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Analytical evaluation of the performance of stabilization systems for polyolefinic materials. Part II: Interactions between hindered amine light stabilizers and thiosynergists

Susanne Beißmann [a,*], Klemens Grabmayer [b], Gernot Wallner [b], David Nitsche [c], Wolfgang Buchberger [a]

[a] Johannes Kepler-University Linz, Institute of Analytical Chemistry, Altenbergerstraße 69, 4040 Linz, Austria
[b] Johannes Kepler-University Linz, Institute of Polymeric Materials and Testing, Altenbergerstraße 69, 4040 Linz, Austria
[c] AGRU Kunststofftechnik GmbH, Ing.-Pesendorfer-Str. 31, 4050 Bad Hall, Austria

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ABSTRACT

In the present study, the applicability of high-performance liquid chromatography hyphenated with highly sophisticated mass spectrometric detection (HPLC-MS) for analysis of hindered amine light stabilizers (HALS), thiosynergists and their conversion products is demonstrated. Degradation pathways as well as interactions between these stabilizer groups were successfully studied by analytical evaluation of model formulations after accelerated aging in the polymer-mimicking solvent squalane. Binary mixtures including HALS and thiosynergist as well as three component systems additionally including a phenolic antioxidant were investigated. Results showed that transformation pathways of HALS are highly influenced by the presence of sulfur-containing compounds and no aminoxyl radicals (typical reactive intermediates of HALS) were observed in these mixtures. To get an understanding of the effect of this altered stabilization mechanism on the protection of the polymer, rating of stabilization efficacies was performed by comparing the amount of degradation products derived from squalane using different formulations.

1. Introduction

During service life, polymers are subjected to degradation, initiated by solar radiation or heat. Stabilizers constitute an important part of commercial polymer formulations to adjust the long term properties under thermal or photochemical exposure. Hindered amine light stabilizers (HALS) have been widely used as additives, as they show a high efficacy both against thermo-oxidative and light-induced degradation of polymers. The high efficacy of HALS is commonly ascribed to a combination of a complex set of reactions. According to the Denisov Cycle the parent amine is oxidized to stable aminoxyl radicals, which act as scavengers of alkyl radicals thereby forming N-alkyloxy compounds. Aminoxyl radicals can be regenerated from these alkoxy amines as they react with peroxy radicals [1–7]. Almost all polyolefin types contain mixtures of stabilizers. As HALS fail as processing stabilizers, they have to be combined with primary antioxidants like hindered phenols and secondary antioxidants like phosphites [8,9]. Another important group amongst the secondary antioxidants are so-called thiosynergists. It has been shown that these sulfur-containing antioxidants have a high contribution to long-term heat protection of polymers [10,11]. It is known that the interaction between additives in a polymeric formulation can be complex and can result in synergism or antagonism [6,12–16]. Between HALS and phenols both synergistic and antagonistic effects have been reported in the literature. Concerning thiosynergists only a reduction of the stabilizing effectiveness of HALS has been reported so far, as the acidic reaction products of these thiosynergists can react with the basic amine compound. In order to avoid antagonistic effects and exploit synergistic effects between stabilizers from different chemical classes it is necessary to study the complex interaction between them. The interpretation of mutual relationships without identification of reaction products of the involved compounds may result in wrong data when proposing stabilizing mechanisms.

In the current work an HPLC method in combination with highly sophisticated MS-detection was developed. With this method it is possible to monitor interactions between HALS and antioxidants in model formulations after exposure to heat. Commercially important low and high molecular weight HALS were selected and aging

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* Corresponding author. Tel.: +43 732 2468 8720.
E-mail address: susanne.beissmann@jku.at (S. Beißmann).

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behavior as well as chemical changes of separately aged HALS were compared to the combination with a thiosynergist. Additionally ternary mixtures including a phenolic antioxidant were investigated. Structural identification of the individual compounds and their degradation products was achieved using a high mass accuracy Q-TOF mass spectrometer. With high mass accuracy, chemically possible elemental compositions are obtained. Together with published knowledge about HALS chemistry feasible chemical structures could be proposed. Thereby new insights into the stabilization mechanism and interactions between stabilizer classes were obtained.

Table 1
Binary gradient for semi-quantitative HPLC-MS detection of stabilizers and their degradation products.

Time/min	Methanol/%	25 mM ammonium formate in water/%
0	60	40
6	80	20
12	97	3
20	97	3
21	100	0
30	100	0

2. Material and methods

2.1. Chemicals

The following polymer stabilizers were included in this work: Irganox PS 800 and Irganox 1330 purchased from Ciba (Basel Switzerland), Tinuvin 770 from BASF (Ludwigshafen, Germany), Cyasorb UV-3529 from Cytec Industries (Woodland Park, USA), and Uvasorb HA 88 from 3V Sigma (Milano, Italy). Corresponding structures are shown in Fig. 1. Squalane was provided by Chrompack (Middelburg, Netherlands), ammonium formate by Sigma–Aldrich (Steinheim, Germany). Toluene and methanol were obtained from VWR (Fontenay-sous-Bois, France), acetonitrile from VWR (Leuven, Belgium). 18 MΩ water was obtained from a Milli-Q water purification system (Millipore, Bedford, MA, USA) was used throughout the work.

2.2. Instrumentation

The chromatographic separation was performed on an Agilent Series 1100 HPLC system coupled with an Agilent 6510 Q-TOF MS (Agilent, Palo Alto, CA, USA). HPLC-MS using positive ion mode for identification of stabilizers and their degradation products. The separation column was a Kinetex C18 (50 × 3.0 mm, 2.6 µm particle size) from Phenomenex (Aschaffenburg, Germany).

2.3. Sample preparation and aging conditions

The apolar solvent squalane was used to serve as liquid model for polypropylene [17–19]. About 10 mg of the stabilizers were added separately to 1 mL of the polymer-mimicking solvent squalane. Additionally binary combinations of the thiosynergist Irganox PS 800 with the hindered amines (Tinuvin 770, Cyasorb UV-3529, Uvasorb HA 88) and ternary mixtures including also the phenolic antioxidant Irganox 1330 were prepared. The solutions were heated in an ambient atmosphere to 130 °C. At various times samples were taken and the stabilizers along with their degradation products were extracted by shaking with methanol (squalane:methanol = 1:10). After separation of the layers, the methanol phase (containing intact stabilizers and degradation products) was 10-fold diluted and analyzed.

2.4. Chromatographic and mass spectrometric conditions

For HPLC separation a binary gradient with methanol/25 mM aqueous ammonium formate at a flow rate of 0.6 ml min^{-1} was used (Table 1). The column was maintained at 37.5 °C. The following optimized parameters were employed: nebulizer gas pressure 35 psi, drying gas flow rate 10 L min^{-1}, drying gas temperature 325 °C and capillary voltage − 4000 V. Full scan accurate mass spectra were obtained from 100 to 3200 Da. The injection volume was 5 µL.

3. Results and discussion

Various HALS-type additives were selected, including Tinuvin 770 with a monomeric structure, and Uvasorb HA 88 as well as Cyasorb UV-3529 with an oligomeric structure. Tinuvin 770 and Uvasorb HA 88 belong to the group of the secondary hindered amines whereas Cyasorb UV-3529, the piperidine ring of which is

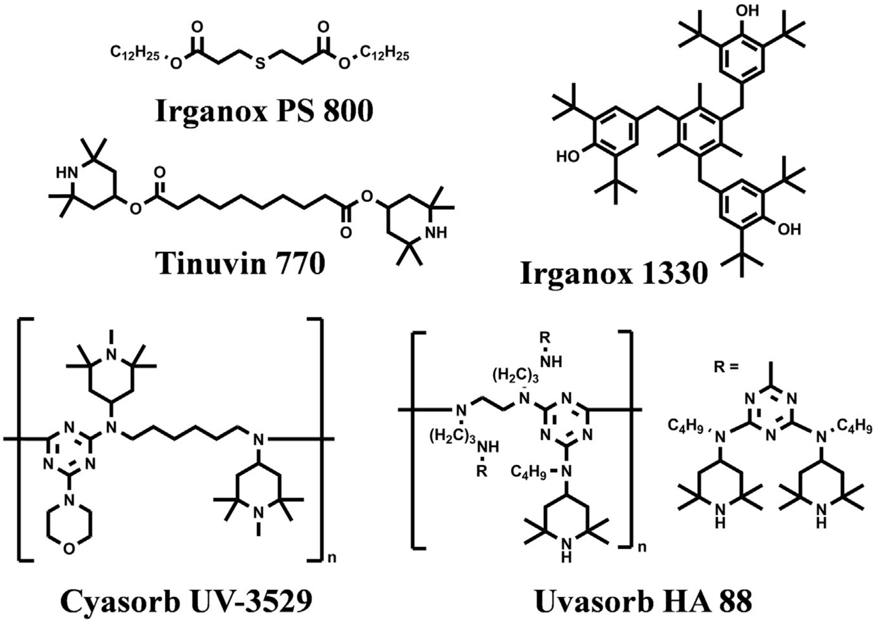

Fig. 1. Chemical structures of investigated analytes.

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alkyl-substituted, only contains tertiary amines. Several antioxidant systems consisting of one of the mentioned HALS in combination with a thiosynergist as well as ternary mixtures additionally including a phenolic antioxidant were subjected to aging tests in squalane (mimicking a polyolefin). To elucidate possible chemical reactions between the different stabilization classes, solutions containing just one stabilizer were prepared as control samples and aged under the same conditions. Decomposition rates as well as chemical changes in the molecular structure of the additives were monitored. Additionally unstabilized squalane was aged to perform a rating of stabilization efficacies of the different additives and their combinations. Aged stabilized and unstabilized squalane solutions were withdrawn at regular intervals and additives were extracted as described in Section 2.3. Stabilizers and their conversion products were monitored by HPLC with MS-detection.

3.1. Stabilization pathway of Irganox PS 800

According to the literature the protection mechanism of thiosynergists consists of the transformation of hydroperoxides ROOH into non-radical, non-reactive and thermally stable alcohols ROH, whereby the original sulfur-based stabilizer is converted into a sulfoxide. Subsequent thermolysis yields sulfenic acid, which further contributes to the protection of the polymer [20]. To get an understanding of possible interactions between different chemical classes, degradation pathways of individual stabilizers have to be elucidated in a first step. Up to now to our knowledge no chromatographic separation of thiosynergists and their degradation products with subsequent MS-detection to prove proposed degradation mechanisms has been presented in the literature.

In the aged squalane solutions stabilized only with Irganox PS 800 a complex mixture of degradation products is formed and several highly abundant degradation products could be clearly separated from the intact stabilizer and were thereby made accessible to structure elucidation. In Fig. 2 the chromatographic separation of Irganox PS 800 from its main degradation products with the corresponding mass spectra is shown. In the present study several degradation products were stable enough to allow extraction from the aging solution as well as chromatographic analysis without further chemical transformation. There may be additional products that just constitute intermediates or undergo further degradation during sample preparation and, thus, could not be detected in the extracts. The identified transformation products helped to propose a complex stabilization mechanism. Following Scheme 1 the first step includes the oxidation of the sulfide (1a) into a sulfoxide (II), whereby the peroxidic ROOH bonds derived from squalane are transformed into a stable alcohol ROH. No sulfoxide (II) was detected in the aged solutions containing only Irganox PS 800, which suggests that it is readily decomposed into a sulfenic acid (III) and an acrylate (1f). At high temperatures sulfenic acid (III) may undergo a condensation reaction yielding a

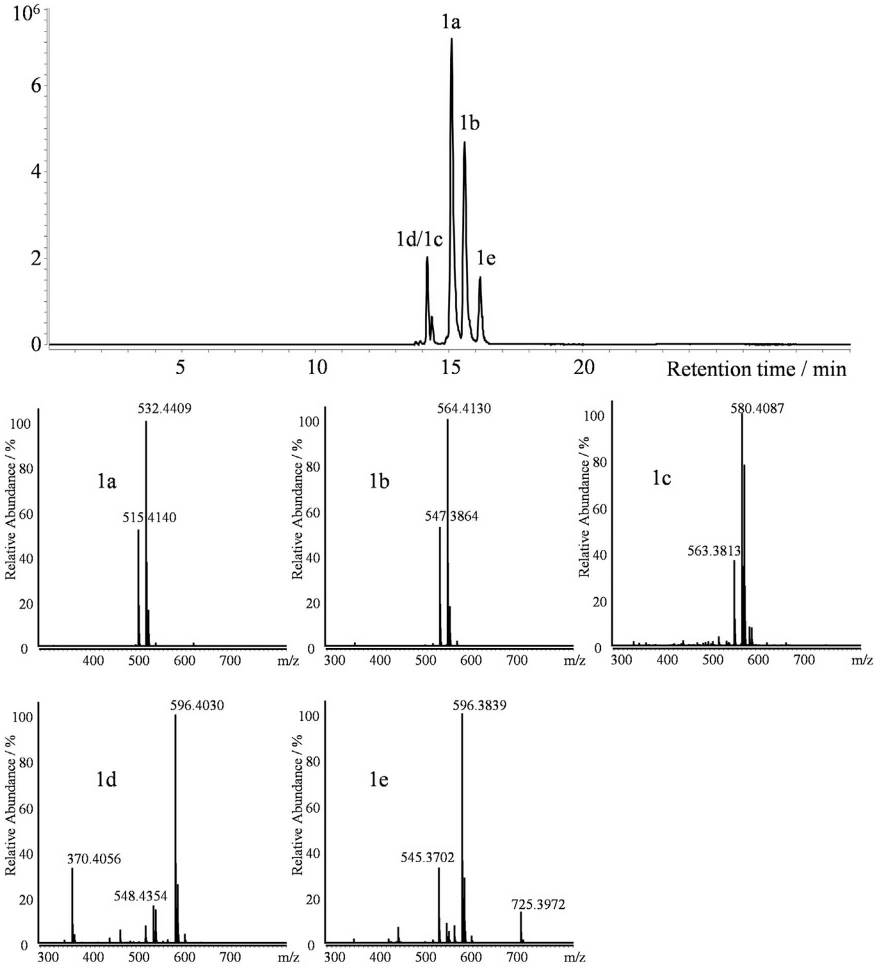

Fig. 2. Extracted ion chromatogram of an extract from squalane aged for 42 days with Irganox PS 800 as stabilizer with corresponding MS spectra of the most abundant peaks (for peak numbering see Table 2).

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thiosulfinate (1c). One possibility is that these thiosulfinates (1c) are further oxidized to disulfoxides (1d) by reaction with hydroperoxides. Another reaction pathway could be thermolysis to a thiosulfoxylic acid (IV) and an acrylate (1f) as already observed in the case of the sulfoxide (II). Additionally to the oxidized products, disulfides (1b) and trisulfides (1e) were formed after exposure to heat. These structures may stem from the reaction of a thiol with the thermolysis products of the sulfoxide and the thiosulfinate (III,IV). Thiols are formed as they are in a chemical equilibrium with the corresponding sulfide according to the so called Michael-addition. Oxidation of sulfides (1a) to sulfones (1g) played a minor role in the solutions containing only Irganox PS 800, as the initially formed sulfoxides (II) were rather thermolyzed as described before.

In combination with a HALS the reaction pathway was somehow different and higher concentrations of sulfones (1g) were found in the mixture but hardly any reaction yielding the other described products was observed.

3.2. Behavior of NH-HALS in the presence of a thiosynergist

It has already been shown in a previous paper that it is possible to chromatographically separate aminoxyl radicals derived from parent HALS compounds. Such radicals constitute the most important intermediates in the HALS stabilization mechanism [21]. In that work the combination with the primary antioxidant Irganox 1330 led to a faster activation of the HALS to its aminoxyl radical, but both stabilizers included were quickly consumed without contributing to the stabilization of the polymer, exhibiting an antagonistic interaction.

Thiosynergists are widely accepted to antagonize the protection efficacy of HALS, whereby different possible reaction mechanisms are proposed [6,10,22–27]. On the one hand the observed antagonism is suggested to stem from a competition between thiosynergists and hindered amines in the reactions with hydroperoxides. Thiosynergists are believed to decompose hydroperoxides faster, thereby retarding or preventing the formation of the active aminoxyl radicals from HALS [23]. Another explanation reports that aminoxyl radicals react with thiyl- or sulfinyl radicals derived from the parent thiosynergist, thereby forming inefficient coupling species [10,27]. Others explained the antagonism by the formation of inactive immonium oxide salts resulting from the reaction of aminoxyl radicals with acidic degradation products from the thiosynergist [25].

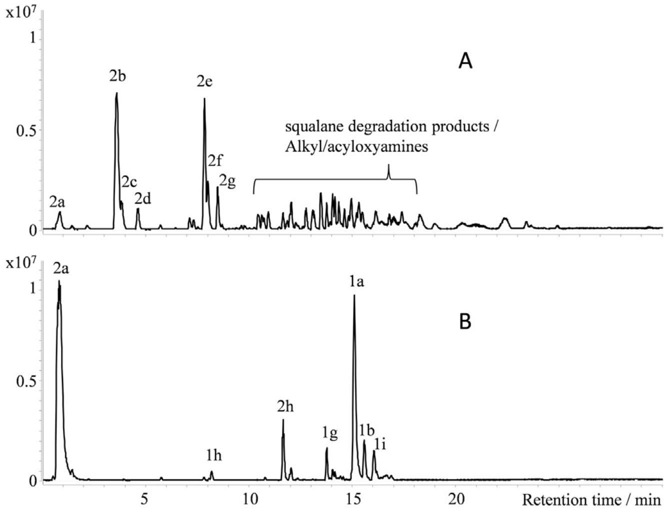
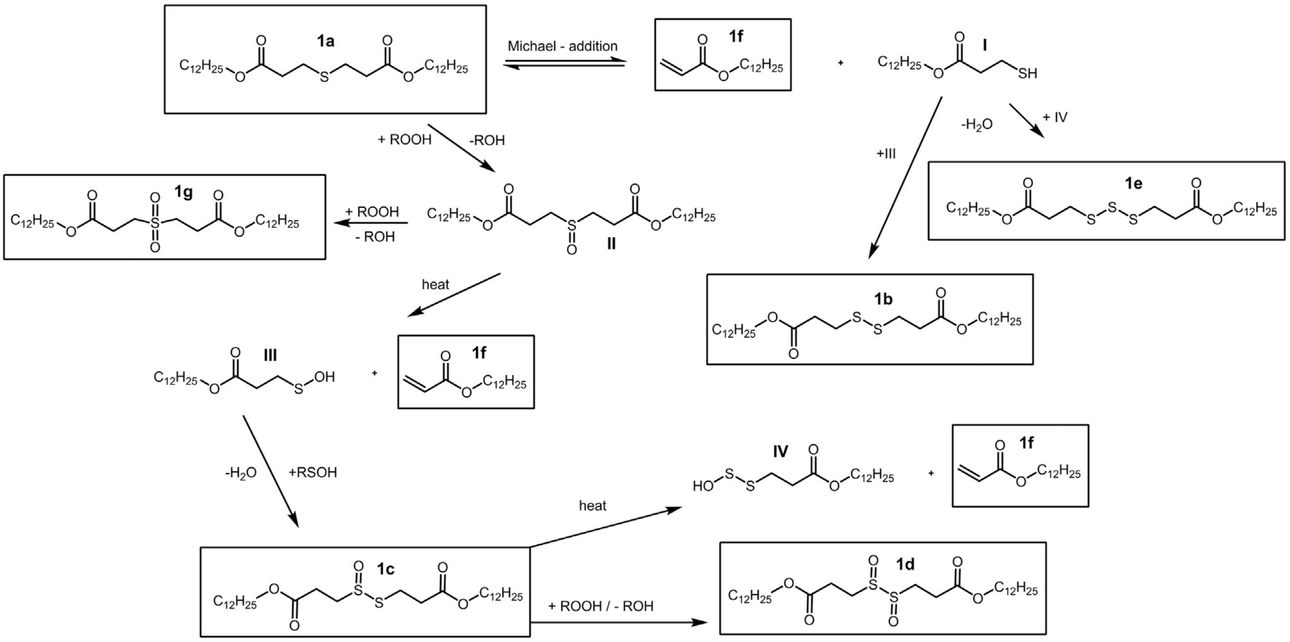


Fig. 3. A: Base peak chromatogram for a squalane extract aged with Tinuvin 770 for 42 days; B: Base peak chromatogram for a squalane extract aged with the binary mixture Tinuvin 770/Irganox PS 800 for 42 days; for peak numbering see Table 2.

In the present study NH-HALS aged separately were compared to combinations with the thiosynergist Irganox PS 800. The obtained chromatograms for Tinuvin 770 and the mixture Tinuvin 770/Irganox PS 800 after aging for 42 days are shown in Fig. 3. It is clearly visible that the observed chromatograms show a significant difference and hardly match each other. The concentration of the intact parent amine (2a) is much higher in the mixture with the



Scheme 1. Degradation pathway of the thiosynergist Irganox PS 800; structures encircled with rectangles were identified by MS-detection; Structures numbered with Roman numerals constitute intermediates and were not stable enough for MS-detection.

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Table 2
Results obtained by LC-MS including measured mass to charge ratios with corresponding molecular formulas of the investigated stabilizers and the identified degradation products after exposure to heat.

	Peak numbering	*m*/*z* measured	Charge state	Molecular formula	Identified substance
Irganox PS 800	1a	532.4409[a]	1	$C_{30}H_{58}O_4S$	Intact Stabilizer (R-S-R)
	1b	564.4130[a]	1	$C_{30}H_{58}O_4S2$	Disulfide (R-S-S-R)
	1c	580.4087[a]	1	$C_{30}H_{58}O_5S2$	Thiosulfinate (R-S(O)-R)
	1d	596.4030[a]	1	$C_{30}H_{58}O_6S2$	Disulfoxide (R-S(O)-S-R)
	1e	596.3839[a]	1	$C_{30}H_{58}O_4S3$	Trisulfide (R-S-S-S-R)
	1f	258.2426[a]	1	$C_{15}H_{28}O_2$	Acrylate (R=)
	1g	564.4307[a]	1	$C_{30}H_{58}O_6S$	Sulfone (R-S(O)$_2$-R)
	1h	539.4077	1		PS 800 degradation product (not identified)
	1i	545.3706	1		PS 800 degradation product (not identified)
Tinuvin 770	2a	241.2044	2	$C_{28}H_{52}N_2O_4$	Intact Stabilizer (HN-R-NH)
	2b	496.3873	1	$C_{28}H_{51}N_2O_5$	Aminoxyl radical (HN-R-NO·)
	2c	497.3960	1	$C_{28}H_{52}N_2O_5$	Hydroxylamine (HN-R-NOH)
	2d	539.4074	1	$C_{30}H_{54}N_2O_6$	Acetylhydroxylamine (HN-R-NOC(O)CH_3)
	2e	511.3749	1	$C_{28}H_{50}N_2O_6$	Diaminoxyl radical (·ON-R-NO·)
	2f	512.3836	1	$C_{28}H_{51}N_2O_6$	Aminoxyl radical, Hydroxylamine (HON-R-NO·)
	2g	554.3938	1	$C_{30}H_{53}N_2O_7$	Aminoxyl radical, Acetylhydroxylamine (·ON-R-NOC(O)CH_3)
	2h	785.5732	1	$C_{43}H_{80}N_2O_8S$	Coupling product with PS 800 (HN-R-NS(O)$_2$-R)
Uvasorb HA 88	3a	259.2402	2	$C_{29}H_{56}N_8$	Degradation product 1 (HN-R-NH)
	3b	337.2600	1	$C_{16}H_{30}N_7O$	Degradation product 2/Aminoxyl radical (HN-R-NO·)
	3c	532.4586	1	$C_{29}H_{55}N_8O$	Degradation product 1/Aminoxyl radical (HN-R-NO·)
	3d	560.4533	1	$C_{30}H_{55}N_8O_2$	Degradation product 3/Aminoxyl radical (HN-R-NO·)
	3e	393.3220	1	$C_{20}H_{38}N_7O$	Degradation product 4/Aminoxyl radical (R-NO·)
	3f	548.4558	1	$C_{29}H_{55}N_8O_2$	Degradation product 1/Aminoxyl radical, Hydroxylamine (HON-R-NO·)
	3g	547.4460	1	$C_{29}H_{54}N_8O_2$	Degradation product 1/Diaminoxyl radical (·ON-R-NO·)
	3h	590.4637	1		Degradation product (not identified)
	3i	421.8717	2		Coupling product with Irganox PS 800 (Structure not identified)
	3j	757.6783	1	$C_{44}H_{84}N_8O_2$	Coupling product with Irganox PS 800 (HN-R-NR)
	3k	821.6432	1	$C_{44}H_{84}N_8O_4S$	Coupling product with Irganox PS 800 (HN-R-NS(O)$_2$-R)
Cyasorb UV-3529	4a	154.1592	1	$C_{10}H_{19}N$	Degradation product 1/Piperidyl - Ring (NH)
	4b	337.1988	1	$C_{15}H_{24}N_6O_3$	Degradation product 2/Trimorpholino-triazine
	4c	447.3338	2	$C_{46}H_{80}N_{14}O_4$	Oligomer 1/dealkylated (HN-R-NH)
	4d	454.3413	2	$C_{47}H_{82}N_{14}O_4$	Oligomer 1/dealkylated (H_3CN-R-NH)
	4e	502.3875	1	$C_{27}H_{47}N_7O_2$	Degradation product 3/(R-NCH_3)
	4f	488.3719	1	$C_{26}H_{45}N_7O_2$	Degradation product 3/dealkylated (R-NH)
	4g	461.3495	2	$C_{48}H_{84}N_{14}O_4$	Oligomer 1/intact form ((H_3CN-R-NCH_3)
	4h	461.3317	2	$C_{47}H_{80}N_{14}O_5$	Oligomer 1/Nitrosonium ion (H_3CN-R-N^+=O)
	4i	468.3386	2	$C_{48}H_{82}N_{14}O_5$	Oligomer 1/Acyl derivative (H_3CN-R-NC(H)=O)
	4j	516.3671	1	$C_{27}H_{45}N_7O_3$	Degradation product 3/Acyl derivative (R-NC(H)=O)
	4k	475.3272	2	$C_{48}H_{80}N_{14}O_6$	Oligomer 1/Acyl derivative (O=(H)CN-R-NC(H)=O)
	4l	475.3574	1		Coupling product with Irganox PS 800 (structure not identified)
	4m	439.3914	1		Coupling product with Irganox PS 800 (structure not identified)
	4n	489.3729	1		Coupling product with Irganox PS 800 (structure not identified)
	4o	350.2371	1		Coupling product with Irganox PS 800 (structure not identified)
	4p	300.2539	1		Coupling product with Irganox PS 800 (structure not identified)
	4q	613.4354	2		Coupling product with Irganox PS 800 (structure not identified)

[a] Detected as $[M + NH_4]^+$.

thiosynergist compared to the separately aged stabilizer. In the presence of Irganox PS 800 none of the degradation products (2b – 2g, for peak numbering see Table 2) identified in the solution containing only Tinuvin 770 are formed. All of these degradation products require the activation of the parent amine into the corresponding aminoxyl radical in a first step. The same behavior was observed for Uvasorb HA 88 (Fig. 4) and no radical species or degradation products (3b – 3h) requiring oxidation of the HALS are formed. The concentration of the intact NH-amine (3a) in the mixture with Irganox PS 800 again exceeded the amount in the solution containing only Uvasorb HA 88. The absence of radical species in the presence of Irganox PS 800 strengthens the theory that thiosynergists are capable hydroperoxide decomposers and therefore oxidation of NH-HALS to aminoxyl radicals is prevented.

However, for both HALS additional peaks occurred which were not observed in the separately aged solutions. A possible explanation is that they originate from coupling products, as the mass to charge ratios were neither observed in the solution containing only HALS nor in the solution containing only thiosynergist. The high mass accuracy of Q-TOF MS measurements helped to verify this assumption and the peaks were identified as coupling products between the particular HALS in the aminoxyl form and a sulfoxyl radical, which is formed during a homolytical cleavage of the sulfoxide as shown in Scheme 2. The corresponding sulfonamides are formed via a rearrangement reaction [10].

In Fig. 5 the degradation of intact Tinuvin 770 and transformation to aminoxyl radicals as well as coupling with the thiosynergist is shown in the separately aged solution (A) and the mixture with Irganox PS 800 (B). It can be seen that the decrease in concentration of intact stabilizer occurs faster in solution containing only Tinuvin 770, and large amounts are transferred into the corresponding aminoxyl radicals. The sum of intact stabilizers and aminoxyl radicals sometimes exceeds 100%, as relative areas and not concentrations were used to calculate cumulative percentages. The areas obtained for the transformation products were set relative to the initial area of intact stabilizer before exposure to heat, thereby allowing comparison of formed amounts in different formulations. It may be possible to determine concentrations of aminoxyl radicals by using ESR spectrosocpy or by using oxidizing agents like *m*-chloroperoxybenzoic acid (mCPBA), or *p*-

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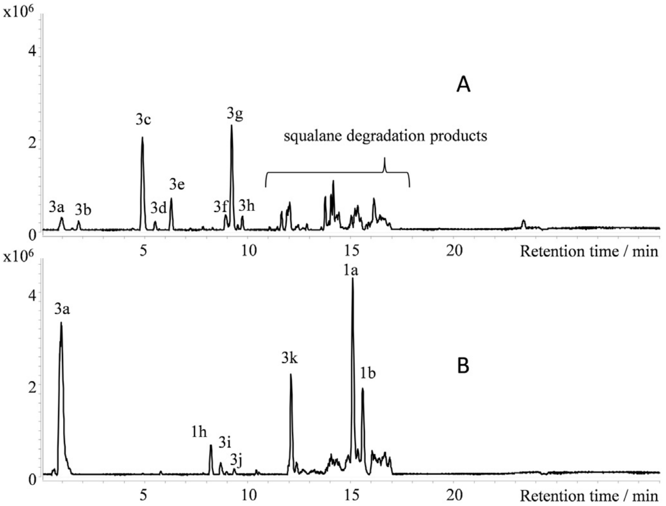


Fig. 4. A: Base peak chromatogram for a squalane extract aged with Uvasorb HA 88 for 42 days; B: Base peak chromatogram for a squalane extract aged with the mixture Uvasorb HA 88/Irganox PS 800 for 42 days; for peak numbering see Table 2.

nitroperoxybenzoic acid (pNPBA) to produce standards, which then can be used to perform a calibration. However, such additional efforts were considered as not fully necessary for the present work. In the presence of Irganox PS 800 aminoxyl radicals (2b, 2d) are not formed within a period of 70 days of aging. The observed small amount of radicals after that time is due to the fact that all of the thiosynergist is consumed and so oxidation of the parent amine is not prevented anymore. The coupling product 2h in the mixture HALS/thiosynergist is observed from the very beginning of aging. These results suggest that the parent amine is transformed into radical species to some extent, but an immediate recombination reaction takes place with highly reactive radicals originating from the sulfoxide as described above.

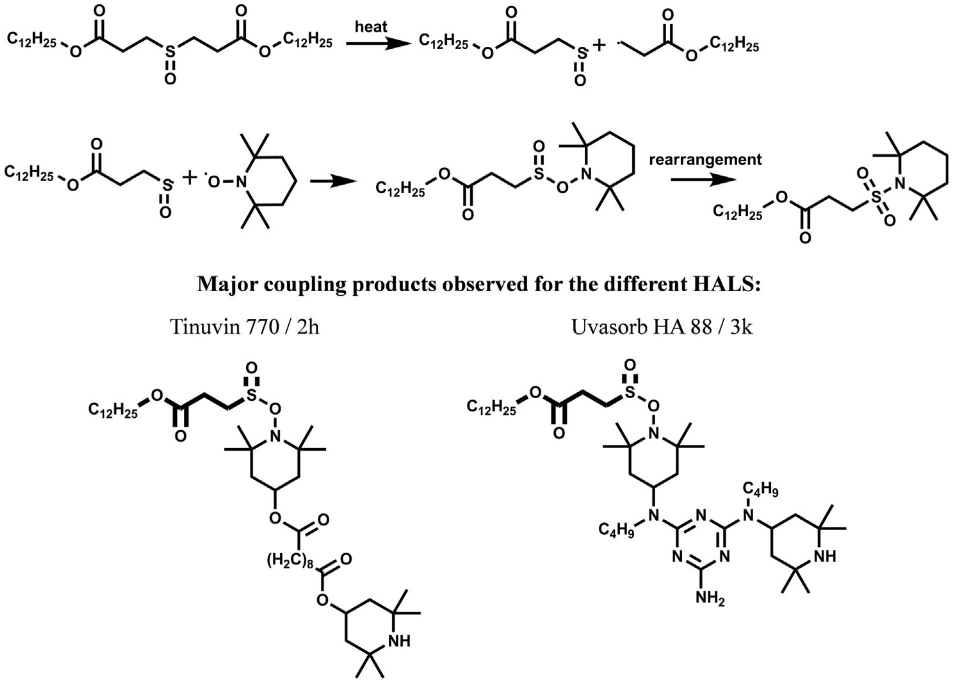
3.3. Behavior of a NCH_3-HALS in the presence of a thiosynergist

In a previous paper it was shown that no aminoxyl radicals were observed for the NCH_3-HALS Cyasorb UV-3529 [21]. Instead dealkylated NH-compounds, acyl-derivatives and nitrosonium ions were formed during exposure to heat.

In the present study the influence of a thiosynergist on the transformation of the N-alkyl group was studied. In Fig. 6 the chromatograms obtained for the separately aged solution and the mixture with Irganox PS 800 after 42 days aging is shown. At low retention times, where the intact stabilizer, dealkylated species and low molecular weight degradation products are eluted, the chromatograms nearly match. For peaks with retention times higher than 5 min clear differences are apparent. In the separately aged solutions highly abundant signals of nitrosonium ion (4h) as well as acyl derivatives (4i – 4k) were observed, which were not formed in the presence of the thiosynergist. Co-stabilizing with Irganox PS 800 led to the appearance of several additional signals eluting between 7 and 14 min (4l – 4q). Although it is assumed that these peaks correspond to coupling products, the exact structures could not be properly determined on the basis of mass spectra. A trend is showing up, as several peaks with a mass difference of 50 Da are detected (4m ↔ 4n; 4o ↔ 4p). A possible explanation may be that in the presence of Cyasorb UV-3529 the sulfoxide is not homolytically cleaved as shown in Scheme 2, but a heterolytically cleavage according to the Retro-Michael addition takes place. Subsequently both degradation products react with the same species derived from a HALS leading to structures with either $C_{15}H_{27}O_3$ or $C_{15}H_{29}O4_S$ attached to molecule. These structures would explain the observed mass difference of 50 Da.

3.4. Ternary stabilizer formulations: HALS/thiosynergist/phenol

In a previous paper it was shown that the phenolic antioxidant Irganox 1330 leads to a decrease in stabilizing efficacy of NH—as well as NCH_3-HALS as both stabilizers are uselessly consumed. However, the investigations showed that activation of the parent



Scheme 2. Reaction pathway for the coupling between NH-HALS and thiosynergist with the corresponding observed coupling products (for compound numbering see Table 2).

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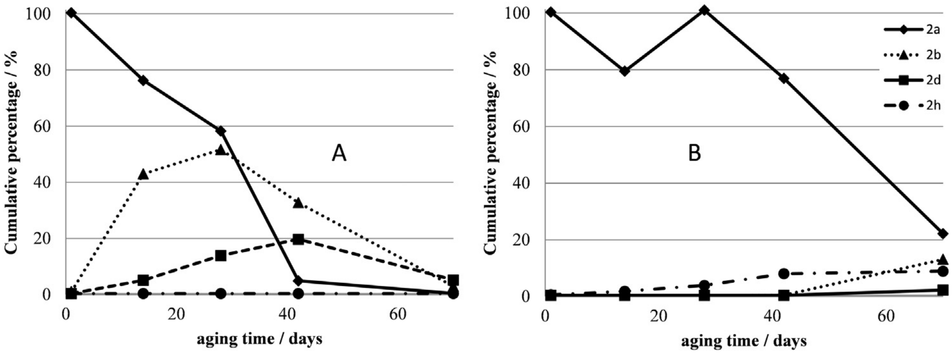

Fig. 5. Conversion rate of Tinuvin 770 to its major degradation products in different stabilizer formulations; A: Tinuvin 770, B: Tinuvin 770/Irganox PS 800; for numbering see Table 2; Cumulative percentage: Areas obtained for the degradation products were set relative to the initial area of intact stabilizer before exposure to heat. Subsequently the relative areas of the different degradation products were summed up.

amine to the corresponding aminoxyl radicals was accelerated in the presence of Irganox 1330 [21]. In the present work, it could be shown that transformation mechanisms of HALS are extremely different in the presence of thiosynergists. In further consequence we were interested what would happen in ternary mixtures containing all three stabilizer groups. Therefore mixtures containing Irganox 1330, Irganox PS 800 and one of the HALS were subjected to aging tests. The results were quite similar to combinations without Irganox 1330. As discussed in the previous sections no aminoxyl radicals were observed for the NH-type HALS and no nitrosonium or acyl derivatives for NCH_3-types. Again several coupling products originating from the reaction of degradation products of Irganox PS 800 with the HALS are formed. The fast degradation of Irganox 1330 in the presence of HALS as discussed in the previous paper was not observed if additionally a thiosynergist is added to mixture. This confirms the assumption that the small amount of aminoxyl radical formed readily reacts with products of Irganox PS 800 and thereby no hydrogen is abstracted from the phenolic antioxidant. Interestingly, all three stabilizers are slower consumed or longer detected in the intact form respectively if used together compared to the separate aging of them.

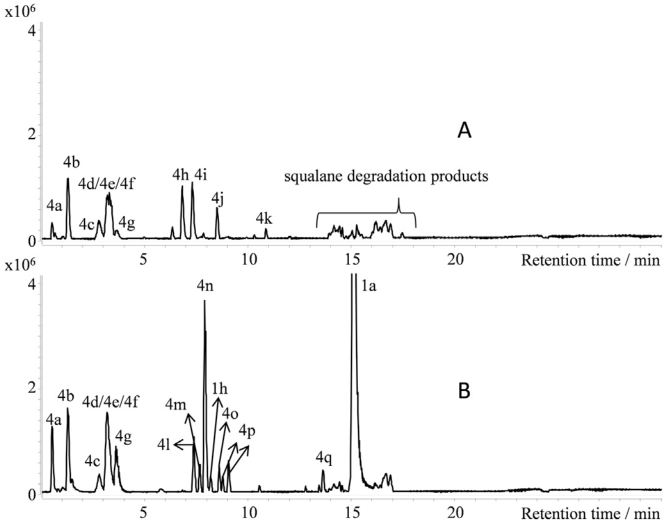

Fig. 6. A: Base peak chromatogram for a squalane extract aged with Cyasorb UV-3529 for 42 days; B: Base peak chromatogram for a squalane extract aged with the mixture Cyasorb UV-3529/Irganox PS 800 for 42 days; for peak numbering see Table 2.

3.5. *Rating of stabilization efficacies*

The efficacy of different stabilizer combinations was evaluated by comparing the amount of degradation products formed from squalane after exposure to heat. Numerous degradation products are formed from which four representatives were chosen (C_{11}, C_{16}, C_{22}, C_{27}) [21]. In Table 3 the comparison of stabilization efficacies according to formed degradation products is presented. In the case of NH-HALS the stabilizing efficacy was in the order HALS < HALS/thiosynergist < thiosynergist < HALS/thiosnyergist/phenol. Cyasorb UV-3529 with tertiary amines acted somehow different and the binary combination with the thiosnyergist showed a better performance compared to the thiosynergist alone. The most striking result emerging from the data is that the highest stabilization efficacy was achieved with the ternary mixture HALS/thiosynergist/phenol for all investigated hindered amines. The results discussed above would suggest a strong antagonism between HALS and thiosynergist because of the absent active aminoxyl radicals. The reason is not fully understood and more investigations are necessary to clarify this phenomenon. The lowest stabilizing effect is given with the use of a HALS alone in the order Tinuvin 770 < Uvasorb HA 88 < Cyasorb UV-3529. Protection of the polymer (squalane) is still the case, as the observed amount of degradation products for unstabilized squalane compared to stabilization with Tinuvin 770 was 5 times higher after aging for 42 days. The reason for the lower stabilizing effect of HALS compared to thiosynergists may have several reason. First of all, it is known that thiosynergists act as so-called inhibitors. This means that the polymer is protected until the stabilizer is fully consumed. Afterwards there is an abrupt loss of mechanical properties. The big advantage of HALS over antioxidants is, that in theory they are not consumed while protecting the polymer. They operate as retarders, meaning that there is a continuous loss of mechanical properties of the polymer from the very beginning of aging, but degradation rate is slowed down [28,29]. Another reason for the lower stabilization efficacy of HALS may be that in the literature a drop of activity is reported if HALS are used above 120 °C [8]. Therefore experiments with Tinuvin 770 and binary as well as ternary mixtures with the other stabilizer classes were repeated at 100 °C to exclude the possibility that some of the observed phenomenon were due to the high temperature used. Degradation mechanism of Tinuvin 770 did not differ from that obtained at the higher temperature and no aminoxyl radicals were observed in mixtures containing Irganox PS 800. Rating of stabilization efficacies did not strictly lead to the same order observed at the higher temperature and was found to be HALS < thiosnyergist < HALS/thiosynergist < HALS/thiosynergist/phenol. The small difference compared to the high temperature can

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Table 3
Comparison of stabilizing efficacies according to the sum of degradation products formed from squalane compared to unstabilized squalane.

Stabilizer formulation	Percentage/% (compared to unstabilized squalane)
Tinuvin 770	20.8
Uvasorb HA 88	9.7
Cysorb UV-3529	1.3
Irganox PS 800	1.1
Tinuvin 770 + Irganox PS 800	9.4
Uvasorb HA 88 + Irganox PS 800	7.1
Cyasorb UV-3529 + Irganox PS 800	0.5
Tinuvin 770 + Irganox PS 800 + Irganox 1330	0.2
Uvasorb HA 88 + Irganox PS 800 + Irganox 1330	0.2
Cyasorb UV-3529 + Irganox PS 800 + Irganox 1330	0.2

be explained by variation in chemical activities depending on the temperature.

4. Conclusions

The purpose of the current study was to develop a method capable of identification of HALS as well as thiosynergists and their major transformation products formed during exposure to heat and resulting from interaction reactions in stabilizer formulations. Structure elucidation of these formed products is of high importance to verify and falsify proposed protection mechanisms as well as theoretical considerations about synergistic or antagonistic effects between stabilizer groups. Up to now, to our knowledge, no such analytical method has been presented. With the developed method a complex reaction mechanism observed for the thiosynergist Irganox PS 800 could be suggested. Combination of HALS with the thiosynergist showed that several conversion products formed in the separately aged solutions were not observed in the presence of Irganox PS 800. These include the aminoxyl radicals, which are said to be the active species in the protection circle of the polymer. Three component systems including an additional phenolic antioxidant showed the same behavior as observed in binary mixtures. Useless consumption of Irganox 1330 in the presence of a HALS as observed in previous investigations was not the case if a sulfur-containing stabilizer is added to the mixture. By comparing degradation products derived from squalane using different additive packages, stabilization efficacies could be rated. More or less the same order was observed for all investigated HALS and stabilizer formulations. HALS alone showed the least effect in protecting the polymer-mimicking liquid squalane compared to the other formulations. Depending on the temperature and type of HALS (secondary, tertiary) this was followed by thiosynergist used separately or the combination HALS/thiosynergist. The best performance was given with the ternary mixture HALS/thiosynergist/phenol. One of the more significant findings to emerge from this study is that the three component stabilizer system provided a degree of stabilization effectively more than the sum of the stabilization effect of the single components. This result suggests a synergistic effect between these stabilizer groups, which was not reported in the literature until now. The protection mechanism leading to these synergistic effects is not fully understood and further investigations including real polymer samples may be necessary.

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