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Interaction between Hindered Amine Light Stabilisers (HALS) and Nickel Complexes in Polypropylene during Thermal Oxidation

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ABSTRACT

The interaction between three commercial hindered amines, Tinuvin 770, Hostavin TM N20 and Cyasorb UV 3346, and two commercial nickel complexes, Rohac Ni PD and Ferro AM 205, in polypropylene (PP), is examined using isothermal TGA, second derivative ultraviolet (UV) spectroscopy, and Fourier Transform infra-red (FTIR) spectroscopy. The results show that at temperatures of 135° and 220°C, all the compounds inhibit carbonyl formation and mass loss of PP, the polymeric hindered amine (Cyasorb UV 3346) being the most efficient. This is in agreement with previous published work. However, the formulations containing the amines and the nickel complexes show different behaviours in relation to the optimum concentration required to achieve maximum stabilisation of the polymer under these conditions. Both synergistic and antagonistic effects are observed, the effect depending on the concentration ratio, the nature of the components and the temperature. In general, during thermal oxidation, the interaction appears to be indirect, the exception being the formulations containing AM 205 where a chemical interaction is observed. The results provide information regarding the use of mixtures of these compounds and have implications with respect to the mechanisms involved in stabilisation.

INTRODUCTION

The mechanism of action of hindered amine light stabilisers (HALS) has been, and continues to be, a subject of extensive study and much debate in

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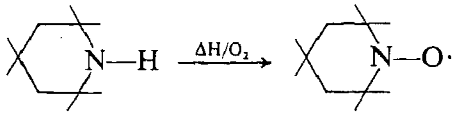
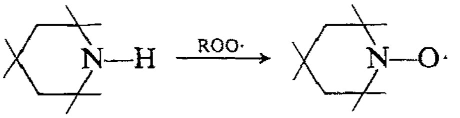
the field of polymer stabilisation.[1-10] The reason for the widespread interest is their excellent performance in polymers such as polyolefins,[1-4] polystyrene,[5] rubbers,[6,7] and acrylic resins.[8-11] Their mechanism of action has been discussed,[1-11] and most authors agree that it proceeds through the initial formation of a nitroxyl radical, thus:[1-11]



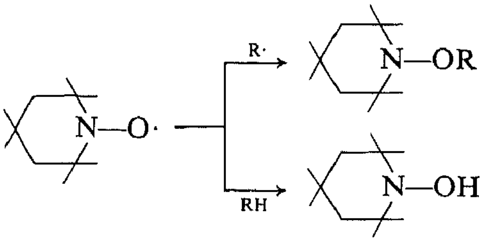
(1)



(2)

(3)

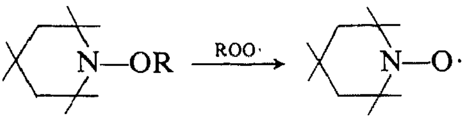
The nitroxyl then reacts with a macroalkyl radical or with the polymer matrix to form a hydroxylamine ether or a hydroxylamine:[1-11]



(4a)

(4b)

The derived hydroxylamine then reacts with a peroxyl radical to regenerate the nitroxyl, thus:[1-11]



(5)

Although this mechanism is now well established, there is a certain degree of controversy regarding the reactive intermediates involved in the stabilisation cycle.[1-11] Some of these aspects will be discussed below.

In recent years the interaction of HALS with other additives has been another subject of increasing relevance. Stabilisers are practically never used individually but rather in combination with other additives to minimise thermal oxidation during the processing operation or during long-term use. Both antagonistic and synergistic effects have been observed.[12-17] Thus, Allen *et al.*[12–15] observed both effects with a series of HALS used in conjunction with 'traditional' antioxidants, such as hindered phenols, phosphites and sulphur-containing antioxidants. Although the study was quite extensive in that it considered a wide range of antioxidants, it only considered a single concentration ratio (50:50), which does not necessarily give the optimum effect.

Chakraborty and Scott[16] originally attributed the antagonism observed between HALS and the dithiocarbamate transition metal complexes to the inhibition of reaction (3) by the latter, thus reducing the yield of nitroxyl from the former. Again, a single concentration ratio (50:50) was used in this study.

In a recent study Allen *et al.*[17] reported on the interactions between some metal complexes and a series of additives which included the commercial HALS, Tinuvin 770. They found[17] that the observed effect depends strongly on the concentration ratio and involves a chemical interaction between the HALS and the metal complexes. More recently, Chakraborty and Scott[18] have shown that the piperidine complex of zinc diethyldithiocarbamate (ZnDEC) is more effective as a UV stabiliser than the metal complex itself.

This study presents results which show that the interaction between HALS and metal complexes, during thermal oxidation, may be of a physical or a chemical nature and depends on the temperature, the molecular weight of the HALS and the concentration ratio of the components.

EXPERIMENTAL

Materials

Polypropylene powder containing no additives was kindly donated by Dr N. S. Allen, Manchester Polytechnic, UK. The hindered amines, Hostavin TM N20 (undisclosed structure), Tinuvin 770 [bis(2,2,6,6-tetramethyl-4-piperidinyl) sebacate], and Cyasorb UV 3346 poly[2-*N*,*N*′-di(2,2,6,6-tetramethyl-4-piperidinyl) hexanediamine-4-(*N*-morpholino) symtriazine], were kindly supplied by Hoechst AG, Frankfurt, FRG, Ciba-Geigy Products, Caracas, Venezuela and Cyanamid de Venezuela, respectively. The nickel complexes, Ferro AM 205 (undisclosed structure) and Robac Ni PD (nickel diethyldithiocarbamate), were kindly supplied by Ferro, USA and Robinson Bros, UK.

The additives were incorporated into the polymer powder by solvent blending with dichloromethane and allowing the solvent to evaporate overnight. Film samples (~100 μm) were prepared by compression moulding (5 min at 180°C).

Oven ageing

Oven ageing was carried out in a draught oven in air at 135°C. Rates of photooxidation were monitored by the established carbonyl index method,[13-15,17] using IR spectroscopy, the rate being expressed as time t, to a carbonyl index of 0·6. Infra-red spectra were obtained using a Nicolet 5DX-C FTIR spectrometer.

Melt oxidation

Oxidation in the melt was carried out in a DuPont 990 Thermal Analyser using a thermogravimetric (TGA) cell (DuPont 951) operating in the isothermal mode (at 220°C). The measurements were made in platinum boats, under aerobic conditions. Mass loss values are measured after 60 min.

Second-derivative ultraviolet (UV) measurements

Second-derivative ($d^2A/d\lambda^2$) UV spectra were measured in a Perkin–Elmer Model 559 UV spectrophotometer.

Solution experiments

Solutions of the HALS and the metal complexes (2% each in carbon tetrachloride) were refluxed for 7 h. They were then cooled to room temperature and analysed by FTIR and UV spectroscopy. They were also examined using thin layer chromatography (TLC).

RESULTS AND DISCUSSION

Figure 1 shows the rates of thermal oxidation of PP (at 135°C) in the presence of the five compounds under study, compared with unstabilised PP. The decreasing order of stability is Cyasorb UV 3346 > Tinuvin 770 > Robac Ni PD > Hostavin TM N20 > control, demonstrating the higher efficiency of the polymeric HALS. This is confirmed in Fig. 2, which shows the mass loss of PP at 200°C in air. The only compound to show an induction period is Cyasorb UV 3346. This greater efficiency of Cyasorb UV 3346 is in agreement with previous reports by Allen and co-workers.[4,19] The results obtained for the interactions between HALS and metal complexes will be discussed in the following sections.

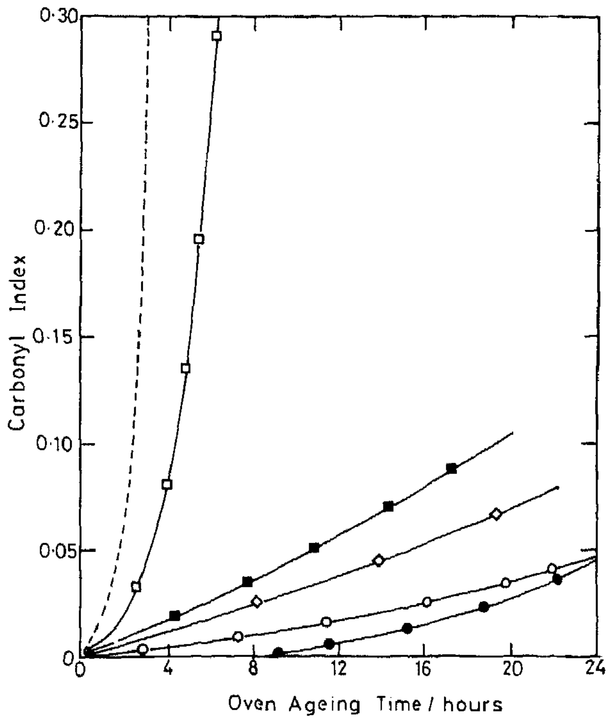


Fig. 1. Rates of thermo-oxidation (at 135°C) of PP films (~100 μm thick) containing: ----, no additives; -□-, AM 205; -◇-, Robac Ni PD; -○-, Tinuvin 770; -■-, Hostavin TM N20; and -●-, Cyasorb UV 3346; at 0·2 wt% each.

Cyasorb UV 3346

Figures 3 and 4 show the interaction between Cyasorb UV 3346 and nickel dithiocarbamate (Robac Ni PD), during oven ageing and high temperature oxidation respectively. Both synergistic and antagonistic effects are observed. However, at melt temperatures, synergism is only observed at a 20/80 ratio of HALS to nickel complex, whereas the opposite behaviour is observed during oven ageing. There were no significant changes observed in the UV spectrum of the nickel complex, nor in its rate of decomposition at 135°C, implying that there is no chemical interaction between the components. The main differences in the conditions at 135 and 220°C are that the rate of hydroperoxide formation is greater at the higher temperature, as is also the ability of the additive to diffuse through the polymer. The latter is of prime importance for polymeric HALS, since at the lower temperature (135°) its mobility in the polymer is severely restricted. This is probably the reason why its efficiency is reduced on a relative basis

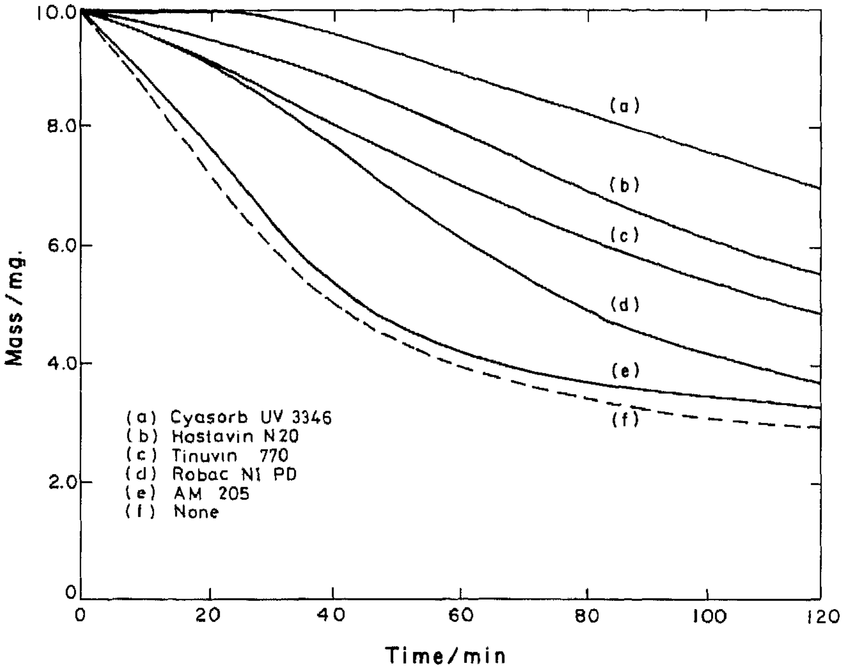


Fig. 2. Rates of mass loss (at 220°C) of PP samples containing 0·2 wt% of the additives.

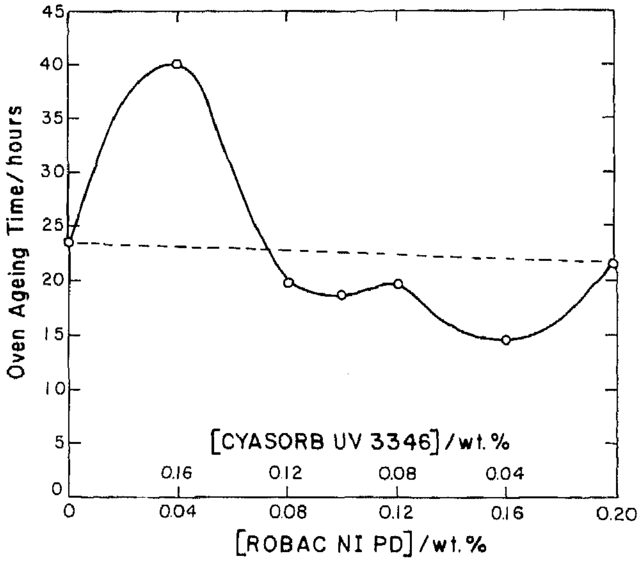


Fig. 3. Interaction between Cyasorb UV 3346 and Robac Ni PD in PP films after oven ageing at 135°C.

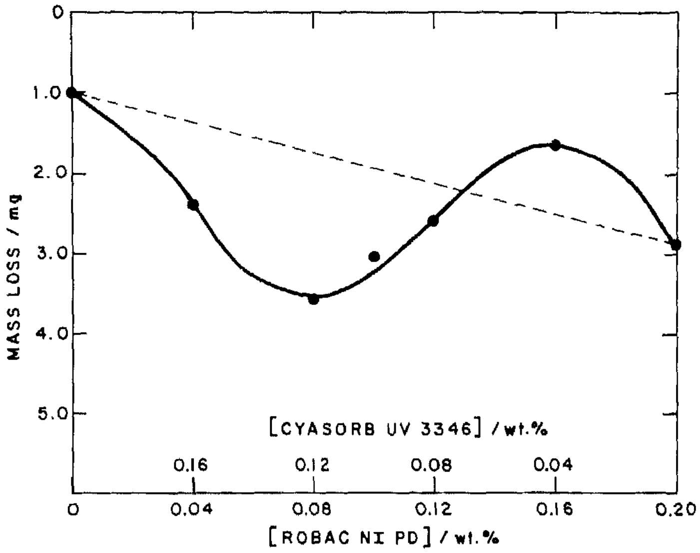


Fig. 4. Interaction between Cyasorb UV 3346 and Robac Ni PD in PP after melt oxidation at 220°C.

compared to the other compounds under study. It has previously been shown that there has to be a balance between compatibility in the polymer and the ability of the additive to diffuse to initiating radicals and/or hydroperoxides.[20] The higher mobility of the amine at melt temperatures will make it compete with the nickel complex more efficiently for hydroperoxides (reaction (3)). At lower temperatures the nickel complex will be more effective, reacting with the hydroperoxides due to its higher mobility, and therefore only when its concentration is relatively low in the mixture will synergism prevail, since its reaction with hydroperoxides will inhibit reaction (3), a vital step in amine-nitroxyl conversion.

The interaction between Cyasorb UV 3346 and AM 205 is shown in Figs 5 and 6, for oven ageing and melt oxidation respectively. AM 205 is a relatively poor thermal antioxidant in PP under the conditions of study, but at melt temperatures it shows synergism with UV 3346 (Fig. 6). During oven ageing, synergism is observed only when there is excess nickel complex (Fig. 5). In this case, direct chemical interaction between the two components was observed during the compression moulding stage, as shown by the second-order derivative UV spectra in Fig. 7. The major absorption band of the nickel complex in this region (at 290 nm) decreases in intensity in the presence of UV 3346 and new bands appear as shown in the figure. In order to try to understand the interaction, carbon tetrachloride solutions of the components were heated for 7 h and then examined using normal and

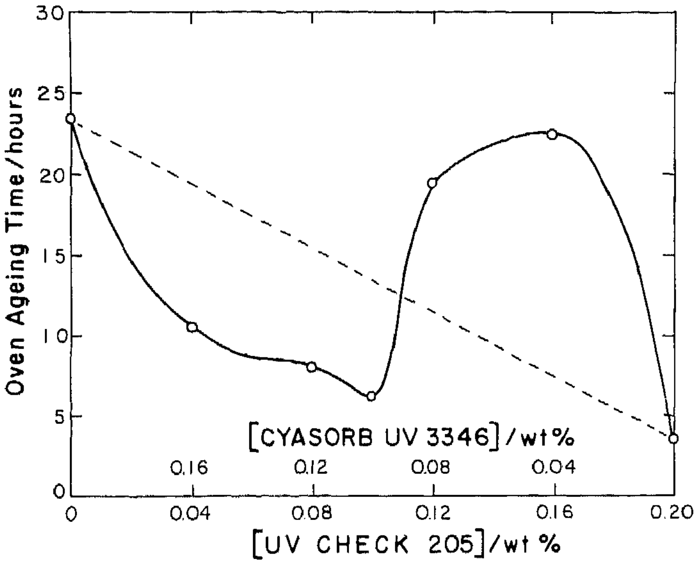


Fig. 5. Interaction between Cyasorb UV 3346 and Ferro AM 205 in PP films after oven ageing at 135°C.

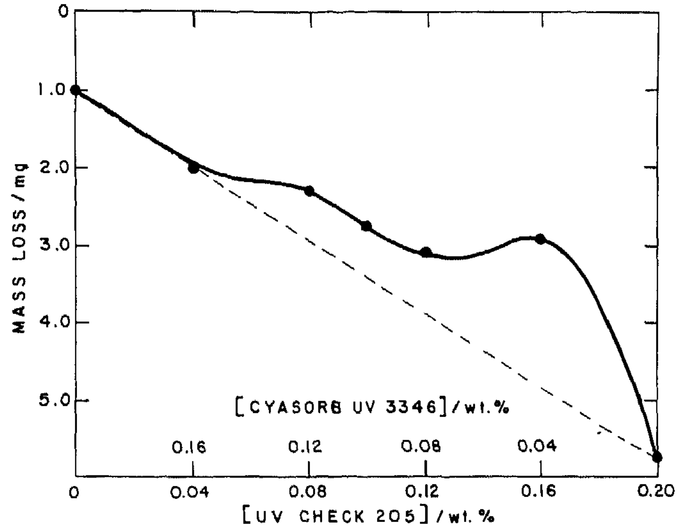


Fig. 6. Interaction between Cyasorb UV 3346 and Ferro AM 205 in PP after melt oxidation at 220°C.

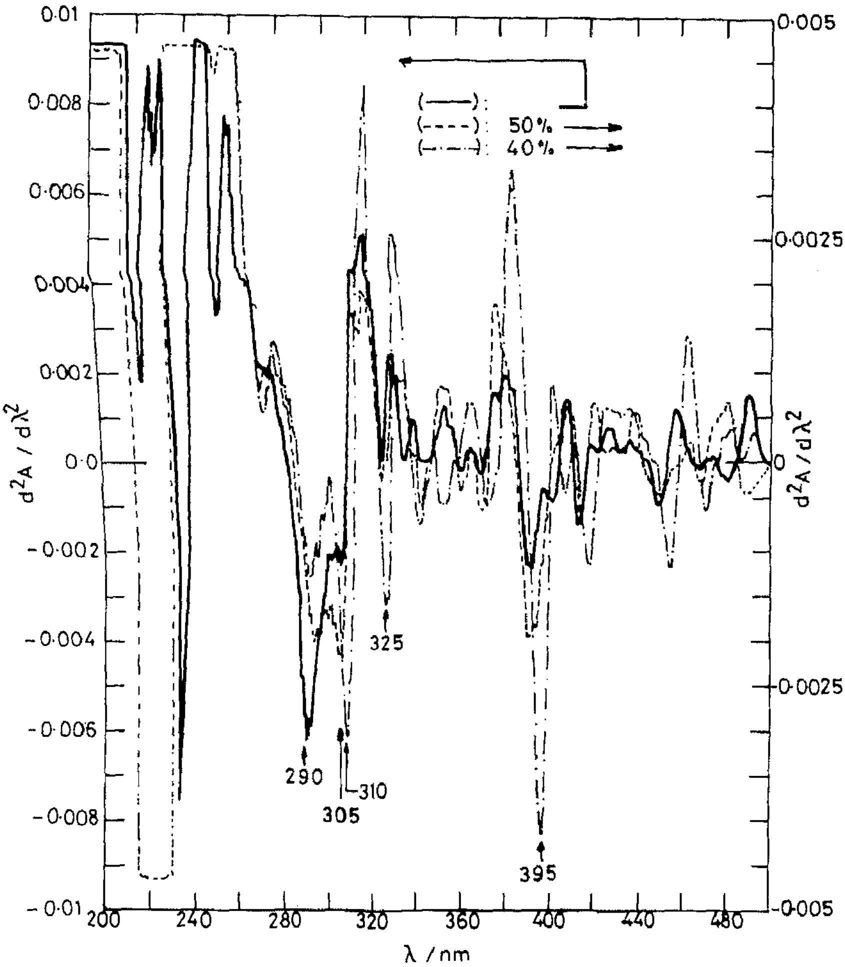


Fig. 7. Second-order derivative UV spectra of Ferro AM 205 in the absence (———) and in the presence of 50% (– – –) and 40% (–·–·–) of Cyasorb UV 3346 in PP films (total additive concentration 0·2 wt%).

second-order derivative UV spectroscopy and Fourier Transform infra-red (FTIR). A slight change in colour of the solution was observed and this is shown in Fig. 8. The changes in the second-order derivative UV spectrum in the 200–500 nm region are shown in Fig. 9. Some of the bands which appear in the mixture correspond to those observed in the polymer, indicating that the changes which occur are similar in both cases. However, high sensitivity FTIR studies showed no structural changes. This can only be explained by the formation of a complex between the amine and the nickel compound at the nickel site. This conclusion is also supported by the fact that TLC carried out in a wide variety of solvents showed no separation, indicating the

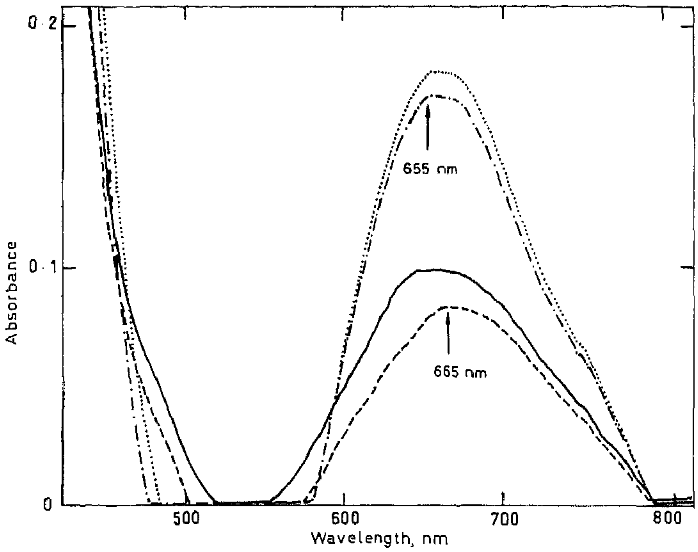


Fig. 8. Ultraviolet absorption spectra of Ferro AM 205 in carbon tetrachloride solutions (2%) before (·—·—·) and after (····) refluxing for 7 h, and in admixture with Cyasorb UV 3346 before (––––) and after (——) refluxing for 7 h.

presence of a single compound in the mixture. Complex formation has previously been observed between the nickel complex 2,2′-thiobis(4-tert-octyl phenolato) *n*-butylamine nickel (II) and cumene hydroperoxide in solution,[21] demonstrating the ability of nickel compounds to form complexes in solution and in the polymer. Furthermore, and as discussed above, Chakraborty and Scott[18] have recently prepared the ZnDEC–piperidine complex and showed it to be a better UV stabiliser that the parent nickel compound. A similar effect may be present here. The formation of the complex is obviously dependent on the concentration ratio and it will have a large influence on the observed interaction.

Tinuvin 770

Figures 10 and 11 show the interaction between Tinuvin 770 and Robac Ni PD, during oven ageing and melt oxidation respectively. In the former case strong synergism is observed, whereas in the latter weak synergism prevails. These results are in direct contrast with those observed by Chakraborty and Scott[16] and therefore with the proposed mechanism of inhibition of reaction (3) by the dithiocarbamate. This obviously implies that amine conversion to nitroxyl through hydroperoxides is strongly dependent on the HALS structure and/or molecular weight, and on the conditions. For Tinuvin 770,

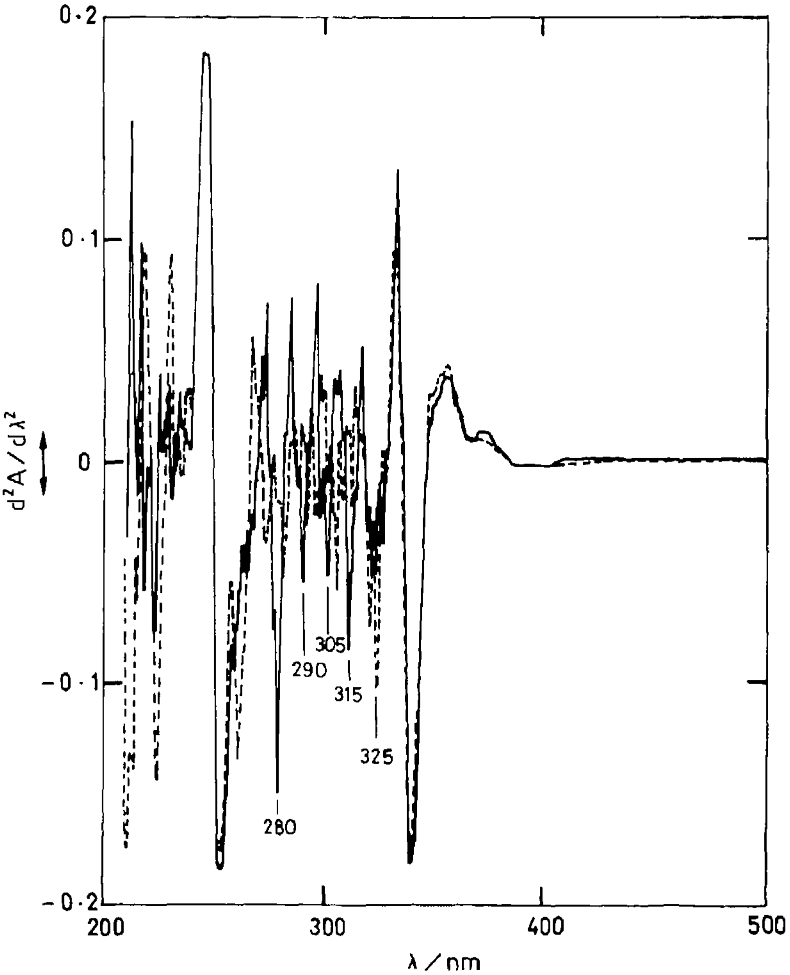


Fig. 9. Second-order derivative UV spectra of Ferro AM 205 in the absence (——) and in the presence (– – – –) of Cyasorb UV 3346 (1 : 1 mixture) in carbon tetrachloride solutions (2%) after refluxing for 7 h.

reaction with radicals to form the nitroxyl (e.g. reaction (2)) may be more important thermally, and thus complementary mechanisms (PD/CB-A) may be responsible for the synergism here. No chemical interaction was observed in this case.

Figures 12 and 13 show the corresponding curves for the interaction between Tinuvin 770 and AM 205, and it is interesting to note that the shape of the curves resembles those observed for UV 3346 and this metal complex. However, no strong chemical interaction was observed, as shown by second-order derivative spectroscopy in the 200–500 nm region, and this is

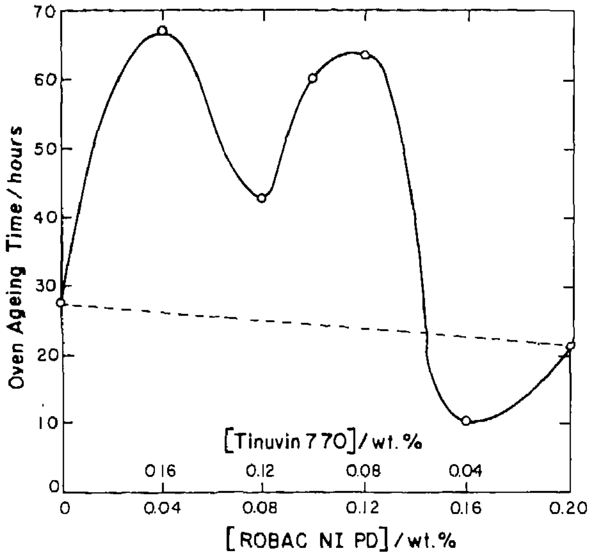


Fig. 10. Interaction between Tinuvin 770 and Robac Ni PD in PP films after oven ageing at 135°C.

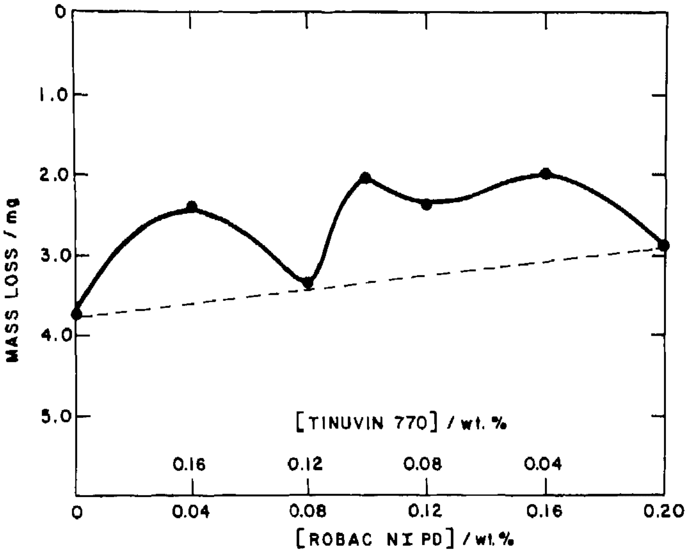


Fig. 11. Interaction between Tinuvin 770 and Robac Ni PD in PP after melt oxidation at 220°C.

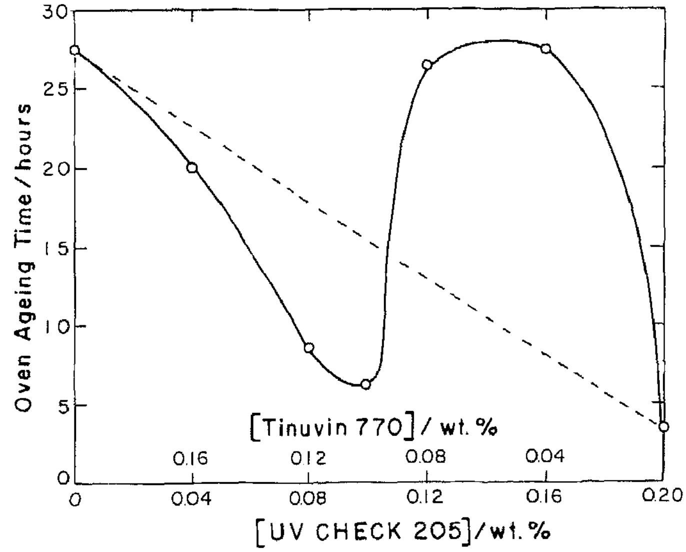


Fig. 12. Interaction between Tinuvin 770 and Ferro AM 205 in PP films after oven ageing at 135°C.

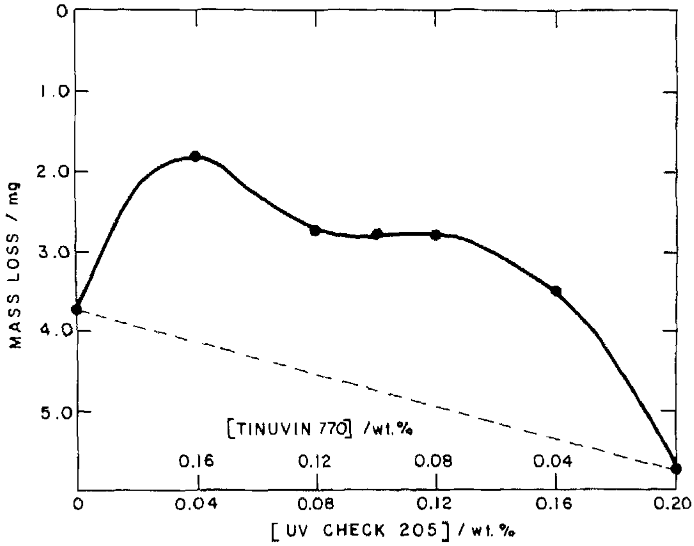


Fig. 13. Interaction between Tinuvin 770 and Ferro AM 205 in PP after melt oxidation at 220°C.

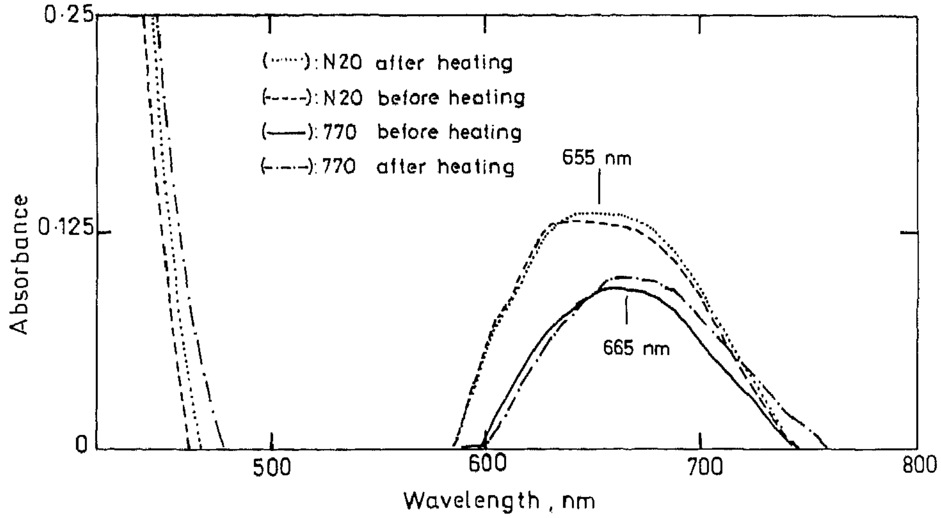


Fig. 14. Ultraviolet absorption spectra of AM 205 in carbon tetrachloride solutions (2%) in admixture (1:1) with Tinuvin 770 before (——) and after (·—·—) refluxing for 7 h, and Hostavin TM N20 before (– – – –) and after (····) refluxing for 7 h.

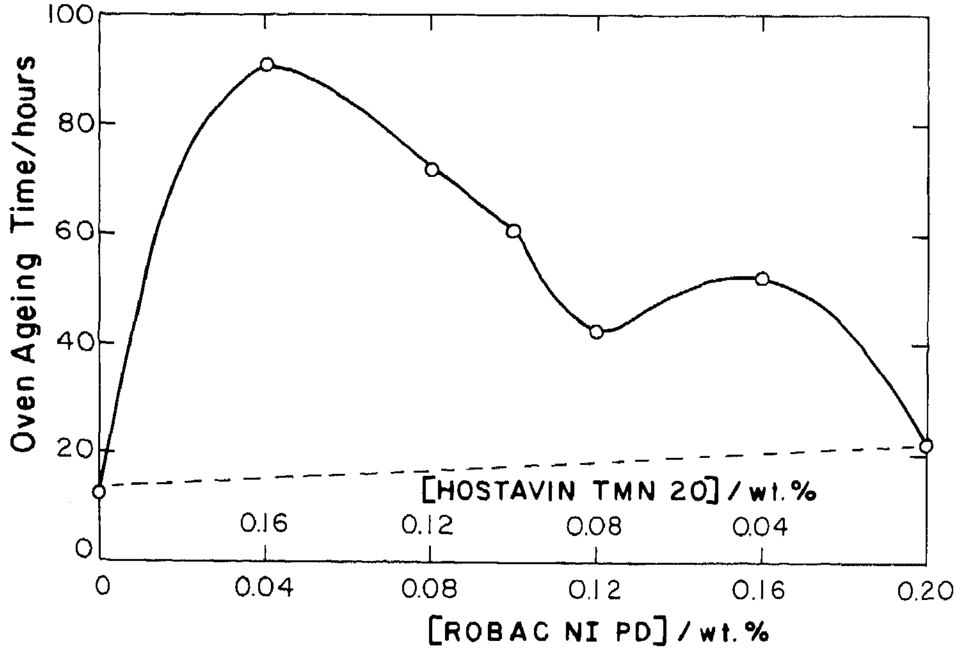


Fig. 15. Interaction between Hostavin TM N20 and Robac Ni PD in PP films after oven ageing at 135°C.

confirmed by the results shown in Fig. 14 for solutions in the region 500–800 nm. Compared with Fig. 8 it is obvious that there is a slight band broadening but no major shift. Thus, at most there is only weak interaction.

Hostavin TM N20

The structure of Hostavin TM N20 is undisclosed. However, it is believed to be a low molecular weight compound of the Tinuvin 770 type. The interaction between N20 and Robac Ni PD is shown in Figs 15 and 16, and as in the case of Tinuvin 770, it is synergistic in both cases. This supports the earlier conclusion that the low molecular weight HALS does not react preferentially with hydroperoxides as this would imply antagonistic behaviour with a peroxide decomposer. Thus, a complementary PD/CB-mechanism must be responsible for the observed synergism as no chemical interaction was observed.

The corresponding results for N20 and AM 205 are shown in Figs 17 and 18. Again, synergism is observed in both cases and the shape of the curves is identical at low and high temperatures, emphasising the decreased importance of mobility restrictions with lower molecular weight additives.

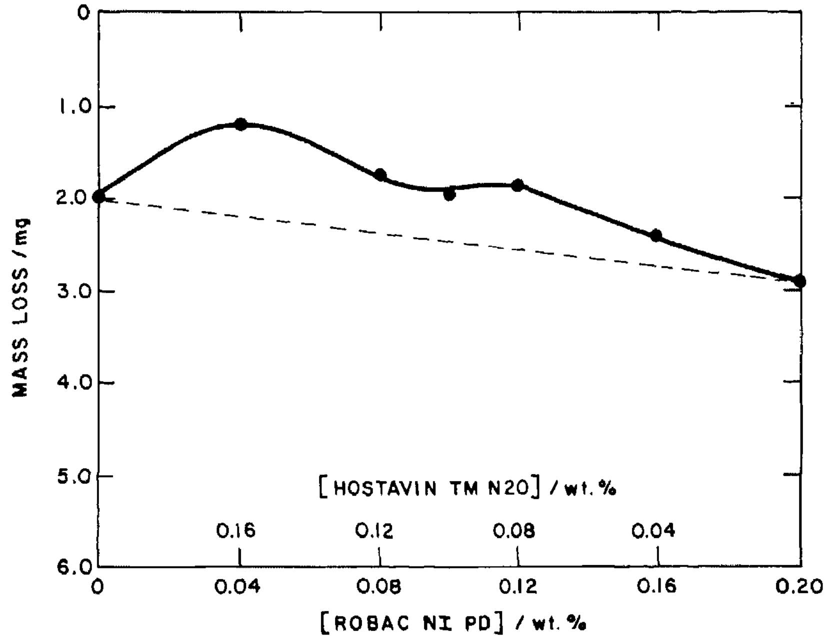


Fig. 16. Interaction between Hostavin TM N20 and Robac Ni PD in PP after melt oxidation at 220°C.

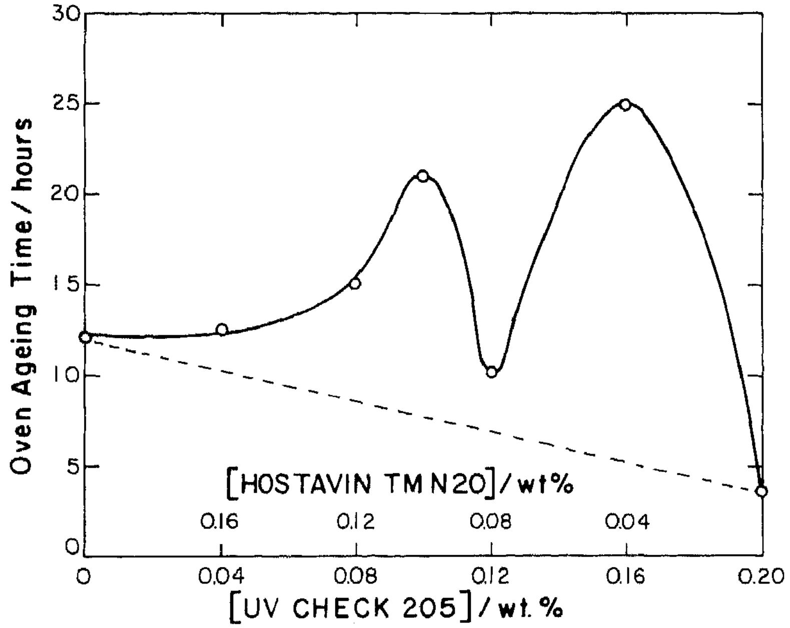


Fig. 17. Interaction between Hostavin TM N20 and Ferro AM 205 in PP films after oven ageing at 135°C.

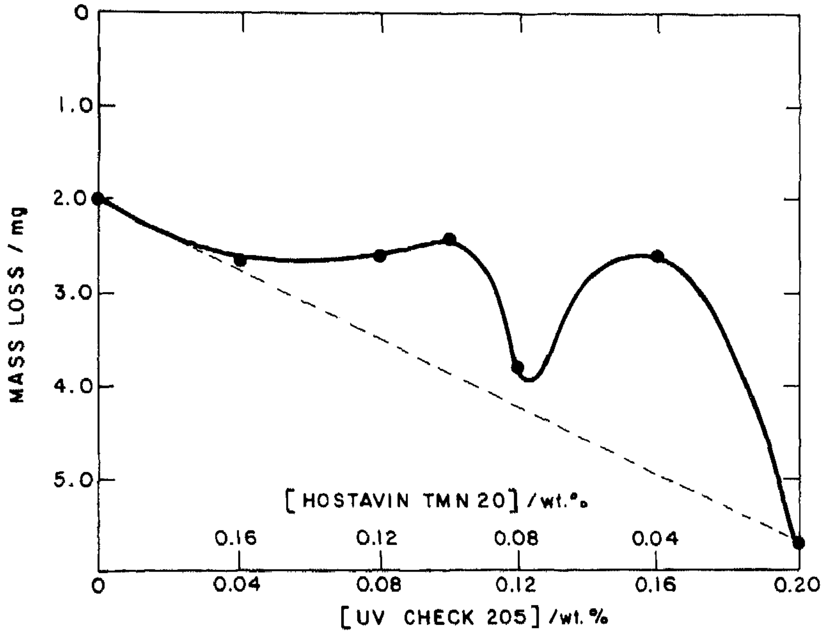


Fig. 18. Interaction between Hostavin TM N20 and Ferro AM 205 in PP after melt oxidation at 220°C.

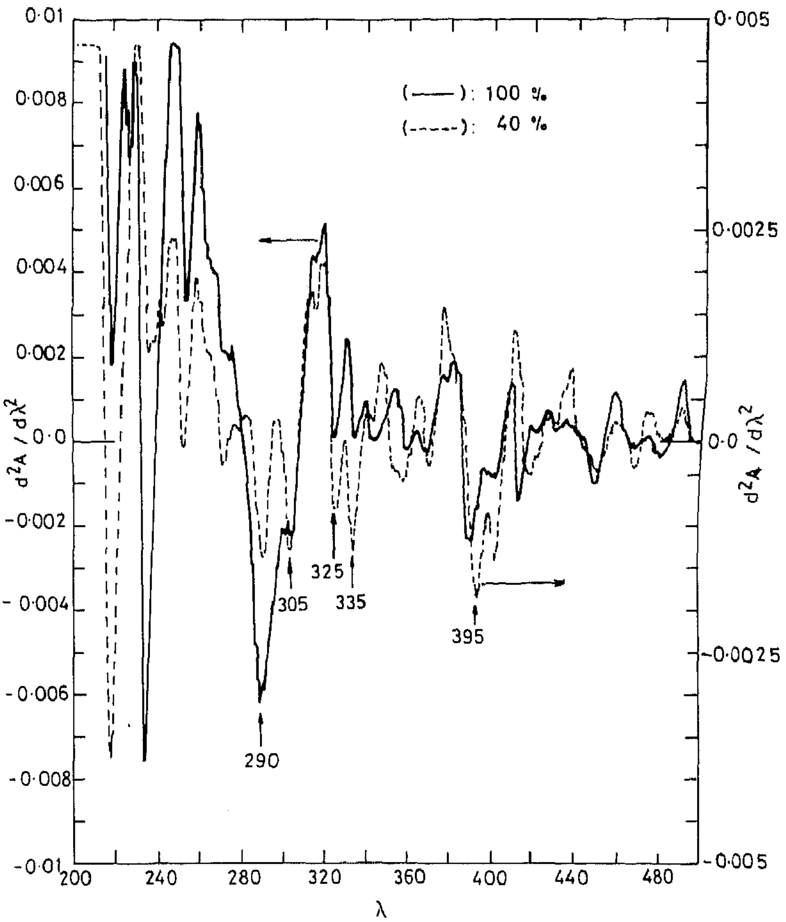


Fig. 19. Second-order derivative spectra of AM 205 in the absence (——) and in the presence (----) of 40% Hostavin TM N20 in PP films (total additive concentration 0·2 wt%).

Some chemical interaction was observed in the polymer as shown by Fig. 19, and this was supported by solution results already presented in Fig. 14 where a band shift towards longer wavelengths is observed. The colour change was visually apparent, indicating complex formation as for the case of UV 3346.

CONCLUSIONS

The results presented are further evidence for complex interaction which occurs when HALS are used with other additives in polymer stabilisation. The synergism or antagonism observed during thermal oxidation depends on (a) the nature of the components, (b) the concentration ratio, (c) the possibility of chemical interaction between them, (d) the stabilisation mechanism(s) involved, and (e) the temperature.

All these factors are important to a greater or a lesser extent and emphasise the complex chemistry involved. The results are also indicative of the effects obtained when these additives are used in conjunction with each other. Although normally the efficiency of these compounds is studied under conditions of UV irradiation, the polymer always has a thermal history prior to its end use.This thermal history is highly important in determining its subsequent lifetime. It has been shown in this paper that beneficial effects can be obtained by choice of a suitable combination of additives and an appropriate concentration ratio.

Experiments are in progress to study the interaction between these additives during photooxidation in PP and in other polymers.

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