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Polymer Degradation and Stability 81 (2003) 483–489
Polymer Degradation and Stability
www.elsevier.com/locate/polydegstab

Aliphatic amines for use as long-term heat stabilizers for polypropylene

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Received 1 March 2003; accepted 1 April 2003

Abstract

It is well known that Hindered Amine Stabilizers (HAS) act as stabilizers preventing the thermo-oxidative degradation of polypropylene (PP). However, different commercial oligomeric HAS that contain a piperidinyl as well as a triazine moiety were found to differ in activity. The main difference between these types of HAS concerned the presence of different types of aliphatic amines in their backbones. We measured the influence of several aliphatic amines on the thermo-oxidative degradation of PP to find out whether this difference can explain the difference in activity of these commercial HAS. In the presence of a HAS or a phenolic antioxidant, aliphatic amines increase the thermo-oxidative stability of PP. This is probably due to their ability to react with aldehydes and in this way prevent the formation of peracids, which are known to increase the degradation rate of PP. The presence of primary or secondary amines in the chemical structure of a HAS in addition to the piperidinyl group has an influence on the activity of the HAS when it is used as a long-term heat stabilizer and may explain the difference in activity observed between some commercial HAS stabilizers.

Keywords: Hindered amine stabilizer; Phenolic antioxidant; Heterogeneous degradation; Thermo-oxidation

1. Introduction

We compared the efficiency of Hindered Amine Stabilizers (HAS) and phenolic antioxidants (AOs) used as stabilizers to prevent the thermo-oxidative degradation of polypropylene (PP) and their ability to reduce the oxidation rate of decalin, squalane and decalin/lauraldehyde mixtures [1,2], which are model compounds for PP. We found that the stabilization mechanism of phenolic antioxidants (AO) differs from that of HAS. Phenolic AOs are able to stop the oxidation of model compounds and PP. They are effective until they have been 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 in which aldehydes do not play a role (decalin). The results obtained with squalane and decalin/lauraldehyde mixtures were fairly well comparable with those obtained for PP [3].

We also found that the effectiveness of HAS is not only related to their piperidinyl group. Different types of oligomeric HAS containing a piperidinyl as well as a triazine moiety were found to differ in activity. HAS-1 and HAS-2 (see Fig. 1 for their chemical structures) were found to be the best HAS stabilizers, whereas HAS-3 had a poor effect on preventing the thermo-oxidation of PP [1]. As all of these HAS contain a triazine moiety (see Fig. 1), this structural part cannot be the reason for the difference in effectiveness. One aspect in which these molecules do differ is the presence of aliphatic amines: they are present in HAS-1 and HAS-2 but absent in HAS-3. In our experiments we therefore focused on the influence of different aliphatic amines on the thermo-oxidation of PP.

2. Experiments

2.1. Materials used

The polypropylene was a copolymer (see Table 1 for its characteristics).

The chemical structures of the antioxidants and hindered amine stabilizers are given in Fig. 1. Depending

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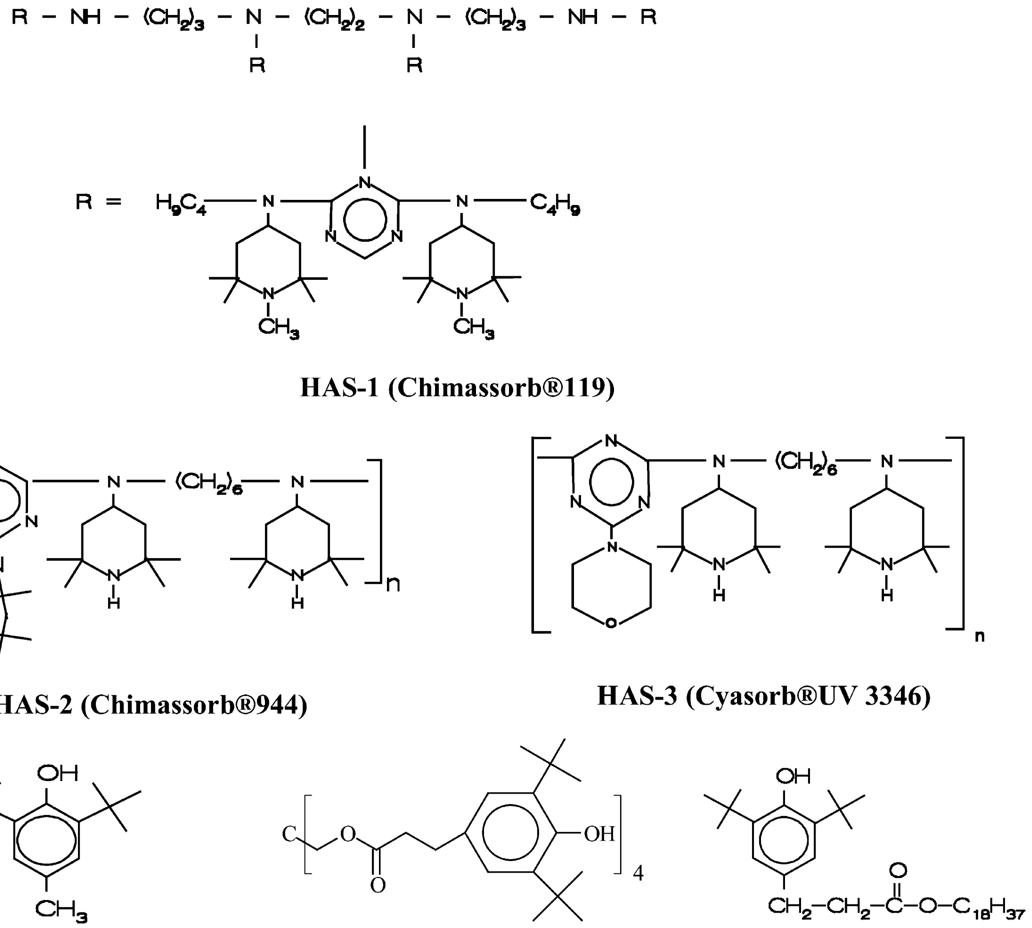
doi:10.1016/S0141-3910(03)00134-4



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. Chemical formulae and trade names of the employed stabilizers.

Table 1
PP powder characteristics

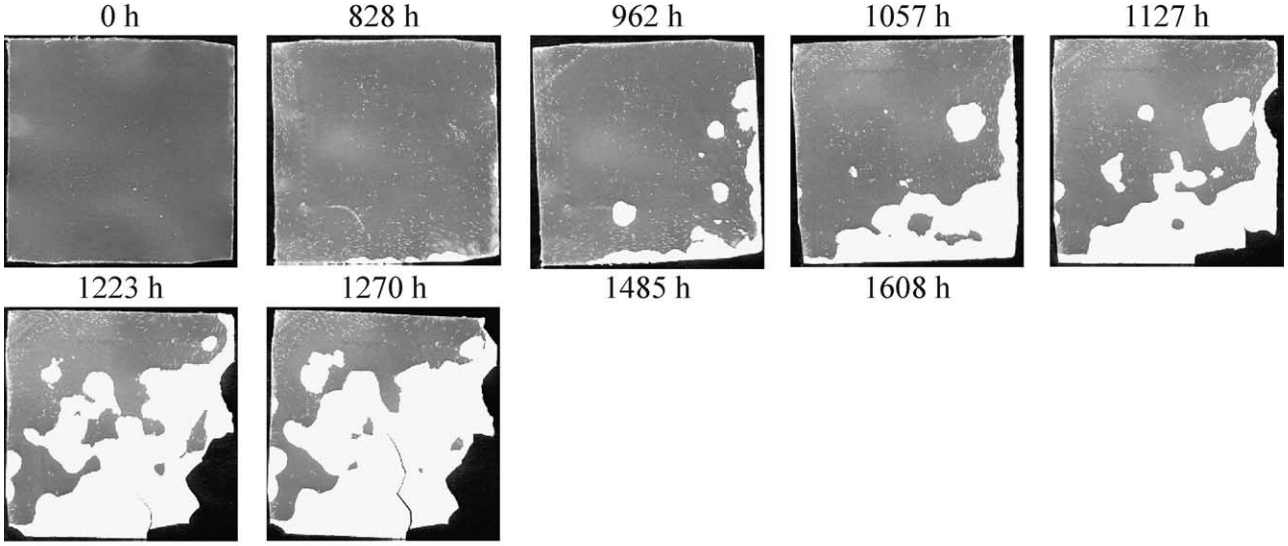
Type of material	PP block copolymer
M_n	65,000
M_w	310,000
Rubber content	21%

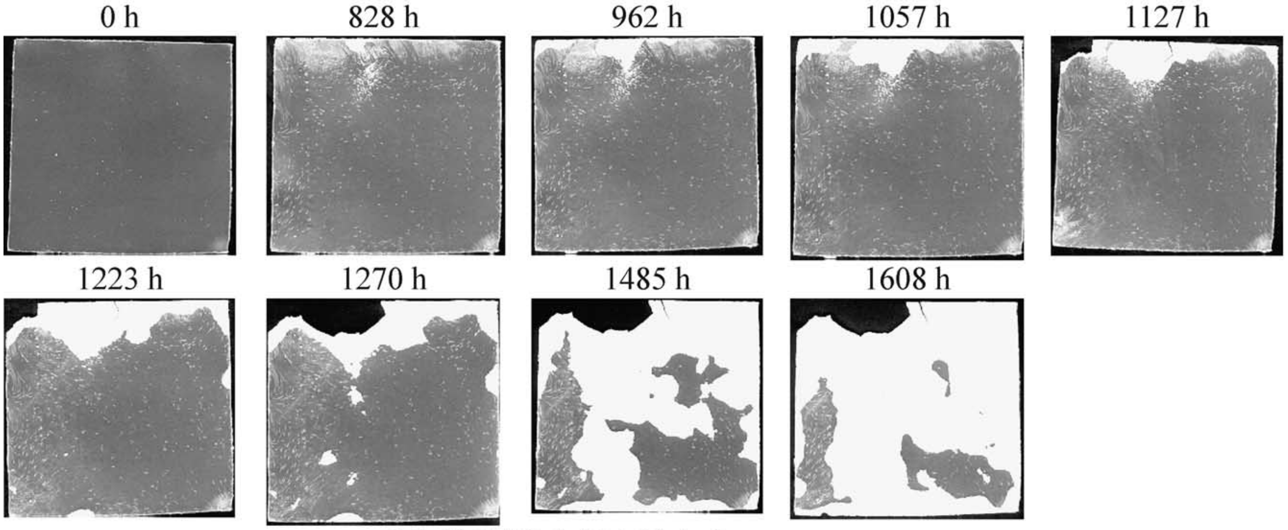
on their molecular weight, the aliphatic amines were evaluated as such or as stearic acid salts. The names and characteristics of the aliphatic amines studied are given in Table 2. The distearate A-2 and the stearate salt A-3 were prepared by dropwise adding a solution of one or two equivalents of stearic acid in ethanol to a one-equivalent solution of the amine in ethanol at room temperature, followed by evaporation of the solvent.

The stabilizers were added to the polymer powder dissolved in dichloromethane. The solvent was removed through evaporation. The stabilized powders were compressed to form films (~150 μm thick, 4 cm^2) at 190 °C. In all cases 0.1 wt.% of AO-1 was added to prevent degradation during processing. AO-1 was used because it would not affect the ageing in the oven due to its high volatility [4].

Table 2
Names and characteristics of the employed amines

Name	Chemical structure	Molecular weight	Supplier
Distearylamine (**A-1**)	$NH(C_{18}H_{37})_2$	522	Fluka
3, 3′-Iminobis(*N*,*N*-dimethylpropylamine) distearate (**A-2**)	$HN[(CH_2)_3N(CH_3)_2]_2 + 2C_{17}H_{35}COOH$	756	Aldrich
N,*N*′,*N*″-Trimethylbis (hexamethylene)triamine stearate (**A-3**)	$CH_3N[(CH_2)_6NHCH_3]_2 + C_{17}H_{35}COOH$	542	Aldrich
Tetraethylenepentamine (**A-4**)	$NH(CH_2CH_2NHCH_2CH_2NH_2)_2$	189	Acros


0.1 % HAS-1


0.1 % HAS-1 + 0.1 % A-1

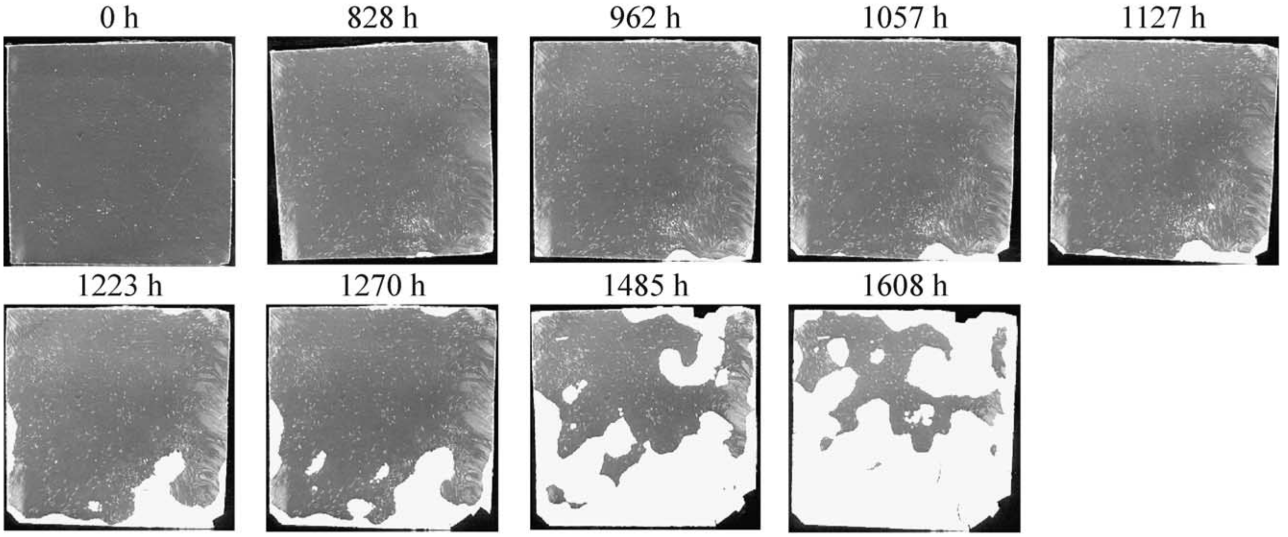

0.1 % HAS-1 +0.1 % A-3

Fig. 2. Scanned images of 150 μm PP films containing: 0.1 wt.% HAS-1 without additional additives (top), with 0.1% A-1 (middle) and with 0.1% A-3 (bottom) aged for different times at 120 °C.

2.2. Thermo-oxidation of PP films

The PP films were thermally aged at 120 °C in a Heraeus D-6450 oven. xperimental temperatures of more than 120 °C lead to results faster, but they are not representative of ageing at the lower temperatures that tend to prevail in the majority of polyolefin applications [5–7].

The chemical changes were measured with the aid of FT-IR. All the determinations were performed on three different films with the same stabilizer composition. The carbonyl absorbance was measured at 1713 cm^{-1}. The absorptions were corrected for baseline changes using the absorption at 1860 cm^{-1}.

The change in visual appearance due to degradation was recorded by scanning a film that had been oven-aged under the same conditions as the films used for the IR measurements.

3. Results

During thermo-oxidative degradation visual images of the films were recorded as a function of the degradation time. The images obtained for HAS-1, AO-2 and AO-3 with and without different aliphatic amines are presented in Figs. 2–4. During degradation part of the films became white; these parts were completely brittle. In the case of the only HAS-1-containing PP film degradation began at the edge of the film, but after 962 h random initiation was visible, too (Fig. 2). The addition of A-1 and A-3 stearate did not have a major influence on the starting time of the degradation, but these aliphatic amines did have an influence on the distribution of the oxidation (Fig. 2). After 1223 h the HAS-1-containing sample without additional aliphatic amine was almost completely brittle, whereas the aliphatic-amine-containing sample only showed degradation at the edge of the

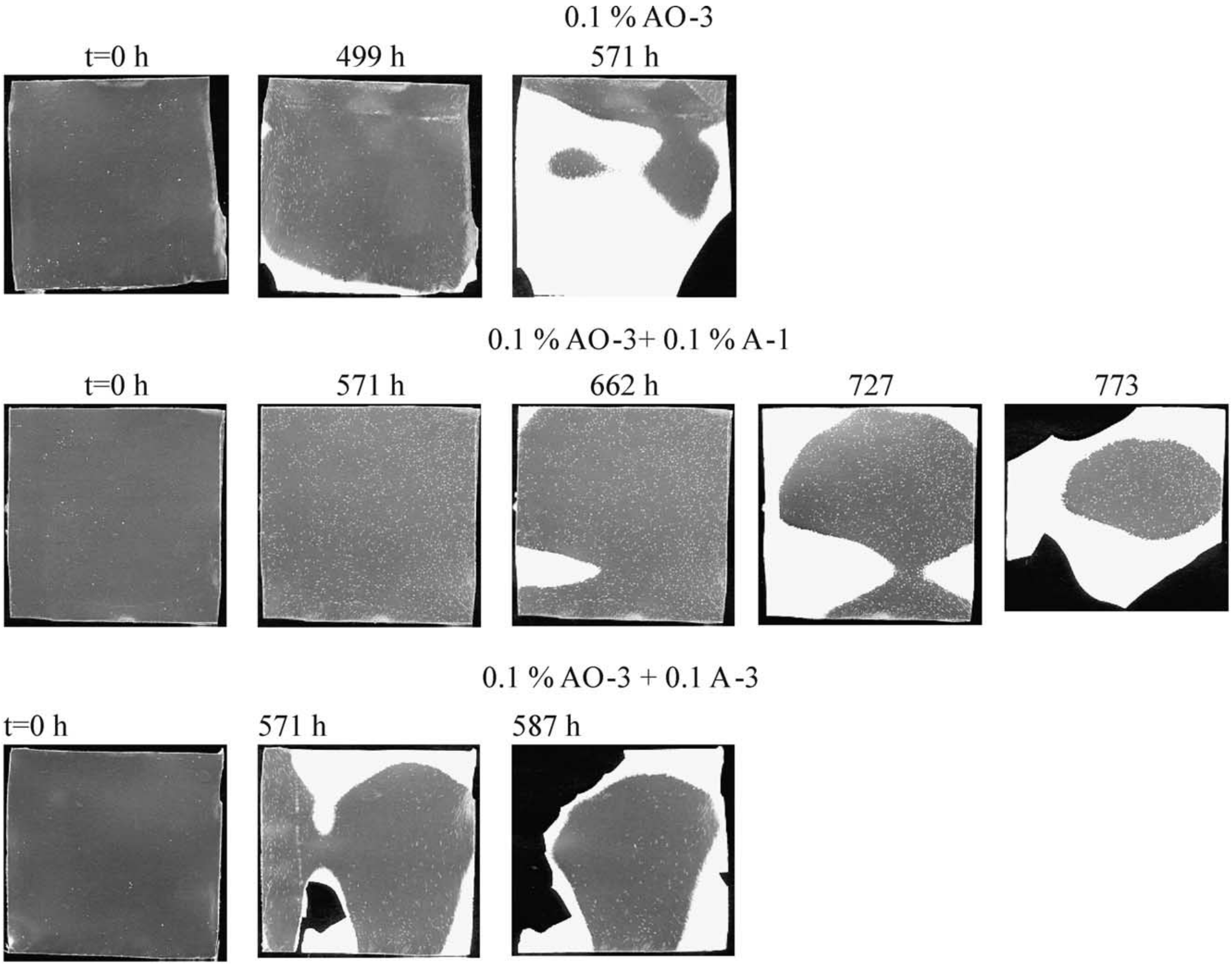


Fig. 3. Scanned images of 150 μm PP films containing: 0.1 wt.% AO-3 without additional additives (top), with 0.1% A-1 (middle) and with 0.1% A-3 (bottom) aged for different times at 120 °C.

film. In the presence of HAS-1 the two aliphatic amines showed more or less the same effectiveness. In the presence of AO-2, A-1 was however more effective than A-3 (Fig. 3).

During thermo-oxidation degradation the carbonyl absorbance increases. So as to be able to compare the different compounds, we measured the amount of time required to realize an increase of 0.1 in the carbonyl absorbance. Because the degradation was heterogeneous, we performed these measurements in triplicate and then calculated the mean value and the standard deviation (see Table 3). Of all the amines used only A-1 had a small influence on the lifetime. All the other evaluated amines had no noticeable influence on the stability of PP. Different results were obtained in the presence of an HAS or a phenolic antioxidant. In the presence of 0.1% HAS-1 the addition of 0.1% of the different amines resulted in longer lifetimes. A-4 was then found to be the most effective. The stability realized by adding 0.1% of the different amines was however poorer than that realized by increasing the concentration of HAS-1 from 0.1 to 0.2%. The effect of the amines seems to be greater in the presence of 0.2% than in the presence of 0.1% HAS-1. When 0.1% A-4 was added to 0.2% HAS-1, 0.1 carbonyl absorbance was reached after 2800 h. A-4 was also effective in the presence of HAS-2. HAS-2 was however much less effective than HAS-1. The different amines were not only effective in the presence of a HAS but also in the presence of an antioxidant. The increase in stability realized in the presence of a HAS was however greater than that realized in the presence of an antioxidant. In the presence of 0.1% AO-3 the addition of A-3 resulted in an increase in stability from about 1900 to 2300 h, whereas in the presence of 0.2% AO-3 the same addition resulted in an increase in stability from about 2800 to 3300 h. AO-3 was less effective than AO-2. But in the presence of this antioxidant aliphatic amines are also capable of increasing stability.

Table 3
Oven-ageing time and standard deviation (S.D.) (based on three measurements) at 120 °C required to reach an increase in the carbonyl absorbance of 0.1 using 150 μm thick pressed PP films containing different stabilizers

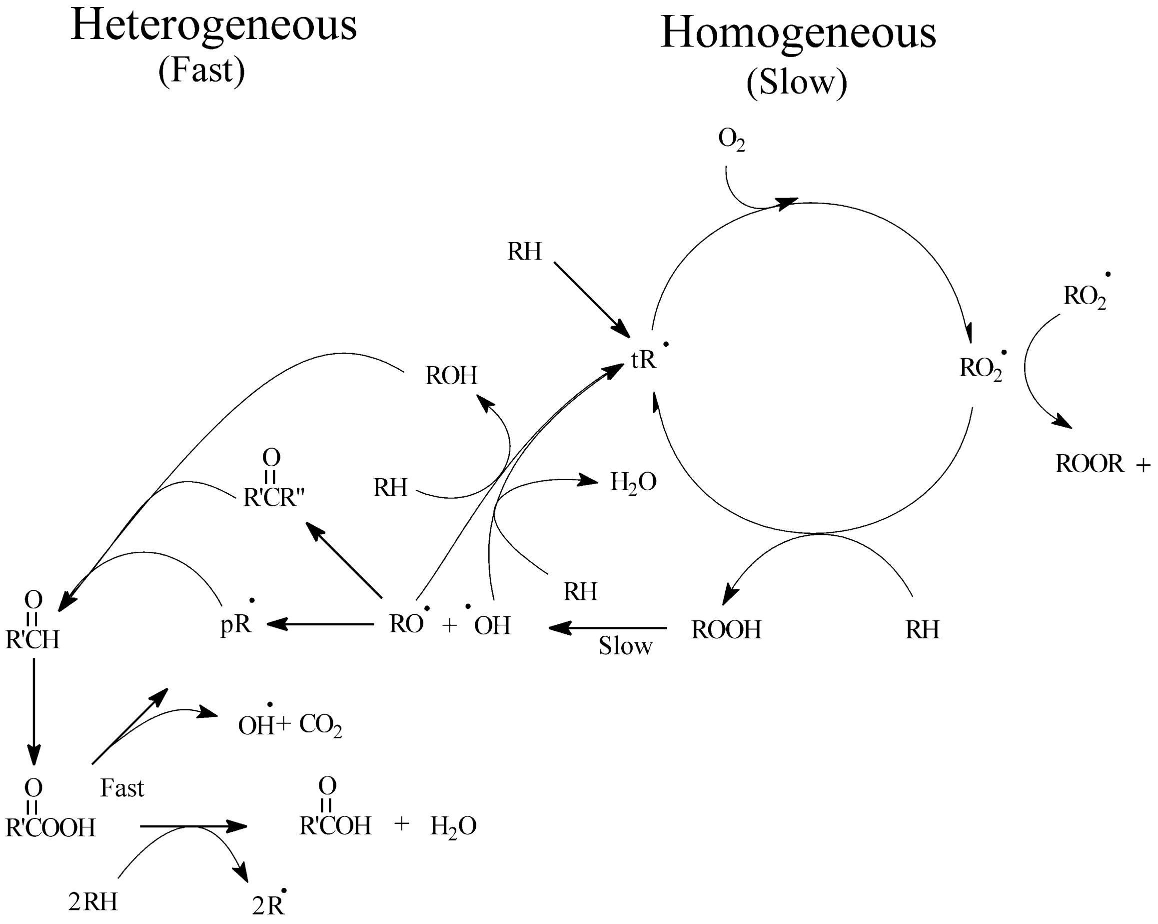
HAS-1	HAS-2	AO-2	AO-3	A-1	A-2	A-3	A-4	Ageing time (h)	S.D.
								<22	
				0.1				70	20
					0.1			<24	
						0.1		<22	
							0.1	14	
0.1								780	90
0.1				0.1				1210	130
0.1					0.1			1020	
0.1						0.1		1210	240
0.1							0.1	>1300	
0.2								1890	140
0.2				0.1				2590	290
0.2						0.1		2800	390
	0.1							485	15
	0.1						0.1	855	75
		0.1						1890	60
		0.1		0.1				2060	50
		0.1				0.1		2310	140
		0.2						2840	230
		0.2		0.1				3070	280
		0.2				0.1		3280	130
			0.1					540	50
			0.1	0.1				595	25
			0.1			0.1		700	50
			0.1				0.1	840	40
			0.2					685	80
			0.2	0.1				770	50
			0.2			0.1		930	10

4. Discussion

According to the generally accepted mechanism underlying the oxidation of PP first described by Bolland and Gee [8,9], the acceleration of the oxidation reaction is due to the formation of hydroperoxides. The decomposition of these hydroperoxides leads to new radicals, which initiate new oxidation cycles. However, this accounts for only part of the degradation mechanism. It was found that the rate of radical formation due to the decomposition of hydroperoxides is too slow to explain the auto-acceleration of the oxidation reaction [10]. This acceleration is probably due to the decomposition of peracids formed in the oxidation of oxidation products (see Scheme 1).

The function of stabilizers such as AOs and HAS is to reduce the oxidation rate of polymers, but this is realized via different mechanisms. AOs are capable of scavenging all the radicals and of interfering in the primary oxidation, but they are consumed in the process. Secondary oxidation begins to play a role only after the greater part of the AO has been consumed. HAS stabilizers are not consumed, but they are not capable of stopping the primary oxidation and are active mainly in the second phase, in which they prevent the acceleration of oxidation by peracids [1,3].

As is already known [1,11,12] and can also be seen in Figs. 3 and 4, when part of a sample begins to oxidize, the oxidation reaction will spread. It was found that the reaction spreads via the gas phase and can even initiate oxidation in adjacent samples [13,14]. It has recently



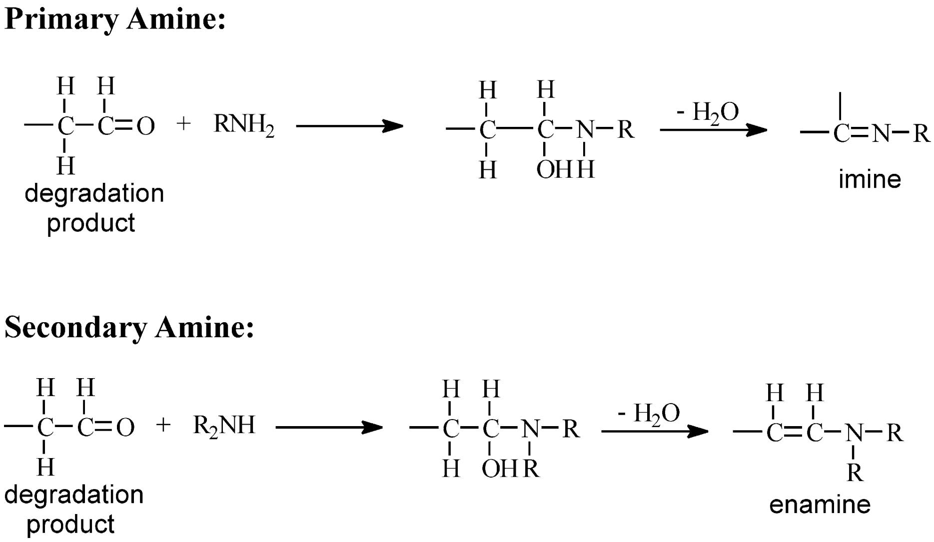
Scheme 1. Mechanism of degradation of PP (from Ref. [3]).

been shown that the rate at which oxidation spreads can be increased by adding formaldehyde to the gas phase [15]. As mentioned earlier, peracids are believed to be responsible for the acceleration of the oxidation of PP, and the main mechanism of action of HAS in preventing thermal oxidation of PP is to stop the oxidation of aldehydes that lead to the formation of peracids. In our study we found that aliphatic amines are effective, but affect mainly the spreading rate and have a smaller effect on the time before the first signs of oxidation become observable. As the spreading rate is determined by aldehydes it is reasonable to assume that the aliphatic amines counteract the influence of the aldehydes.

It is known that aliphatic amines can react with aldehydes to form more stable imines or enamines (see Scheme 2 [16]). In this way aliphatic amines prevent the formation of peracids, which explains their stabilizing effect.

The difference in activity between amines containing AOs and those containing HAS can also be explained on the basis of this mechanism. In the presence of AOs the greater part of the stabilizer is consumed in preventing homogeneous degradation, as shown in Scheme 1. So it is largely consumed before the peracids begin to play a role. After this consumption period the oxidation rate will be high, resulting in rapid consumption of the aliphatic amines. This implies only a small stabilizing effect. HAS act mainly against the heterogeneous oxidation part of Scheme 1 and they are not consumed. Further reduction of this part of the oxidation scheme by scavenging aldehydes results in greater improvement of the stability than can be realized in the presence of an AO.

Thus, besides the piperidinyl function, which is present in almost all hindered amine stabilizers, other functions in the molecules can influence stability. Especially primary and secondary amines, which are able to prevent the formation of peracids by scavenging aldehydes, are important groups that can increase the thermo-oxidative stability of PP. Besides the piperidinyl group, HAS-1 and HAS-2 contain a secondary amine. Such a group is not present in HAS-3. This difference might explain the poorer effectiveness of HAS-3 in preventing thermo-oxidative degradation of PP in relation to HAS-1 and HAS-2.



Scheme 2. Deactivation of PP degradation products by aliphatic amines.

5. Conclusions

It has been shown that in the presence of a HAS or a phenolic antioxidant aliphatic amines can increase the thermo-oxidative stability of PP. This is probably due to their ability to react with aldehydes and thus prevent the formation of peracids. The presence of amine functionality in the molecular structure (besides the piperidine group) can have a strong influence on the activity of Hindered Amine Stabilizers used as long-term heat stabilizers and may explain the difference between some commercial HAS stabilizers.

Acknowledgements

Sabic-EuroPetrochemicals b.v. is gratefully acknowledged for allowing us to publish the results presented in this paper.

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