

# Thermal and Photooxidation of Polyolefins in the Presence of 3,5-Ditertiarybutyl 4-Hydroxybenzyl Thioglycollate, Zinc Diethyldithio Carbamate, and Irganox 1076

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## Synopsis

Three types of additives for polymers have been studied in polystyrene and poly(methyl methacrylate). The effects of a novel thermal stabilizer 3,5-ditertiarybutyl 4-hydroxybenzyl thioglycollate (DBHBT), zinc diethyldithiocarbamate (ZnDEC) have been compared with the commercial antioxidant Irganox 1076. It has been found that the new antioxidant was far more superior to the commercial antioxidant. It also acts as a peroxide decomposer. It also gave considerable synergistic effects with ZnDEC both under thermal and photo degradations. Its use is being recommended instead of the present commercial ones.

## INTRODUCTION

The stability of polymers is of critical importance and interest to manufacturers, and understandably polymer degradation and stabilization has received considerable attention.<sup>1-6</sup> In actual fact, any article made from polymers coming to tropical Africa calls for proper stabilization because of the very aggressive environment of ours on these polymeric materials; even those common polymers that are taught to be fairly stable to environmental degradation in temperate countries have been found not to be able to stand the test of time here in tropical Africa.<sup>7</sup> Consequently, polymer technologists have in recent years directed their efforts towards improving the stability of the common polymers. In the course of such studies it has been found necessary to achieve deeper understanding of the chemical mechanisms involved in the degradation of polymers, particularly of the ways in which additives modify the properties that lead to degradation or stabilization.

In the present work, the author reports on two of the most commonly used polymers in Nigeria's developing polymer industry—polystyrene and poly(methyl methacrylate). When polystyrene is subjected to UV irradiation or thermooxidative degradation, it undergoes a rapid yellowing and becomes brittle and sometimes insoluble. Industrially, these are obviously important adverse effects on the aging of polystyrene, particularly during outdoor exposure. Most of the articles made from polystyrene in the country today are used outdoor. The photooxidation and thermal oxidation of polystyrene had been extensively studied by many authors.<sup>8-16</sup> A general concensus on the mechanism of degradation is that both thermal oxidation and photooxidation of PS follows a free radical mechanism. Based on the rate of molecular weight measurements, the overall reaction could be explained in terms of initiation at the chain ends, fol-

lowed by unzipping, which produces monomer, intramolecular transfer from which dimer, trimer, and tetramer are derived, and this explains the rapid initial decrease in molecular weight. Crosslinking and insolubility may also result from combination of the macroradicals.<sup>17</sup>

Similarly, the degradation of PMMA had been studied extensively.<sup>2-14,18-23</sup> Available evidences support a free radical mechanism. Photodegradation of PMMA at low temperatures (from room temperature up to  $T_g$ ) is characterized by chain scission of the main chain carbon-carbon bonds. At high temperatures  $>T_g$  degradation is a typical depolymerization reaction. Burlant<sup>24</sup> has demonstrated that incorporation of styrene as a comonomer stabilized PMMA. Lead stearate and aromatic compounds were also found to act as protectants for PMMA.<sup>25</sup> Also a great deal of stabilization of PMMA is achieved by copolymerization with a small concentration of a second monomer which is incapable of being liberated from the polymer chain by depolymerization. Acrylates were found to be effective for this purpose and have been used industrially. As little as 1 part in 400 of PMMA of copolymerized acrylonitrile was found to inhibit degradation completely. Grassie and Melville<sup>20</sup> have also found that 1,4-diamino anthraquinone powerfully inhibited the degradation of PMMA.

In this study, the author has reacted a newly synthesized antioxidant with PS and PMMA to see whether it will act as a good thermal stabilizer for saturated polyolefins. The effectiveness of this antioxidant as a thermal stabilizer and peroxide decomposer has been compared with some of the commercially available ones.

## EXPERIMENTAL

### Materials

The polymers used in the present study were polystyrene (PS) granular (beads) and poly(methyl methacrylate) (PMMA) granular (beads) form, containing no additives. The polymers were supplied by Polysciences, Inc. They were further purified by reprecipitations. The molecular weights were determined from solution viscosity; polystyrene,  $M_v = 28,000$ , PMMA,  $M_v = 25,300$ . Irganox 1076, a commercial antioxidant, was supplied by Ciba-Geigy. The zincdiethyldithiocarbamate (ZnDEC) was prepared by double decomposition of a 10% solution of the corresponding sodium salt with a saturated solution of zinc sulphate. The new antioxidant 3,5-ditertiarybutyl 4-hydroxybenzylthioglycollate (DBHBT) was prepared, as described elsewhere.<sup>26</sup>

### Compounding

The various additives were mixed with the polymers in our new Rheocord EU, Torque Rheometer supplied by HAAKE, Inc., Saddle Brook, NJ, using closed chambers using a standard quantity of material (50 g batches of polymer). The processed samples were cooled immediately and stored in the dark.

### Preparation of Film

Films were compression-molded using stainless steel glazing plates. The plates were thoroughly cleaned before use to ensure a smooth surface and to prevent film sticking. Antistick mold-release lubricant was also used for this purpose. Film thickness was controlled by using a standard quantity of polymer. About 2 g of polymer was found to produce a film approximately  $5.0 \times 10^{-3}$  cm thick. The weighed amount of processed polymer-additive mixture was placed between the glazing plates and inserted into the press. The plattens were maintained at 150–155°C in the case of PS and 120–125°C in the case of PMMA. After pressing, the glazing plates were removed and allowed to cool at room temperature. The films were then removed and stored in the dark. Portions having uniform thickness were cut off for testing.

### Methods of Following Degradation

It is obviously preferable, where possible, to make the comparison of the weatherability of commercially available plastics with reference to those properties of practical importance, especially the mechanical properties. However, the marked dependence of mechanical properties on test procedure and test piece history, unrelated to weathering, introduces a lot of errors into the test results to such an extent that assessment of comparative stability is very difficult if not impossible. Because of this difficulty, it was decided to monitor the chemical changes in the microstructure occurring during degradation by the use of infrared spectroscopy. All spectra were recorded using a Perkin-Elmer Infrared Grating Spectrophotometer Model 1000.

### Testing Procedure

#### *Thermal Oxidation*

The accelerated thermal oxidation of processed polymer films was carried out in a Wallace air oven at 100°C. Each sample was contained in a separate cavity. The degradation was followed by running the IR spectra of the films at regular time intervals.

#### *Photooxidation*

Accelerated photooxidation of the polymer films was carried out by exposing the films to UV light of wavelength 254 nm at 30°C. The degradation was followed by running the IR spectra at regular time intervals.

### Embrittlement Test

The specimens were tested at 8-h intervals for embrittlement. The test was carried out by bending the specimen twice at 180°C. The first bending was performed towards the irradiated surface, and the second was carried out next but towards the unirradiated surface.

## IR Spectroscopy

The degradation was expressed quantitatively in terms of carbonyl index and Hydroxyl index. These indices were calculated as previously described.<sup>17,26</sup>

## RESULTS AND DISCUSSION

The stabilizing effects of 3,5-ditertiarybutyl 4-hydroxybenzyl thioglycollate (DBHBT) have been compared with zinc diethyldithiocarbamate (ZnDEC) and Irganox 1076, both being commercial antioxidants. The degradation of PS and PMMA during oven aging, UV irradiation, and natural weathering with and without these additives have been studied. Synergistic mixtures have also been investigated.

## Thermal Oxidative Degradation of Polystyrene

When polystyrene was degraded in an air oven at 100°C, the degraded samples exhibited growths in the bands corresponding to the carbonyl at 1740  $\text{cm}^{-1}$  and a peak at 1680  $\text{cm}^{-1}$ , which corresponds to unsaturated carbonyls. As degradation continued, the peak at 1680  $\text{cm}^{-1}$  became a shoulder to the peak at 1740  $\text{cm}^{-1}$ . The sharp band in the IR spectra at 3600  $\text{cm}^{-1}$  due to —OH stretching of the free hydroperoxide was also seen to grow as degradation continued.

Figure 1 shows the dependence of the hydroxyl index on time of oven aging. The control has an induction period of about 35 h and an embrittlement time of about 300 h. When the commercial phenolic antioxidant Irganox 1076 was incorporated into PS, the thermal stability of the polymer was greatly improved. An induction period of almost 135 h was obtained with an embrittlement time of over 1000 h. However, in the presence of ZnDEC and DBHBT, the hydroxyl index can be seen to fall initially; this is then followed by a constant value and then finally a rise. The fall in the hydroxyl index corresponds to the consumption of hydroperoxide formed during processing. Thus we see that the additives have

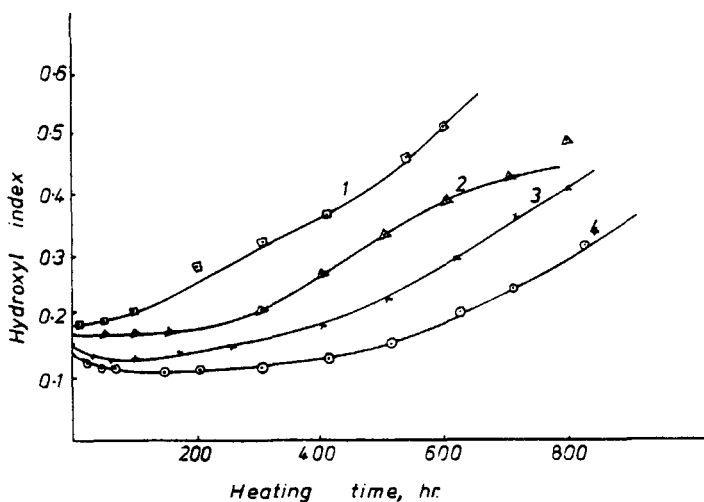


Fig. 1. Effect of antioxidants and stabilizers on the rate of thermal oxidation of PS at 100°C (all additives at  $4.0 \times 10^{-3}$  mol/100 g): (1) control (no additives), (2) PS + Irganox 1076, (3) PS + ZnDEC, (4) PS + DBHBT.

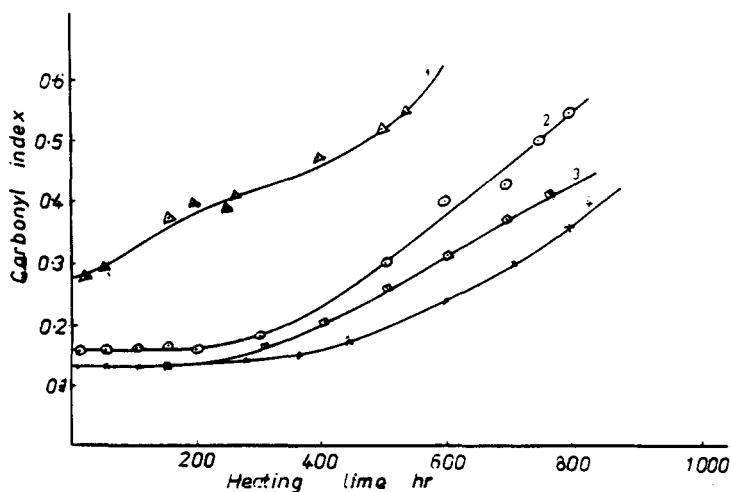


Fig. 2. Effect of antioxidants and stabilizers on the rate of oxidation of PS at 100°C. The ordinate indicates the carbonyl index; the abscissa indicates heating time (h): (1) control, (2) Irganox 1076, (3) ZnDEC, (4) DBHBT.

abilities to decompose hydroperoxides as they are formed, i.e., hydroperoxides formed during processing and those formed from the hydroxyl group which generate during oxidation are consumed by these additives. This behavior is found with all the samples containing either DBHBT or ZnDEC or their mixtures but absent in the samples containing Irganox 1076. It does appear that both ZnDEC and DBHBT act by similar mechanisms different from Irganox 1076 in their stabilization of PS.

Figure 2 shows the plot of carbonyl index against heating time. Of the three additives it can be seen that the newly synthesized antioxidant performed best. Table I compares the efficiency of these additives.

A most interesting aspect of a work of this nature is to find a stabilizer or a combination of stabilizers which will give rise to synergism. The extent of

TABLE I  
Comparison of Antioxidants in Polystyrene (Concentration of All Additives  
 $4.0 \times 10^{-3}$  mol/100 g)

Antioxidant	Induction period (h)	Calculated effect based on additivity law (h)	% Synergism <sup>a</sup>
Control (no additive)	35	—	—
Irganox 1076	135	—	—
ZnDEC	180	—	—
DBHBT	225	—	—
Irganox 1076 + ZnDEC	405	315	51
Irganox 1076 + DBHBT	365	360	14
ZnDEC + DBHBT	615	405	73

$$^a \text{ \% synergism} = \frac{I_s + I_c - I_1 - I_2}{I_1 + I_2 - 2I_c} \times 100$$

where  $I_s$  = induction period of synergist,  $I_c$  = induction period of control,  $I_1$  = induction period of antioxidant 1,  $I_2$  = induction period of antioxidant 2.

synergism as illustrated in Table I is not extremely high, but, nevertheless, is significant, particularly with ZnDEC and DBHBT combination. From Figure 3, it can be seen that, in the case of Irganox 1076 and ZnDEC combination, the postinduction slope is rather steep whereas, in the other two combinations, the slopes rise very gently after the induction period. This means that the synergistic mixtures will not only be good at protecting the polymer during fabrication but that the products so produced will have a long service life. The embrittlement times were seen also to follow the order of the induction periods.

### Photooxidation of Polystyrene

The dependence of the carbonyl group development during UV irradiation (254 nm) on time is illustrated in Figures 4 and 5. It can be seen that the conventional antioxidant Irganox 1076 imparts some UV stability to PS under UV degradation. It has been shown that both thermal oxidation and photo oxidation of PS follow a free radical mechanism.<sup>12,13</sup> Therefore, even though Irganox 1076 is not classified as a UV stabilizer, it can still impart UV stability by interacting with polystyryl radicals and thereby terminating chain reactions. Both ZnDEC and DBHBT impart considerable UV stability to PS. The UV stability activity of these additives is attributable to the sulphur products in part and to some energy transfer processes, particularly in the case of ZnDEC. Result of the synergistic mixtures are presented in Figure 5 and Table II.

The control had an embrittlement time of about 200 h whereas the combination of additives gave embrittlement periods several times more than the control. The combination ZnDEC and Irganox 1076 proved a better synergist than the Irganox 1076—DBHBT combination. However, the ZnDEC—DBHBT mixture gave the highest percent synergism.

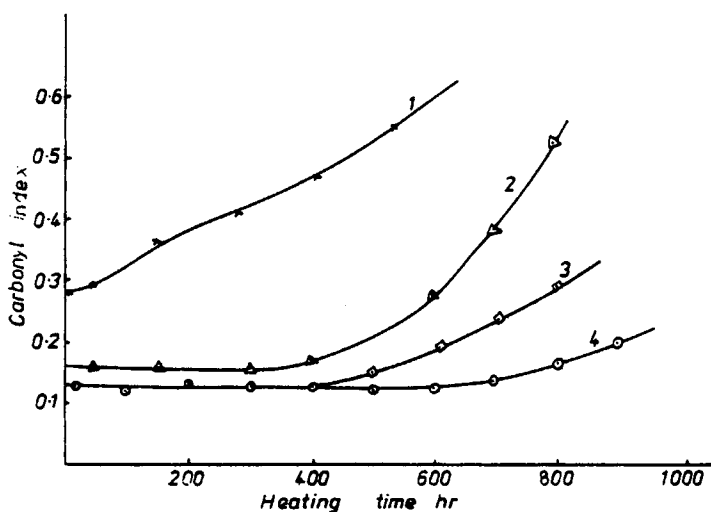


Fig. 3. Effects of combination of antioxidants and stabilizers on thermal oxidation of PS (concentration of all additives at  $4.0 \times 10^{-3}$  mol/100 g): (1) control, (2) Irganox 1076 + DBHBT, (3) Irganox 1076 + ZnDEC, (4) DBHBT + ZnDEC.

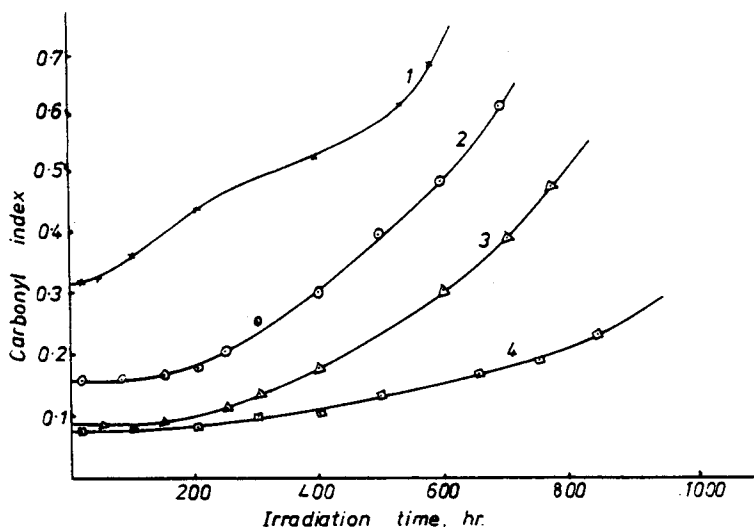
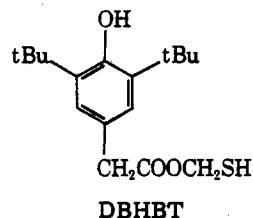
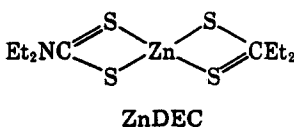
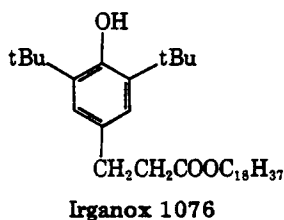


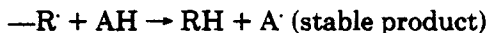
Fig. 4. Effect of additives on the rate of photo oxidation of PS at a 254 nm: (1) control, (2) PS + Irganox 1076, (3) PS + DBHBT, (4) PS + ZnDEC.

### Stabilizing Activities of the Additives

The structure of the additive is believed to play very significant roles in the stabilization activities in the polymers. The structure of the additives are shown as follows:



Irganox 1076 is known to act by interrupting the chain reactions by combining with propagating free radical species<sup>27</sup> and thus forming a non-reactive stable product.



Here R $\cdot$  represents the polystyryl radical and AH the Irganox 1076. The lack of activity of the reaction product derives from resonance stabilization or possible hydrodimerization with other species. So structurally, both Irganox 1076 and DBHBT should behave as good antioxidants both acting by a chain-breaking mechanism. These antioxidants operate by removing from the reaction medium the two important species normally involved in chain propagation step, i.e., alkyl peroxy and alkyl radicals. In addition to its ability to act as a chain-breaking antioxidant through its phenol group and resonance stabilization, DBHBT is able to act as peroxide decomposer. It removes peroxide radicals as soon as they

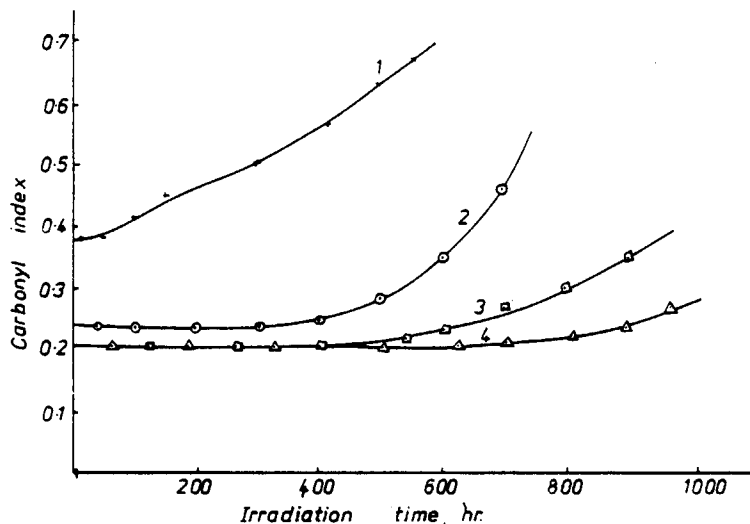
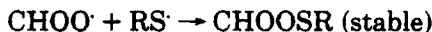
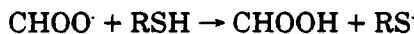


Fig. 5. Effects of combination of additives on the rate of photo oxidation of PS at 254 nm (concentration of all additives at  $4.0 \times 10^{-3}$  mol/100 g): (1) control, (2) Irganox 1076 + DBHBT, (3) Irganox 1076 + ZnDEC, (4) ZnDEC + DBHBT.

are formed, thereby arresting hydroperoxide photolysis from beginning:



In effect, it means that DBHBT is able to act both as a primary and a secondary stabilizer. This explains why it behaves as a very good thermal stabilizer.

Nickel compounds have been found to interact with photoexcited molecules, deactivating them by dissipating excess energy as IR radiations. Briggs and McKeller<sup>28</sup> in their work with polypropylene and Scott<sup>27</sup> have also demonstrated the effectiveness of a series of nickel complexes as UV stabilizers. Chakraborty and Scott<sup>29</sup> have also shown that the effectiveness of nickel dialkyldithiocar-

TABLE II  
Photooxidative Stability of Polystyrene in Presence of antioxidants (Concentration of All Additives  $4.0 \times 10^{-3}$  mol/100 g)

Antioxidant	Embrittlement time (h)	Calculated effect based on additive law	% synergism*
Control	200	—	—
Irganox 1076	540	—	—
ZnDEC	600	—	—
DBHBT	900	—	—
Irganox 1076 + ZnDEC	1500	1140	75
Irganox 1076 + DBHBT	1656	1440	40
ZnDEC + DBHBT	2452	1500	105

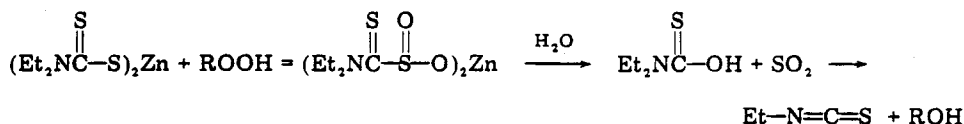
$$* \% \text{ synergism} = \frac{E_s + E_c - E_1 - E_2}{E_1 + E_2 - 2E_c} \times 100$$

where  $E_s$  = embrittlement time for synergist,  $E_c$  = embrittlement time for control,  $E_1$  = embrittlement time for antioxidant 1,  $E_2$  = embrittlement time for antioxidant 2.



bamates as UV stabilizers is a function of their role as catalysts for the nonradical decomposition of hydroperoxides and that Irganox 1076 synergizes with NiDBC as a thermal stabilizer.

The action of ZnDEC in thermal oxidation and photooxidation of PS is thought to be due to a combination of its stability to decompose peroxides direct by absorbing UV light and quenching the polymer-excited states by energy transfer mechanism. The ability of ZnDEC to decompose hydroperoxide in a nonradical mechanism may be represented as follows:



It is presumed that synergism arises because inhibition can be affected at different stages in the oxidative reaction. Therefore, combinations of additives which suppress oxidation at different stages will be particularly effective. DBHBT suppresses the rate of initiation, but, as each oxidative chain is terminated, a molecule of peroxide is formed. Decomposition of peroxides which would yield radical and make the reactions autocatalytic is prevented in the presence of DBHBT or ZnDEC. In this way additional radicals are not formed, and these additives are preserved, thus yielding excellent stabilization.

The activities of DBHBT and ZnDEC are also enhanced because they act as reservoirs of potentially available sulphur oxides which could act as powerful antioxidants when they diffuse into the polymer and act as UV stabilizing agents. This assertion is also reinforced by the work of Amin and Scott<sup>30</sup> on low-density polyethylene. They showed that zinc, nickel, and cobalt complexes are relatively stable to oxidative treatments at high temperatures and that the processes leading to their destruction involves reaction with hydroperoxides and the products formed, notably SO<sub>2</sub>/SO<sub>3</sub>, which are powerful antioxidants. Because DBHBT and ZnDEC or the other combinations shown in Tables I and II interfere at different points in the autooxidation processes, they mutually reinforce one another, leading to an effect greater than the sum of the effects of each additive alone. This is synergism.

As well as being complementary in mechanism, the two classes of antioxidants also complement each other in their response to environmental conditions, thereby giving rise to protection over a broader period of time and a wider range of environmental conditions, which we experience in Nigeria.

### Thermal Oxidation of Poly(methyl Methacrylate)

The above-mentioned additives have also been incorporated into PMMA. The interest here is centered on how the newly synthesized antioxidant compares with the market samples. In the study with PMMA, the development of the hydroxy content of the thermally degraded and photodegraded samples have been monitored.

Figures 6 and 7 and Table III is a summary of the results obtained from the

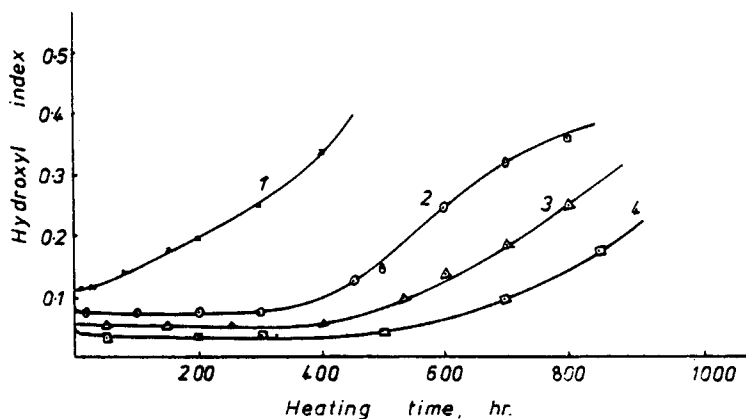


Fig. 6. Effects of combination of additives on the thermal oxidation of PMMA: (1) control (no additives), (2) PMMA + Irganox 1076 + DBHBT, (3) PMMA + Irganox 1076 + ZnDEC, (4) PMMA + ZnDEC + DBHBT.

experiments. Figure 6 shows a plot of the hydroxyl index against the time of thermal oxidation in an air oven. The unstabilized sample is seen to degrade very fast with an induction period of 25 h. Again, as in the case of PS, an initial fall in the hydroxyl index was observed. This means that during the thermal processing some hydroperoxide groups were formed, and these were later consumed by the DBHBT. When incorporated individually into PMMA, the thermal efficiency of the additives follow the order.

Irganox 1076 < ZnDEC < DBHBT. This, is in the case of PS, shows that the new antioxidant is superior to the commercially available ones. This has been found to be true when incorporated into ABS<sup>26</sup> and when grafted into Nigeria natural rubber.<sup>31</sup> Figure 6 shows the combination effect of the additives when heated in air oven. The greatest stabilization is obtained with the system con-

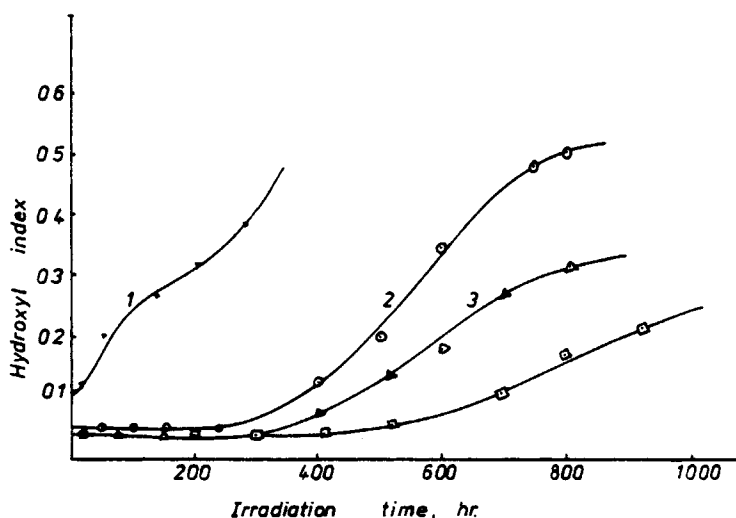


Fig. 7. Effects of combination of additives on the photo oxidation of PMMA at 254 nm (concentration of all additives at  $4.0 \times 10^{-3}$  mol/100 g): (1) control, (2) Irganox 1076 + DBHBT, (3) Irganox 1076 + ZnDEC, (4) ZnDEC + DBHBT.

TABLE III  
Effect of Combination of Additives on Thermal Oxidation and Photooxidation of PMMA  
(Concentration of All Additives at  $4.0 \times 10^{-3}$  mol/100 g PMMA)

Antioxidant	Embrittlement time (thermal oxidation) (h)	Embrittlement time (photooxidation) (h)
Control	100	140
Irganox 1076	430	380
ZnDEC	600	500
DBHBT	800	500
1076 + ZnDEC	1972	1135
1076 + DBHBT	1624	1070
ZnDEC + DBHBT	1884	1492

taining the ZnDEC—DBHBT combination, and the system containing the Irganox 1076—DBHBT mixture gave the worst performance. Similar observations have been made with PS. This is, however, surprising given the fact that DBHBT is a better thermal stabilizer than ZnDEC. One would have expected it to give a better thermal performance with Irganox 1076—DBHBT than with Irganox 1076—ZnDEC, which is obtained in this result. It is suggested that both Irganox 1076 and DBHBT are structurally similar, except that the latter contains a terminal sulphur group which can itself impart additional stabilization. On the other hand, the addition of Irganox 1076 to a structurally different additive, and one that acts by a different mechanism, ZnDEC, brings to play a higher mutual enhancement of their stabilization effects. This is why one obtains a greater synergistic effect with Irganox 1076/ZnDEC than with Irganox 1076/DBHBT.

### Photodegradation of PMMA

Figure 7 and Table III show the effect of UV irradiation at 254 nm on the hydroxyl group development of PMMA film samples. The figure and the table illustrate the synergistic activities of these additives. Table III shows that ZnDEC offers the greatest stability to PMMA under UV irradiation. However, a combination of ZnDEC and DBHBT gives the best protection to the polymer films under UV irradiation. Table III also shows that PMMA is more stable under thermal oxidation than under UV degradation. This again goes to prove the superiority of new antioxidant to the commercially available ones.

### CONCLUSIONS

From the results of the investigations with PS and PMMA, it can be concluded that under thermal oxidative degradation, the effectiveness of the additives is in the order DBHBT > ZnDEC > Irganox 1076. Presently, Irganox 1076 is used commercially; the use of DBHBT as a substitute is highly recommended. Its presence in polymers, both unsaturated<sup>26</sup> and saturated, allows for longer processing time and at high temperatures if so desired. A two-component stabilizer of ZnDEC and DBHBT performed much better than DBHBT alone both under thermal and UV oxidation. DBHBT is easier to prepare and has a high yield. Its use will be of economic value.

## References

1. *Chemistry of High Polymer Degradation Processes*, N. Grassie, Ed., Interscience, New York, 1956.
2. *Degradation of Vinyl Polymers*, H. H. Jellinek, Ed., Academic, New York, 1955.
3. *Elements of Polymer Degradation*, L. Reich and S. Stivals, Eds., McGraw-Hill, New York, 1971.
4. *Atmospheric Oxidation and Antioxidants*, G. Scott, Ed., Elsevier, New York, 1965.
5. *Polymer Stabilization*, W. L. Hawkins, Ed., Interscience, New York, 1972.
6. *Thermal Degradation of Organic Polymers*, S. L. Madorsky, Ed., Interscience, New York, 1964.
7. E. G. Kolawole, unpublished results.
8. N. Grassie and N. A. Weir, *J. Appl. Polym. Sci.*, **9**, 963 (1965).
9. J. L. Bolland and P. Tentare, *Discuss. Faraday Soc.*, **2**, 252 (1947).
10. J. H. Adams, *J. Polym. Sci.*, **8**, 1077 (1970).
11. H. C. Beachell and L. H. Smiley, *J. Polym. Sci.*, **5**, 1635 (1967).
12. J. F. Rabek and B. Ranby, *J. Polym. Sci.*, **12**, 273 (1974).
13. B. Ranby and J. F. Rabek, in *Photodegradation, Photooxidation and Photostabilization of Polymers*, Wiley, New York, 1975, pp. 165-184.
14. J. B. Lawrence and N. A. Weir, *J. Polym. Sci.*, **11**, 105 (1973).
15. J. Lucki and B. Ranby, *Polym. Degr. Stabilization*, **1**, 1 (1979).
16. J. Lucki, J. F. Rabek, and B. Ranby, in *IUPAC Symposium on Long Term Properties of Polymers and Polymeric Materials*, Stockholm Aug. 30-Sept. 1, 1976.
17. E. G. Kolawole and M. O. Agboola, *J. Appl. Polym. Sci.*, to appear.
18. I. C. McNeill, *Eur. Polym. J.*, **6**, 373 (1970).
19. I. C. McNeill, *Eur. Polym. J.*, **4**, 21 (1968).
20. N. Grassie and H. W. Melville, *Proc. Roy. Soc. (Lond.) A*, **199**, 1 (1949).
21. P. R. E. J. Cowley and H. W. Melville, *Proc. Roy. Soc. (Lond.) A*, **210**, 461, (1968).
22. N. Grassie, I. C. McNeill, and I. Cooke, *J. Appl. Polym. Sci.*, **12**, 831 (1968).
23. I. C. McNeill and D. Neil, *Eur. Polym. J.*, **6**, 143 (1970).
24. W. D. Burlant, *J. Appl. Polym. Sci.*, **1**, 296 (1959).
25. D. G. Gardner et al., *J. Chem. Phys.*, **34**, 1653 (1961).
26. E. G. Kolawole and J. B. Adeniyi, *Eur. Polym. J.*, to appear.
27. G. Scott, in *Developments in Polymer Degradation*, N. Grassie, Ed., Applied Science Publishers, London, 1977, Vol. 1.
28. P. J. Briggs and J. F. McKeller, *J. Appl. Polym. Sci.*, **12**, 1825 (1968).
29. K. B. Chakraborty and G. Scott, *Eur. Polym. J.*, **13**, 1007 (1977).
30. M. U. Amin and G. Scott, *Eur. Polym. J.*, **10**, 1019 (1974).
31. G. Ebi, M. Sci. dissertation, Ahmadu Bello University, Zaria, Nigeria, 1982.

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