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Hindered amine stabilisers as long-term heat stabilisers for polypropylene

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Abstract

A comparison is made between the efficiency of hindered amine stabilisers (HAS) and phenolic antioxidants as stabilisers against the thermo-oxidative degradation of polypropylene (PP) and their ability to reduce the oxidation rates of decalin, squalane and decalin/lauraldehyde mixtures. The stabilisation mechanism of phenolic antioxidants differs from that of HAS. Phenolic AOs are able to stop the oxidation of model compounds and PP. They are effective until they are consumed. The effectiveness of HAS depends on the system into which they are incorporated. When aldehydes can be formed (squalane and PP) or are added (decalin/lauraldehyde mixture) HAS are more effective than in cases where aldehydes do not play a role (decalin). The results with squalane and decalin/lauraldehyde mixtures are comparable to those with PP. The best comparison is found for squalane. © 1999 Elsevier Science Ltd. All rights reserved.

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1. Introduction

The service life of polypropylene (PP) is determined by its oxidative stability. Due to an autoxidative process the molecular structure of the polymer changes, which results in an impairment of the mechanical properties. The mechanism leading to the deterioration of PP is still a topic of discussion. Gijsman et al. [1] suggested that the autocatalytic behaviour of the oxidation of PP at relatively low temperatures is not due to the accumulation of hydroperoxides as proposed by Bolland and Gee [2,3], but to the formation of peracids. It was suggested [1] that at low-temperature PP oxidises in two stages. In the first stage, 'normal' oxidation takes place. In this period the rate of degradation is controlled by the rate of decomposition of hydroperoxides and oxidation products are formed. In the following stage, due to the restricted mobility, these oxidation products will be oxidised preferentially leading to peracids. When these peracids are present, they start to control the oxidation rate. Thus, at low temperatures the sudden increase in the oxidation rate is not due to the accumulation of hydroperoxides as expected but to the formation of peracids.

High molecular weight hindered amine stabilisers (HAS), which are well known as UV-stabilisers, have been promoted as long-term heat stabilisers for polymers, especially for polyolefins [4]. Gijsman [5] found that HAS and their nitroxides can reduce the oxidation rate of decalin/lauraldehyde mixtures, which are model compounds for oxidised PP, while they hardly reduce the oxidation rate of decalin alone, which is a model compound for PP. From these results it was concluded that HAS can prevent the oxidation of aldehydes leading to peracids, which explains the good performance of HAS at low temperatures.

In this paper, the stabilisation of PP against thermo-oxidative degradation is investigated. A comparison is made between the efficiency of HAS and phenolic antioxidants as stabilisers against the thermo-oxidative degradation of PP and their ability to reduce the oxidation rate of decalin, squalane and decalin/lauraldehyde mixtures.

2. Experimental

2.1. Thermo-oxidation of PP films

The characteristics of the PP used are given in Table 1. The stabilisers studied are three high molecular weight

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Table 1
PP powder characteristics

Material type	PP block copolymer
M_n	65.000
M_w	310.000
Rubber content	21%

HAS (1,3,5-triazine-2,4,6-triamine, *N,N‴*-[1,2-ethanediylbis [[[4,6-bis[butyl(1,2,2,6,6-pentamethyl-4-piperidinyl)amino]-1,3,5-triazine-2-yl]imino]-3,1-propanediyl]]-bis[*N′,N″*-dibutyl-*N′,N″*-bis(1,2,2,6,6-pentamethyl-4-piperidinyl) (HAS-1), poly[[6-[(1,1,3,3-tetramethylbutyl)-amino]-*s*-triazine-2,4-diyl][2,2,6,6-tetramethyl-4-piperidinyl)imino]hexamethylene [(2,2,6,6-tetramethyl-4-piperidinyl)imino]]} (HAS-2), poly[(6-morpholino-s-triazine-2,4-diyl)[2,2,6,6-tetra-methyl-4-piperidyl)imino]-hexamethylene[(2,2,6,6 tetra-methyl-4-piperidyl)imino]] (HAS-3)) and two phenolic antioxidants (tetrakis [methylene (3,5-di-t-butyl-4-hydroxyhydrocinnamate)] methane (AO-2) and benzenepropanoic acid, 3,5-bis(1,1-dimethylethyl)-4-hydroxy-octadecyl ester (AO-3)) that are well known as thermal stabilisers [4]. Their chemical structures are shown in Fig. 1. All the evaluations were done with 0.1 wt% of one of the stabilisers. The stabilisers were added to the polymer as solutions in dichloromethane. The solvent was removed by evaporation. The stabilised powders were pressed into films (~150 μm thick) at 190°C. In all the cases 0.1 wt% of Butylated Hydroxy Toluene (AO-1) was added to prevent degradation during processing. AO-1 was used because due to its high volatility it does not contribute to the oven-lifetime [6].

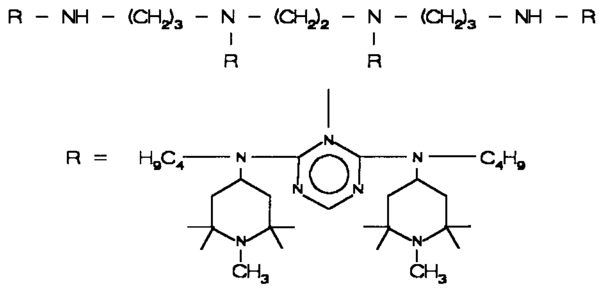
PP films were thermally aged at 120°C in a Heraeus D-6450 Hanau oven. Test temperatures above 120°C lead to results faster, however these are not representative of ageing at lower, more realistic, use-temperatures for the majority of polyolefin applications [7–9].

The chemical changes were measured with FT-IR. All the determinations were done on three different films containing the same stabiliser composition. The carbonyl absorbance was measured at 1713 cm^{-1}. Every absorption was corrected for baseline changes using the absorption at 1860 cm^{-1}.

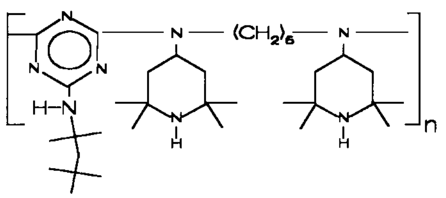
The change in the visual appearance of degradation was recorded by scanning a film that was oven-aged under the same conditions as the films on which the IR measurements were done.

2.2. Oxidation of the model compounds

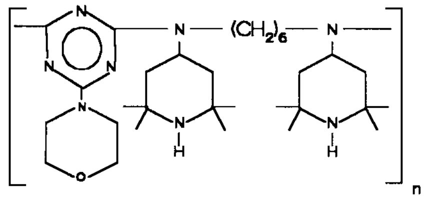
The influence of 0.1 wt% of the stabilisers mentioned in Fig. 1 was studied on the oxidation of three different



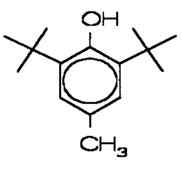
HAS-1 (Chimassorb®119)



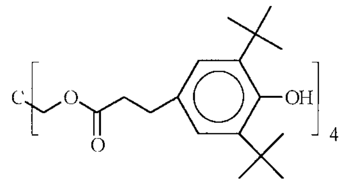
HAS-2 (Chimassorb®944)



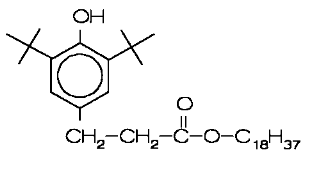
HAS-3 (Cyasorb®UV 3346)



AO-1 (BHT)



AO-2 (Irganox®1010)



AO-3 (Irganox®1076)

Fig. 1. Stabiliser chemical formulae and trade names.

model compounds: decalin (Baker), a mixture of 10% lauraldehyde (Aldrich) in decalin and squalane (Aldrich). Every reaction was initiated with 1% of *t*-butylhydroperoxide (Aldrich).

The reactions were done in a closed system filled with pure oxygen. In the closed vessel a molecular sieve (5 Å) was included in order to adsorb low molecular weight polar oxidation products. The top of the vessel was connected to a pressure transducer. The oxygen uptake expressed in mmol/kg was calculated from the pressure drop. The mixture was continuously stirred with a magnetic stirrer (380 rpm). The experiments were done in an oil bath at 100 and 120°C ± 2°C at least in duplicate.

3. Results

3.1. Model compounds

3.1.1. Decalin

Fig. 2 shows the oxygen uptake of decalin with and without different stabilisers at 120°C. The only stabilisers that are able to inhibit the autoxidation of decalin alone are the phenolic antioxidants AO-2 and AO-3. In the presence of these stabilisers there is an induction period before the oxidation starts. This induction time is longer for AO-2 than for AO-3. The different HAS stabilisers have almost no effect on the decalin oxidation rate; only HAS-1 has a small effect.

3.1.2. Decalin and lauraldehyde mixtures

In Figs. 3 and 4 the results for the oxygen uptake of decalin/lauraldehyde mixtures with different stabilisers at 100 and 120°C, respectively, are plotted. The degradation of decalin/lauraldehyde mixtures without stabiliser starts immediately (see Fig. 3). All the stabilisers evaluated reduce the autoxidation rate of this mixture. The times to 200 mmol/kg oxygen uptake are given in Table 2. At both temperatures HAS-3 performs worse than HAS-2, although there is only a small difference in their chemical structure. At 100°C, HAS-3 is by far the weakest in preventing the oxidation of the mixture. HAS-2 and AO-3 show about the same results; HAS-1 is more effective than AO-2. The order of efficiency at 120°C is about comparable. The only difference is that AO-2 is more effective than HAS-1.

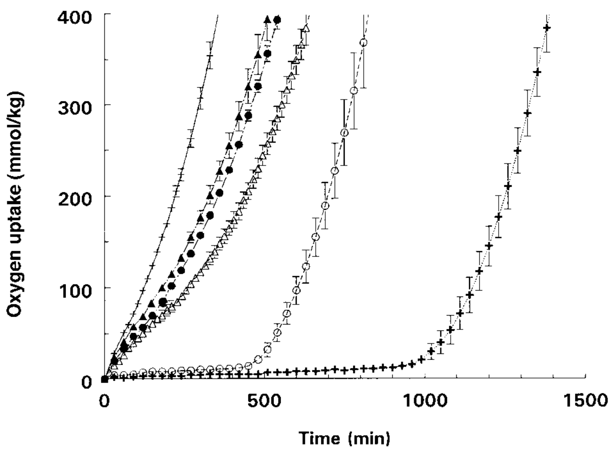


Fig. 2. Influence of 0.1 wt% of stabiliser on the oxidation rate of decalin at 120°C. Control (+), HAS-1 (△), HAS-2 (▲), HAS-3 (●), AO-2 (+) and AO-3 (○). Bars show the standard deviation.

3.1.3. Squalane

Fig. 5 shows the oxygen uptake of squalane with and without different stabilisers at 120°C. Every stabiliser studied is able to inhibit the autoxidation of squalane. Surprisingly, HAS-1 is by far the most effective here. It performs even better than AO-2. The order of increasing efficiency is AO-3, HAS-3, HAS-2, AO-2 and HAS-1.

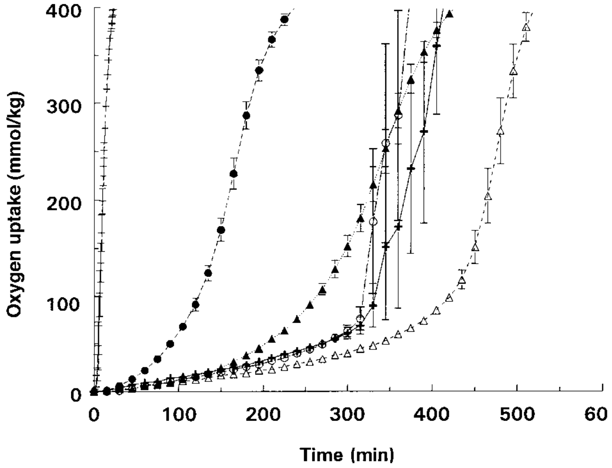


Fig. 3. Influence of 0.1 wt% of stabliser on the oxidation rate of a decalin/lauraldehyde mixture at 100°C. Control (+), HAS-1 (△), HAS-2 (▲), HAS-3 (●), AO-2 (+) and AO-3 (○). Bars show the standard deviation.

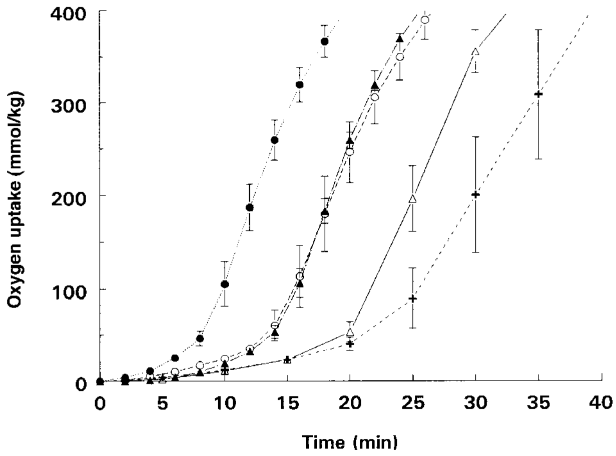


Fig. 4. Influence of 0.1 wt% stabiliser on the oxidation rate of a decalin/lauraldehyde mixture at 120°C. HAS-1 (△), HAS-2 (▲), HAS-3 (●), AO-2 (+) and AO-3 (○). Bars show the standard deviation.

Table 2
Time and standard deviation (SD) in min. to reach an oxygen uptake of 200 mmol/kg for decalin, decalin/lauraldehyde mixtures and squalane containing 0.1 wt% of stabilizer

	Decalin		Decalin/lauraldehyde mixture				Squalane	
	120°C		100°C		120°C		120°C	
	Time	SD	Time	SD	Time	SD	Time	SD
Control	225	10	10	1	< 5		350	50
AO-2	1250	40	375	30	29	7	4350	80
AO-3	705	45	345	25	18	2	2500	250
HAS-1	445	25	465	15	25	2	6790	350
HAS-2	330	20	320	15	18	1	3830	160
HAS-3	355	5	160	10	12	1	3600	220

3.2. Thermal ageing of PP films

During thermo-oxidative degradation the carbonyl absorbance increases. To compare the different compounds, the time to reach an increase of 0.1 in the carbonyl absorbance was used. These times are given in Table 3. According to this criterion, AO-2 is by far the most effective long-term heat stabiliser. HAS-2 is the second best. The lifetime of the compound containing HAS-2 is half that of the compound containing AO-2. The order of increasing efficiency is AO-3, HAS-3, HAS-1, HAS-2 and AO-2.

Besides the carbonyl increase, the stability of the compound was also determined visually and scanned images were made. During degradation, parts of the films became white [see Fig. 6(a) and (b)]. These white parts are totally brittle. The behaviour of the samples differs, depending on the type of stabiliser. Every phenolic-antioxidant-containing sample starts to degrade at the edges followed by the propagation of the degradation into the film [see Fig. 6(a) and (b)]. The HAS-containing films behave differently. The degradation starts more randomly and does not show the same spreading as that found for the AO-containing samples [see Fig. 6(c)–(e)]. The spreading rate is also different for the AO- and HAS-containing samples. It is quite slow for HAS-containing PP films whereas it is very fast for AO-containing samples. For example, AO-3-containing PP film is completely degraded within 200 h after the time at which the first changes are visible, while for HAS-1-containing PP film it takes 400 h. There is also a difference in the appearance of degradation between HAS-2 and HAS-1. The first appearance of degradation is earlier for the samples containing HAS-2 than for films containing HAS-1. In the presence of HAS-2 the degradation looks more homogeneous than with HAS-1. The spreading rate is also different, this is much higher in the presence of HAS-1 than with HAS-2.

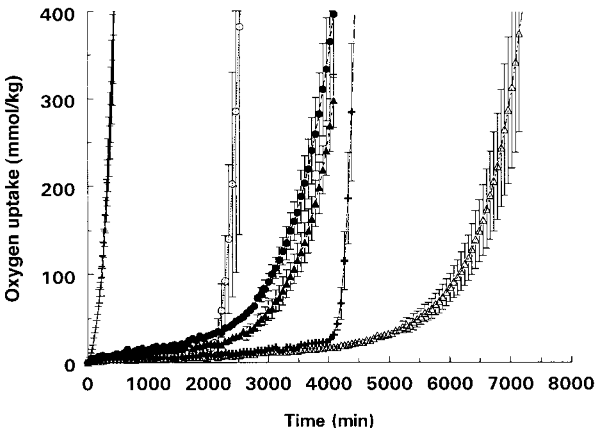


Fig. 5. Influence of 0.1 wt% of stabiliser on the oxidation rate of squalane at 120°C. Control (+), HAS-1 (△), HAS-2 (▲), HAS-3 (●), AO-2 (+) and AO-3 (○). Bars show the standard deviation.

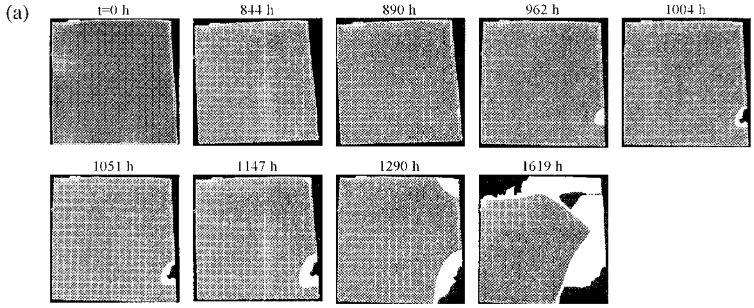
4. Discussion

4.1. Model compounds

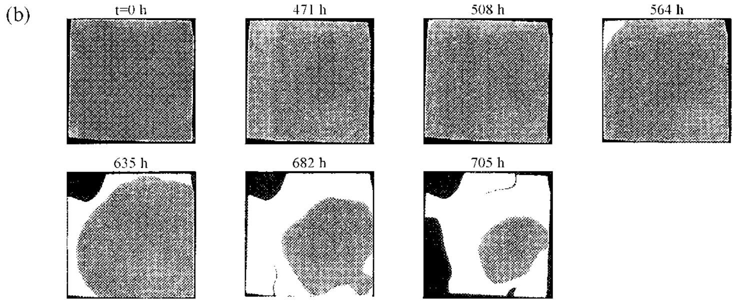
The experiments done with decalin at 120°C show an induction period in the presence of an AO. These stabilisers are able to stop the autoxidation of decalin, whereas HAS are not able to prevent it. However, when AOs are completely consumed the degradation is very fast.

Table 3
Oven-ageing time at 120°C (in h) to reach an increase in the cabonyl absorbance of 0.1 for 150 μm thick pressed PP films containing 0.1 wt% of stabiliser

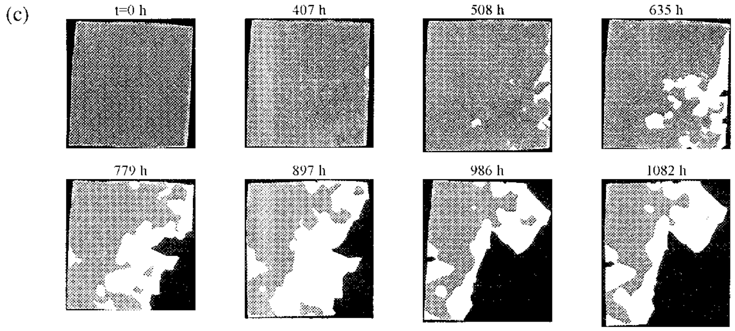
	Time (h) to 0.1 carbonyl absorbance increase	Standard deviation (h)
Control	< 24	
AO-2	> 1300	
AO-3	540	50
HAS-1	680	100
HAS-2	760	80
HAS-3	550	80



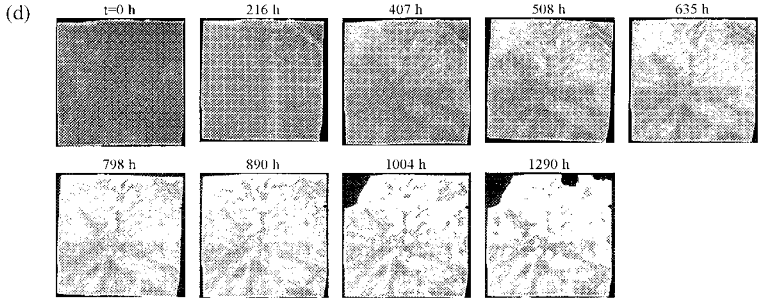
0.1 wt.% of AO-2



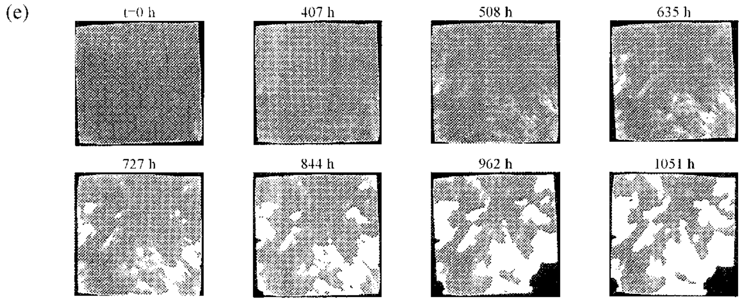
0.1 wt.% of AO-3



0.1 wt.% of HAS-1



0.1 wt.% of HAS-2



0.1 wt.% of HAS-3

Fig. 6. Scanned images of differently stabilised 150 μm thick pressed PP films after oven-ageing for different times (h) at 120°C.

Experiments carried out with decalin/lauraldehyde mixtures show that HAS are able to prevent the oxidation of aldehydes.

Although HAS are not able to stop the oxidation of the hydrocarbon decalin, they are able to stabilise squalane.

The efficiencies of the different stabilisers are highly dependent on the model system (see Table 2). AOs are effective in every system, but HAS are not effective in decalin. The oxidation of decalin takes place at the tertiary and secondary carbons leading to cyclodecanone and a mixture of decahydronaphthol isomers, therefore no aldehydes are formed [10]. The addition of 10% of lauraldehyde to decalin causes oxidation to start earlier. In these mixtures HAS are effective as stabilisers. HAS-1 becomes even more effective than AO-3. Squalane is a hydrocarbon containing secondary and tertiary hydrogens like decalin. However, the oxidation rate of squalane is slower than that of decalin. This difference becomes even more pronounced when stabilisers are added. Although squalane is a hydrocarbon, HAS are effective in reducing its oxidation rate even without the addition of aldehydes. HAS-1 is even more effective in squalane than AO-3. The difference between the oxidation of squalane and decalin might be that the oxidation of squalane will lead to aldehydes, while it was shown that the oxidation of decalin does not. The oxidation of squalane will lead to alkoxy radicals, which can lead to methyl ketones and primary radicals. The latter can be oxidised to aldehydes (see Scheme 1).

Besides a difference in oxidation rate, there is also a difference in the shape of the oxygen uptake versus time curve between HAS and phenolic antioxidants, especially in squalane (Fig. 5). In the presence of an AO there is a period of no oxygen uptake followed by a fast oxygen uptake, while in the presence of a HAS (especially HAS-2 and 3) there is oxygen uptake from the beginning followed by a smaller increase. This is consistent with the idea that AO can stop the oxidation of hydrocarbons completely, while HAS can only prevent the rapid oxidation of aldehydes.

4.2. Oven-ageing of PP films

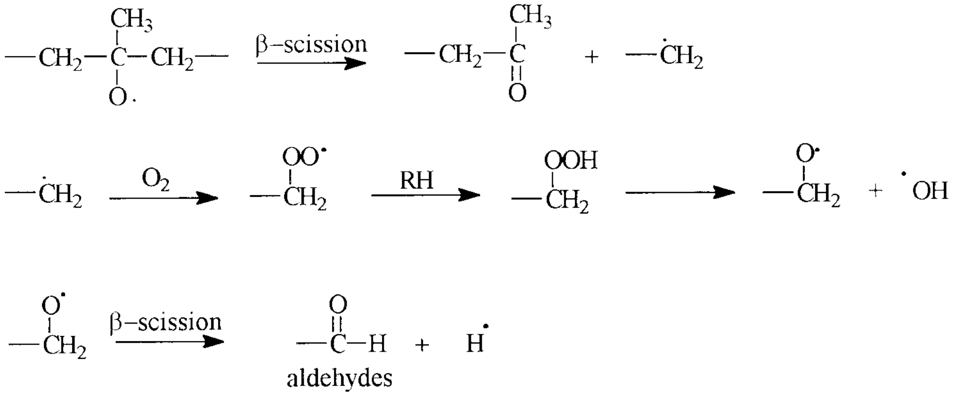
The difference in appearance of the thermo-degradation shows that there is a difference in the mechanism of action between phenolic AOs and HAS. During oven-ageing of PP, AOs are able to prevent the degradation completely for a long time. However, when the oxidation is started they are not able to stop the spreading of the oxidation probably because they are consumed while they are acting. HAS are not able to prevent the degradation of PP completely. Therefore the degradation starts early. However, they are more capable of decreasing the spreading rate than AOs. An advantage of HAS over AOs is that they are not consumed while they are doing their job. That is probably why they appear to be good retardants of the process.

Besides the chemical aspects discussed above, there is also a physical aspect. There is a difference in the degradation appearance between PP films containing HAS-1, HAS-2 and HAS-3. Although HAS-2 and HAS-3 have approximately the same chemical structure, a difference in molecular weight (see Table 4) might cause the difference in activity found.

4.3. Relationship between the oxidation of model compounds and PP

The degradation of the model compounds and PP with phenolic AOs differs from the degradation with HAS. The activity of AOs is independent of the model system. In every system they are able to stop the oxidation, which leads to an induction period followed by a fast oxidation. This is comparable to the degradation of PP. In the presence of AOs the degradation starts on the film edges and it propagates fast until the whole polymer is degraded.

The activity of HAS is highly dependent on the system. In a system in which no aldehydes can be formed, HAS are not effective. In the first stages of PP oxidation no aldehydes are formed, which is comparable to the degradation of decalin. In this period HAS are not effective. This results in an early initiation of PP oxidation



Scheme 1. Oxidation of squalane.

Table 4
Molecular weight of HAS used as long-term heat stabilisers of PP

	Molecular weight (g/mol)
HAS-1	2286
HAS-2	2500–4000
HAS-3	1600 ± 10%

as expected. However, when aldehydes can be formed or are added, HAS become effective and reduce the oxidation rate. Thus, when in PP aldehydes are formed the effectiveness of HAS increases, which causes a decrease in the propagation of the degraded spots formed initially. This is clear for HAS-2 and 3. HAS-1 is slightly different. It seems that its behaviour is intermediate between the other HAS and the AOs. This is probably because HAS-1 has low effectiveness against the oxidation of hydrocarbons as shown in the decalin experiments.

It is known that the relative effectiveness of HAS and AOs depend on ageing temperature. By decreasing the temperature from 120 to 100°C HAS-1 becomes more effective than AO-2 in PP. The same is found for the degradation of decalin/lauraldehyde mixtures.

Results obtained with squalane are about the same as for the oven-ageing of PP films. The only surprising result is that in squalane HAS-1 is more effective than AO-2, which is not the case in PP. However, in the decalin/lauraldehyde mixtures and in PP at 120°C the relative effectiveness of HAS-1 and AO-2 is the same.

For the comparison between the model experiments and the oven-ageings besides chemical parameters, physical ones like evaporation might also be important. On this point there is a big difference between PP and model compound degradation. The degradations with the model compounds were done in a closed system; in this case evaporation is not important at all. However, for the degradation of PP, evaporation might be very important. Thus the molecular weight of the stabilisers is more important for the degradation in PP than in the model compounds.

5. Conclusions

The stabilisation mechanism of phenolic AOs differs from that of HAS. AOs are able to stop the oxidation of model compounds and PP until they are consumed. After this period there is no effective stabiliser left, which results in a dramatically fast degradation. The effectiveness of HAS depends on the system into which they are incorporated. When aldehyde oxidation is important HAS are more effective than in cases where aldehydes do not play a role. As no aldehydes are formed during the first step of PP oxidation or during decalin oxidation, HAS are not effective in preventing the initiation of the degradation. However, when aldehydes are formed (PP or squalane) or added (to decalin), HAS become effective and reduce the oxidation rate. In the case of PP this results in an early but slow degradation. This oxidation is comparable to the oxidation of squalane and decalin/lauraldehyde.

The results with squalane and decalin/lauraldehyde mixtures are comparable to those with PP, especially for the results with PP and squalane. The model can be used to determine differences in chemical activity. However physical properties, like evaporation, will be more important for the degradation of PP than for the degradation of the model compounds.

The high effectiveness of HAS-1 in squalane might be caused by its double effectiveness. It is very active against the degradation of lauraldehyde/decalin mixtures but it also has a small effect against the degradation of decalin, so it is also able to prevent the oxidation in the early stages (before aldehydes are formed).

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