

THE EFFECT OF 3,5-DITERT.BUTYL-4-HYDROXYBENZYLTHIOGLYCOLLATE AND TINUVIN P ON THE THERMAL, PHOTO AND NATURAL DEGRADATION OF ABS

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Abstract—A newly synthesized antioxidant 3,5-ditert.butyl-4-hydroxybenzyl thioglycollate (DBHBT) and Tinuvin P have been used as additives for normal ABS. The thermal and photo-oxidative stabilities of the polymer containing these additives have been compared with those for unstabilized ABS. It is concluded that the new additive gives very good thermal stability to ABS and acts as a peroxide decomposer. It was found that it could be grafted on to the polymer backbone during processing. Synergism was obtained with a combination of Tinuvin P and DBHBT. It was found that considerable protection was offered to the base polymer when ABS containing these additives was exposed to weathering.

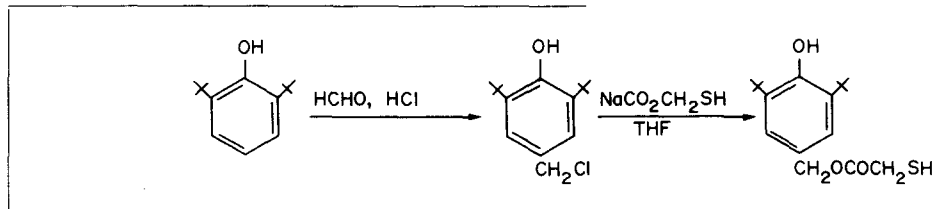
INTRODUCTION

It is known that acrylonitrile-butadiene-styrene (ABS) is a terpolymer which exhibits a desirable combination of mechanical, thermal, chemical and electrical properties together with ease of processing and moderately low cost; the performance of the polymer

further purification. The new thermal stabilizer 3,5-ditert.-butyl-4-hydroxybenzylthioglycollate (DBHBT) was synthesized in our laboratory.

Preparation of 3,5-ditert.butyl-4-hydroxyl-benzylthioglycollate (DBHBT)

The following two stage procedure was followed:



as regards weatherability outdoors is, however, very poor. This is obviously a serious technological problem; hence the stabilization and degradation of ABS have been the subject of several recent studies [1-4]. In our earlier paper, we investigated the stabilization of ABS through masterbatch additives [5]. In this paper we report on the effect of Tinuvin P (a commercial u.v. stabilizer) and a newly synthesized thermal stabilizer—3,5-ditert.butyl-4-hydroxybenzylthioglycollate (DBHBT) on ABS. This work has involved processed films to which these additives have been added at appropriate stages.

EXPERIMENTAL

Materials

The ABS polymer was supplied by Borg-Warner Chemicals Ltd as Cylolac R211; Tinuvin P 2-(2H-benzotriazol-2-yl)-p-cresol, a commercial stabilizer, was used without

(i) A known weight of 2,6-ditert.butyl phenol and 0.002% w/w ferric chloride:phenol were placed in a three-necked flask. 0.5% w/w of paraformaldehyde-phenol was added to the flask. This was immediately followed by 500 cm³ of concentrated HCl and vigorously stirred. HCl gas was also passed into the mixture. The mixture was stirred for several hours at the end of which it separated into two layers and the lower aqueous layer was discarded. The organic top layer was extracted with ether, washed neutral with Na₂CO₃ solution. The extract was dried with anhydrous MgSO₄ and the ether was distilled off by rotary evaporation. Finally, the 3,5-ditert.butyl-4-hydroxybenzylchloride was collected by vacuum distilling at 141° as a red liquid.

(ii) The 3,5-ditert.butyl-4-hydroxybenzylchloride was converted by the process of thioacetylation into the thio derivative. Sodium salt of thioglycollate was made in ethanolic medium. Excess of solvent was removed to avoid solvolysis of the very reactive benzyl halide derivative. Dry redistilled THF was put into the flask containing the sodium thioglycollate and this was followed by the halide. The mixture was refluxed for some hours under N₂. The solid which separated was purified in hexane. The melting point was 110°.

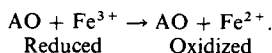
Chemical determination of bound antioxidant

The method used was one based on that developed by Metcalf and Tomlinson [6] with slight modification.

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Essentially, the method involves oxidation of the antioxidant under controlled conditions using ferric ions.



In the reaction, the Fe^{2+} ions produced react with 2,2-bipyridyl to form coloured complexes with intensity proportional to the concentration of the antioxidant.

Method. Processed ABS (10.0 g) containing DBHBT was ground into fine powder and extracted continuously with hot benzene in a Soxhlet extractor for 48 h.

The extract was rotary evaporated and the residue dissolved in 10 cm³ toluene (AR). Alcohol (10 cm³) was added to precipitate any residual polymer. The solution was filtered and made up to 50 cm³ with absolute alcohol.

Two dry 10-cm³ volumetric flasks painted with several layers of black paint were immersed in a water bath at $25 \pm 0.5^\circ$. Filtrate (1.0 cm³) was pipetted into one and 1.0 cm³ 25/75 (v/v) toluene-ethanol mixture into the other. Dipyrldyl solution (0.5 cm³) was added to the flasks and made up to the volume with toluene-ethanol mixture. The flasks were allowed to stand for 1 h in the thermostat. The optical density of the solution was measured at 520 nm and the concentration read from a calibration curve previously prepared. From this, the amount of bound DBHBT was obtained. It was found that up to 40% of the added antioxidant was bound to the polymer.

Processing and film pressing. Mechanical mixtures of ABS with and without additives were homogenized in a RAPRA torque rheometer at 190° . Samples containing the additives were processed for various periods between 2 and 10 min. Films (0.0025–0.003 in.) were moulded for 1½ min (after preheating for 1½ min) under pressure at 190° .

Testing. The degradation of commercially available plastics has often been monitored in terms of the changes in mechanical properties. However, the results are markedly dependent on test procedure and on the test-piece history which in themselves are unrelated to weathering. This feature introduces errors into test results to such an extent that assessment of comparative stability becomes unreliable and often irreproducible. This irreproducibility and dependence of results of mechanical studies on factors besides weathering have prompted the authors to direct attention to monitoring of the chemical changes during degradation by means of i.r. spectroscopy.

The advantages of this method of monitoring degradation arise because examining thin films by transmission spectroscopy permits the course of degradation to be followed without damage to or interference with the test area. Also, the use of transmission spectroscopy minimizes any intensity loss due to reflection at the outer and inner surfaces. It is also a non-destructive test and eliminates from the results the specimen-to-specimen variation inseparable from destructive tests. All spectra were recorded using a Perkin-Elmer i.r. spectrophotometer model 1000.

Oven ageing. Accelerated thermal oxidation of ABS films was carried out by mounting samples on specially prepared cardboard holders which were suspended with Cu wires in the cavity of the Wallace air-oven at 100° . Each sample film was contained in a separate cavity. The degradation was followed by running the i.r. spectra at regular intervals.

Irradiation procedure. Accelerated indoor weathering of ABS films were carried out by exposing films to u.v. light of 254 nm at 30° . Again, degradation was followed by running i.r. spectra.

Infra-red spectroscopy measurement. The measurements of carbonyl, hydroxyl and *trans*-1,4-polybutadiene absorbances were carried out by recording the spectra between 4000 and 600 cm⁻¹. The peak at 2222 cm⁻¹ corresponding to the CN group of the acrylonitrile was used as a reference peak. The growth or decay of the monitored peaks were expressed as indices. The indices were defined as the ratio of the absorbance of the growing or diminishing peaks to that of the reference peak.

RESULTS AND DISCUSSION

A common feature is that the spectra of degraded samples exhibited growth in the bands corresponding to the carbonyl group (1720 cm⁻¹) and hydroxyl group (3450 cm⁻¹) with decrease in the bands corresponding to poly*trans*-1,4-butadiene and polycyclic 1,4-butadiene at 965 and 910 cm⁻¹. During the heating of the films in the Wallace oven, the nitrile and the phenyl absorbances at 2222 and 1960 cm⁻¹, respectively, showed no changes, indicating that splitting of the phenyl or nitrile group does not occur.

A yellow discoloration was also observed in the films during degradation, the intensity increasing with

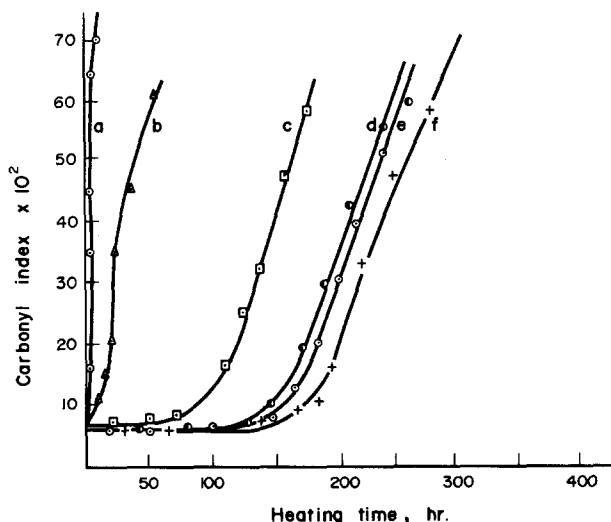


Fig. 1. Thermal oxidation of ABS. Dependence of carbonyl index upon heating time for ABS containing varying concentrations of DBHBT. (a) Control—normal ABS; (b) ABS + 0.2% DBHBT; (c) ABS + 0.5% DBHBT; (d) ABS + 2.0% DBHBT; (e) ABS + 1.5% DBHBT; (f) ABS + 1.0% DBHBT.

Table 1. Induction periods produced by addition of 1% w/w DBHBT-ABS and then processed for various periods

g DBHBT-100 g ABS	Processing time (min)	Induction period (h)
1.0 (3.6×10^{-3})	2	60
1.0 (3.6×10^{-3})	3	175
1.0 (3.6×10^{-3})	5	120
1.0 (3.6×10^{-3})	7½	90

Figures in parentheses are the molar concentrations of the added stabilizers per 100 g polymer.

increasing time of exposure. The degraded samples also became insoluble in dichloromethane and acetone indicating some cross-linking [7].

For ABS containing additives, the bands of interest exhibited initial induction periods after which the peaks at 965 and 910 cm^{-1} diminished while those at 1720 and 3450 cm^{-1} increased. Induction period is taken to mean the time during which the added stabilizer or antioxidant has an arrestive power on the degradation of the polymer sample.

Thermal oxidative degradation

Part of the present study involves the incorporation of a new antioxidant DBHBT into ABS to prevent formation of hydroperoxide which would otherwise be formed and lead to auto-oxidation of ABS. We wish to discover how this new antioxidant protects ABS under long processing periods and also to examine the effect of concentration.

In addition to the peaks mentioned above, other bands were observed to increase at 1650 and 1820 cm^{-1} during the initial stages of heating. The peaks probably correspond to unsaturated acids and ketones, respectively. They later became shoulders to

the main peak at 1720 cm^{-1} on prolonged heating. Another significant peak occurred at 1587 cm^{-1} . Shimada and Kabuki [1] reported that the stretching frequency of carbon-carbon double bonds does not change during low-temperature degradation; we find, however, that the carbon-carbon stretching band of the terminal bond at 1587 cm^{-1} increases very slightly after some time.

In order to determine the effect of concentration on the stability of ABS towards thermal oxidative degradation, various amounts of DBHBT have been added to ABS before processing for 3 min. It can be seen from Fig. 1 that the sample which contains 1% w/w DBHBT-ABS performed best. Industrially, however, amounts of this antioxidant exceeding 1% w/w in the base polymer will not be economically viable.

The thermal stability of the antioxidant DBHBT has also been investigated. Table 1 shows the results obtained when ABS containing 1% w/w DBHBT was processed for various periods. The stability has been measured in terms of the induction periods. It is clear that the sample processed for 3 min gives the best result. The poor stability for samples processed for longer periods is believed to be due to excessive oxidation of the polymer during processing.

On the other hand, 2 min processing is too short because antioxidant will not be evenly mixed with the base polymer. This effect may lead not only to agglomeration of the antioxidant and under-utilization but could also lead to loss by volatilization during processing.

Figure 2 compares the effect of the two additives during thermal treatment for the unextracted and extracted samples. It can be seen that, while the unstabilized polymer shows no induction period, DBHBT offers very considerable protection to the polymer during heating. Tinuvin P, although not a thermal stabilizer, offers some protection to ABS. In this figure, the additives are present at 1% w/w

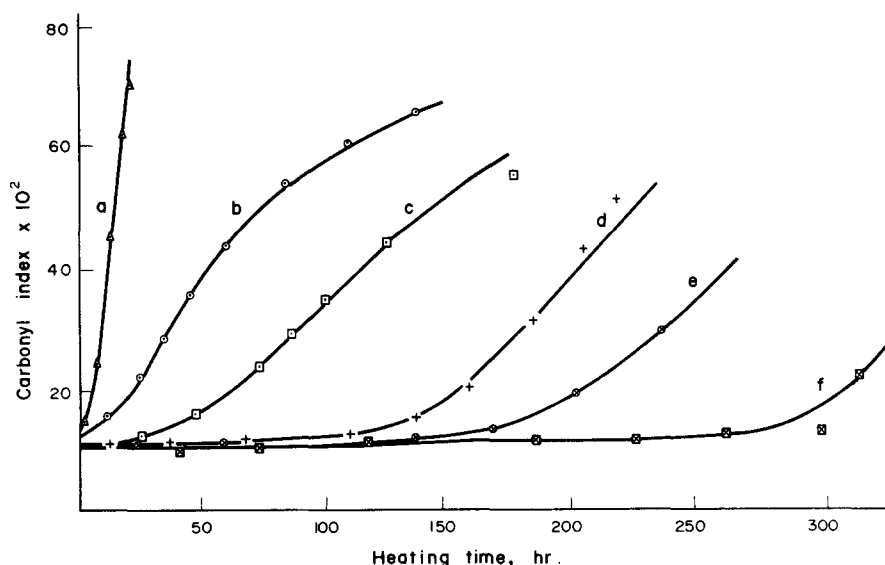


Fig. 2. Comparison of extracted and unextracted samples of ABS containing different additives. (a) Control—normal ABS; (b) ABS + Tinuvin P (after extraction); (c) ABS + 1% Tinuvin P (before extraction); (d) ABS + DBHBT (after extraction); (e) ABS + 1% DBHBT (before extraction); (f) ABS + DBHBT/Tinuvin P (1:1).

Table 2. Combination effects of additives in ABS (concentration of all additives 1 g/100 g ABS)

Additive mole/100 g ABS	Induction period before/after extraction	% Synergism*
Control	3/3	—
Tinuvin P (4.4×10^{-3})	26/3	—
DBHBT (3.6×10^{-3})	175/125	—
DBHBT + Tinuvin P	300/250	52

$$\% \text{ Synergism}^* = \frac{(I_s - I_c) - [(I_1 - I_c) + (I_2 - I_c)]}{[(I_1 - I_c) + (I_2 - I_c)]} \times 100,$$

where I_s is induction period of the synergistic mixture, I_c is induction period of the control, I_1 is induction period of the stabilizer (Tinuvin P), I_2 is induction period of the anti-oxidant (DBHBT).

DBHBT-ABS concentration. Also in this study, various ratios of the two additives have been mixed with ABS and the thermal stability tested. In each case, synergism was observed. Figure 2(f) illustrates this effect for ABS containing 1% w/w DBHBT-ABS and 1% w/w Tinuvin P-ABS. In each case, the polymer was processed for 3 min and then heated in the air oven. It was seen that the synergistic mixture offers considerable protection to ABS. An induction period of about 300 h has been obtained compared with an induction period of only 3 h for the control. Also from the additivity law, a total induction period of 201 h was obtained for the films containing the two separate additives. It can also be seen that, even after the end of induction period for the sample containing the synergistic mixture, the rate of change in the slope is very small compared with the other graphs where auto-oxidation sets in at the end of the induction periods. The low rate of change of slope means a higher degree of protection.

Both extracted and unextracted samples have been

studied as shown in Fig. 2. In each case, the extracted samples degraded more quickly than the unextracted samples. However, from the graph it appears that some substantial grafting of DBHBT to ABS must have taken place. The efficiency falls by about 29% in the case of DBHBT in ABS, as demonstrated in Table 2.

It is also seen that, even after extraction, synergism is also observed. An induction period of 250 h is observed for the sample containing the synergistic mixture as compared to a total of 128 h obtained from the additivity law.

Figure 3 shows the dependence of hydroxyl index on the heating time. Here, all samples contain 1% DBHBT and have been processed for various periods. It is seen that there is an initial fall in the hydroxyl index with heating time. This initial fall is followed by a period of induction after which growth is again observed. This observation could be explained as follows. The hydroxyl groups produced during the processing of the polymer are converted to hydroperoxi-

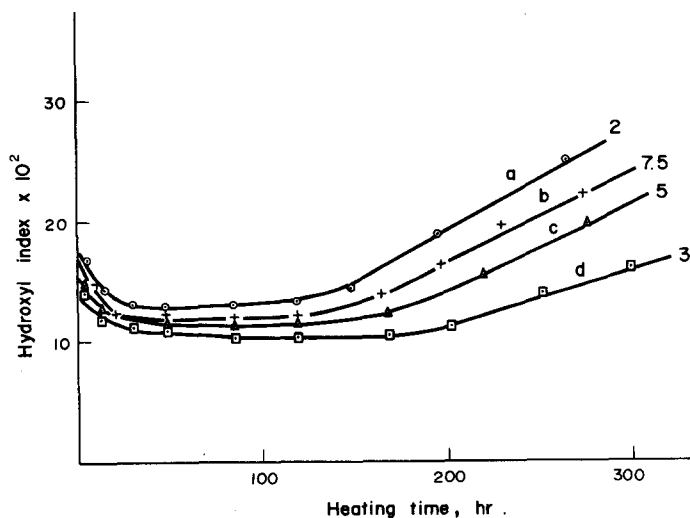
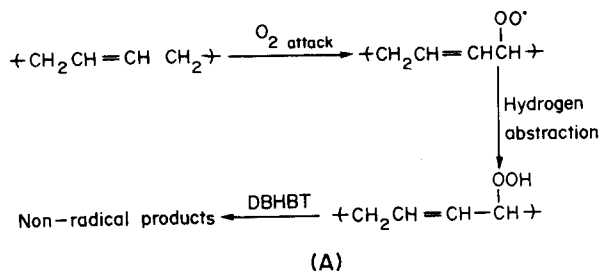


Fig. 3. Dependence of hydroxyl index on heating time. ABS + 1% DBHBT and processed for various periods (min) as indicated on the graphs.

ides which are themselves subsequently consumed by the anti-oxidant (Scheme A).

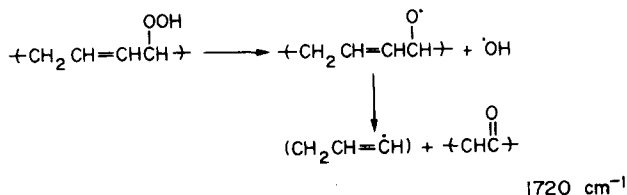
is much easier to prepare than BIBM. It is, in fact, an ester of BIBM. Therefore, considering the ease of



However, when the level of the anti-oxidant has fallen substantially, the hydroperoxides grow and are gradually converted to carbonyls and this is then reflected by an increase in the peak at 1720 cm^{-1} (Scheme B).

handling, cost and time required for preparation, the use of DBHBT in place of BIBM will be of great technological advantage.

Figure 4 shows the first-order plots of the various



This observation suggests that DBHBT acts as a peroxide decomposer. This observation is similar to an earlier conclusion where the initial decrease and subsequent constancy in the hydroxyl peak absorption was observed in ABS in the presence of BIBM [5]. These results show that DBHBT is a good thermal stabilizer. DBHBT has an added advantage in that it

indices on heating the polymer in an air oven. The straight lines obtained after an induction period show that thermal oxidative degradation of ABS in the presence of these additives follows a first-order process. Calculated values of the first order rate constants k , show that

$$k_{\text{C}=\text{C}} = 12.34 > k_{\text{OH}} = 11.31 > k_{\text{C}=\text{O}} = 9.67.$$

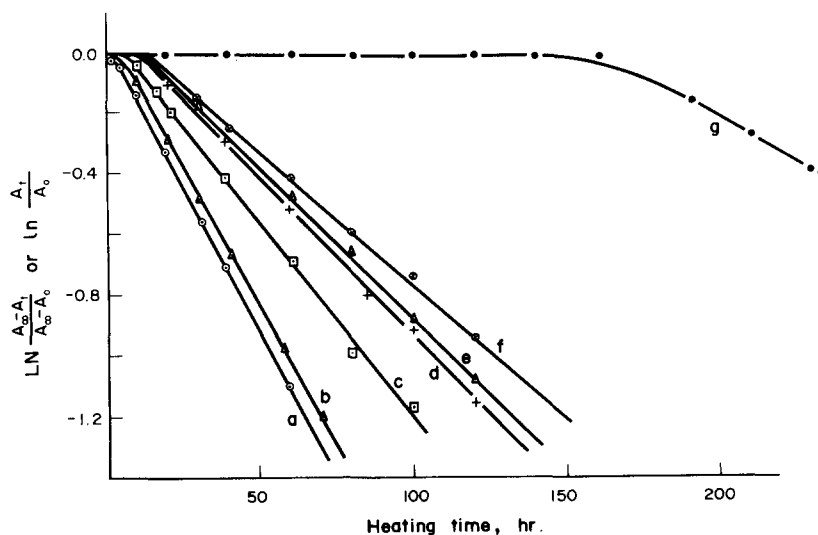


Fig. 4. First-order plots showing changes in the functional groups during heating. ABS without additives: (a) $\text{—C}=\text{C—}$; (b) —OH ; (c) $>\text{C}=\text{O}$; ABS + 1% Tinuvin P; (d) $\text{—C}=\text{C—}$; (e) —OH ; (f) $>\text{C}=\text{O}$; ABS + DBHBT; (g) $>\text{C}=\text{O}$.

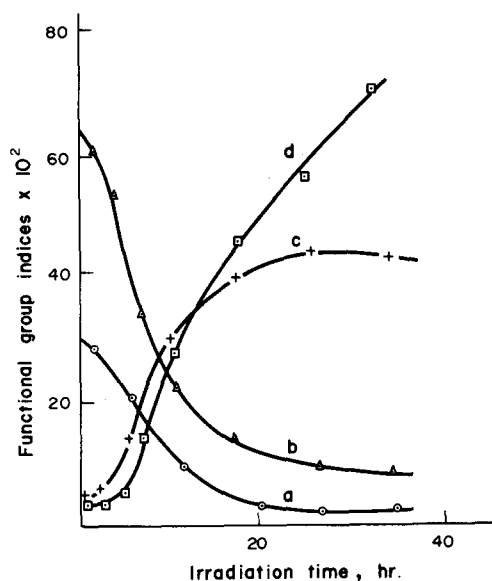


Fig. 5. Photo-oxidation of ABS. Dependence of functional group indices on time of u.v. irradiation of unstabilized ABS; (a) Carbon-carbon bond at 910 cm⁻¹; (b) Carbon-carbon bond at 965 cm⁻¹; (c) Hydroxyl index; (d) Carbonyl index.

This shows the dependence of the hydroxyl group on the initial destruction of the carbon bonds. The rate constants for carbonyl is the smallest in agreement with the result obtained during u.v. irradiation of the films. Essentially, it further confirms that degradation of ABS begins with the destruction of the double bonds but is then propagated by the formation of hydroperoxides. This conclusion is in agreement with the mechanisms proposed by Bevan and Phillips [7].

Photo-degradation of ABS

Figure 5 shows the changes during u.v. irradiation of unstabilized ABS films. Evidently, polytrans-1,4-butadiene degrades more quickly than polycis-1,4-butadiene. There appears to be no induction period, i.e. degradation begins as soon as the films are exposed to u.v. irradiation. The hydroxyl groups begin to build up after a 2-h induction period while the carbonyl appears shortly after.

Development of carbonyl group is by β -scission of the alkoxy radical [7]. Also it appears that the hydroxyl group grows more quickly than the carbonyl group at the beginning of oxidation. This result suggests that carbonyl compounds are secondary breakdown products of hydroperoxides. The hydroxyl peak reaches a maximum at about the time when polybutadiene unsaturation is completely destroyed. The continued growth in the carbonyl peak even beyond the time the hydroxyl peak has reached a maximum indicates a slow conversion of the hydroxyl groups to the carbonyl groups. The same observation was made for the thermal oxidation of ABS. As stated earlier, the oxidation of ABS is due to the destruction of the polybutadiene backbone. All data presented so far are in line with this statement and in agreement with the suggestion of Bevan and Phillips [7] that the mechanisms for initial photo-oxidation and thermal oxidation of polybutadiene are identical.

Figures 6-8 demonstrate the effect of u.v. irradiation on the unstabilized and stabilized ABS polymers. Figure 6 shows the first order plots of the effect of u.v. irradiation on the functional groups in ABS films with and without Tinuvin P. A similar plot has been constructed for ABS containing DBHBT and irradiated by u.v. light.

For the growing bands of —OH and —C=O, $\log \frac{A_\infty - A_t}{A_\infty - A_0}$ is plotted as a function of time; A_∞ is the maximum absorbance, A_t is the absorbance at any time t , A_0 is the absorbance of the initial peak.

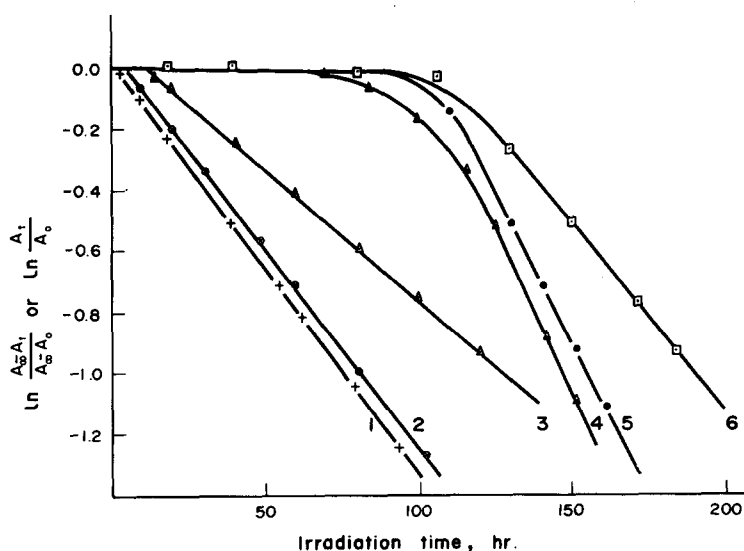


Fig. 6. First-order plots showing dependence of functional group indices upon u.v. irradiation. ABS without additives: (1) —C=C—; (2) —OH; (3) >C=O; ABS + 0.5% Tinuvin P; (4) —C=C—; (5) —OH; (6) >C=O.

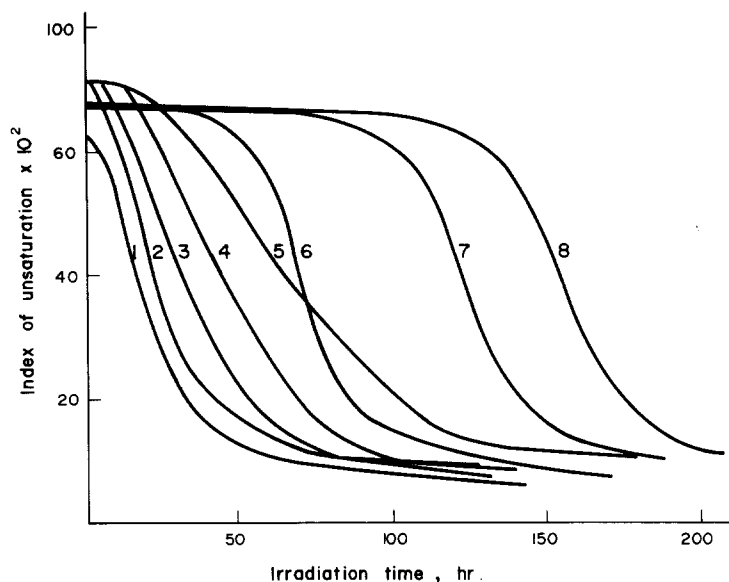


Fig. 7. Photodegradation of ABS. Dependence of loss of unsaturation upon irradiation time for ABS containing various additives. (1) Control; ABS with DBHBT; (2) ABS + 0.2% DBHBT; (3) ABS + 0.4% DBHBT; (4) ABS + 0.5% DBHBT; (5) ABS + 1.0% DBHBT. ABS with Tinuvin P; (6) ABS + 0.2% Tinuvin P; (7) ABS + 0.4% Tinuvin P; (8) ABS + 0.5% Tinuvin P.

For the diminishing band of —C=C— , $\log A_t/A_0$ has been plotted vs time of exposure. The graphs are linear after initial induction periods. This suggests that photo-oxidation of ABS in the presence of these additives is a first-order process. It is also noted that, although DBHBT is not really a u.v. stabilizer, it imparts some stability to ABS when irradiated by u.v. (figures in parenthesis in Table 3 below). Table 3 shows that the rate of formation of hydroxyl groups is quite similar to the rate of destruction of carbon-carbon double bonds. The rate of carbonyl development is quite low. This again confirms our earlier

Table 3. Rate of degradation of various function groups under u.v. light

Additive	<i>k</i> values ($\times 10^6$ s)		
	—C=C—	—OH	—C=O
Control	13.69 (none)	12.08 (2)	7.69 (3)
Tinuvin P	3.55 (85)	3.49 (100)	2.60 (120)
DBHBT	8.67 (10)	8.60 (20)	5.33 (26)

Figures in parenthesis show the corresponding induction periods for the additives.

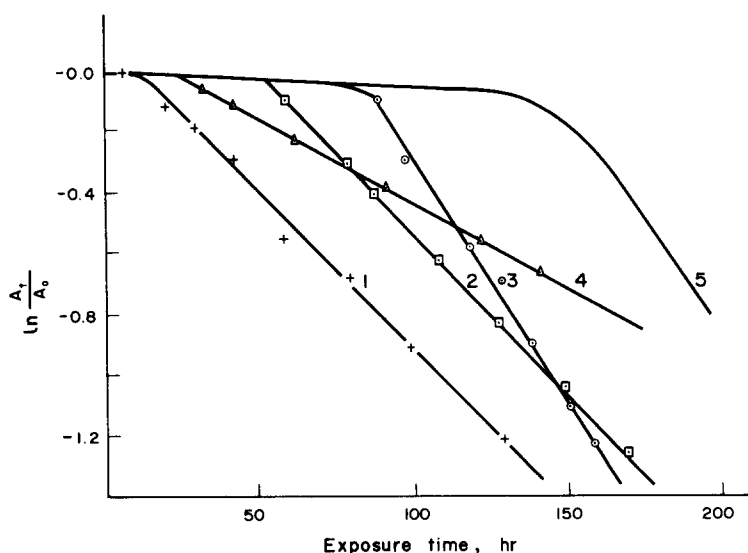


Fig. 8. First-order plots showing the effects of Tinuvin P and DBHBT on the destruction of double bonds at 965 cm^{-1} under various degradative conditions. (1) ABS + 1% Tinuvin P (oven ageing); (2) ABS + 1% DBHBT (natural weathering); (3) ABS + 1% Tinuvin P (natural weathering); (4) ABS + 1% DBHBT (u.v. irradiation); (5) ABS + DBHBT under oven ageing.

Table 4. Induction periods produced by Tinuvin P when added to normal ABS and processed for 3 min and then exposed to u.v. irradiation

g Stabilizer/100 ABS	Induction period (h)
Control	3
0.25 (0.90×10^{-3} M)	120
0.50 (1.80×10^{-3} M)	150
1.00 (3.6×10^{-3} M)	197
2.00 (7.2×10^{-3} M)	197

suggestion that photo-oxidation of ABS starts with the destruction of double bonds at 965 cm^{-1} . Also there is an initial rapid formation of hydroxyl groups which are later converted to carbonyl groups.

Table 4 shows the effect of stabilizer concentration on the u.v. stability of ABS. It is clear that the higher the concentration of Tinuvin P the greater the induction period. It can be seen that, even at a 0.25% w/w Tinuvin P-ABS level, substantial stability is imparted to ABS. The most economical level of application would be about 1% concentration. Higher concentrations do not have any effect on the induction period.

Figure 7 shows the dependence of unsaturation index on the time of irradiation. This figure compares the effectiveness of Tinuvin P and DBHBT under u.v. irradiation. It is clear that Tinuvin P is much superior to DBHBT as a u.v. stabilizer. For example, at 0.25% level of each, DBHBT gave an induction period of 16 h while Tinuvin P gave an induction period of 120 h.

Figure 8 shows the first-order plots of the dependence of loss of unsaturation on time. The figure compares the accelerated weathering conditions with natural outdoor weathering. All additives were present at 1% concentration. It is seen that the sample containing Tinuvin P performs better outdoors than the sample containing DBHBT, i.e. Tinuvin P has an induction period of about 90 h, to be compared with 45 h obtained for DBHBT. Again, the sample containing 1% DBHBT and 1% Tinuvin P shows synergism when exposed to outdoor weathering. In all cases, degradation in the accelerated weathering conditions is much faster than that of the natural weathering. It should be mentioned, however, that this comparison is not strictly valid because the u.v. source used here emits radiation at 254 nm which is not related to sunlight.

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