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SYNTHESIS AND THERMAL AND PHOTO-OXIDATIVE BEHAVIOUR OF NOVEL AMINATED 2-HYDROXYBENZOPHENONE STABILIZERS IN POLYOLEFIN FILMS

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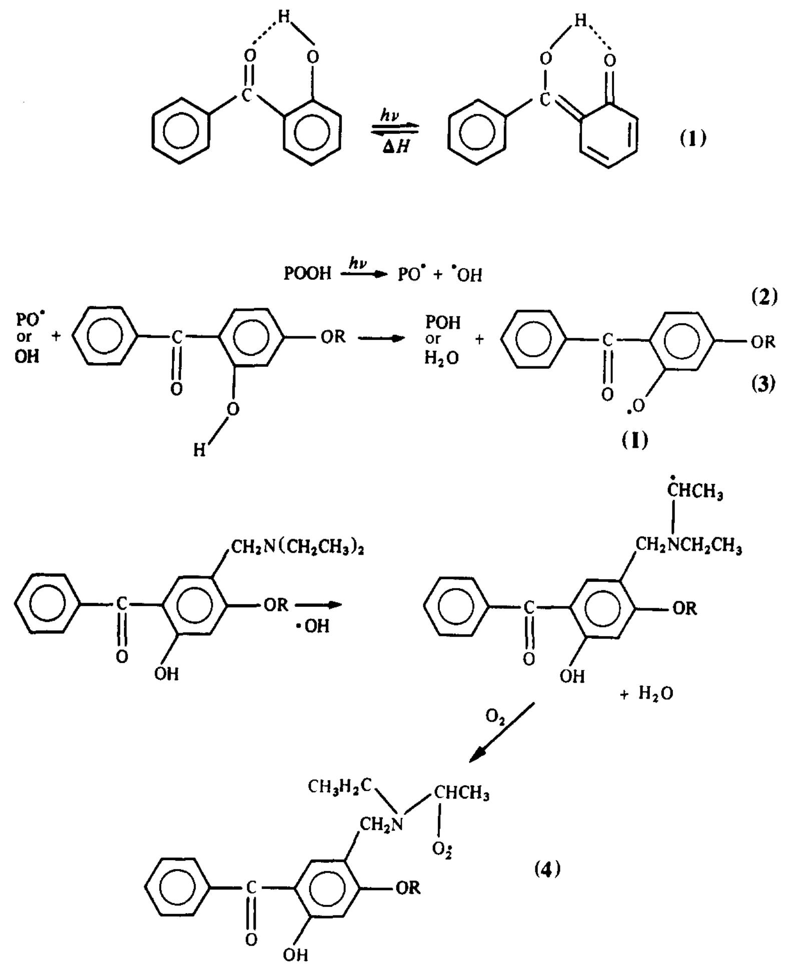
Abstract—Three light stabilizers have been prepared and characterized, based on the substitution of a tertiary amine group into the 3- and 5-positions of 2,4-dihydroxybenzophenone (DHBZ) and 2-hydroxy-4-n.octoxybenzophenone (HOBZ) via the Mannich reaction. The derivatives prepared by this method were, the 3-*N*,*N*-diethylaminomethyl of the former and the 5-*N*,*N*-diethylaminomethyl and 5-morpholinomethyl derivatives of the latter. The thermal and photo-oxidative stabilization activities of the three compounds have been examined and compared with those of DHBZ and HOBZ in medium density polyethylene and polypropylene films at 0.1% w/w concentration using i.r. absorption and fluorescence spectroscopy and hydroperoxide analysis. In medium density polyethylene, all three aminated derivatives are weak antioxidants with the diethylaminomethyl derivative of DHBZ being the most effective. The commercial light stabilizers DHBZ and HOBZ were also weak antioxidants but less effective than the aminated derivatives. In polypropylene, similar results were obtained but in this case both the Mannich derivatives of HOBZ were effective. In the presence of a hindered phenolic antioxidant, Irganox 1010, all the stabilizers except the HOBZ were synergistic in the thermal oxidation of polyethylene whereas in polypropylene the effects were antagonistic. On photo-oxidation, the effects were reversed with antagonism being observed in the case of polyethylene and synergism in polypropylene but only in the case of the morpholinomethyl derivative of HOBZ. Surprisingly, the three aminated derivatives were less effective as light stabilizers than the two simple commercial benzophenone stabilizers HOBZ and DHBZ. Hydroperoxide formation is markedly reduced on oven-ageing of polypropylene by the aminated derivatives and is consistent with the ability of the tertiary amine group to scavenge oxygen and free radicals. Fluorescence quenching studies on the same polymer also show that the aminated derivatives are more effective quenchers than the corresponding commercial HOBZ and DHBZ stabilizers.

INTRODUCTION

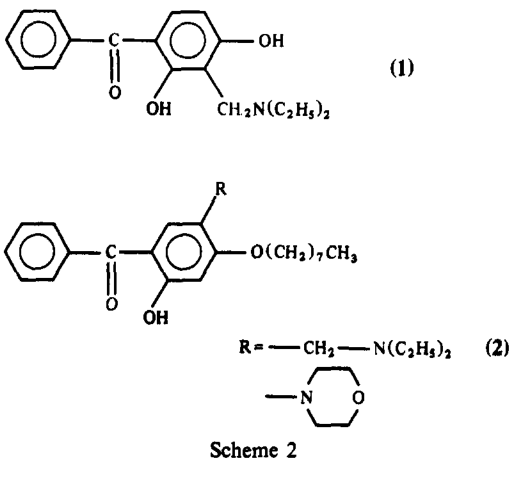
Ortho-hydroxy substituted aromatic compounds based on benzophenone are known to function as light stabilizers through their ability to absorb preferentially the harmful u.v. radiation in the solar region 290–350 nm and then harmlessly dissipate the absorbed energy through one or more non-radiative processes [1–8]. Taking the 2-hydroxybenzophenones as examples, they dissipate the absorbed light energy through a mechanism that involves the reversible formation of a six membered hydrogen-bonded ring system (Scheme 1). Here, the two tautomeric forms (keto-enol) in equilibrium provide a facile pathway for deactivation of the excited state induced by the absorption of light. The result of this mechanism of light absorption and dissipation thus leaves the stabilizer chemically unchanged and still able to undergo a number of these activation–deactivation cycles. However, the concept of photostabilization in commercial polymers by u.v. absorption has become unacceptable from both a theoretical and practical basis [9, 10]. In fact, high concentrations of an absorber are required on the surface of a polymer system for it to operate efficiently in this way since photooxidation reactions in polymers occur on the near surface [11].

In order to account for the high stabilization efficiency of a number of these light stabilizers being greater than that simply associated with absorption, other mechanisms have been proposed. The ability of these stabilizers to quench the excited states of active chromophores in polymers through either trivial, short or long range energy transfer processes has been proposed through experimental observations on model systems and in polymers [12, 13]. More recent theories however, have centred on the activity of these types of stabilizers to act as weak antioxidants either thermally or photochemically [14–16]. In this regard they are known to act as chain-breaking donors for the termination of alkoxy and hydroxyl radicals produced in the photolysis of hydroperoxides as depicted in Scheme 2. It is in this regard therefore that we have examined here the thermal and photochemical effects in polyolefins of substituting a tertiary amine functionality in the 2-hydroxybenzophenone chromophore via the well-known Mannich reaction [17] to give structures **1** and **2** respectively. Amines are well-known scavengers of oxygen and free radicals, as borne out by the efficiency of the hindered piperidine light stabilizers [1–3]. In fact, in recent work on multifunctional acrylated coatings, the substitution of a tertiary amine functionality was found to improve markedly the light stability of the



Scheme 1

resin system [18, 19]. On this basis therefore it was of interest to examine the effect of amine substitution on the stabilizing efficiency of the 2-hydroxybenzophenone chromophore using i.r. and fluorescence spectroscopy and hydroperoxide analysis. The results are also discussed in terms of the efficiencies of structures **1** and **2** and that of a commercial hindered phenolic antioxidant, Irganox 1010 (Ciba-Geigy Ltd, Switzerland).



Scheme 2

EXPERIMENTAL PROCEDURES

Materials

Medium density polyethylene and polypropylene powders containing no commercial additives were supplied by BP Chemicals, U.K. and ICI Chemicals and Polymers Group Ltd, U.K. respectively. Irganox 1010 [pentaerythrityl tetrakis(3,5-di-t-butyl-4-hydroxyphenyl)propionate] (Ciba-Geigy Corp., Switzerland), Aduvex 12 (2,4-dihydroxybenzophenone; DHBZ) (International Biosynthetics Ltd; Widnes, U.K.) and Cyasorb UV531 (2-hydroxy-4-n.octoxybenzophenone; HOBZ) (American Cyanamid Co., U.S.A.) were obtained as gifts from the respective manufacturers. Sodium iodide, glacial ethanoic acid, chloroform, 2-propanol, acetone, petroleum ether (60–80°), methanol, pentane and diethyl ether were obtained (Aldrich Chemical Co., U.K.) in Analar quality. Magnesium sulphate, conc. hydrochloric acid, paraformaldehyde, diethylamine and morpholine were also obtained (Aldrich Chemical Co., U.K.) as standard laboratory grade materials.

Mannich reaction

In a typical preparation, paraformaldehyde (0.06 M), diethylamine (0.06 M), conc. hydrochloric acid (0.5 cm^3) and methanol (60 cm^3) were refluxed for 20 min in a 250 cm^3 flask followed by the addition of DHBZ (0.03 M). The whole was then refluxed for a further 24 hr followed by cooling and vacuum evaporation of the methanol. The residue was then dissolved in chloroform and the excess amine removed with dilute hydrochloric acid (1 M) (2 × 25 cm^3). The organic layer was then washed with

Table 1. Analytical and preparative information on aminated benzophenone derivatives

Compound	Mpt (°C)	Yield (%)	% Expected C	% Expected H	% Expected N	% Found C	% Found H	% Found N
MAN/Aduvex 12	84	74	72.2	7.0	4.7	72.0	6.9	4.7
MAN/Cyasorb UV531	108	70	75.9	9.1	3.4	75.3	8.9	3.3
MORPH/Cyasorb UV531	181	75	73.4	8.3	3.3	73.3	8.3	3.3

distilled water followed by drying over anhydrous magnesium sulphate. The chloroform was then evaporated on a steam bath followed by trituration with 10 cm^3 of diethyl ether to give a creamy white precipitate recovered by filtering. The product was purified using flash chromatography with chloroform as the eluant. The product was recrystallized using a mixture of petroleum ether (60–80) and chloroform (50:50 v/v).

The melting points, yields of individual reactions and carbon and hydrogen contents are shown in Table 1. The use of a Jeol 270 MHz NMR instrument confirmed the presence of the methylene chain linking the amino substituents through both proton and carbon^{-13} analysis as well as mass spectrometry (VG 30/70 Spectrometer). I.r. spectroscopy was carried out using a Mattson Alpha-Centauri FTIR instrument. In the latter case, the spectra of the aminated derivatives showed an increase in the alkane C—H substitution at 2900 cm^{-1} compared with that for the HOBZ and DHBZ.

Polymer sample preparation

The stabilizers were incorporated in the polymers by solvent blending with dichloromethane. The solvent was removed by rotary evaporation. The polymer powders were then compression moulded into films (200 μm thick) using temperatures of 170 and 200° for polyethylene and polypropylene respectively for 1 min at 10 tons/in^2 followed by quench cooling in water.

Thermal and photooxidation

The polymer films were heated in air draught ovens at 110 and 130° for polyethylene and polypropylene respectively. The film samples were also irradiated in a Microscal unit utilizing a 500 watt high pressure mercury/tungsten lamp (wavelengths > 300 nm, 50°) (Microscal Ltd, London).

Rates of oxidation

Rates of polymer oxidation were measured by monitoring the rate of formation of the non-volatile carbonyl oxidation products in the region 1500–1800 cm^{-1} using the Mattson FTIR spectrometer described above. Carbonyl growth in this region of the spectrum is determined by using an index defined as follows [3, 11]:

$$\text{Carbonyl index} = [\text{Log}_{10}(I_0/I_t)/d] \times 100$$

where d, film thickness in microns; I_0, initial light intensity; I_t, transmitted light intensity.

Embrittlement times for both polymers were taken at a carbonyl index value of 0.06 for reference purposes only.

U.v./visible absorption spectra

U.v. absorption spectra of the compounds were obtained using a Perkin–Elmer Lambda-7 spectrophotometer.

Hydroperoxide analysis

Hydroperoxide determinations were carried out on the polypropylene films using the standard iodometric method described previously [15–17]. Briefly, 1 g of finely cut polymer film was refluxed in a mixture of 2-propanol/glacial ethanoic acid (9:1 cm^3) together with 0.5 g of sodium iodide for 1/2 hr. The generated I^{3-} was then measured spectrophotometrically at 420 nm on the absorption curve in order to avoid interference due to extracted stabilizers.

Fluorescence analysis

Fluorescence spectra were recorded using a Perkin–Elmer LS-5 spectrofluorimeter equipped with a front face accessory.

RESULTS AND DISCUSSION

Analysis of the Mannich reaction products using NMR spectroscopy indicated that, in the case of the DHBZ (Aduvex 12), substitution occurred at the 3-position by the *N*,*N*-diethylaminomethyl group whereas in the case of the HOBZ (Cyasorb UV531) substitution occurred at the 5-position in both cases. In the latter case, this was associated with steric hindrance by the 4-n.octoxy group.

Several interesting features were observed with regard to the properties of these aminated 2-hydroxybenzophenone stabilizers. The first is related to their absorption maxima and in particular extinction coefficients. In relation to the HOBZ (Cyasorb UV531) and DHBZ (Aduvex 12), it is seen that the main absorption maximum does not show any significant red shift with regard to the nature of the substituent and the extinction coefficients for all three stabilizers remain virtually unaffected (Table 2). This corresponds to the main π–π^* transition of the benzenoid rings and clearly indicates that, despite the electron-donating ability of the tertiary amine substituents, *meta* substitution has little or no influence on the chromophoric intensity.

The thermal antioxidant performance of these derivatives is particularly important with regard to their mode of action on photostabilization. Carbonyl

Table 2. Absorption maxima and extinction coefficients of aminated 2-hydroxybenzophenones, Aduvex 12 and Cyasorb UV531 in chloroform and 2-propanol

Compound	2-Propanol Wavelength (nm)	2-Propanol Extinction coefficient (m^2 mol^{-1})	Chloroform Wavelength (nm)	Chloroform Extinction coefficient (m^2 mol^{-1})
Aduvex 12	288	1379	288	1372
Cyasorb UV531	290	1206	290	1599
MzAN/Cyasorb UV531	284	1206	285	1426
MORPH/Cyasorb UV531	284	1170	284	1449
MAN/Aduvex 12	288	1271	289	1210

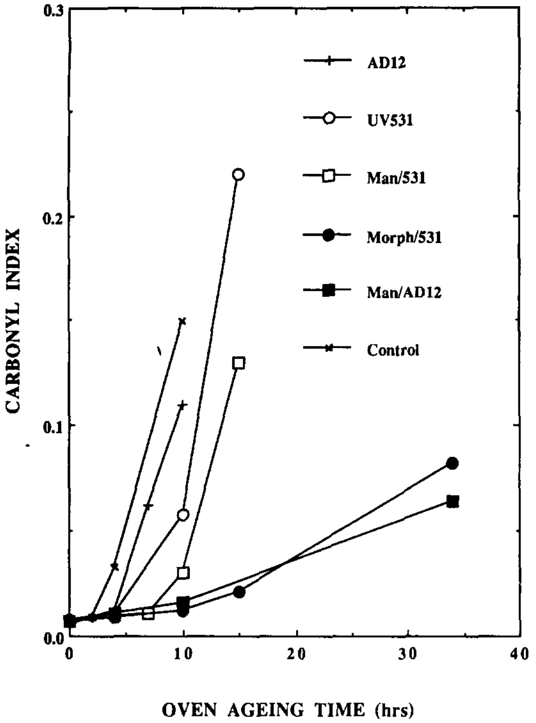


Fig. 1. Carbonyl index vs oven-ageing time (hr) of polyethylene film (200 μm thick).

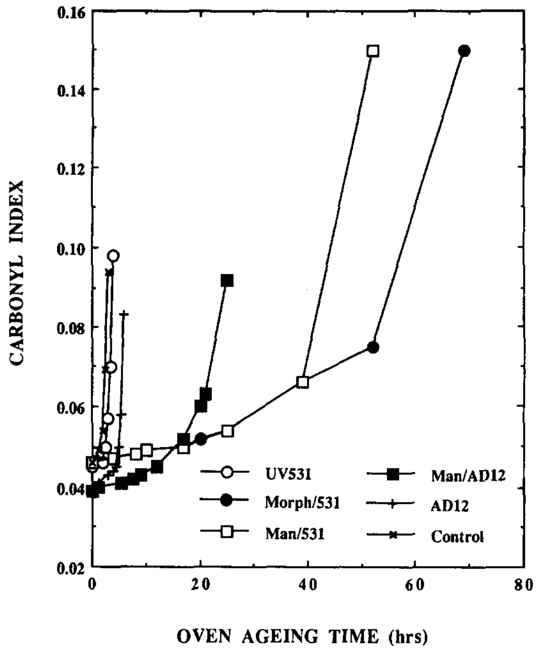


Fig. 2. Carbonyl index vs oven-ageing time (hr) of polypropylene film (200 μm) thick.

index growths in stabilized polyethylene and polypropylene films during oven ageing at 110 and 130° are shown in Figs 1 and 2 respectively. Actual embrittlement times in hours of the polymer films with and without the antioxidant Irganox 1010 are compared in Table 3. Compared with the control polymer films, all the stabilizers operate as mild antioxidants on their own and from Figs 1 and 2 appear to be auto-retarding carbonyl formation. Figure 1 shows that both the Mannich products of Aduvex 12 and 5-morpholino derivative of Cyasorb UV531 are particularly effective in this regard in polyethylene whereas the DHBZ is the least effective due to its incompatibility. Thus, in polyethylene, although both DHBZ and HOBZ exhibit some antioxidant behaviour, the enhanced performance of the aminated derivatives is certainly due to the ability of the tertiary amine group to scavenge oxygen and terminate free radicals as shown in Scheme 1 reaction (4). In polypropylene, the effects are similar and as can be seen from the plots of carbonyl index in Fig. 2 the DHBZ and HOBZ are the least effective antioxidants. All three aminated derivatives are highly effective in auto-retarding carbonyl formation indicating that the macroalkyl radicals are being terminated before they are able to react with oxygen. Furthermore, the role of hydroperoxide groups is known to be more important in polypropylene than in polyethylene [1]. In this regard the most interesting results however are the times to embrittlement in the presence of Irganox 1010 shown in Table 3. In polyethylene, strong synergism was observed whereas in polypropylene the effects were all antagonistic. Again the primary importance of hydroperoxides in the latter polymer may be responsible for the observed effects. It is clear that in this case the two types of stabilizers do not operate in a complimentary way whereas in polyethylene they do. Transformation products from the phenoxy radical of the Irganox 1010 are quite important in further stabilization and in polypropylene may be interacting with the alkylamino radicals from the tertiary amino group Scheme 1 reaction (4). In polyethylene the hydroperoxides are much less stable under the ageing conditions used here compared with polypropylene.

Table 3. Thermal embrittlement times (at 0.06 carbonyl index) for polyethylene (110°) and polypropylene (130°) films (200 μm) containing aminated 2-hydroxybenzophenones, Cyasorb UV531 and Aduvex 12 (0.1% w/w) with and without Irganox 1010 (0.1% w/w)

	Polyethylene		Polypropylene	
Compound 0.1% w/w	No Irganox 1010	With Irganox 1010	No Irganox 1010	With Irganox 1010
Control	6	1750	2	3400
Cyasorb UV531	11	1750	3	2600
Aduvex 12	7	1900	6	2600
MAN/Aduvex 12	33	2600	20	3000
MAN/Cyasorb UV531	12	3500	30	2450
MORPH/Cyasorb UV531	22	3480	31	3000

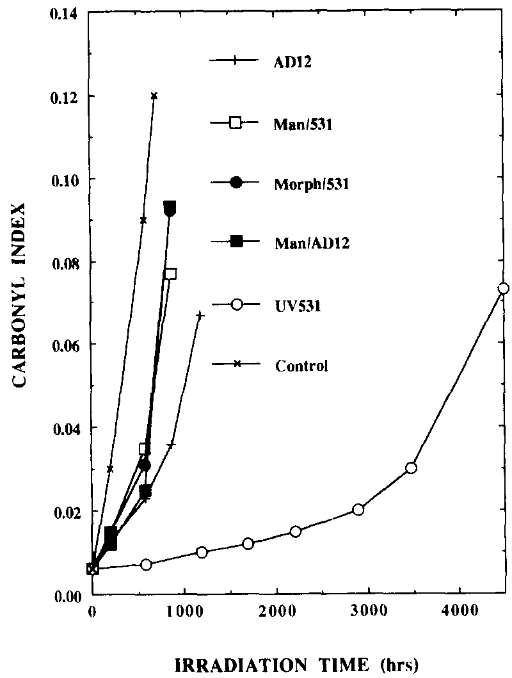


Fig. 3. Carbonyl index vs irradiation time in the Microscal Unit (hr) of polyethylene film (200 μm thick).

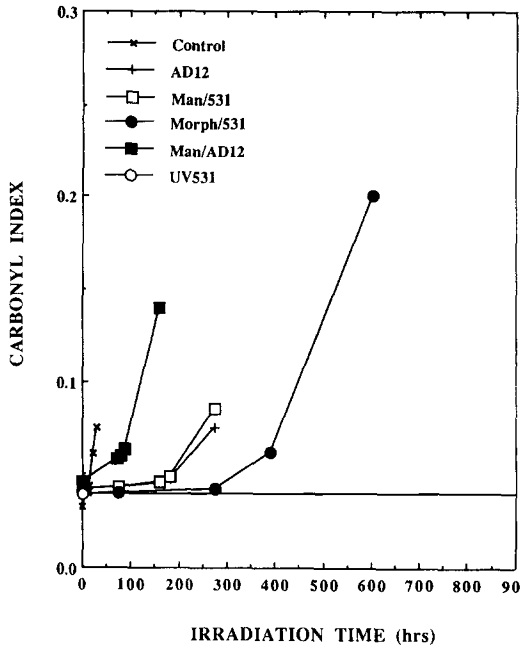


Fig. 4. Carbonyl index vs irradiation time in the Microscal Unit (hr) of polypropylene film (200 μm thick).

Thus, the chain-breaking donor mechanism in Scheme 2 may be more important in polyethylene than polypropylene on thermal oxidation.

The photostabilization efficiencies of the aminated 2-hydroxybenzophenone derivatives in comparison with both DHBZ and HOBZ in polyethylene and polypropylene films are shown by the carbonyl index plots in Figs 3 and 4 respectively. It is seen that, whilst all three aminated derivatives operate as effective stabilizers, they are not as effective as either HOBZ or even the small molecular DHBZ (Aduvex 12) in both polymers. This result is surprising since these compounds are effective as chain-breaking donors in scavenging oxygen and macroalkyl radicals. The increased molecular size and possibly lower solubility of these derivatives in both polymer systems are unlikely to be responsible for their lower stabilization efficiencies. Furthermore, some degree of intermolecular interaction or self-quenching of the benzophenone chromophores may also be possible through either salt formation or some type of weak triplet–exciplex between the tertiary amine group and aromatic ketone.

In contrast to the effects seen in thermal stabilization, all the aminated 2-hydroxybenzophenone stabilizers are antagonistic with Irganox 1010 in polyethylene whilst with polypropylene synergism is observed in only one case with the 5-morpholinomethylene derivative. In this case, salt formation between the basic aminated derivatives and the acidic hindered phenolic antioxidant would be responsible for the observed antagonism.

The importance of hydroperoxide groups in polypropylene and their interplay in the stabilization mechanism is further supported by the hydroperoxide analysis data shown in Table 5 for the polypropylene samples before and after 2 hr of oven ageing. Thus, the presence of higher concentrations of hydroperoxides produces polymers with a lower stability, essentially confirming the importance of Scheme 1, reaction (4) and Scheme 2 in thermal and photochemical stabilization. The results in Table 5 show that, even on compression moulding of polymer film, all three Mannich derivatives suppress hydroperoxide formation compared with that of the control polymer without any stabilizer. This effect of hydroperoxide

Table 4. Photoembrittlement times (at 0.06 carbonyl index) for polyethylene (110°) and polypropylene (130°) films (200 μm) containing aminated 2-hydroxybenzophenones, Cyasorb UV531 and Aduvex 12 (0.1% w/w) with and without Irganox 1010 (0.1% w/w)

Compound 0.1% w/w	Polyethylene		Polypropylene	
	No Irganox 1010	With Irganox 1010	No Irganox 1010	With Irganox 1010
Control	380	1000	21	550
Cyasorb UV531	4200	4500	5000	5000
Aduvex 12	1100	900	225	425
MAN/Aduvex 12	710	1050	170	500
MAN/Cyasorb UV531	740	1250	215	580
MORPH/Cyasorb UV531	710	1200	390	980

Table 5. Hydroperoxide concentrations (μg/g) in polypropylene films (200 μm) before and after 2 hr thermal oxidation at 130° containing aminated 2-hydroxybenzophenones, Cyasorb UV531 and Aduvex 12 (0.1% w/w)

Compound 0.1% w/w	Hydroperoxide (μg/g) 0 hr	2 hr
Control	146	800
Cyasorb UV531	158	694
Aduvex 12	117	691
MAN/Cyasorb UV531	84	393
MORPH/Cyasorb UV531	93	108
MAN/Aduvex 12	122	480

inhibition is also extended on oven ageing. In this regard stabilization efficiency follows the order 5-morpholino–HOBZ > 5-*N*,*N*-diethylamino–HOBZ >·3-*N*,*N*-diethylamino–DHBZ matching the order in both their thermal oxidation and light stabilization efficiencies shown in Figs 2 and 4 respectively.

One final aspect regarding the efficiency of stabilizers is their influence on the potentially photo-active luminescent species in the polymer. The fluorescent species in polyolefins have been connected with the presence of unsaturated carbonyl compounds with excitation and emission wavelength maxima at 284 and 345 nm [3, 11]. The effect of the 2-hydroxybenzophenone stabilizers on this emission is shown in Fig. 5. Here it is seen that, compared with the DHBZ and HOBZ stabilizers, the corresponding aminated derivatives are more effective in quenching the emission over the concentration range studied. Although much of the quenching seen here may be trivial in nature and due to the high extinction coefficients of the stabilizers, the enhanced effect of the aminated derivatives may be due to a weak exciplex between the tertiary amine group and the excited carbonyl species.

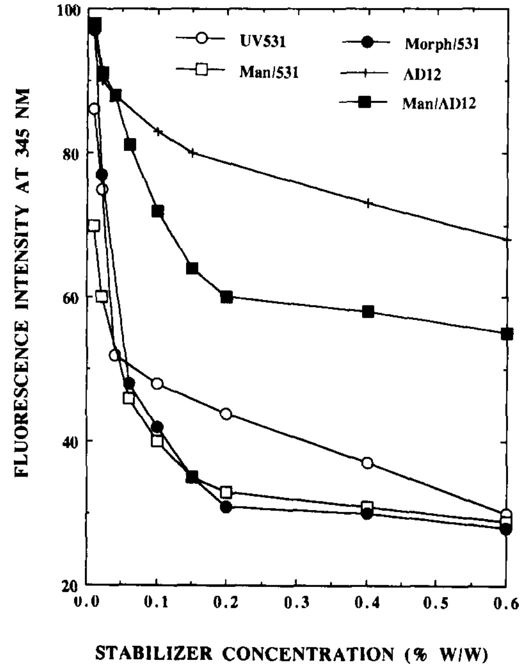


Fig. 5. Fluorescence intensity of polypropylene film (200 μm thick) vs concentration in % w/w.

CONCLUSIONS

The results clearly show that, whilst the products of substitution of a tertiary amine group into the 3- or 5-positions of 2-hydroxybenzophenone chromophores are less effective in the photostabilization of polyolefins than the simpler unsubstituted stabilizers, they are more effective as thermal antioxidants. Intermolecular complex formation via some type of exciplex may be responsible for the reduced efficiency as well as possible salt formation. However, the aminated 2-hydroxybenzophenones show several features in their stabilization efficiency consistent with a chain-breaking donor mechanism playing a role in both thermal and photochemical oxidation. The degree of complexation with the antioxidant Irganox 1010 is important in controlling both thermal and photochemical oxidation of polyethylene and polypropylene. Quenching of the fluorescent chromophores is also more effective by the aminated derivatives possibly through an exciplex with the excited carbonyl species and the amine group.

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