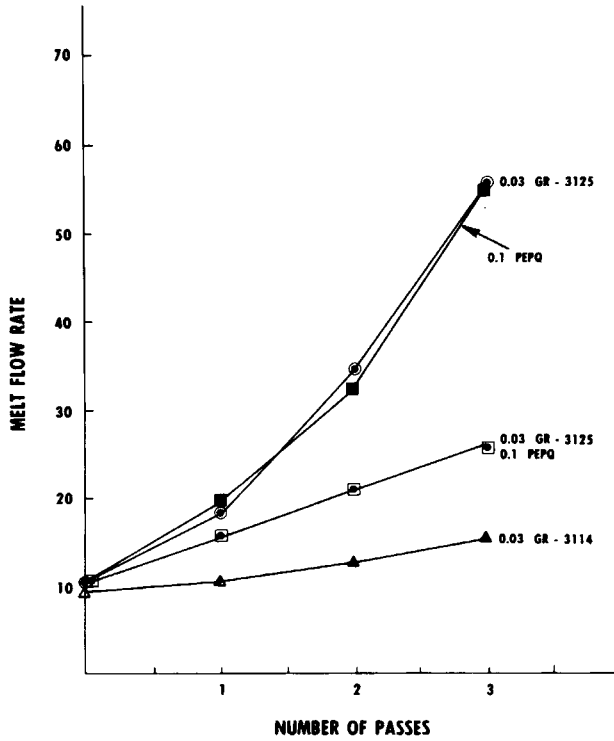


Fig. 3. Melt stability of polypropylene.

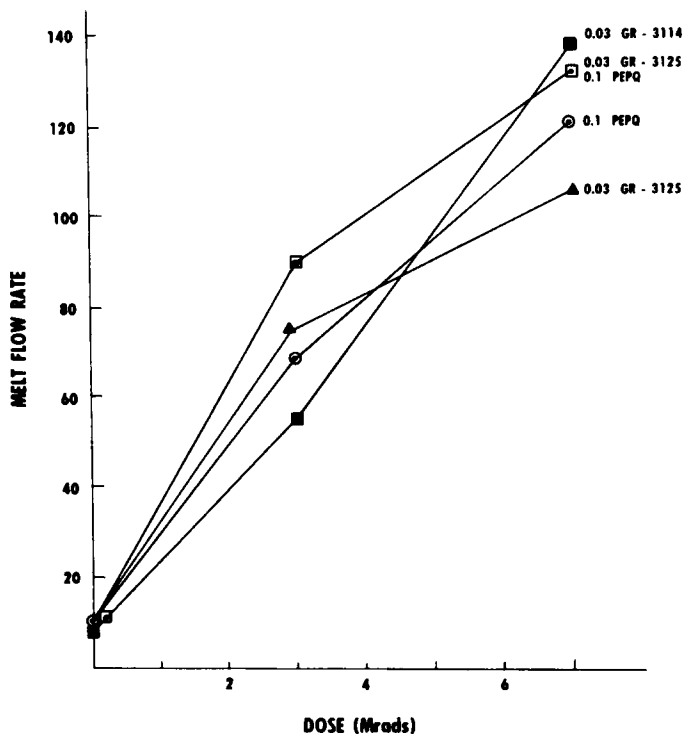


Fig. 4. Melt flow rate as a function of irradiation dose for polypropylene formulations.

addition of phenolic antioxidants which are definitely required with well-known hydroperoxide decomposers such as the thioester derivatives.

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