*Pure & Appl. Chem.*, Vol. 55, No. 10, pp. 1637-1650, 1983.
Printed in Great Britain.

0033-4545/83 \$3.00+0.00
Pergamon Press Ltd.

# SYNERGISM OF ANTIOXIDANTS

C.R.H.I. de Jonge

Akzo Research, Corporate Research Department, Arnhem,
The Netherlands

Abstract - Synergism of antioxidants has found wide-spread use since differences in stability of vegetable oils and fats were found when antioxidants were added. A huge amount of synergistic combinations has been found empirically. In some cases synergism of stabilizers has a high practical value in the stabilization of polymers. Nevertheless little is known about the chemistry involved. A short general overview of synergism of antioxidants and some chemical rules by which synergism is governed are given. Recent results in our studies on synergism of antioxidants indicate that e.g. on the basis of model reactions chemical explanations can be used to demonstrate synergism of antioxidants in polyolefins.

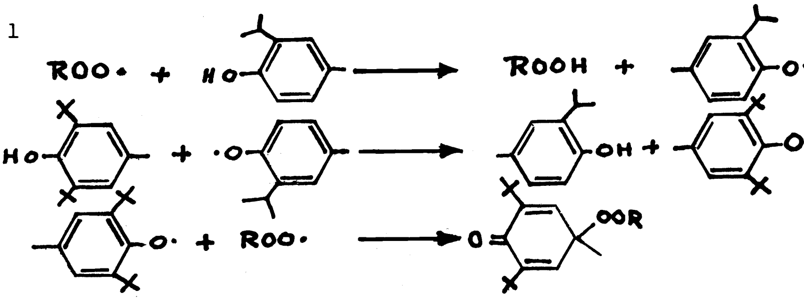
## INTRODUCTION

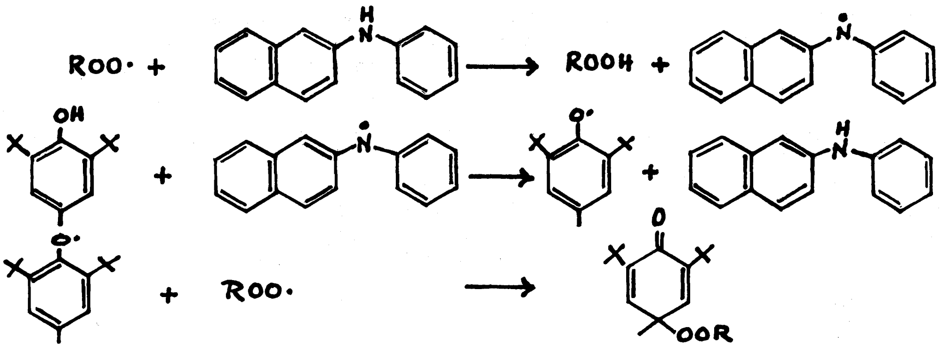
Most organic polymers, being sensitive to oxidative degradation, require the addition of stabilizers to provide protection during processing and end-use. Combinations of stabilizers often show remarkable phenomena where the cooperative action displays a stabilizing effect greater than the sum of the individual effects, taken independently. This phenomenon is defined as synergism.
Two mechanistically distinct types of synergism1) can be considered:
Homosynergism, involving two compounds operating by the same mechanism and Heterosynergism, arising from the cooperative effect of antioxidants acting by different mechanisms.
Especially the latter category has found wide-spread application in the stabilization of hydrocarbon polymers, viz. combinations of chain-breaking antioxidants and preventive antioxidants of various types.

## GENERAL CONSIDERATIONS

In the case of a combination of two different chain-breaking antioxidants (homosynergism) that function by donation of hydrogen to a peroxy radical, the most likely mechanism of synergism would involve transfer of hydrogen from one inhibitor to the radical formed in the reaction of the other inhibitor with a peroxy radical.
Typical examples are combinations of hindered phenols with other phenols2), ascorbic acid3), dialkylphosphonates4) and aromatic amines5). The latter example has been studied in detail. In all these cases it is believed that the stronger inhibitor is regenerated from its radical by the less powerful inhibitor, serving as a reservoir of hydrogen for regeneration of the more effective chain-breaking antioxidant. It was also shown that the concentration of the more effective antioxidant remains constant during the oxidation until complete consumption of the weak inhibitor has occurred (see Scheme 1, for synergism of two phenols differing in the bulkiness of the ortho-substituents and for a phenol-aromatic amine combination).

SCHEME 1





The use of homosynergistic systems in the commercial stabilization of polyolefins is however not widely applied. Despite this it was this concept of economically regenerating the chain-breaking antioxidant from its radical which was the basis for our work on novel antioxidant systems, and will be described later on.

The mechanism of synergism observed with a wide variety of combinations of chain-breaking antioxidants and preventive antioxidants can be explained by consideration of the specific ways in which these different types of stabilizers function to retard or inhibit the oxidation reaction. The free radical chain stopping reaction of the chain-breaking antioxidant (a phenol or an amine) will retard the formation of peroxides by termination of the kinetic chain, thus eliminating chain propagation. However, one molecule of hydroperoxide will be formed in the transfer of hydrogen to a peroxy radical. If the hydroperoxide formed is converted by a preventive antioxidant to form non radical products, rather than to decompose thermally to form chain initiating free radicals, there is a further reduction in the oxidation rate.

SCHEME 2

---

ROO. + AH ⟶ ROOH + A. (1)
ROOH + peroxide decomposer ⟶ non radical products (2)
A. + ROO. ⟶ ROOA (3)

A. + $O_2$ ⟶ AOO. ⟶ etc. (4)
A. + peroxide decomposer ⟶ AH + products (5)

---

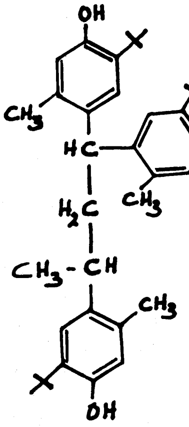
From scheme 2 it can be seen that for effective heterosynergism reactions (3) and (4) are undesired side reactions, wasting the corresponding radical of the chain-breaking antioxidant. In this case the primary antioxidant (AH) is consumed and can play no further role in stabilization of the system. Therefore it seems to be of importance that the chain-breaking antioxidant in reaction (1) is capable of forming a radical, which is highly reactive towards hydrogen donating species existing in the peroxide decomposer molecule, to give according to reaction (5) a regeneration of the chain-breaking antioxidant.

In such a case high levels of synergistic action can be obtained when the preventive antioxidant is not only a hydroperoxide decomposer, but also a reservoir for hydrogen donation to the corresponding radical of the chain-breaking antioxidant. However, the use of antioxidants and synergistic combinations is not only governed by favourable chemical interactions but can also be restricted by evaporation, extraction and incompatibility with the substrate to be protected. There are however, methods to avoid such physical losses, e.g. by increasing the molecular weight of antioxidants to such an extent that even under severe test conditions losses are minimised or even prevented. Prevention of physical losses can be obtained by chemical bonding of an antioxidant to the polymer chain[6]. For optimal synergism of a combination of antioxidants, the antioxidant system should also show a mu-

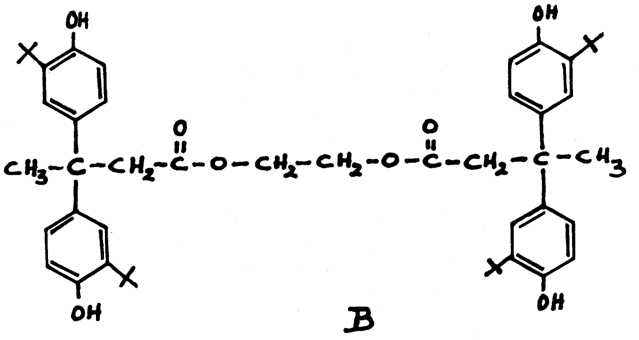
tual regeneration of the individual compounds or active derivatives. Antioxidant wasting side reactions have to be avoided.
Moreover, especially for service life conditions, the antioxidants should have a low volatility and a high compatibility with the substrate.
For commercial applications the antioxidant should not or to a very low extent be extracted e.g. by hot water and the individual components should be non-toxic.

## SOME ANTIOXIDANTS-SYSTEMS USED IN PRACTICE

There are a few synergistic systems used in practice, e.g. 1,1,3-Tris-(5-tert.-butyl-4-hydroxy-2-methylphenyl)-butane (A) with dilaurylthiodipropionate (DLTDP) or distearylthiodipropionate (DSTDP) and Ethyleneglycol-bis-[3,3-bis-(3'-tert.butyl-4'-hydroxyphenyl)-butyrate] (B) with DLTDP or DSTDP.

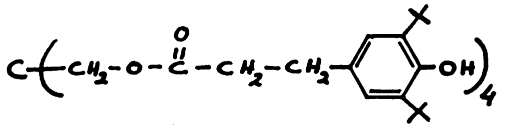


A



B

When antioxidant (A) is used in combination with DLTDP synergism is observed[7)] when tested in polypropylene sheet (1 mm) at 135°C (see Fig. 1). Comparing this combination with an excellent chain-breaking antioxidant, which shows hardly synergism, viz. pentaerythrityl-tetratris-3-(3,5-di-tert. butyl-4-hydroxyphenyl)-propionate (C) it becomes evident that the use of synergistic combinations can be of a limited value, when compared with a high-performance chain-breaking antioxidant.



C

Moreover in a lot of applications the use of thioethers as DLTDP or DSTDP is not wanted.
The level of synergistic action (SA) observed for antioxidant (A) with DLTDP is not so high, probably due to the fact that the corresponding radical of antioxidant (A) is not stable towards oxygen (see Scheme 2, reaction 4).

$$\text{S.A.} = \frac{\text{induction period (chain-breaking a.o. + preventive a.o)}}{\text{induction period chain-breaking a.o. + ind. period preventive a.o.}}$$

An interesting chemical question remains, when comparing the test results of antioxidant (A) and (C) viz. why is compound (A) showing synergism with DLTDP and compound (C) not. Later in in the discussion of model reactions some indications are given. The question why in some cases synergism occurs prompted us to investigate the chemistry more basically, especially along the lines given in the Section General Considerations (vide supra). This investigation coincided closely with our work on the development of diphenylphenol based antioxidant systems.

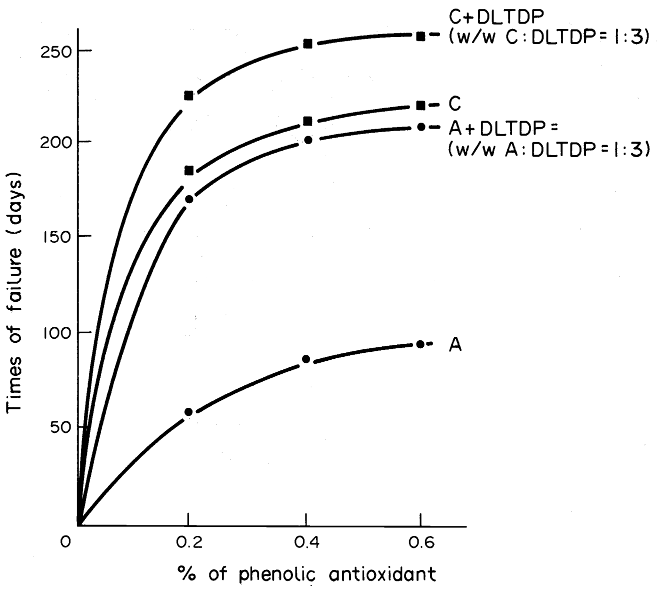


Fig. 1. Times of failure (days) of polypropylene sheet (1 mm) at 135°C, stabilized with antioxidants A and C.

## 2,6-DIPHENYL SUBSTITUTED PHENOLIC ANTIOXIDANTS

It is known that stabilization of a phenoxy radical can be obtained not only by steric hindrance, but also by electron delocalisation. When such a phenomenon could be applied to phenols, effective antioxidants could result.

In the course of our investigations into 2,6-diphenylphenol chemistry we found that some 2,6-diphenylphenol radicals, when properly substituted in the 4-position, were extremely stable even in the presence of oxygen[8]. When 4-methoxy-2,6-diphenylphenol (D) is oxidized to the corresponding radical (F), the oxidation product is obtained as the dimeric form of the radical (E). This dimer can even be purified by recrystallisation. In solution the dimer dissociates giving the green-coloured phenoxy radicals (F), which are stable in an oxygen atmosphere. It was especially this behaviour which opened new possibilities for the synthesis of highly novel phenolic antioxidants.

Initially the study of the 4-alkoxy-2,6-diphenylphenols was disappointing since low levels of activity were displayed when the phenolic antioxidants were tested at the usual ageing temperatures (140-150°C). However it was found that in the presence of a preventive antioxidant like DLTDP or DSTDP the combination became highly active and that the system displayed unusual characteristics[9,10]. In particular maximum synergistic effects were observed at very low phenol concentrations. This is shown in Fig. 2a. For comparison a high performance hindered phenol (C) has also been studied (Fig. 2b).

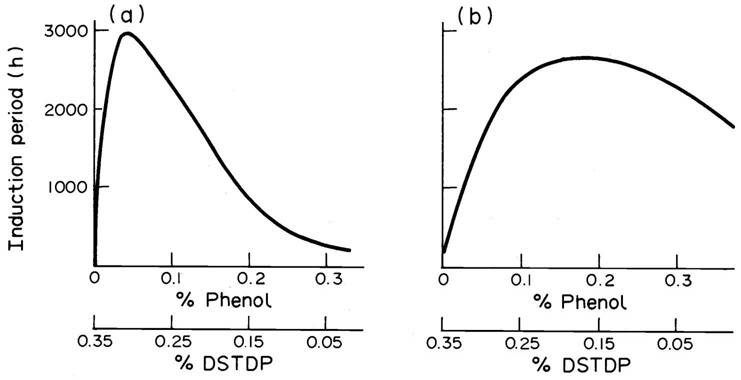
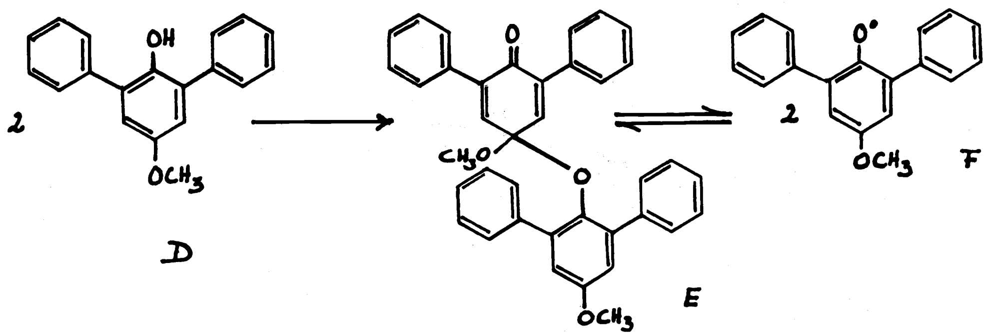
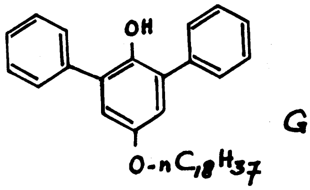


Fig. 2 Measured induction period at 140°C for polypropylene oxidation for samples containing phenolic antioxidants in combination with DSTDP. a) antioxidant (G) b) antioxidant (C).



Further advantages were observed when the processing characteristics of polypropylene containing a mixture of 4-stearoxy-2,6-diphenylphenol (G) and DSTDP were studied. On multiple passes through an injection moulding machine at 270°C little decrease of the concentration of phenolic antioxidant (G) was observed.



G

Comparative studies with the high molecular-weight hindered phenolic antioxidant (C) again in the presence of DSTDP showed a marked decrease in the phenolic antioxidant concentration (Fig.3).

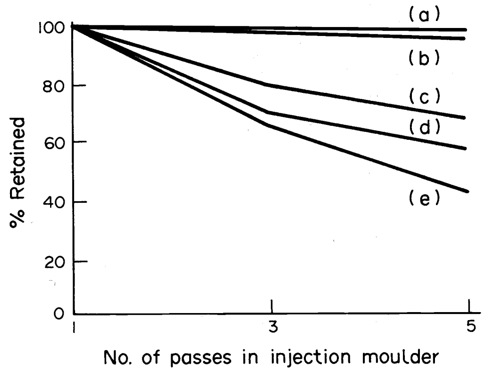
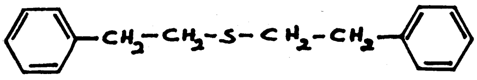


Fig. 3 Effect of processing on the phenolic antioxidant concentration in the presence of DSTDP
a) 0.03 % G + 0.32 % DSTDP
b) 0.12 % G + 0.23 % DSTDP
c) 0.12 % C + 0.23 % DSTDP
d) 0.09 % C + 0.26 % DSTDP
e) 0.06 % C + 0.29 % DSTDP

## MODEL COMPOUNDS IN PRACTICAL TESTS

To understand the phenomena described above it was decided to study in detail the chemical changes occurring during processing and ageing and in particular the fate of the sulphur component (the preventive antioxidant). To simplify this study 4-methoxy-2,6-diphenylphenol (D) and diphenyldiethylsulphide (H) were chosen and it was found that they behaved in an analogous manner to the combination of antioxidant (G) and DSTDP.



H

To study the extrusion effect, polypropylene stabilized with 0.1 % of D and 0.25 % of H was passed five times through an extruder at 200°C. After five passes the concentration of D was not changed. However the concentration of H had decreased to 80 % of the original value (Fig. 4)

The samples obtained after five passes through an extruder where then aged at 150°C in an oxygen atmosphere. At regular time intervals samples were taken from the polymer and the gas stream. The polypropylene samples were extracted and combined with solutions of sublimates formed during the ageing process. Using GLC the concentrations of D and H were quantitatively determined. Results are shown in Fig. 5.

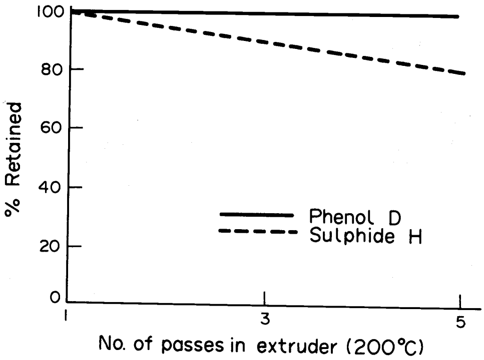


Fig. 4

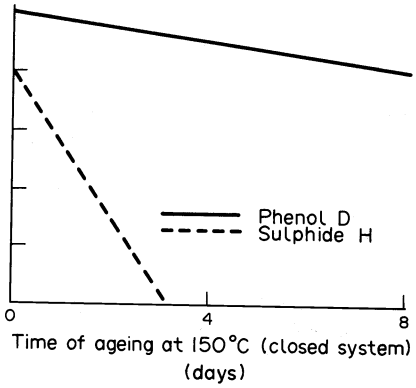


Fig. 5

Fig. 4 Effect of extrusion on the model system.

Fig. 5 The effect of ageing of extruded polypropylene samples containing antioxidant (D) and suplhide (H). The samples were previously extruded five times at 200°C.

From the results presented in Fig. 4 and 5 it was clear that the behaviour of the model compounds (D) and (H) was similar to that shown in earlier oxidation experiments. It was also shown that the sulphide component (the peroxide decomposer) was consumed during the ageing in a manner typical of the behaviour of a hydrogen donor in a homosynergistic system.

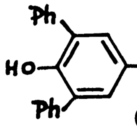
## OVEN-AGEING OF PHENYLSUBSTITUTED PHENOLS AND SYNERGISTIC COMBINATIONS

In Table 1 the results obtained with some 4-alkoxy-2,6-diphenylphenols in combination with DSTDP are summarised.

### The effect of volatility of the chain-breaking antioxidants

With respect to the increasing length of the alkylchain in the alkoxy moiety of the 4-alkoxy-2,6-diphenylphenols it was found that the induction period increased, although the OH-content decreased. Since all of the compounds were soluble in squalane (a model compound for polypropylene), which can be a measure for compatibility with polypropylene, the increasing induction periods can be ascribed to decreased volatility.
TGA-measurements show that $T_{10\%}$ weight loss of 4-n-decanoxy-2,6-diphenylphenol = 256°C and $T_{10\%}$ weight loss of 4-octadecanoxy-2,6-diphenylphenol = 332°C (heating rate: 5°C/min; air: 50 ml/min). The most promising results obtained thus far were those where 4-octadecanoxy-2,6-diphenylphenol (G) and DSTDP were used as chain-breaking antioxidant and preventive antioxidant respectively.
Further investigation with respect to the optimum ratio of chain-breaking antioxidant and preventive antioxidant, comparison with commercial systems, influence of sample thickness, etc. are reported elsewhere10,11)

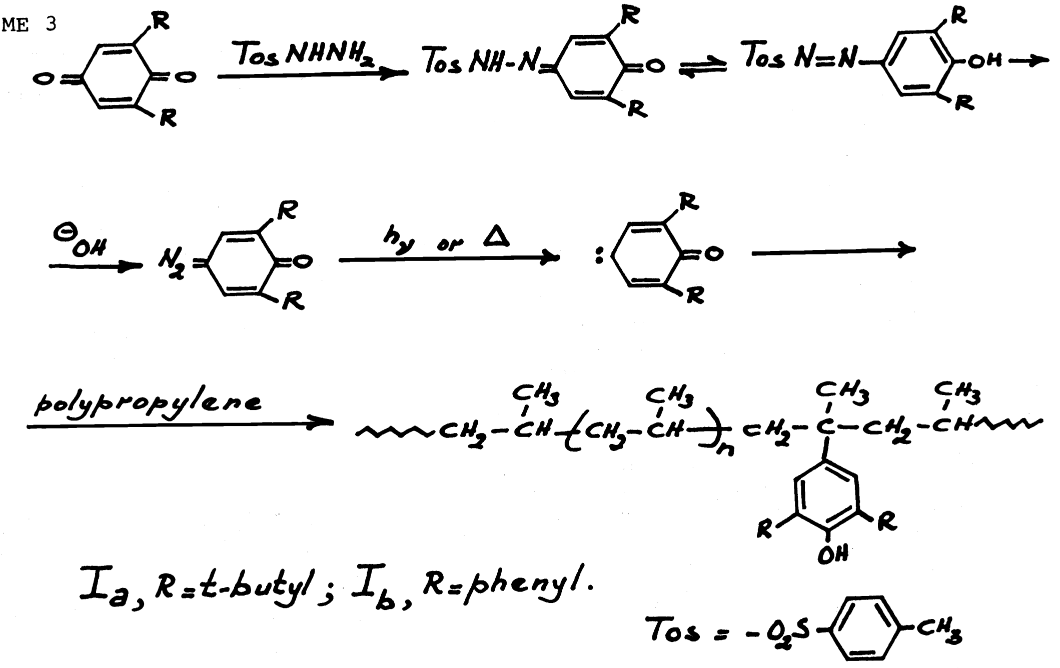
Table 1 Times of failure (h) of PP films* (150 µm stabilized with 4-alkoxy-2,6-diphenylphenols and synergists at 140, 120 and 80°C.

|  (0.1%) | 140°C | | | 120°C | | | 80°C | | |
|---|---|---|---|---|---|---|---|---|---|
| | | DLTDP (0.25%) | DSTDP (0.25%) | | DLTDP (0.25%) | DSTDP (0.25%) | | DLTDP (0.25%) | DSTDP (0.25%) |
| -- | 5 | 18 | 15 | 20 | 280 | 210 | 300 | 1300 | 1100 |
| R=-n-$C_{10}H_{21}$ | 15 | 230 | 375 | 70 | 840 | 1450 | 860 | 7100 | 8000 |
| R=-n-$C_{12}H_{25}$ | 15 | 350 | 580 | 55 | 1275 | 2250 | 1350 | 7400 | 10000 |
| R=-n-$C_{18}H_{37}$ | 15 | 780 | 2000 | 60 | 2500 | 5800 | 2500 | 7600 | 14000 |

* Films obtained by 2' compression moulding (200°C).
Type PP: Experimental PP.

A way to minimise or even to prevent volatility of a chain-breaking antioxidant is binding the 2,6-diphenylphenol moiety to the polymer chain. This procedure was carried out by generation of the related carbene from 6-diazo-2,4-diphenyl-1,4-cyclohexadiene-3-one. Comparative studies were carried out using the related 2,6-di-tert.butylanalogue$^{6b)}$. The synthetic route is shown is Scheme 3.

SCHEME 3



In practice the carbenes were generated by mixing the quinonediazide and polypropylene followed by a normal processing procedure. To remove the by-products the resulting polymer was extracted with boiling methanol. When DSTDP was added the polymer was recompounded to incorporate the preventive antioxidant. The oven-ageing results are shown in Table 2.

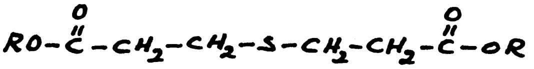
Table 2 Times of failure (h) of PP films (150 µm) stabilized with bonded antioxidants*

| Stabilizer | Extra additives** | Oven ageing at 140°C (h) |
|---|---|---|
| - | DSTDP | 60 |
| Ia | - | 4 |
| Ib | - | 5 |
| Ia | DSTDP | 72 |
| Ib | DSTDP | 740 |

* Bonded antioxidant is the primary a.o. (0.1 wt%) ** DSTDP (0.25 wt%)

## The effect of volatility of the preventive antioxidants

From the preceeding section it can be concluded that 4-stearoxy-2,6-diphenylphenol (G) is an extremely powerful antioxidant when used in combination with a thioether as preventive antioxidant. Therefore it was of interest to determine the effect of this thioether structure on the antioxidant activity. To study the effect of volatility thiodipropionates with different molecular weights were used.



$$RO-\overset{O}{\overset{\|}{C}}-CH_2-CH_2-S-CH_2-CH_2-\overset{O}{\overset{\|}{C}}-OR$$

J

| | | Mol. weight | TGA (5°C/min in air) 10% wt.loss | 50 % wt.loss |
|---|---|---|---|---|
| a. | R = $CH_3$ | 206 | | |
| b. | R = $nC_4H_9$ | 290 | | |
| c. | R = $nC_7H_{15}$ | 374 | | |
| d. | R = $nC_8H_{17}$ | 402 | | |
| e. | R = $nC_{12}H_{25}$ | 514 | 255°C | 295°C |
| f. | R = $nC_{18}H_{37}$ | 682 | 280°C | 330°C |

In Table 3 the results of oven-ageing of polypropylene films (150 µm) stabilized with 4-stearoxy-2,6-diphenylphenol (G) and β-activated thioethers (Ja-f) at 145°C and 100°C are shown. It is clearly shown that compounds with molecular weights $<$ 400 do not show any synergism, which has to be attributed to the high volatility of the thioether.

Table 3 Times of failure (h) of PP films* (150 µm) stabilized with G and β-activated thioethers at 145°C and 100°C.

| β -activated thioeether 0.25% | 145°C | | 100°C | |
|---|---|---|---|---|
| | - | 0.1% G | - | 0.1% G |
| - | 5 | 55 | 40 | 1800 |
| Ja | 10 | 60 | 100 | 1820 |
| Jb | 10 | 60 | 120 | 1820 |
| Jc | 10 | 60 | 190 | 1820 |
| Jd | 10 | 60 | 310 | 2100 |
| Je | 70 | 430 | 2600 | 4880 |
| Jf | 90 | 1000 | 2200 | 9750 |

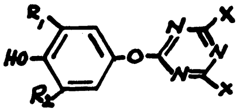
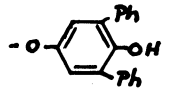
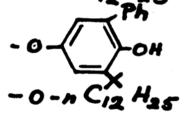
* Samples prepared by compr. moulding 2' (200°C)
PP: Propathene HF-20 (ICI)

This effect was also demonstrated in the study of the stabilization of polypropylene by combination of 4,4'-butylidene-bis-(3-methyl-6-t-butylphenol) with various di-n-alkylsulphides[12]).

## The effect of compatibility of the chain-breaking antioxidants

The effect of compatibility of the chain-breaking antioxidants with polypropylene on the induction period can be well established by e.g. comparison of results shown in Table 4. In the case when one phenylgroup is replaced by a t-butylgroup ($K_a$ and $K_c$) the induction period of $K_c$ is increased to a considerable extent in combination with DSTDP. It was also demonstrated by stability measurements in squalane that $K_c$ is easily soluble ($\geq$ 10 %), whereas $K_a$ is hardly soluble under the same conditions ($<$ 0.3 %).
Comparing $K_a$ with $K_b$ it is evident that, although the OH-content of the chain-breaking antioxidant is drastically decreased, the induction period of the latter increased. These phenomena have to be attributed to a better compatibility of these compounds in comparison with $K_a$, since no distinct differences in volatility of all the compounds in Table 4 are observed (TGA-measurements).

Table 4 Times of failure of PP films* (150 µm) stabilized with triazine based phenolic antioxidants and synergists at 140°C.

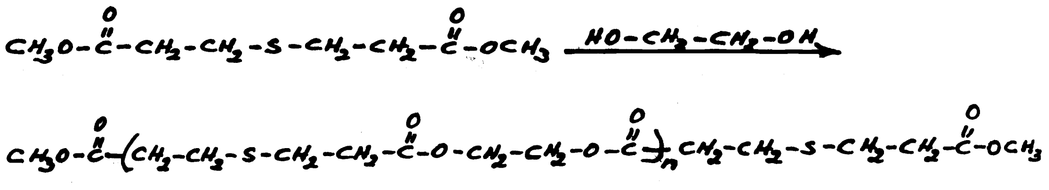
| K  (0.1%) | 140°C | | |
|---|---|---|---|
| | - | DLTDP (.25%) | DSTDP (.25%) |
| - - | 5 | 18 | 15 |
| a. $R_1=R_2=Ph$, x=  | 15 | 650 | 1400 |
| b. $R_1=R_2=Ph$, x= $-O-n\,C_{12}H_{25}$ | 15 | 480 | 1700 |
| c. $R_1=Ph, R_3=+$, x=  | 15 | 980 | 2900 |
| d. $R_1=Ph, R_2=+$, x= $-O-n\,C_{12}H_{25}$ | 15 | 700 | 2400 |
| e. $R_1=R_2=+$, x= $-O-n\,C_{12}H_{25}$ | 30 | 70 | 120 |

* Films obtained by 2' compression moulding (200°C)
Type PP: Experimental PP

## The effect of compatibility of the preventive antioxidants

Although volatility is markedly decreased when β-activated thioethers are transesterified with e.g. ethyleneglycol, it is noteworthy to mention that the synergistic interaction with 4-alkoxy-2,6-diphenylphenols is drastically decreased.

Oligomers of the series La-e were prepared as shown below.



$$CH_3O-\overset{O}{\overset{\|}{C}}-CH_2-CH_2-S-CH_2-CH_2-\overset{O}{\overset{\|}{C}}-OCH_3 \xrightarrow{HO-CH_2-CH_2-OH}$$

$$CH_3O-\overset{O}{\overset{\|}{C}}\left(CH_2-CH_2-S-CH_2-CH_2-\overset{O}{\overset{\|}{C}}-O-CH_2-CH_2-O-\overset{O}{\overset{\|}{C}}\right)_n CH_2-CH_2-S-CH_2-CH_2-\overset{O}{\overset{\|}{C}}-OCH_3$$

La, n = 1
Lb, n = 2
Lc, n = 3
La, n = 4
Le, n = 5

Comparing TGA-measurements with those obtained in the J-series, we found that the compounds of the L-series were less volatile than those of the J-series. Nevertheless no or less synergistic action was observed with 4-stearoxy-2,6-diphenylphenol (G) (see Table 5).

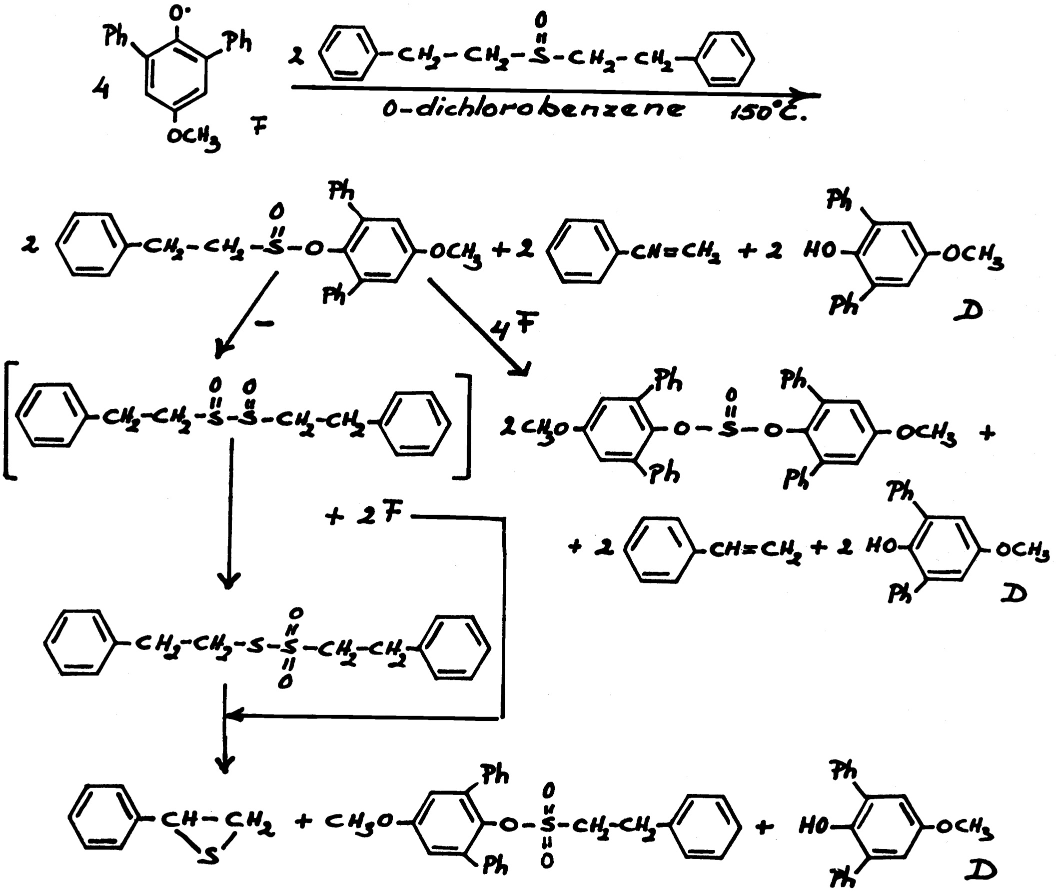
Table 5 Times of failure (h) of PP films* (150 µm) stabilized with G and β-activated thioethers at 145°C and 100°C.

| β -activated thioeether 0.25% | 145°C | | 100°C | |
|---|---|---|---|---|
| | - | 0.1% G | - | 0.1% G |
| - | 5 | 55 | 40 | 1800 |
| La | 10 | 60 | 300 | 2450 |
| Lb | 10 | 240 | 520 | 3250 |
| Lc | 15 | 240 | 360 | 4000 |
| Ld | 10 | 240 | 300 | 4000 |
| Le | 10 | 300 | 300 | 4050 |

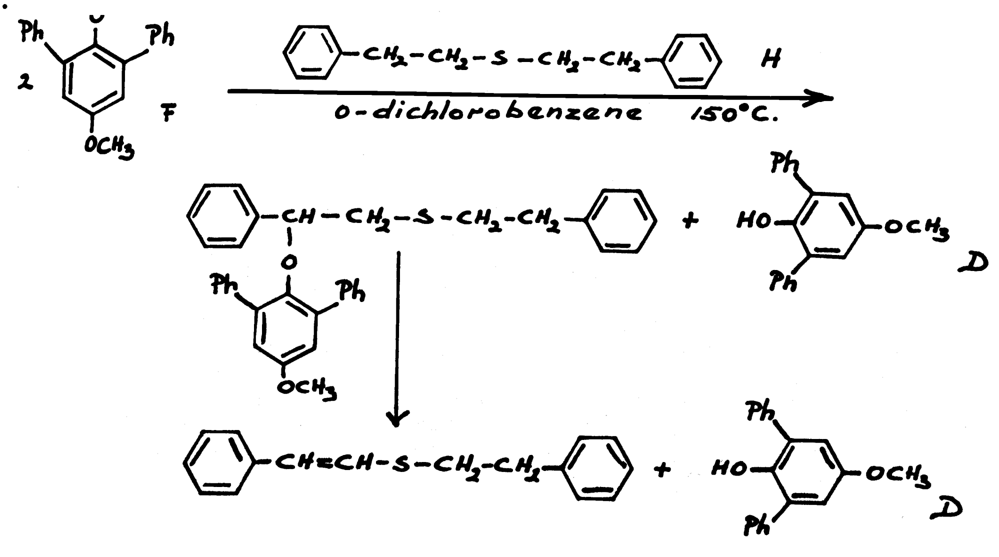
* Samples prepared by compr. moulding 2' (200°C)
PP: Propathene HF-20 (ICI)

## STUDIES OF MODEL COMPOUNDS IN SOLUTION

To understand the chemical interactions in a synergistic mixture of chain-breaking and preventive antioxidants and their reaction products model reactions were carried out in o-dichlorobenzene at 150°C13).
The chemical pathways are shown below.



When 4-methoxy-2,6-diphenylphenoxyl reacts with the corresponding sulphoxide of (H) products arise which are again capable of acting as chain-breaking and preventive antioxidants. All products were identified, after separation with HPLC, with IR, NMR and mass spectrometry.
However, as mentioned before, the ratio of the chain-breaking and preventive antioxidants for optimal synergistic action is in most cases 1 : 5.
Therefore it was also of practical importance to study the interaction of 4-methoxy-2,6-diphenylphenoxyl (F) and β-activated thioether (H).
The products arising from this reaction are shown in the reaction scheme below.

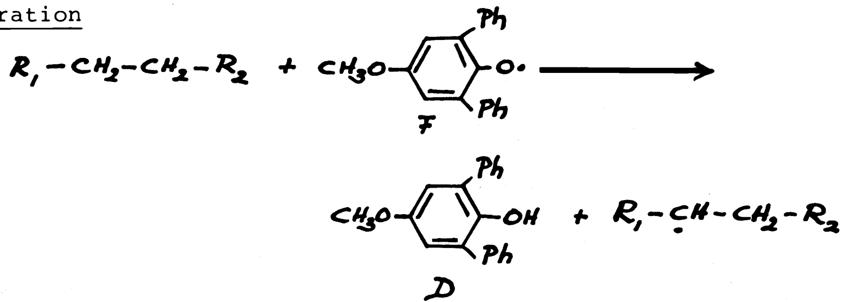


From these experiments it was concluded that the 2,6-diphenylphenol antioxidant (D) can be regenerated by the H-donating action of the preventive antioxidant.

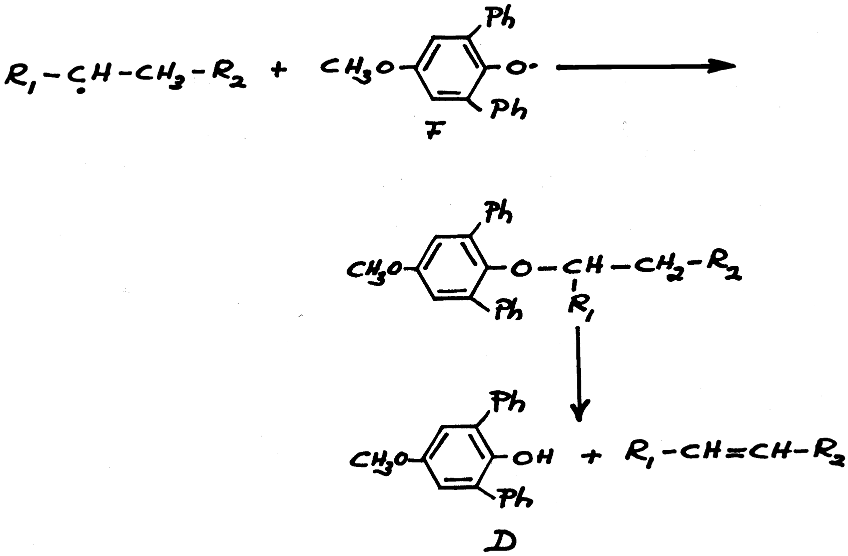
## MECHANISM OF SYNERGISM

For effective regeneration of the chain-breaking antioxidant, several important features are required in the regenerating species.
The substrate must have active hydrogens which can be abstracted by the phenoxyl radical leading to the first stage regeneration of the chain-breaking antioxidant.
Further reaction of the newly formed radical leads to the formation of an adduct with a second phenoxyl radical.
In some cases effective elimination leads to a second stage regeneration of the chain-breaking antioxidant.
From model studies it was found that many active methylene species were effective in the first stage regeneration process; only the $\beta$-active thioethers showed synergism. This effect can be attributed to a second stage regeneration, but also to the peroxide decomposing ability of the thioether.
Following Scheme 2 we can asssume that the hydroperoxides are effectively decomposed and that reaction (5) is the homosynergistic first and second stage regeneration reaction in a heterosynergistic system.
Moreover in the phenylsubstituted phenol synergistic interactions antioxidant wasting side reactions (3) and (4) are absent.
Taking all the above considerations into account, it is not surprising that the 4-alkoxy-2,6-diphenylphenol-$\beta$-activated thioether system is a highly effective synergistic system.

First stage regeneration



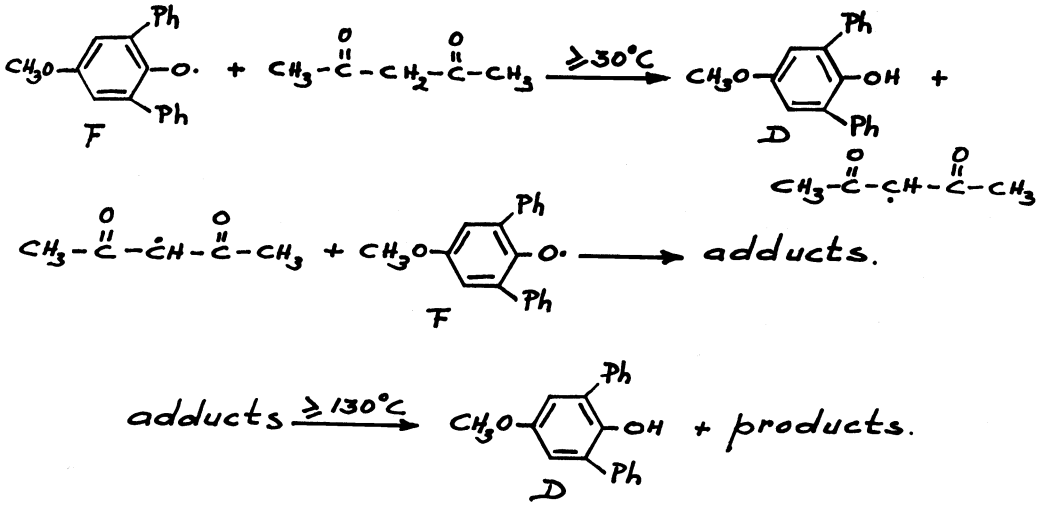
Second stage regeneration



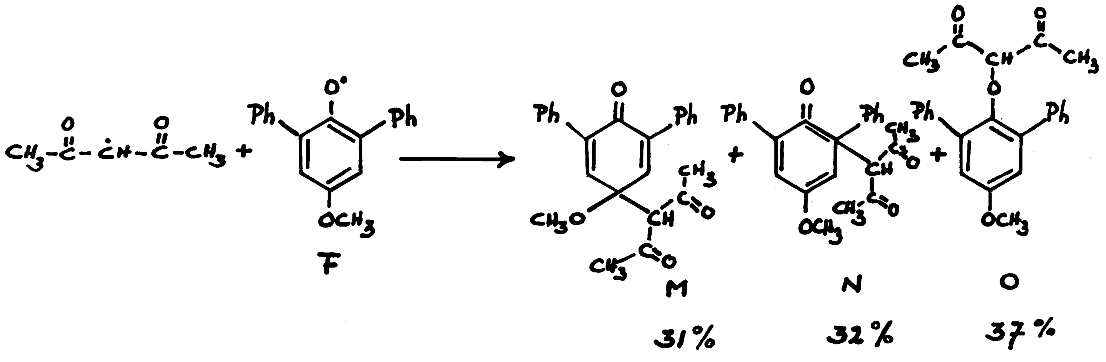
First stage regeneration could easily be demonstrated by a model reaction between the stable phenoxyl radical (F) and an H-donating species.
Quantitative analysis by GLC showed the regeneration of phenol (D).
Second stage regeneration however, showed a more complicated reaction pattern from which the end result is shown above. In the next section the underlying chemistry of the second stage regeneration is outlined.

## First and second stage regeneration reactions

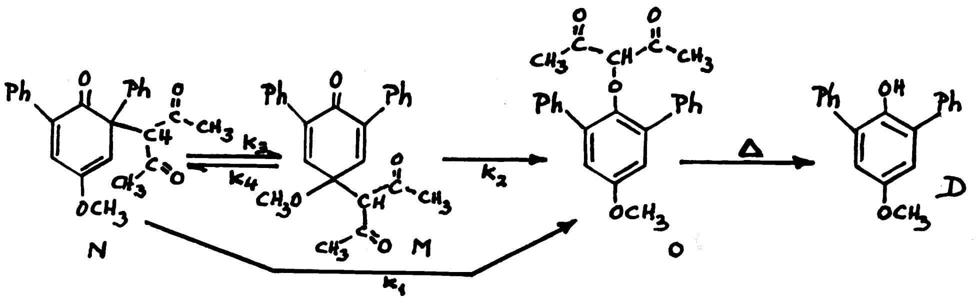
These reactions were simulated by the reaction between 4-methoxy-2,6-diphenylphenoxyl (F) and 2,4-pentanedione as an H-donor.



From the reaction scheme above it can be concluded that first stage regeneration takes place even at moderate temperatures (≥ 30°C).
This reaction was followed and HPLC showed that a complete first stage regeneration had taken place.
The chemical nature of the second stage regeneration proved to be rather complex. With the aid of preparative HPLC and structure analysis of the products of the adduct mixture we found the following reaction sequence[14]:



Thermal treatment of the mixture of these adducts and of the components individually showed the following reaction scheme to be operative:

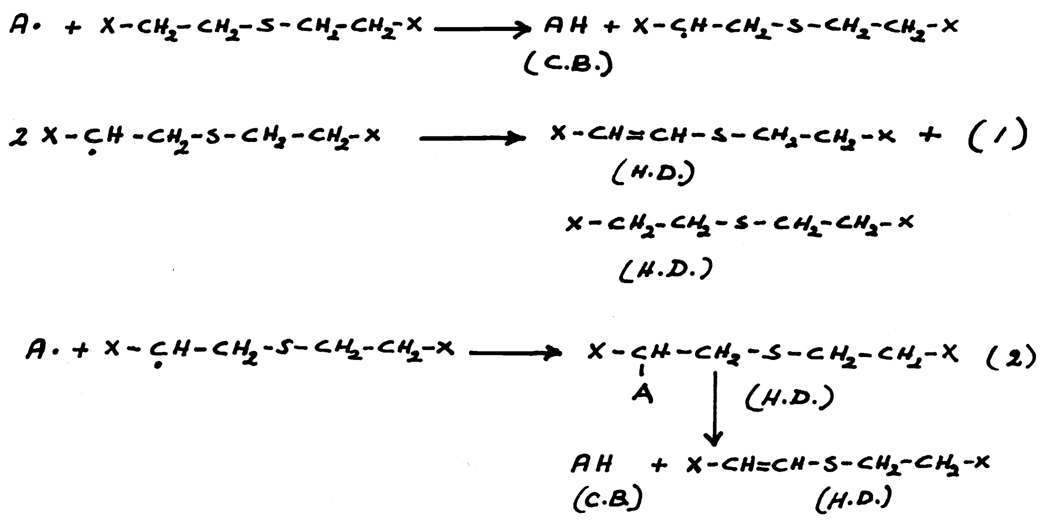


The o-p-dienone-aromatic ether rearrangements were followed in a temperature range of 90 - 130°C. $E_a$ = 130 kJ/mole.
From the above experiments we could conclude that a kinetic equilibrium mixture of M, N and O of 31:32:37 and a thermodynamic equilibrium mixture of 0:0:100 was obtained. At $\geqslant$ 130°C we observed that the aromatic ether (O) produced 4-methoxy-2,6-diphenylphenol (D).

## Synergism of phenolic antioxidants and preventive antioxidants

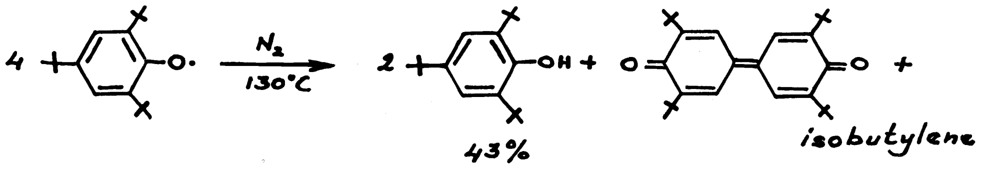
An important aspect for synergism of chain-breaking and preventive antioxidants is the first and second stage regeneration of the chain-breaking antioxidant as shown in Scheme 4.

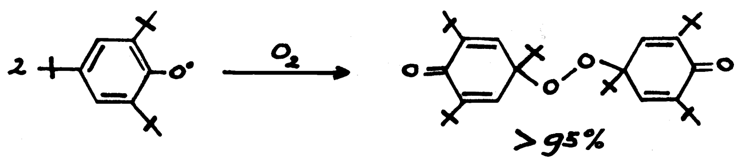
Scheme 4



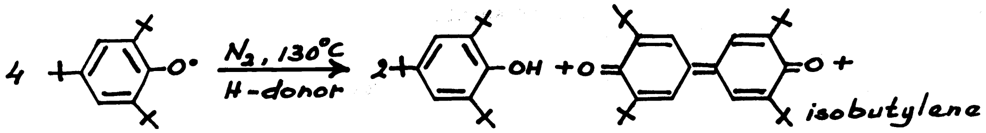
C.B. = chain-breaking antioxidant
H.D. = hydroperoxide decomposer (preventive antioxidant)

The same reactions are also possible with the corresponding sulphoxide to give regeneration of the chain-breaking antioxidant and to form related hydroperoxide decomposers. The two reactions occur with sterically less hindered phenols e.g. 4-sterearoxy-2,6-diphenylphenol (G), 1,1,3-tris-(5-t-butyl-4-hydroxy-2-methylphenyl)-butane (A) and ethyleneglycol-bis- [3,3-bis(-3'-t-butyl-4'-hydroxyphenyl)-butyrate] (B). The presence of reactions (1) and (2) (Scheme 4) is a prerequisite for synergism. Sterically hindered phenols e.g. 4-substituted-2,6-di-t-butylphenols are, depending on the nature of the 4-substituent, in some cases excellent chain-breaking antioxidants as such (see Fig. 1 compound C). Their behaviour in synergistic interactions is however very poor. This can be attributed to the fact that reaction sequences (1) and (2) (Scheme 4) for first and second stage regeneration are absent in these cases.

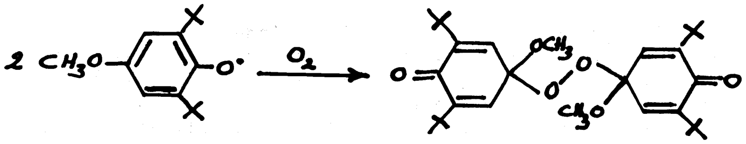




In the presence of H-donors e.g. toluene, β-activated thioethers (Ja) etc., it was observed that first and second stage regeneration did not take place15).



The same was observed with 4-methoxy-2,6-di-t-butylphenoxyl and H-donors. Moreover it is known that in the presence of oxygen 4-methoxy-2,6-di-t-butylphenoxyl is extremely unstable16).



On the basis of our studies on the interaction of species, originating from inhibition by chain-breaking antioxidants and reaction products of preventive antioxidants after hydroperoxide decomposition or the preventive antioxiodants themselves we were able to rationalize the synergistic effects observed. It was also possible to understand why in some cases synergism is poor or even absent.

The level of synergism is a.o. determined by chemical characteristics of intermediate species e.g. elimination of the chain-breaking antioxidant from the second stage regeneration adduct, stability of the phenoxyl radicals and physical characteristics e.g. volatility and compatibility of the compounds involved.

## REFERENCES

1a. G. Scott, Atmospheric Oxidation and Antioxidants (1965) Elsevier, Amsterdam.
b. N.M. Emanuel, E.T. Denisov, Z.K. Maizus, Liquid-phase Oxidation of Hydrocarbons (1967) Plenum, New York.
c. J.R. Shelton, Polymer Stabilization, W.L. Hawkins, Ed (1972) Wiley, New York.
d. C.R.H.I. de Jonge et al., Stabilization and Degradation of Polymers, D.L. Allara amd W.L. Hawkins, Eds. Adv. Chem. Series 169, 399-425 (1978).
e. L. Jirackova, J. Pospisil, Angew. Makromol. Chem., 82, 197 (1979).
2. See ref. 1b.
3. H.S. Olcott, H.A. Mattill, Chem.Rev. 29, 257 (1941).
4. G.C. Knapp, H. Orloff, Amer. Chem. Soc. Pap. 5, 11 (1960).
5. G.V. Karpukhina, Z.K. Maizus, M.Ya. Meskina, N.M. Emanuel, Zh.Fiz.Khim., 44, 1377 (1970).
6a M.L. Kaplan, P.G. Kelleher, G.H. Bebbington, R.L. Hartless, J.Polym.Sci. Polym. Lett. Ed. 11, 357 (1973).
b C.R.H.I. de Jonge, G. Hoentjen, V.V. Ershov, G.A. Nikiforov, Makromol. Chem. 180, 1077 (1979).
7. R. Gächter, H. Müller, Kunststoffadditive, p20-21.
8. C.R.H.I. de Jonge, H.J Hageman, W.G.B. Huysmans, W.J. Mijs, J.Chem.Soc. Perkin Trans.2 1973, p1276
9. C.R.H.I. de Jonge, H.J Hageman, W.G.B. Huysmans, W.J. Mijs, Amer. Chem. Soc. Div. Org. Coat. & Plast. Chem. Pap. 34, 107 (1974).
10. C.R.H.I. de Jonge, E.A. Giezen, F.P.B. van der Maeden, W.G.B. Huysmans, W.J. de Klein, W.J. Mijs, Polym. Prepr. Amer. Chem. Soc. Div. Polym. Chem. 18, 458 (1977).
11. C.R.H.I. de Jonge, P. Hope, Developments in Polymer Stabilization - 3, Ed. G. Scott, Applied Science Publishers Ltd. London 1980, p21-54.
12. E. Spirk, P. Rosner, S. Kamenar, I. Krivosik, Angew. Makromol. Chem. 84, 137 (1980).
13. C.R.H.I. de Jonge, F.P.B. van der Maeden, M.E.F. Biemond, W.G.B. Huysmans, W.J. Mijs, J.Polym.Sci.Polym.Symp. 57, 197 (1976).
14. C.R.H.I. de Jonge, to be published
15. E. Müller, A. Rieker, A. Schick, J.Liebigs Ann. der Chem. 673, 41 (1964).
16. E. Müller, K. Ley, Chem. Ber. 88, 601 (1955).