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Reactions of Sulfur Containing Phenolic Antioxidants for Elastomers

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Alkyl-hydroxybenzylthioethers are efficient storage and processing stabilizers for elastomers and adhesives. Especially alkyl-(2-hydroxybenzyl)thioethers represent an intramolecular combination of a primary and secondary antioxidant, i.e. a phenolic and a thioether moiety in an optimized spatial arrangement. The mechanism of their intramolecular synergism was investigated. The best overall stabilizers are 2,4-bis(alkylthiomethyl)-6-methylphenols, e.g. AO1, in contrast to 2,6-dialkyl-4-alkylthiomethylphenols(B), 4-alkyl-2,6-bis(alkylthiomethyl)phenols C.



1. Introduction

The goal of this paper is to present and discuss the relevant reactions of sulfur containing phenolic antioxidants for elastomers during stabilization and grafting.

2. Critical Steps in Stabilization of Elastomers

Degradation

The degradation of the majority of synthetic elastomers based on polydienes consists mainly in crosslinking of the polymer, caused by accumulation of C-centered polymeric radicals P which are formed in a similar way as with other hydrocarbon based polymers according to a widely accepted mechanism¹⁴ (scheme 2). According to this mechanism, initially generated C-centered radicals add molecular oxygen in a fast step, giving rise to macroalkylperoxy radicals. These radicals abstract hydrogen atoms from the polymer hydrocarbon chains, thereby forming new C-centered radicals (first cycle) and macroalkylhydroperoxides. The latter undergo homolytic scission of the O-O bond, especially at temperatures above 100°C and give rise to macroalkoxy and hydroxy radicals (scheme 2). These radicals are even more active than hydroperoxy radicals and propagate the chain by hydrogen abstraction and formation of C-centered radicals in a second cycle. After consumption of oxygen, the accumulated radicals can either undergo crosslinking reactions or chain scission reactions (e.g. with tertiary alkylperoxy radicals). Depending on the nature of the polyene or polydiene, one type of degradation predominates; most polydienes except polyisoprene tend to an overall crosslinking. Inhibition

Primary antioxidants, e.g. BHT, AO1 or other phenols with substituted ortho- and para-positions can break the first cycle of the chain reactions by donating a hydrogen atom to macroalkylperoxy radicals (this leads to more stable phenoxy radicals which do not propagate the radical chain). Secondary antioxidants, e.g. thioethers, on the other hand, prevent the second cycle by reduction of the macroalkylhydroperoxides to the corresponding alcohols. These two reactions are assumed to be the most important steps which contribute to a net stabilization of the polymer against thermooxidative degradation ¹⁴(scheme 2a).

The allylic C-H bonds in polybutadiene, a typical elastomer, are attacked at a higher rate than C-H bonds in simple polyalkenes such as polypropylene². Therefore, autoxidation and crosslinking occurs already at relatively low temperatures.





Scheme 2a: Primary and Secondary antioxidants

Primary Antioxidants (Phenois, Amines):



Secondary Antioxidants (Synergists: S and P compounds):

POOH + R-S-R' ----- POH + R-S(=0)-R'

e.g. TS1 = S-(CH₂CH₂COOC,
$$_{2}$$
H₂,)₂ = DLTDP

Critical in polydiene production and processing are the drying step (ca. 80-120°C) and the processing of the raw polymer in a Banbury mixer (ca. 160°C) before vulcanization (scheme 3). The second step is more critical; classical phenolic antioxidants, e.g. AO2 cannot provide any substantial stabilization, even in combination with common secondary antioxidants, for instance TS1(induction times of oven ageing at 80°C and of processing in Brabender extruder at 160°C, substrate: polybutadiene (BR), table 1, cf. scheme 2a).

Scheme 3: Antioxidants in Rubber Production



RAW RUBBER e.g. BUTADIENE RUBBER



VULCANIZED RUBBER



Stabilizer 1	Stabilizer 2	Brabender (160°C) t(ind)[min]	Oven Test (80°C) t(ind)[weeks]
0.25 % AO2 (classical phenol)		4	2
0.25 % AO2 (classical phenol)	0.5 % TS1 (thiosynergist)	4	22
0.25 % AO1 (sulfur containing phenol)		50	26

Table 1: Classical and Sulfur Containing Phenolic Antioxidants in BR

3. Autosynergistic Sulfur Containing Phenols

It was found by Scott² Pospisil³ that the efficiency of phenolic stabilizers is improved if they contain a thioether function. Recently, we proved the intramolecular nature of the synergism in AO1 by comparing its efficiency with that of a mixture of O-methyl-AO1 and 2,4-didecyl-6-methylphenol⁵. We could show that in most elastomers 2,4bis-functionalized phenols such as AO1 provide the best overall protection amongst a variety of tested sulfur containing phenols⁵.

Influence of structure on efficiency at 80°C (oven test) and 160 °C (Brabender test): AO1 reaches distinctly higher induction times in the Brabender test than all 4-functionalized phenols AO3-AO5, the 2,6-bis-functionalized products AO6, AO6a and AO7, the monofunctionalized phenol AO8 with unsubstituted ortho-position as well as the commercial product AO9, which is a product by process containing AO7 and AO8 as major sulfur containing phenols (table 2).

The results of compounds AO6, AO6a, AO6b, AO7 and AO11 show that for orthofunctionalised phenols tertiary alkyl groups in the ortho- or para-position reduce the antioxidant activity significantly. A similar reduction is observed for compounds with free ortho- or para-positions(AO8 and AO10), which are prone to other oxidative processes, providing C,C-coupling products $\frac{54}{2}$.

The para-cresol derivative AO6b reaches similar efficiency in the Brabender test; however, to obtain an optimal antioxidant activity in the oven test at 80°C, a paraalkylthiomethyl group is required apparently, more or less independent of the nature of the alkyl ring substituent(cf. table 2).

Also the relative hydrogen transfer rates $k(rel)^{50}$ (measured with DPPH as a model for macroalkylhydroperoxy radicals, see table 2; mesitol(2,4,6-trimethylphenol): k(rel) = 17.1, oven test/Brabender test: 2 weeks/3 min; BHT(2,6-di-t-butyl-para-cresol): k(rel) = 0.36; oven test/Brabender test: 2 weeks/3 min; 0 fthe different phenols do not seem to have an influence on the stabilizer efficiency in the oven test. However, it seems that in order to obtain a high antioxidant activity in the Brabender test, the hydrogen transfer rate has to be within an optimal range. A very slow trapping of peroxy radicals would possibly be equivalent with a starting competition between substrate C-H and inhibitor O-H bonds for hydrogen abstraction.

The outstanding results of AO1, AO6b and AO10a in the Brabender test clearly demonstrate the presence of an ortho-effect under processing conditions.

Recent tests have shown that the length of the spacer between the phenolic moiety and the thioether group is critical. AO10b and AO10c, homologs and of AO10a with two and three methylene groups, respectively, (AO10a with side chain -(CH₂)₂SC₈H₁₇ and -(CH₂)₂SC₈H₁₇, respectively, instead of -CH₂SC₈H₁₇) showed a reduced Brabender activity as compared to that of AO10a: t(ind) (Brabender test at 160°C in BR) AO10b 4 min; AO10c 16 min (c(antioxidant) = 0.25 %), cf. table 2.

4. Mechanistic Explanation of the ortho-Effect in AO1

We assume that AO1 traps macroalkylperoxy radicals POO efficiently in a kind of "tandem reaction" ⁵. Abstraction of a hydrogen atom from AO1("primary antioxidant") and reduction of the resulting POOH to POH("secondary antioxidant") are either simultaneous or the reduction step immediately follows the hydrogen abstraction (scheme 4): the cage reaction (cf. ⁶) is apparently much faster than the corresponding escape reaction. In contrast to this, synergistic mixtures of a phenol and a thioether do not suppress the formation and cleavage of "free" POOH fast enough under processing conditions and thus the propagation of the radical chain reaction. An "ortho-effect" accounts for the much more efficient stabilization by 2-alkylthiomethylphenols as compared to the corresponding para-functionalized derivatives in the Brabender test (see table 2): the ratio k(cage reduction)/k(escape) is plausibly larger due to the shorter initial distance between the two reaction sites(scheme 4).

The above mentioned homologs of AO10a with a slightly larger spacer -(CH₂)_nSC₈H₁₇, bearing a side chain with n = 2(AO10b) or n = 3 (AO10c) have a significantly lower activity than AO10a (n = 1). The predominance of the cage reaction is probably reduced due to the longer spacer group. In the case of AO10b, however, a strong pro-oxidative effect of a transformation product (see chapter 7) might supersede the expected reduced antioxidant effect of the phenolic thioether.

Stabilizer (k(rei), Hydrogen Transfer Rate to DPPH *)	Structure	Oven Ag ei ng 80°C (weeks)	Brabender (160°C): t(ind)[min]
AO1 (1.0) (R = CH ₂ S-Octyl, R' = CH ₃)		26	50
AO3 (0.27)	HOLD SOL	25	16
AO4 (0.1)	Image: state	17	12
AO5 (7.94)	H0	35	6
AO6 (0.26) R = t-butyl	Dass- HO Coss-	15	27
AO6a (0.48) R = t-octyl	s. AO6	17	30
AQ6b (0.57) R = CH3	s. AO6	13	51
AO7 (0.32)	Dodacyl S HO- Dodacyl S	14	24
AO8	Dedicy-S- HO	n.a.	20
AO9 (commercial)	A07 + A08 + other components	15	31
AO10, R = H, R' = CH, (2.95)	s. AO1	8	40
AO10a, $R = R' = CH_0$ (1.05)	s. AO1	20	49
AO11, R = CH ₂ S-Octyl, R' = t-Butyl (0.55)	s. A01	12	24

Table 2: Brabender Induction Period of Butadiene Rubber Stabilized with 0.25 % AO(160°C) and Oven Ageing Induction Period (80°C) with 0.25 % AO



Scheme 4: Reaction of Macroalkyl Peroxy Radicals with AO1

5. Oxidation Products of AO1

By extraction with acetone, AO1-o-SO (besides a small amount AO1-p-SO, see fig. 5a and scheme 5b) was shown to be the primary transformation product found in the aged polymer (oven ageing at 60 and 80°C)⁵ whereas at elevated temperature (>150°C) neither of the oxidation products could be detected in the extract. AO1 also provides more AO1-o-SO than AO1-p-SO, if the oxidation is carried out in a solvent with H_2O_2 or an organic hydroperoxide. This is obviously the result of an intramolecular acid catalysis by the phenolic OH group^{56, 7}.

Both, AO1-o-SO and AO1-p-SO, are still active antioxidants (Brabender 160°C, c = 0.25 %: t(ind) = 28 and 17 min, respectively).





Scheme 5b: Oxidation Products of AO1 Found in the Substrate



6. Grafting of AO1

Sulfur analysis of extracted polybutadiene indicated that during ageing a part of the antioxidant AO1 is grafted to the polymer (fig. 6; cf. experimental part, table 6). Since this grafting is much faster with the transformation product AO1-o-SO, we assume that the latter is the key intermediate for grafting. Subsequently, ¹H-NMR studies of the polymer revealed that the same grafting product A is formed after ageing under various conditions if AO1 or the corresponding "ortho-sulfoxide" AO1-o-SO is added to the polymer before ageing. A typical singlet at ca. 3.6 ppm(assigned to benzylic protons of the (unchanged) para substituent) as well as two aromatic meta protons around 6.9 ppm(all other signals are either masked by the polymer or expected to be very broad) are in agreement with (a) a Diels-Alder addition product or (b) a radical addition product to the intermediate ortho-quinone methide (OQM) (formation of graftable intermediates, see scheme 7).

Analysis of the ¹H-NMR integrals of -CH₂CH₃ resonances indicates that at least part of the intermediate octyl sulfenic acid is also grafted. Since the polymer itself also contributes to the -CH₂CH₃ integral, a clear proof has been established with ¹⁹F-NMR spectroscopy and ¹⁹F marked side chains (see paragraph 10 and experimental part, table 6).



Fig. 6: Decrease of AO1 and AO1-o-SO and Increase of Non-Extractable Sulfur Content in BR



The intermediate formation of OQM is confirmed by the isolation of a small amount of the Diels-Alder adduct DA1 in a preparative thermolysis of the model sulfoxide AO10a-o-SO at 165°C in vinylene carbonate (VC) (scheme 8) (see experimental part).

Scheme 8. Model DA reaction



7. Thermal Behavior of AO1-o-SO and Related Compounds

The hydrogen transfer rates from DPPH(see table 2) and the oxidation rates of the isomeric thioethers AO1(linear side chain) and AO12(α -branched tertiary side chain) to the sulfoxide(s) (in perdeuterated acetonitrile solution with cumylhydroperoxide at 60 °C ⁶ⁿ) are of the same order of magnitude. We found, however, a striking difference in the processing stabilizer activities of the two isomeric compounds (table 3).

Stabilizer	Structure	k(rel), Hydrogen Transfer Rate to DPPH	Brabender (160°C): t(ind)[min]
AO1	HO-S-DCtyl	1	50
AO12	HO-S-LOCTY	0.82	8

Table 3. n-Alkyl vs. t-Alkyl Benzylthioethers

This directed our attention to the stability of the corresponding sulfoxides and/or the nature of the products formed by thermolysis of the sulfoxides.

Consequently, we studied the thermal decomposition of sulfoxides AO1-o-SO, AO12o-SO and related compounds (table 4) as well as the influence of the sulfoxide structure on elastomer stabilization at processing temperatures.

It has been demonstrated that sulfoxides, as primary oxidation products of thioethers, themselves are not the active species in catalytic non-radical decomposition of hydroperoxides in model experiments^{8, 8a}. However, sulfenic acids, e.g. t-C,H₉-SOH generated in situ by sulfoxide thermolysis, immediately decompose hydroperoxides⁸. Activity in hydroperoxide decomposition in model systems (<100°C) was shown to be related to the thermal instability of the sulfoxide formed ^{8+e}. Dialkyl sulfoxides thermally give rise to alkenes and alkanesulfenic acids⁸. Furthermore, the nature of sulfacia caid produced from sulfoxides can play an important role^{8d}.

The data in table 4 demonstrate the influence of the structure of the sulfur substituent on Brabender induction times.

Oven ageing of AO1-o-SO and AO10a-o-SO in BR with high stabilizer concentration (1-2%) and at an elevated temperature allowed us to estimate their rates of decomposition. At 180°C the estimated half-lifes ($t_{1/2}$) of AO1-o-SO and AO10a-o-SO are 20 and 23 min, respectively.

Surprisingly, at 180°C the decomposition rates for the sulfoxides AO1-o-SO and AO10a-o-SO with a linear alkyl substituent on sulfur are higher by a factor of two than those of linear dialkyl sulfoxides ^{5a}. These findings can be rationalized by the elimination of the ortho-quinone methide OQM(scheme 7) predominating over alkene elimination from the alkyl side chain(cf. scheme 9). This is also the reason for the lack of alkenes as major volatile decomposition products. At this temperature,

rearrangement reactions leading to formation of aldehydes and thiols via a homolytic pathway were not observed. These reactions are reported to be much slower and require significantly higher temperatures than alkene elimination⁸⁷.

Sulfoxide	Structure	Brabender (160°C): t(ind)[min]
without		4
A01-o-S0		28
A010a-o-SO	OH S-CeHin O	40
A012-0-50	OH S-t-C ₆ H ₁₇	7
A013-o-SO		7
AQ14-o-SO		3

Table 4: Brabender Induction Period of BR Stabilized with 0.25 % Sulfoxide

In contrast to the sulfoxides with linear alkyl sulfur substituents (AO1-o-SO, AO10ao-SO), the major volatile product of the (concerted) unimolecular thermal elimination reaction of the sulfoxide AO 12-o-SO, bearing a t-octyl sulfur substituent, is an alkene (Scheme 9; TG-FTIR- and ¹H-NMR-evidence).

The estimated half life $(t_{1/2})$ of AO12-o-SO at 180°C is only about 0.18 min, i.e. about hundred times smaller than that of AO1-o-SO. Similar results were obtained from thermolysis of AO13-o-SO (see table 5).





Table 5: Half Lifes t1/2 of Sulfoxides at Different Temperatures

Stabilizer	Temperature [°C]	Half Life t _{1/2} (min)
AO1-o-SO (1.5 % in BR) ^{a)}	180	20
AO10a-o-SO(1.7 % in BR) ^{a)}	180	23
AO12-o-SO (neat) b)	180	0.18
AO12-o-SO (neat) b)	160	0.67
AO13-o-SO (neat) 0)	180	0.13
AO13-o-SO (neat) b)	160	0.64
AO14-o-SO (neat) cj	160	14 ^{c)}

^{a)} oven ageing ^{b)}TG-FTIR ^{c)} TG-FTIR/GLC-MS still under investigation

Even though AO14-o-SO is a sulfoxide with a linear alkyl sulfur substituent, a fluorinated alkene could be detected as one of the major thermolysis products (TG-FTIR).

Due to the electron withdrawing proporties of the perfluoroalkyl group in the side chain, the decomposition rate of AO14-o-SO is accelerated and thus the formation of the perfluoroalkylalkene is "promoted". Similar effects found with other electron withdrawing groups are reported by Shelton and coworkers³⁰.

The decomposition rate of the linear alkyl thioether AO10a (a model compound for AO1) is by four orders of magnitude slower than that of the sulfoxide AO12-o-SO and by two orders of magnitude slower than that of AO1-o-SO or AO10a-o-SO (DSC/GLC-MS evidence).

Therefore, n-alkyl 2-hydroxybenzyl thioethers such as AO1 can be considered as thermally stable under normal rubber processing conditions.

At first sight it seems that a short half life of the sulfoxide at processing temperature is equivalent with poor processing stability. The more stable AO1-o-SO and AO10a-o-SO, probably give rise to traces of strong acids which decompose hydroperoxides <u>catalytically</u> under processing conditions (via a non-radical pathway according to ¹. This could explain the surprisingly high efficiency of

n-alkyl 2-(hydroxybenzyl)-thioethers, in addition to the "tandem mechanism" (chapter 4).

In the case of the less stable sulfoxides we assume an antagonism between phenolic thioethers and sulfenic, sulfinic or sulfonic acids(formed by thermolysis of sulfoxides (and subsequent oxidation)) in high concentration $^{6, 6a}$. Common alkane sulfenic acids are known to be thermally unstable and eliminate water, giving rise to thiolsulfinates, which dissociate to radicals if they are derived from simple alkane sulfenic acids, the major isolated products being dialkyl disulfides 8 . We could observe formation of variable amounts of dioctyldisulfide in all grafting experiments with AO1, AO1-o-SO and AO10a-o-SO (see experimental part, table 6) which increase with longer ageing periods

Benzylic thiolsulfinates, however, such as those formed from t-alkylbenzylsulfoxides (scheme 9), are reported to be decomposed already at 100°C to benzylic sulfenic acid and thiobenzaldehydes¹⁴, which most probably are active chain propagators (scheme 9a).

Another unusual behavior is observed in the case of 2,4-dimethyl-6-(2'-octylthioethyl)phenol (AO10b; see chapter 3). We assume that a fast formation of the corresponding sulfoxide AO10b-o-SO occurs during processing, the thermolysis of which should give rise to a styrene derivative(scheme 9b, cf.¹⁴). The latter is expected to propagate the radical chain significantly and therefore its pro-oxidative effect seems to supersede the antioxidative effect of the thioether AO10b. Further work is planned to confirm this assumption.

Scheme 9a

2 R-S-OH _____ [R-S(=O)-S-R] (thiolsuffinate) general reaction

R = Alkyl: thiolsuffinate ---- R-S'+ R-S(=0)

Thivi radical R-S- ----- grafting

Sulfinyl radical R-S(=O) ----- poor grafting



Chain Propagation

Ar-CH=S+P' ---- Ar-CH(-S-P)'

Ar-CH(-S-P) + P-H ---- Ar-CH2-S-P + P

Scheme 9b



8. Reaction of Phenoxy Radicals in Solution (CIDNP Experiments)

In CIDNP experiments nuclear spin polarization is observed for products related to radical pair reactions immediately after formation of the product (i.e. between 100 ns and a few seconds). CIDNP experiments with AO1 and BHT lead to the following conclusions: In the absence of the elastomer substrate, these antioxidants preferably dimerize to C,O-dimers, e.g. D1 and D2 (scheme 10)^{5, 6a}. No polarizations were observed for the disproportionation products AO1 and BHT, respectively and the corresponding para-quinone methides, e.g. PQM1^{5, 6a}. This indicates that

disproportionation is much slower than dimerization. However these disproportionation products can be formed from the dimer as intermediate. Similar experiments were performed with BHT and peroxy radicals, leading to the analog radical recombination products^{2h}.

Thus, in the substrate, i.e. in the presence of macroalkylperoxy radicals P-OO, the phenoxy radical AO1 could give rise to a C,O-coupling product E - in analogy to the formation of dimers D1 - which in turn could be decomposed, e.g. to PQM1 and a macroalkyl hydroperoxide P-OOH(scheme 10).

If one follows the phenoxy radicals in ESR-experiments for a time interval larger than a few seconds, one observes that the phenoxy radical arising from AO1 is less stable than that arising from BHT; this indicates that depending on the surrounding matrix and the radical concentrations, reactions - mainly on the thioether side chain - start to compete with dimerization.

9. para-Quinone Methides from AO1

We recently reported an efficient addition of C-centered radicals to the substituted para-quinone methide PQM1(scheme 10), obtained by oxidation of AO1 with K₃Fe(CN)₆, a member of a class of interesting synthons for 4-hydroxybenzaldehydes, asymmetric 4-hydroxybenzaldehydedithioacetals and 4-hydroxytrithioorthobenzoates⁹. This demonstrates that quinone methides are efficient traps for Ccentered radicals and thus could be grafted to the polymer chain (cf. scheme 7, path (b)). Even PQM1 is also an active processing stabilizer in polybutadiene (Brabender $160^{\circ}C$, c = 0.25%: t(ind) = 20 min). It could, however, not yet be estimated to what degree PQM1 contributes to stabilization in the substrate; under processing conditions, PQM1 is too reactive to be detected.



Scheme 10: Reactions of the Radical AO1' (R = Octyl)

10. The Grafting of the Side Chain

AO1

Brabender experiments with AO1-o-SO in polybutadiene and subsequent ¹H-NMR experiments (see chapter 6) proved the intermediate formation of an ortho-quinone methide and octanesulfenic acid (scheme 7). While the ¹H-NMR spectra showed clearly that an important part of the quinone methide is grafted to the polybutadiene backbone, there was no unambiguous answer about the grafting of the sulfenic acid. In order to answer this important question, we carried out Brabender ageing experiments of polybutadiene, using stabilizer AO15-o-SO which bears a partially fluorinated alkyl group (with no β -hydrogen atoms) on the sulfur atom(scheme 11).

Scheme 11

CF, ັ້ງ ເວັ່ງ

n = 0: AO15 n = 1: AO15-o-SO

After compounding of the polymer on a roll mill or in a Brabender, respectively, and exhaustive extraction with acetone(cf. table 6 in experimental part), the ¹⁹F-NMR spectrum of the polymer revealed two groups of resonances at approximately -61.2 ppm and -66.6ppm vs. CPCl₃, the integral of the second group being distinctly larger than the one of the first. While the chemical shift values are the same in different experiments, the relative intensities (integrals) of the individual resonances depend on the parameters of the ageing experiment. The ¹⁹F-NMR spectra indicate that grafting in polybutadiene is a well defined process occurring at certain polymer sites. Comparing the ¹⁹F- chemical shift values in the polymer with those of AO15 (-66.5 ppm) and AO15-SO (-60.8 ppm) leads to the assignement of the polymer resonances to the two sulfur oxidation states, with the conclusion that both oxidation states are present in the side chains grafted to the polymer, the larger component being of the thioether type. This could mean that the sulfenic acid R-SOH is transformed into sulfinyl radicals R-S', which are grafted to a large extent, and sulfinyl radicals R-S(=O)', which are grafted to a smaller extent(scheme 9a). Such a reaction would be in agreement with the common assumption that thiyl radicals are more reactive in grafting than sulfinyl radicals. The grafted thioether side chains will certainly contribute to the stabilization of the polymer. It is therefore plausible to assign the ¹⁹F-NMR signals at 61.2 ppm mainly to products of a partial oxidation of the major grafting products.

11. Conclusions

To our knowledge, AO1 is the best overall processing and storage stabilizer for most elastomers. It is an optimized compound in the family of sulfur containing phenols. It undergoes different reactions most of which contribute to a high net stabilizing effect. A striking feature of the stabilizer AO1 is that nearly all transformation products are themselves active antioxidants.

A part of the stabilizer is also grafted to the polymer; this is most likely to occur through the intermediacy of the ortho-quinone methide OQM, formed by thermal cleavage of the corresponding "ortho-sulfoxide" AO1-o-SO. There are strong indications that in the case of n-alkylthiomethylphenols also the transformation products of the unstable alkane sulfenic acids are substantially grafted. As for processing stabilizer activity the following observations were made: Bulky substituents in the ortho- as well as the para-position lead to a drop of the antioxidant activity; most of the 2,6-bisfunctionalized products, e.g. AO8, a major component of the commercial stabilizer AO9 show a significantly lower performance. Unsubstituted ortho- or para-positions also seem to reduce the antioxidant activity.

n-Alkanesulfenic acids, which are slowly formed from the more stable sulfoxides such as AO1-o-SO, and/or their reaction products seem to catalyse a non-radical decomposition of hydroperoxides(cf.^{8, 84}). This catalytic process and a fast stoichiometric cage process ("tandem reaction") seem to contribute to a net stabilizing effect and enhance the performance of AO1 and its family under processing conditions by an order of magnitude as compared to combinations of classical phenols and thiosynergists.

In contrast to *n-alkyl*-2-hydroxybenzylthioethers, *tertiary alkyl* analogs show a striking breakdown of the processing stabilizer activity; obviously the corresponding intermediate sulfoxide undergoes a different elimination reaction, giving rise to an olefin and a benzylic sulfenic acid.

We assume an antagonism between phenolic thioethers and high concentrations of acidic thermolysis products of the unstable sulfoxides and/or thiobenzaldehydes, respectively.

We acknowledge Ciba Specialty Chemicals for supporting this work.

Experimental Part

Application tests: Oven ageing induction time [weeks] at a given temperature is defined as oven ageing time of 10 mm compression molded rubber sheets until gel content exceeds 2.0% $(w/w)^{5}$.

Brabender ageing: The induction time is defined as time [min] to an increase of the torque by 1 Nm after the minimum 5 .

Grafting experiments(butadiene rubber): Sulfur content by elemental analysis. Extractions of polybutadiene: The rubber was compression molded to 2mm sheets after grafting experiments and subsequently extracted 3 days with acetone in a Soxlet apparatus. The concentration of the products was determined by HPLC of acetone extracts.

ESR-experiments: in toluene solution, DPPH = 2,2-diphenyl-1-pikrylhydrazyl radical ⁹.

The CIDNP experiments were performed on a Bruker AM-200 wide bore spectrometer with probe heads modified for in situ irradiation. The light source was a Lambda Physics dye laser operated with diphenylstilbene (404.5 nm) which was pumped by a Questek excimer laser (XeCl, 308nm). ¹H- and ¹⁹F-NMR-experiments with dissolved polymers were carried out on a Varian

'H- and 'F-NMR-experiments with dissolved polymers were carried out on a Varian Unity 500 (500 Mhz) spectrometer.

TG-FTIR: Experiments were performed on a Netzsch Thermo-Microbalance TG 209, coupled to a Bruker FTIR Spectrometer IFS 28. The isothermal TG measurements with 2.5 mg samples were carried out at different temperatures (116-164°C) in a dynamic N₂ atmosphere. The FTIR spectra were recorded in the wave number range 4500-550 cm⁻¹ and 20 spectra coadded every 7 seconds. With this range of data, it was possible to estimate the half-life $(t_{1/2})$ for further temperatures.

DSC/GLC-MS: A 1.5 mg sample in a hermetically sealed pan (under N₂ atmosphere) was treated thermally in a Differential Scanning Calorimeter (Perkin Elmer DSC 7). After cooling down, the pan was opened and the reaction mixture dissolved in CH_2Cl_2 .

GLC-MS data was obtained using a FISONS Instruments GC 8000 gas chromatograph coupled to a MD 800 quadrupole mass spectrometer (mass range 10-800).

Synthesis

General: see ⁵; TLC: [A] = bexane/ethyl acetate 49:1; [B] = bexane/ethyl acetate 19:1; [C] = bexane/ethyl acetate 4:1. AO1 ⁵; AO3 ³, AO4 ¹⁰; AO5 was synthesized in analogy to AO4 ⁵, yield 74.2 %, b.p. 182-185°C/0.04 mbar, yellowish oil. ¹H-NMR: 6:90(s, 2 arom. H), 3.59 (s, Ar-CH₂), 2.41(t, J = 7, CH₂CH₂S), 2.21 (s, Ar-CH₃), 1.56(quintet, J = 7, CH₂CH₂S), 1,26(m, (CH₂)₃), 0.88 (t, J = 7, CH₃CH₂). Anal. calc. for C₁₇H₂₈OS (280.47), C 72.80; H 10.06; S 11.43; found C 72.86; H 10.25; S 11.19. AO6, AO6a (=2,6-Bis-(octy)thiomethyl) -4-(1,1,3,3-tetramethylbutyl)phenol) and and AO6h ¹¹; AO7 and AO8 were synthesized in analogy to AO6, using a 1:1:1 molar ratio of p-t-nonylphenol, dodecanethiol and para-formaldehyde (0.115 mol); separation of the reaction mixture on a silicagel column provided 5.37 g (14%) of AO7 as a colorless liquid, R_f [A] = 0.34. ¹H-NMR: 7.04 (s, OH); 6.86-6.69(m, 2 ar. H), 3.57(s, ArCH₂S), 2.2-2.1 (m, SCH₂CH₂); 1.40-1.25(m, SCH₂CH₂), 1.02 und 0.56(m, t-C₃H₁₇); anal. calc. for C₄₁H₇₆OS₂ (649.15), C 75.86; H 11.80; S 9.88; found C 77.09; H 12.02; S 8.71

and 12.31g (27 %) of AO8 as a colorless liquid, Rf [A] = 0.23. H-NMR: 7.06 (s, OH), 7.0-6.3(m, 3H); 3.60(s, ArCH2S), 2.14(m, SCH2CH2); 1.50-0.50(m, SCH2CH2 and t-C9H17). Anal. calc. for C28H50OS(434.77), C 77.35; H 11.59; S 7.37; found C 77.81; H 11.57; S 6.77. AO10 was synthesized according to ¹²: yield 45 %, b.p. 112°C/0.01mbar. ¹H-NMR: 7.15-7.05 and 6.9-6.7 (m, 3 aromat.H); 4.75(br. s, OH); 3.78 (s, Ar-CH2-S); 2.37 (t, J = 7, SCH2CH2); 2.25 (s, Ar-CH3); 1.53(quintet, J = 7, SCH_2CH_2 ; 1.23 (m, 10H); 0.87 (t, J = 7, CH₂CH₂). Anal. calc. for C₁₆H₂₆OS(226.45): C 72.13; H 9.64; S 12.03; found C 72.13; H 9.80; S 11.70. AO10a 5. AO11 13 AO10b: This phenol was prepared in a multistep sequence from 5,7-Dimethyl-3Hbenzofuran-2-one which was synthesized in analogy to ^{13a}, yield 19 % (sublimation at 120-140°C/0.002 mbar), m.p. 123-125°C. 1H-NMR: 6.88(s, 2 aromat. H); 3.65(s, CH₂); 2.28 and 2.25 (2s, Ar-CH₃). Anal. calc. for C₁₀H₁₀O₂ (162.19), C 74.06; H 6.21; found C 73.86; H 6.15. 2,4-dimethyl-6-(2'-hydroxyethyl)phenol; The benzufuranone was reduced in methanolic solution with NaBH4 and the product was purified after the standard work-up by recristallization from toluene, yield 78 %, m.p. 77-78°C. 1H-NMR: 7.47(s, OH), 6.78 and 6.65 (2br. s, aromat. H); 3.89(quartet, J = 7, O-CH2); 2.77(t, J = 7, Ar-CH2); 2.24(m, OH); 2.16(s, Ar-CH3). Anal. calc.for C10H14O2 (166.22), C 72.26; H 8.49; found C 72.18; H 8.32.). 2,4-dimethyl-6-(2'bromoethyl)phenol: A solution of 2,4-dimethyl-6-(2'-hydroxyethyl)phenol (9.97 g, 60 mmol) in 78 ml 33 % HBr in AcOH was stirred for 1 h at 100°C. After standard workup, the residue was submitted to bulb to bulb distillation (100°C/0.01 mmbar) and further purified by flash chromatography on silicagel (cluant hexane/ethyl acetate 9:1), brownish liquid, yield 15 %, R1[C] = 0.51. H-NMR: 6.77 and 6.72 (2 br. s, aromat. H); 4.53(s, OH); 3.52(t, J = 7, Br-CH2); 3.07(t, Ar-CH2); 2.15 and 2.14(2s, Ar-CH3). The product was further purified and the OH group protected by a standard treatment

with 1 equivalent of CISiMe3 and Et3N, yield after bulb to bulb distillation (105°C/0.02 mbar) 73 % (2,4-dimethyl-6-(2'-bromoethyl)-O-trimethylsilylphenol), colorless liquid; ¹H-NMR: 6.82 and 6.75 (2 br. s, aromat. H); 3.48(t, J = 7, Br-CH₂); 3.06(t, Ar-CH2); 2.19 and 2.14 (2s, Ar-CH3); 0.24(s, Si(CH3)3). 5.36 g (17.8 mmol) of this product was dissolved in 30 ml toluene and allowed to react for 37 h at 100°C with 17.8 mol of the sodium salt of octanethiol (prepared from 3.1 ml octanethiol and sodium hydride). After filtration of the reaction mixture, standard work-up and bulb to bulb distillation, the crude 2,4-dimethyl-6-(2'-octylthioethyl)-O-trimethylsilylphenol (1.75 g, 27 %; ¹H-NMR: 6.79 and 6.77 (aromat. H); 2.70 (A2B2-system, 4H, Ar-CH2-CH₂); 2.52(t, J = 7, S-CH₂-C₁H₁₈); 2.21 and 2.15 (2s, Ar-CH₃); 1.57(m, C₆H₁₃-CH₂-CH2-S); 1.25 (m,(CH2)s); 0.87(t, J = 7, CH3CH2); 0.24(s, Si(CH3))) was hydrolyzed to the corresponding phenol: 1.69 g(4.6 mmol) of the crude trimethylsilyl derivative was treated for 45 min with 5ml 2N HCl in 5 ml of acetone at 55°. Then after standard work-up the residue was submitted to bulb to bulb distillation; yield 1.10 g (82 %), b.p. 150°C/0.008 mbar, yellowish liquid, R_t [C] = 0.63. ¹H-NMR: 6.73 and 6.68 (2 br. s, aromat. H); 5.49(s, OH); 2.79 and 2.70 (A2B2-system; 4H, Ar-CH2-CH2); 2.45 (t, J = 7, S-CH₂-C₇H₁₈); 1.49(m, C₆H₁₃-CH₂-CH₂-S); 2.13(s, Ar-CH₃); 1.18(m,(CH₂)₅); 0.80(t, J = 7, CH₃CH₂). Anal. calc. for C₁₈H₃₀OS(294.50): C 73.41; H 10.27; S 10.89; found C 73.49; H 10.89; S 10.96.

AO10c: A solution of 5g (30.8 mmol) 2-allyl-4.6-dimethylphenol ^{13b}, 4.51 g (30.8 mmol) and 101 mg Azo-isobutyronitril (AIBN) in 20 ml toluene was stirred for 62 h at 60°C (cf. ^{13c}). After evaporation of the solvent the residue (7.5 g) was submitted to bulb to bulb distillation. The major fraction distilled at 135-140°C (0.005 mbar), 6.45 g (68%), yellowish liquid, R_t [B]= 0.73. ¹H-NMR: 6.58 (m, 2 aromat. H); 5.21 (br. S, OH); 2.50 (t, J = 7, Ar-CH₂); 2.33(quartet, J = 7, S-CH₂); 2.02 (s, Ar-CH₃); 1.69 (quintet, J = 7, C₆H₁₃-CH₂-CH₂-S); 1.1 (m, (CH₂)₅); 0.69(t, J = 7, <u>CH₂</u>-CH₂). Anal. calc. for C₁₉H₃₂OS(308.52): C 73.97; H 10.45; S 10.38.

AO11¹³; AO12¹³⁴; AO13, AO14 and AO15 were synthesized in analogy to ¹⁴. AO13: From 1,1,3,3-tetramethylbutanethiol, 98 %, yellowish oil, R_{f} [B]= 0.57. ¹H-NMR: 6.85 and 6.79 (m, 2 aromat. H); 3.77 (s, Ar-CH₂-S); 2.20 (s, Ar-CH₃); 1.68 (s, 2H); 1.47 (s, 6 H); 1.03(s, 9H). Anal. calc. for C₁₇H₂₄OS(280.47): C 72.80; H 10.06; S 11.43; found C 72.35; H 10.10; S 11.03. AO14: From Lodyne 921A (major component: C₄F₁₃CH₂CH₂-SH), 76 %, colorless liquid, b.p. 100-105°C/0.005mbar. ¹H-NMR: 6-86 and 6.73 (s, 2 aromat. H); 5.74 (s, OH); 3.77 (s, Ar-CH₂S); 2.6-2.5 (m, 2H); 2.4-2.1 (m, 2H); 2.20 (s, Ar-CH₃). Anal. calc. for C₁₇H₁₅F₁₃₀C(514.34): C 39.70; H 2.94; F 48.02; S 6.23; found C 39.67; H 3.08;F 48.16; S 6.19. AO15: From 2.2,2trifluoroethanethiol, 71%, colorless oil, b.p. 65°C/0.01mbar. ¹H-NMR: 6.91 and 6.75 (s, 2 aromat. H); 5.54 (s, OH); 3.85 (s, Ar-CH₂S); 2.94 (quartet, J(H,F) = 10, SCH₂CF₃); 2.21 (s, Ar-CH₃). Anal. calc. for C₁₁H₁₃F₁₃OS(250.28): C 52.79; H 5.24; F 22.77; S 12.81 found C 53.18; H 5.26; F 22.19; S 12.67.

Oxidation products: AO1-o-SO and AO1-p-SO ¹⁵. AO10a-o-SO, AO12-o-SO, AO13-o-SO, AO14-o-SO and AO15-o-SO were synthesized in analogy to ¹⁴. AO10a-o-SO from AO10a, yield 77 %, colorless liquid, R_{f} [A]= 0.27. ¹H-NMR: 9.1(s, OH); 6.93 and 6.64 (s, 2 aromat. H), 4.35 and 3,76 (AB-system, J = 14, Ar-CH₂-SO); 2.75-2.5 (m, SCH₂CH₂); 2.24 (s, Ar-CH₃); 1.8-1.6 (m, SCH₂CH₂); 1.5-1.2 (m, 10 H); 0.88 (t, J = 7, CH₃CH₂). Anal. calc. for C₁₁H₂₈O₂S (296.47): C 68.87; H 9.52; S 10.81; found C 68.93; H 9520; S 10.62. AO12-o-SO from AO12: 46.3 %, mp. 107.5-108.5 °C(from CH₂Cl₂). ¹H-NMR: 9.17 (OH), 7.06 and 6.93(s, 2 aromat. H), 4.18 and 3.53 (AB-

system, J = 13, Ar-CH₂-SO), 3.66(s, Ar-CH₂-S); 2.88 (s, Ar-CH₃); 1.8-1.4 (m, 16H), 1.09 and 1.04 (s, 18 H,(CH₃)₃C). Anal. calc. for C₂₃H₄₄O₂S₂ (440.73): C 68.13; H 10.06; S 14.55; found C 68.13; H 10.27; S 14.56.

AO13-o-SO from AO13: 79 %, m.p. 129.5-130.0 °C (from hexane). ¹H-NMR: 8.93 (s, OH); 6,90 and 6.74 (s, 2 aromat. H); 4,18 and 3,47(AB-system, J = 13,_

Ar-CH₂-SO); 2.21 (s, Ar-CH₃); 1.75 and 1.52 (AB-system, J = 14, (CH₃)₃C-CH₂); 1,42 and 1,44 (s, (CH₃)₂C); 1.07 (s, (CH₃)₃C). Anal. calc. for C₁₇H₂₈O₂S(296.47): C 68.87; H 9.52; S 10.89; found C 68.71; H 9.73; S 10.89.

A014-o-SO from A014: 61 %, m.p. 92.5-93°C (from acetone); ¹H-NMR: 8.30 (OH); 6.95 and 6.68 (s, 2 aromat. H); 4.42 and 3.84 (AB-system, J = 14, Ar-CH₂-SO); 2.95-2.8(m, 2H); 2.7-2.35 (m, 2H), 2.23 (s, , Ar-CH₃). Anal. calc. for

C₁₇H₁₅F₁₃O₂S(530.34): C 38.50; H 2.85; F 46.57; S 6.05; found C 38.53; H 2.92; F 46.68; S 6.06. AO15-o-SO from AO15: 60 %, m.p. 106.5-107.5°C(from

cyclobexane/toluene); ¹H-NMR: 8.16 (s, OH); 6.98 and 6.67(s, 2 aromat. H); 4.60 and 3.82(AB-system, J = 14, Ar-CH₂-SO); 3.55-3.20 (m, SCH₂CF₃); 2.23(s, Ar-CH₃). Anal.. calc. for: $C_{11}H_{13}F_3O_2S(266.28)$: C 49.62; H 4.92; F 21.40; S 12.04; found C 49.73 H 4.97; F 21.10; S 12.09.

Thermolysis of the model sulfoxide AO10a-o-SO (scheme 8). DA1: 5 g (0.0169 mol) AO10a-o-SO and 1.5 g (0.0174 mol) vinylenecarbonate were heated for 4 h to 165°C. Distillation at 140°C (0.01 mbar) provided 0.06g(1 %) of the Diels-Alder adduct DA1 as white needles, m.p. 132-132.5°C (bexane); IR (KBr): 1799, 1785 (C=O).¹H-NMR: 6.92 and 6.80(s, 2 aromat. H); 6.31(d, J = 7, O-CH-O); 5.26(dxdxd, J₁ = 7, J₂ = 3, J₁ = 2, CH₂-CH-O); 3.07 and 2.91 (AB-part of ABMX-system, J(AB) = 16, J(AM) = 3, J(BM) = 2, CH₂). MS: 220. Anal. calc. for C₁₂H₁₂O₄ (220.22): C 65.45; H 5.49; found C 65.29; H 5.41. Column chromatography (hexane) of the distillation residue . gave besides 0.27 g of dioctyl disulfide (GLC, IR) 1.65 g(35 %) of a white solid. identified as 6,8-dimethyl-2-heptyl-3-thischromane (TC), m.p. 49-50°C; ¹H-NMR: 6.84 and 6.71 (s, 2 aromat. H); 5.08(dxd, $J_1 = 7$, $J_2 = 5$; O-CH-S); 4.15 and 3.62 (ABsystem, J = 16, S-CH₂); 2.21 and 2.16 (s, Ar-CH₃); 2.1-1.9 (m, CH₂-CH); 1.7-1.5 (m, 2H); 1.4-1.2(m, 8H); 0.89 (t, J = 7, CH₃CH₂). MS: 278. Anal. calc. for C₁₇H₂₆OS (278.45): C 73.33; H 9.41; S 11.51; found C 73.45; H 9.54; S 11.44, N.B. The formation of the thiochromane compound TC(Pummerer rearrangement) will be discussed in a subsequent paper. PQM1 ⁹.

Stabilizer (Concentration [%])	Ageing •)	Ageing Temperature(°C) /Time [min]	Sulfur Content After Extraction [%] ^{*)} (by Elemental Analysis)	Stabilizer Found After Ageing (in % of Initial Con- centration) ^{c)}
AO1 (1.78)	Oven	80/4w, 8w, 12w, 16w, 20w, 30w ^{b)}	1, 2, 3.1, 4.3, 5.8 and 13.3	99, 96.3, 92.3, 90.2, 83, 66.8
AO1-0-SO (2.00)	Oven	80/4w, 8w, 12w, 16w, 20w, 30w ^{b) •)}	8.5, 15, 21, 30, 36.7 and 46.7	84.3, 59.5, 47.8, 25.6, 7.3, <0.4
AO1 (2.11)	Oven	180/120	6.25	80.3 ·
AO1 (2.39)	Oven	180/480	31	28
AO1-0-SO (1.54)	Oven	180/60	55	12.2
AO10a-o-SO (1.67)	Oven	180/60	45.6	16.5
AO1 (2.11)	Brab.	160 ⁴⁾ /7	2.2	83
AO1 (1.87)	Brab.	160 7/90	17	71
AO1-0-SO (2.07)	Brab.	160 0/7	34	47.1
AO15-0-SO(2.0)	Brab.	160 0)/15	56 (F: 52 %)	n.a.

Table 6: Results of Grafting Experiments in Butadiene Rubber:

^{a)}Brab. ~ Brabender ^{b)} w = weeks ^{c)} by HPLC ^{d)}mass temperature ca. 180°C

^{•)} dioctyl disulfide content [ppm] (GLC): 4w: 120, 8w: 520, 12w: 1120, 16w: 2430 and 20w: 2770 ppm ⁷% of initial concentration

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