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The Mechanism of the Action of Antioxidants and the Synergism of Mixed Antioxidants

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The review considers the mechanism by which various types of inhibitors act in the oxidation processes of carbochain polymers and also mixtures of inhibitors exhibiting a synergistic effect. In conclusion a new and promising class of stabilisers (polyfunctional inhibitors) is considered.
The bibliography includes 85 references.

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I. INTRODUCTION

The effective protection of polymers against thermo-oxidative degradation is an important theoretical and technical problem. The oxidation of organic compounds, including polymers, may be sharply inhibited by the introduction of small amounts of inhibitors or antioxidants. Antioxidants protect polymers from oxidative degradation during their processing at high temperatures and increase the useful life of articles made of polymers.

Mixtures of antioxidants have found application in recent years in the stabilisation of polymers and lubricating oils, since the effect of many mixtures proved to be much greater than would be expected from the additive effects of their components. Numerous studies have been devoted to this phenomenon, called synergism, and also to the search for effective inhibitor compositions.

A number of monographs[1-3] and reviews[4-6] published in recent years deal with the mechanism by which inhibitors of free-radical processes act but the problem of the mechanism of the action of phosphites and sulphur-containing compounds has been hardly touched upon. The mechanisms of the synergism of mixtures comprising inhibitors of free-radical processes and agents decomposing hydroperoxides have been very incompletely treated in the monographs and reviews published hitherto.

The present review deals with the mechanism by which inhibitors terminate kinetic oxidation chains (phenols and amines) and inhibitors suppressing chain branching (phosphites and sulphur-containing compounds); the possible mechanisms of the action of their mixtures, which exhibit synergistic effects, are also discussed.

II. THE MECHANISM OF THE ACTION OF INHIBITORS

1. Phenols and Amines

The oxidation of carbochain organic compounds and in particular of polymers involves a radical chain mechanism with degenerate branching[8], which can be described as follows[7]. Initiation takes place as a result of the reaction of oxygen with the hydrocarbon:

$$RH + O_2 \xrightarrow{w_u} \dot{R} + H\dot{O}_2$$

or

$$2RH + O_2 \xrightarrow{w_u} 2\dot{R} + H_2O_2 .$$

The kinetic chain is propagated and branches via the reactions

$$1.\ \dot{R} + O_2 \xrightarrow{k_1} R\dot{O}_2 ,$$

$$2.\ R\dot{O}_2 + RH \xrightarrow{k_2} \dot{R} + ROOH ,$$

$$3.\ ROOH \xrightarrow{k_3} R\dot{O} + H\dot{O} ,$$

$$3'.\ ROOH + RH \xrightarrow{k'_3} \dot{R} + \dot{R}O + H_2O .$$

The chains are destroyed as a result of the recombination of the radicals $R\dot{O}_2$, since in the presence of oxygen $[\dot{R}] < [R\dot{O}_2]$:

$$4.\ R\dot{O}_2 + R\dot{O}_2 \xrightarrow{k_4} ROOR + O_2 .$$

In the presence of inhibitors of free-radical processes (phenols and amines), there is linear termination of the $R\dot{O}_2$ radicals by the inhibitor[8-10]:

$$5.\ R\dot{O}_2 + InH \xrightarrow{k_5} ROOH + In ,$$

with formation of a hydroperoxide and a relatively inactive inhibitor radical, as shown in subsequent studies using ESR[11,12].

Semenov[7] showed that, when the above process mechanism operates, there should exist a critical inhibitor concentration defined by the equation

$$[InH]_{cr} = \frac{k_2[RH]}{k_5} . \qquad (1)$$

The presence of critical inhibitor concentrations has been established in a number of studies on the oxidation of liquid hydrocarbons[13,14] and polypropylene[15].

Eqn. (1) was derived on the assumption that reaction (5) yields stable products; nevertheless, the hydroperoxide formed is a branching agent in the chain process. When this is taken into account, then, as shown by Neiman[2], there should be no critical inhibitor concentration. Since the critical concentration is in fact observed experimentally and, within the framework of the oxidation process mechanism adopted by Semenov, Eqn. (1) is not entirely exact, it has been suggested[15] that the hydroperoxide

reacts with the hydrocarbon[16] and ultimately the radicals $R\dot{O}_2$ are formed with a probability δ by the reaction

$$ROOH + RH \begin{cases} \nearrow R\dot{O} + \dot{R} + H_2O \\ \searrow ROR + H_2O \end{cases} \xrightarrow{RH,O_2} \delta R\dot{O}_2 .$$

After this modification, the following expression was obtained[2,17] for the critical inhibitor concentration:

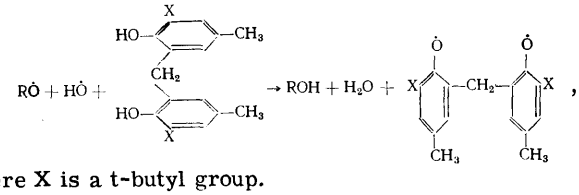
$$[InH]_{cr} = \frac{\delta}{(1-\delta)} \frac{k_2}{k_5} [RH] , \qquad (2)$$

from which it follows that the critical concentration of the antioxidant can obtain only when $\delta < 1$. Up to the critical antioxidant concentration the oxidation reaction takes place under non-steady-state conditions and above it under steady-state conditions[13-15,17].

Hydroperoxides are known to react with phenols and amines at a higher rate than with hydrocarbons. Ingold showed that phenols and amines accelerate the decomposition of the hydroperoxides formed in the oxidation of mineral oil[18]. It has also been established[19,20] that amines sharply reduce the activation energy for the decomposition of polypropylene hydroperoxide: in the absence of amines the activation energy for the decomposition of the hydroperoxide is 25 kcal mole^{-1}, while in the presence of diphenylamine it is 17 kcal mole^{-1} and in the presence of *N*-cyclohexyl-*N'*-phenyl-*p*-phenylenediamine it is only 14 kcal mole^{-1}. Consequently, in the presence of such inhibitors the hydroperoxide reacts not with the hydrocarbon but with the inhibitor to form ultimately active $R\dot{O}_2$ radicals with a probability δ according to the mechanism

$$3'.\ ROOH + InH \begin{cases} \nearrow R\dot{O} + \dot{In} + H_2O \\ \searrow RO{-}In + H_2O \end{cases} \xrightarrow{RH,O_2} \delta R\dot{O}_2 .$$

It is easy to show that, when account is taken of this reaction, the preceding equation (2) is obtained for the critical antioxidant concentration. The antioxidants in whose presence $\delta \geq 1$ cannot at any concentration ensure a slow steady-state occurrence of the inhibited reaction. In their presence the reaction always takes place under non-steady-state conditions with appreciable acceleration. This acceleration cannot be detected from the absorption of oxygen, since it is too slight, but it can be observed from the decrease of the molecular weight of the polymer. If the antioxidant does not have a critical concentration, in its presence the molecular weight of the polymer falls sharply during the induction period. Thus in the presence of monohydric phenols, which do not have a critical concentration, the molecular weight of polypropylene falls much more appreciably than in the presence of bisphenols which do have a critical concentration[21]. Moreover, monophenols are much less effective than bisphenols (several times and not by a factor of two as would be expected on the basis of the number of hydroxy-groups). The different effectiveness of monophenols and bisphenols in the inhibited oxidation of polypropylene is probably associated with the participation of antioxidants in chain branching. It has been suggested[22] that effective antioxidants should have two active groups located close to one another in order to react simultaneously with the two radicals formed in the decomposition of the hydroperoxide, for example in a cage according to the mechanism



where X is a t-butyl group.

This process results in the formation of a single relatively inactive biradical. If the antioxidant has one active group, then in the cage it can react with only one radical. The second radical cannot recombine, which increases the probability of chain branching.

The dependence of the induction period (τ) in the oxidation of polypropylene on the concentration of 2,2'-methylenebis-(6-t-butyl-4-methylphenol) as an antioxidant in the presence and absence of 4-methyl-2,6-di-t-octylphenol has been investigated[23]. It was shown that in the presence of the monophenol τ for the bisphenol diminishes and the critical concentration increases. Other monophenols had a similar effect.

According to the authors, the increase of the critical concentration of the bisphenol in the presence of the monophenol is due to an enhanced probability of chain branching in the oxidation of polypropylene. However, the increase of the critical concentration and the decrease of τ for the bisphenol can also be caused by the reaction of the monophenoxy-radical with polypropylene:

$$\dot{In} + RH \rightarrow InH + R .$$

If the monophenoxy-radical participates in chain propagation, then, as shown by Likhtenshtein and Urman[24,25], the critical concentration of the inhibitor increases. Possibly the inhibitor (monophenol) radicals are more active in the initiation of oxidation than the bisphenol radicals[12] and consequently increase the critical concentration of the latter. Under the conditions of identical reactivities of the monophenol and bisphenol inhibitor radicals, theoretical calculations show that the critical concentration is increased by the enhanced probability of branching. At low oxidation temperatures the inhibitor radicals are destroyed by recombination; at an elevated temperature there is a greater probability of their participation in chain propagation.

Thus it has been shown[26] that the critical concentration of an effective bisphenol increases both in the presence of an ineffective monophenol and an ineffective bisphenol (monohydroxybenzophenone and dihydroxybenzophenone). Probably chain transfer to the photostabiliser radicals plays an appreciable role.

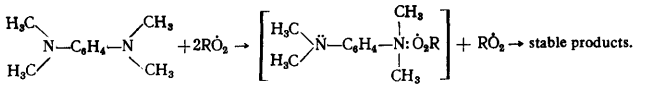
Oxidation may be initiated also as a result of the direct oxidation by oxygen of an antioxidant molecule, for example, a monophenol, via the mechanism $InH + O_2 \rightarrow \dot{In} + H\dot{O}_2$ with formation of the relatively active radical $H\dot{O}_2$. On interaction with the hydrocarbon, the latter yields hydrogen peroxide, which breaks down into radicals and causes chain branching. As a result of this reaction, the critical concentration of the inhibitor should increase, as shown theoretically by Likhtenshtein and Urman[24]. Thus the increase of the critical concentration of the bisphenol in the presence of a monophenol can be caused both by the participation of the monophenol in degenerate branching and by the initiation of the oxidation process by the inhibitor radical and the inhibitor oxidation products.

It has been established in a number of investigations that the mechanism of inhibition by amines which contain a mobile hydrogen atom in the amino-group consists in linear termination of radicals:

$$R\dot{O}_2 + R''NHR' \rightarrow R'\dot{N}R'' + ROOH .$$

This mechanism of inhibition by amines is confirmed by the formation of inhibitor radicals[11,12] and the expected final oxidation products[1-6]. Thus in the oxidation of cumene in the presence of *NN'*-diphenyl-*p*-phenylenediamine, the latter is 80–95% converted into *NN'*-diphenyl-*p*-quinone-di-imine. However, it is known that tertiary

amines also strongly inhibit the oxidation. It has been shown that in the oxidation of cumene in chlorobenzene solution each tetramethyl-*p*-phenylenediamine molecule terminates two oxidation chains:



This involves the intermediate formation of a radical complex [27]. Probably aromatic hydrazines which do not have mobile hydrogen atoms should fulfil a similar role. Further study of such compounds will undoubtedly be of great interest.

2. Sulphur-containing Compounds

Sulphur-containing compounds without amino- and phenolic groups inhibit the oxidation process by the decomposition of hydroperoxides with formation of stable molecules [28-31]:

$$6.\ \mathrm{ROOH} + \mathrm{R'_2S} \xrightarrow{k_6} \mathrm{ROH} + \mathrm{R'_2SO}\ .$$

In a study of the kinetics of the reaction of a hydroperoxide with sulphides, it was shown that the reaction is of first order with respect to the hydroperoxide [32]. Sulphides are oxidised further to sulphones [33-35]:

$$\mathrm{ROOH} + \mathrm{R'_2SO} \rightarrow \mathrm{ROH} + \mathrm{R'_2SO_2}\ .$$

Apart from the reactions mentioned above, sulphides are oxidised by peroxy-radicals without chain termination [28,30,31]:

$$\mathrm{RO_2^{\cdot}} + \mathrm{R'_2S} \rightarrow \mathrm{RO^{\cdot}} + \mathrm{R'_2SO}\ .$$

In this secondary reaction sulphides are consumed, which reduces their effectiveness.

Mercaptans inhibit oxidation via the mechanism

$$\mathrm{RO_2^{\cdot}} + \mathrm{R'SH} \rightarrow \mathrm{ROOH} + \mathrm{R'S^{\cdot}}\ .$$

Thiyl radicals can probably also interact with peroxy-radicals in the following way [36]:

$$\mathrm{RO_2^{\cdot}} + \mathrm{R'S^{\cdot}} \rightarrow \mathrm{R'(O)-S-O-R},$$

and can recombine with formation of disulphides. Aryl disulphides are as a rule more effective than aryl sulphides. However, in the presence of certain disulphides the molecular weight of polypropylene was found to diminish sharply during the induction period [37]. Probably at 200°C the aromatic disulphide breaks down into thiyl radicals which in the presence of oxygen cause the breakdown of the polymer.

In the first oxidation stage disulphides and hydroperoxides form intermediate thiosulphoxides:

$$\mathrm{R'S-SR''} + \mathrm{ROOH} \rightarrow \mathrm{R'S(O)SR''} + \mathrm{ROH},$$

which on further oxidation are converted into thiosulphones [35,38,39]. The sulphides themselves are rarely used to stabilise mineral oils and polymers, since their effectiveness is low but, when mixed with inhibitors of free-radical processes, they sharply increase the effectiveness of the latter. Among sulphur-containing compounds, sulphides, mercaptans, polysulphides, etc. are used in mixtures with phenols and amines. The most powerful synergistic effect is produced by esters of thiocarboxylic acids such as dilauryl and distearyl thiodipropionates and esters of thiovaleric acid. The synergistic effect of mixtures of free-radical process inhibitors with sulphides is widely used to stabilise various organic substances, including polymers.

3. Phosphites

Phosphite esters are widely used to stabilise polymers both in a pure form and in mixtures with phenols. In contrast to amines and phenols, phosphites do not colour polymers and therefore may be used in the manufacture of light-coloured articles. The mechanism of their action and the effectiveness of aromatic phosphites as a function of the structure of their phenoxy-residues have been little investigated.

It is known that aliphatic phosphites, like sulphides, break down hydroperoxides virtually without the formation of free radicals [40,41]:

$$7.\ \mathrm{ROOH} + (\mathrm{RO'})_3\mathrm{P} \rightarrow \mathrm{ROH} + (\mathrm{RO'})_3\mathrm{PO}\ .$$

Therefore it is suggested that phosphites inhibit oxidation only by suppressing chain branching. Furthermore, it has been shown [42] that at 130°C aliphatic phosphites are oxidised by peroxy- and oxy-radicals to phosphates without chain termination:

$$8.\quad \begin{aligned} &\mathrm{RO_2^{\cdot}} + (\mathrm{R'O})_3\mathrm{P} \rightarrow \mathrm{RO^{\cdot}} + (\mathrm{R'O})_3\mathrm{PO}\ , \\ &\mathrm{RO^{\cdot}} + (\mathrm{R'O})_3\mathrm{P} \rightarrow \mathrm{R^{\cdot}} + (\mathrm{R'O})_3\mathrm{PO}\ . \end{aligned}$$

Table 1. Effectiveness of phosphites in the oxidation of polypropylene at 200°C and an oxygen pressure of 200 mmHg [43].

No.	Phosphite	Induction period at a concn. of 0.05 mole kg^{-1} min
1	Tri(nonylphenyl) phosphite	30
2	Iso-octyl diphenyl phosphite	35
3	Phenyl *o*-phenylene phosphite	60
4	Tri-(4-t-butylphenyl) phosphite	90
5	α-Naphthyl *o*-phenylene phosphite	190
6	2,6-Di-t-butyl-4-methylphenyl *o*-phenylene phosphite	260
7	2,4,6-Tri-t-butylphenyl *o*-phenylene phosphite	400
8	2,6-Di-isobornyl-4-methylphenyl *o*-phenylene phosphite	1000

The effectiveness of action of the phosphites by this mechanism must be low. Indeed, it follows from the data in Table 1 [43-46] that aliphatic and aromatic phosphites without alkyl substituents in the phenoxy-residue have a low antioxidant activity.

Table 1 shows that the introduction of a t-butyl and particularly an isobornyl group into the *ortho*-position of phenol in *o*-phenylene phosphite sharply increases the induction period. A study of the kinetics of the absorption of oxygen in the oxidation of polypropylene in the presence of phosphites showed that relatively ineffective phosphites do not have a critical concentration (Fig. 1) [37]. Consequently they inhibit the oxidation, like sulphides, by breaking down the hydroperoxides without linear termination of peroxy-radicals [1,7]. On the other hand, effective phosphites have a critical concentration and therefore they inhibit the oxidation process by linear termination of

radicals and possibly by breaking down the hydroperoxides (Fig. 2) [37].

The kinetics of the reactions of aromatic phosphites with the diphenylpicrylhydrazyl radical and with t-butyl hydroperoxide at room temperature have been investigated [47,48]. It was found that phosphites (6) and (7) (see Table 1) react rapidly, compound (4) much more slowly, and compound (3) and triphenyl phosphite hardly react at all with the diphenylpicrylhydrazyl radical [47]. Thus the reactivity towards radicals and the effectiveness of phosphites increase sharply on introduction of alkyl substituents into the phenoxy-residue. On the other hand, the reactivity of aromatic phosphites towards hydroperoxides bears an inverse relation, i.e. the lower the antioxidant activity of phosphites the faster they react with the hydroperoxide [48].

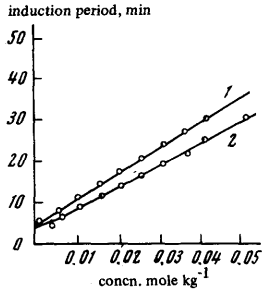


Figure 1. Variation of the induction period in the oxidation of polypropylene with the concentration of tri(nonylphenyl) phosphite (*1*) and iso-octyl diphenyl phosphite (*2*) at 200°C and P_{O_2} = 200 mmHg.

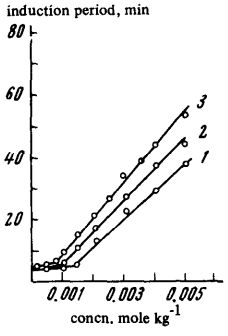


Figure 2. Variation of the induction period in the oxidation of polypropylene with the concentration of α-naphthyl *o*-phenylene phosphite (*1*), 2,6-di-t-butyl-4-methylphenyl *o*-phenylene phosphite (*2*), and 2,4,6-tri-t-butylphenyl *o*-phenylene phosphite (*3*) at 200°C and P_{O_2} = 200 mmHg.

The reaction of peroxy- and oxy-radicals with aromatic phosphites has not been investigated at all. Walling and coworkers suggested [49] that in the reaction of aromatic phosphites with aliphatic RO radicals a double decomposition reaction is possible:

$$R\dot{O} + (R'O)_3P \rightarrow (R'O)_2POR + R'\dot{O}$$

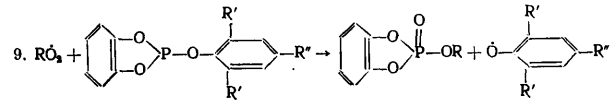
in consequence of the formation of the more stable phenoxy-radical. Almost simultaneously it was shown [50] that in the reaction of diethyl peroxide with triphenyl phosphite at 130°C ethyl phenyl ether ($C_2H_5OC_6H_5$) and a phosphate with the probable structure $C_2H_5OP(O)(OC_6H_5)_2$ are formed. These products may be formed by the exchange of radicals via an intermediate quadrivalent phosphorus compound:

$$C_2H_5O + (C_6H_5O)_3P \rightarrow C_2H_5OP(OC_6H_5)_3 \xrightarrow{C_2H_5\dot{O}} \rightarrow (C_6H_5O)_2P(O)(OC_2H_5) + C_2H_5OC_6H_5$$

and probably in the reaction of the undecomposed diethyl peroxide with triphenylphosphite via an intermediate quinquevalent phosphorus compound:

$$C_2H_5OOC_2H_5 + (C_6H_5O)_3P \rightarrow (C_6H_5O)_3P\begin{matrix}OC_2H_5\\OC_2H_5\end{matrix} \rightarrow C_6H_5OOC_2H_5 + (C_6H_5O)_2\overset{O}{\overset{\|}{P}}-OC_2H_5 .$$

Probably the reaction of pentoxy-radicals with aromatic *o*-phenylene phosphite esters with t-butyl groups in the phenoxy-residue can occur at an elevated temperature via a radical exchange mechanism with formation of a phosphate and a stable phenoxy-radical [43]:



This mechanism is consistent with the high reactivity of these phosphites towards diphenylhydrazyl radicals and their enhanced antioxidant effectiveness compared with other phosphites [37,43]. However, this mechanism is inconsistent with the experimental studies on the kinetics of the reaction of $R\dot{O}_2$ radicals with aromatic phosphites in ethylbenzene at 60°C using a chemiluminescence technique [51]. In these experiments it was shown that aromatic phosphites (5), (6), and (7) (Table 1) cause chain termination, but fifty phosphite molecules are required for the termination of a single $R\dot{O}_2$ radical. Possibly at the experimental temperature the phosphites only react slowly with peroxy-radicals and therefore do not affect the effectiveness of the luminescence. On the other hand, it would appear that the weak termination of peroxy-radicals in the presence of aromatic phosphites might be explained by the presence of hydrolysis products. On this basis, it was suggested that phosphites inhibit oxidation by the hydrolysis products formed in the oxidation process [5]. Nevertheless, this hypothesis is inconsistent with a number of observations. The hydrolysis products of *o*-phenylenephosphite esters do not have a critical concentration under the experimental conditions in the oxidation of polypropylene, like screened phenols, α-naphthols, and *o*-phenylene phosphorous acid, while the phosphite itself does have such a concentration (Fig. 2). Moreover, the effectiveness of phosphites (6), (7), and (8) (Table 1) would be almost the same if the oxidation of polypropylene were inhibited by the hydrolysis products, since the effectiveness of the latter differs little. It was further established that the effectiveness of phosphite (7) is much higher than that of any equimolar mixture of the hydrolysis products [37]. Probably at a high temperature phosphites enter into reactions (7), (8), and (9) with different probabilities (depending on the structure). Possibly aliphatic and aromatic phosphites with unscreened phenoxy-groups inhibit oxidation only by suppressing chain branching [reaction (7)] and are mainly consumed in reaction (8). On the other hand, aromatic phosphites with screened phenoxy-groups in the molecule may inhibit oxidation by

radical termination via reaction (9). If the phenoxy-radicals formed propagate the oxidation chain via the reaction $\dot{In} + RH \rightarrow InH + \dot{R}$ with a lower probability, then the effectiveness of the phosphite will be high, and conversely. Moreover, at an elevated temperature effective aromatic phosphites, like aliphatic phosphites, probably react with hydroperoxides to form stable products. Experiments on the oxidation of polypropylene in the presence of a mixture of 2,6-di-t-butyl-4-methylphenyl-*o*-phenylene phosphite and dilauryl thiodipropionate showed that this mixture exhibits a synergistic effect, which, however, is much smaller than that of a mixture of phenols with the same sulphide[37]. Consequently, such sulphides inhibit chain branching to some extent as well. Moreover, effective phosphites can probably be partially consumed also by reaction (8).

The above mechanism of inhibition by screened phosphites is consistent with their high antioxidant activity and the critical concentrations observed in experiments on the oxidation of polypropylene.

III. THE MECHANISM OF THE SYNERGISM OF INHIBITOR COMPOSITIONS

When two or more inhibitors are introduced into the substance being oxidised, an antioxidant effect in excess of the additive value is frequently observed. Such an effect of the mixture is usually called synergism and is defined by the expression $\tau_{1,2} < \tau_1 + \tau_2$, where $\tau_{1,2}$, τ_1, and τ_2 are the induction periods for the mixture and the individual components respectively. Furthermore, the synergistic effect should be defined as one in which the antioxidant efficiency of the induction period for the mixture are higher than for any one component taken separately at a concentration equal to the overall concentration of the mixture (Fig. 3) [37,52]. On the other hand, strictly speaking, the phenomenon of synergism should be understood as the enhancement of the effectiveness of the active component by a completely inactive component.

With this definition of synergism, it is possible to establish both the magnitude of the effect and its maximum as a function of the molar ratio of the components. The synergistic effect for mixtures of inhibitors is observed in those cases where the mixture components inhibit oxidation by different mechanisms. Therefore we shall consider the possible mechanisms of the action of inhibitor compositions for which the synergistic effect is known to apply or may be postulated.

1. Mixtures of Inhibitors of Free-radical Processes with Sulphides.

The most powerful synergistic effect is usually shown by mixtures of two inhibitors one of which terminates the oxidation chain and the other breaks down hydroperoxides[15,32-34,36,37,52-55]. The considerable enhancement of the inhibiting effect can be explained in terms of this mechanism by the fact that one of the inhibitors reduces the yield of hydroperoxides, which, on decomposing into radicals cause chain branching, while the second breaks down the hydroperoxides and thereby both inhibitors protect one another from rapid consumption. However, hydroperoxide decomposing agents are evidently themselves oxidised by peroxy-radicals in the inhibition process.

This mechanism was confirmed[15] by kinetic data. Thus, when polypropylene is stabilised by a mixture of a chain terminating oxidant and a sulphide which decomposes hydroperoxide, the critical concentration of the antioxidant diminishes as that of the sulphide is increased, according to the equation

$$[InH]_{cr} = \frac{\delta k_2 k_4 [RH]^2}{(1-\delta) k_4 k_5 [RH] + k_6 [R_2S]} \cdot \qquad (3)$$

In the absence of the sulphide or another hydroperoxide decomposing agent, Eqn. (3) transforms into Eqn. (2) derived above.

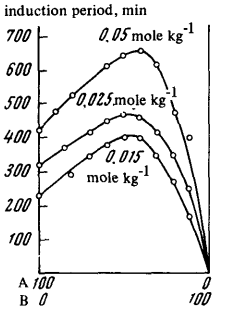


Figure 3. Variation of the induction period in the oxidation of polypropylene with the composition of a mixture of 2,2'-methylenebis-(6-t-butyl-4-methylphenol) (*A*) and dilauryl thiodipropionate (*B*) at different overall concentrations, 200°C, and P_{O_2} = 200 mmHg.

In the same investigation it was shown that 2,4,6-tri-t-butylphenol does not have a critical concentration in the oxidation of polypropylene (200°C, oxygen pressure 300 mmHg); in this case the induction period is short. However, in the presence of a sulphide[15] or a phosphite[46] (at a sufficiently high concentration) a critical concentration is observed and the effectiveness of the monophenol increases sharply. If the antioxidant has a critical concentration, then in the presence of a hydroperoxide decomposing agent it diminishes and the effectiveness of the antioxidant increases[15,46].

Mixtures of monophenols, bisphenols, and thiobisphenols with hydroperoxide decomposing agents show a marked synergistic effect[15,37,54,55-58]. Fig. 3 shows as an example the variation of the induction period of the oxidation of polypropylene as a function of the molar composition of a mixture of 2,2,-methylenebis-(6-t-butyl-4-methylphenol) and dilauryl thiodipropionate at different overall concentrations. It is seen that the induction period for the mixture is much longer than for the bisphenol at the concentration equal to the overall concentration of the mixture. It is interesting that the sulphur in the thiobisphenol molecule does not decompose the hydroperoxide, since thiobisphenols in a mixture with a sulphide exhibit an appreciable synergistic effect. The synergistic effect depends on the activity of the synergist. The most active synergist among the sulphides investigated proved to be dilauryl thiodipropionate[54], but, as shown by the present authors' experiments, thiovaleric esters are also active synergists; thioacetic esters are less active. The activity of thioacid esters increases with the number of carbon atoms in the aliphatic residue[58].

Synergistic mixtures of phenols with sulphur-containing compounds are widely used to stabilise polymers, largely polyolefins. There are more than 200 patents for the application of these synergistic mixtures. Certain mixtures effectively protect polyolefins during processing at a high temperature and under the conditions of their use[55-57]. Synergistic mixtures of phenols with thiophosphoric compounds and phosphites do not colour polymers or weaken them appreciably and they are very important in the manufacture of light-coloured high-quality articles.

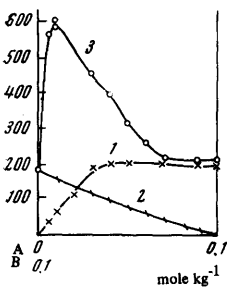


Figure 4. Variation of the induction period in the oxidation of polypropylene with the composition of a mixture of *p*-hydroxyphenyl-β-naphthylamine (*A*) and mercaptobenzimidazole (*B*) (*3*) and with the concentrations of the components (*1* and *2*) at 200°C and P_{O_2} = 200 mmHg.

Beside phenols, amines mixed with agents which decompose hydroperoxide exhibit a synergistic effect. For example (Fig. 4), the effectiveness of a mixture of *p*-hydroxyphenyl-β-naphthylamine with mercaptobenzimidazole (MBIA) is three times greater than the effectiveness of the most active component at the concentration equal to the overall mixture concentration[52]. It is interesting that the maximum effect is observed when MBIA is present in the mixture in an appreciable excess.

The synergistic effect is observed in different ways depending on the activity of the inhibitor of free-radical processes. Fig. 5 shows that a mixture of β-naphthylphenylamine with MBIA is not more effective than the initial amine[53]. A synergistic effect in respect of additivity is observed only at a low amine concentration. Probably at a high concentration the amine suppresses chain branching.

The different synergistic effects of the last two mixtures evidently depend also on the different rates of the direct oxidation of the amines employed according to the mechanism

$$InH + O_2 \rightarrow In^{\cdot} + HO_2^{\cdot} \xrightarrow{RH} In^{\cdot} + H_2O_2 + R^{\cdot}\ .$$

Indeed the curves relating τ to the antioxidant concentration (curves *1* in Figs. 4 and 5) show in the first place the attainment of a limiting induction period as the concentration is increased, while in the second case a limit is not reached. This shows that *p*-hydroxyphenyl-β-naphthylamine is vigorously oxidised by oxygen as the concentration increases[32]. The presence of an agent which decomposes hydroperoxide sharply decreases the yield of free radicals $\dot{R}$, leading to an appreciable enhancement of the effectiveness of the mixture.

Thus certain mixtures consisting of a weak inhibitor and a synergist may be as effective as compositions comprising a strong inhibitor and the same synergist, i.e. the synergistic effect is greater the weaker is the inhibitor free radical process.

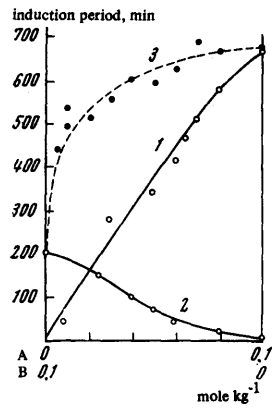


Figure 5. Variation of the induction period in the oxidation of polypropylene with the composition of a mixture of β-naphthylphenylamine (*A*) and mercaptobenzimidazole (*B*) (*3*) and with the concentrations of the components (*1* and *2*) at 200°C and P_{O_2} = 200 mmHg.

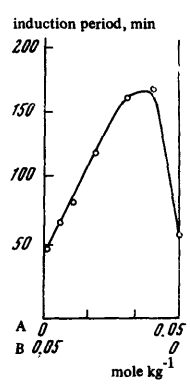


Figure 6. Variation of the induction period in the oxidation of polypropylene with the composition of a mixture of 2,4,6-tri-t-butylphenol (*B*) and dilauryl thiodipropionate (*A*) at 200°C and P_{O_2} = 200 mmHg.

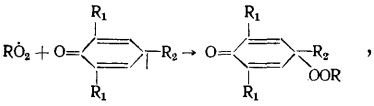
If a strong inhibitor, for example a bisphenol or a diamine, binds both free radicals on interaction with the hydroperoxide in a cage, in the presence of a hydroperoxide decomposing agent the synergistic effect should be absent or small. However, Fig. 3 shows that a mixture of a bisphenol with dilauryl thiodipropionate exhibits an appreciable synergistic effect. Consequently bisphenols do not bind in a cage all the free radicals formed on decomposition of the hydroperoxide. Comparison of the synergistic effect of a mixture of a monophenol and a sulphide (Fig. 6) with that of a mixture of a bisphenol with the same sulphide (Fig. 3) shows that it is greater in the first mixture[15,37,46]. This finding evidently shows that in the presence of the bisphenol, the yield of radicals in

the decomposition of the hydroperoxide is lower than in the presence of the monophenol. In principle, it is possible that polyphenols and polyamines which have either adjacent functional groups or well separated ones capable of approaching one another in space may completely suppress chain branching. Thus certain tetraphenols (for example Irganox 1010 produced by the Geigy Co., Switzerland) mixed with sulphides and oxides do not exhibit a synergistic effect, which probably shows that they suppress chain branching. Inhibitors capable of chain termination and suppression of chain branching should exhibit a high antioxidant activity provided that they are not oxidised by oxygen under these conditions. The search for such inhibitors is of considerable interest both from theoretical and practical points of view.

2. Mixtures of Phenols with Phosphites

It is known that aliphatic and aromatic esters of phosphorous acid, like sulphides, interact with hydroperoxides to form stable products[40,41]. Moreover, it has been shown[42] that phosphites react with peroxy-radicals without chain termination by reaction (8) and therefore are rapidly consumed. In the presence of inhibitors of free-radical reactions the consumption of phosphites by reaction with peroxy-radicals should diminish, which should increase the importance of phosphites in the suppression of chain branching. As a result of the above reactions, the effectiveness of the mixture components increases significantly and the mixture may exhibit a synergistic effect. However, this general inhibition mechanism probably depends on the structure of the alkoxy- and phenoxy-residues of the phosphite esters. Aliphatic phosphites mixed with phenols are relatively ineffective, although they rapidly decompose hydroperoxides with a low yield of free radicals[59]. Evidently this can be explained by the more rapid consumption of phosphites by reaction (8) so that they suppress chain branching only to a small extent. Nevertheless, mixtures of monophenols and bisphenols with iso-octyl diphenyl phosphite (Figs. 7 and 8) and with tri(nonnylphenyl) phosphite show a powerful synergistic effect[46], whose magnitude is greater for monophenols. Probably this is because bisphenols are more likely to suppress chain branching than monophenols. As mentioned above, this is also observed in mixtures of monophenols and bisphenols with dilauryl thiodipropionate.

The structure of phosphites has a very pronounced effect on the synergistic effect in mixtures of phenols with *o*-phenylene phosphite esters. Thus a mixture of a monophenol with 2,4,6-tri-t-butylphenyl *o*-phenylene phosphite does not show an appreciable additional effect[37], in contrast to the mixture of the same monophenol with iso-octyl diphenyl phosphite (Fig. 7). At the same time an appreciable synergistic effect is observed in mixtures of *o*-phenylene phosphite esters with bisphenols and thiobisphenols[37,44,60]. The absence of the synergistic effect from mixtures of monophenols with *o*-phenylene phosphite esters and conversely its occurrence in mixtures with bisphenols and thiobisphenols indicate a complex inhibition mechanism. In the inhibition of oxidation phosphite esters, like sulphides[15], do not exhibit a critical concentration[46]. Therefore both inhibit oxidation by suppressing chain branching and at the same time are oxidised by the peroxy-radicals with formation of stable products and an oxy-radical, i.e. without chain termination[31,42]. On the other hand, *o*-phenylene phosphite esters do have a critical concentration, which shows that they are responsible for linear termination of peroxy-radicals. The mechanism of the action of these phosphites was examined above and it was postulated that at a high temperature *o*-phenylene phosphite esters undergo reaction (9) with peroxy-radicals to form a phosphate and a phenoxy-radical. On the other hand, the phenoxy-radical can react with another peroxy-radical:



forming a peroxide, which, on decomposing at an elevated temperature into radicals, gives rise to chain branching.

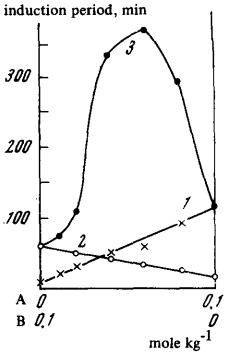


Figure 7. Variation of the induction period in the oxidation of polypropylene with the composition of a mixture of 2,4,6-tri-t-butylphenol (*A*) and iso-octyl diphenyl phosphite (*B*) (*3*) and with the concentrations of the components (*1* and *2*) at 200°C and P_{O_2} = 300 mmHg.

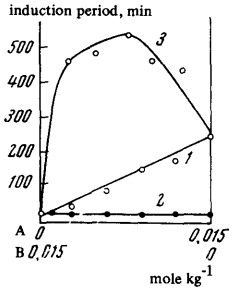


Figure 8. Variation of the induction period in the oxidation of polypropylene with the composition of a mixture of 2,2'-methylenebis-(6-t-butyl-4-methylphenol) (*A*) and iso-octyl diphenyl phosphite (*B*) (*3*) and with the concentrations of the components (*1* and *2*) at 200°C and P_{O_2} = 300 mmHg.

The different effects observed in the presence of bisphenols and monophenols can probably be explained by the different probabilities of the suppression of chain branching by these compounds. Bisphenols, which have two functional groups, are more likely to bind both

radicals formed from the peroxide and thereby suppress chain branching, while monophenols can bind only one radical, the other continuing the chain propagation process.

This mechanism of the synergistic effect is consistent with the finding that it is a maximum at a high concentration of the bisphenol. However, for the final determination of the mechanism by which mixtures of screened *o*-phenylene phosphite esters with bisphenols act, it is necessary to investigate the elementary reactions of the peroxy-radical with these phosphites at an elevated temperature.

3. Mixtures of Inhibitors of Free Radical Processes

When mixtures of inhibitors of free radical processes inhibit only by linear termination of peroxy-radicals, they cannot exhibit a synergistic effect. However, such mixtures may have an antioxidant effect greater than the additive value in consequence of the hydrogen transfer reaction from the weaker inhibitor to the radical of the stronger inhibitor after the latter has given up its hydrogen to the peroxy-radical, according to the reaction

$$In_1 + In_2H \rightarrow In_1H + In_2 .$$

Such a reaction is possible, since even the least active inhibitor will then give rise to a resonance-stabilised radical. Reactions of this class have been observed between 2,4,6-tri-t-butylphenoxy-radicals and phenols, naphthols[61], and also 4-substituted phenols[62].

When the concentrations of both components are equal, the effectiveness of the mixture, which increases only by virtue of the hydrogen transfer reaction, cannot exceed the effectiveness of the strongest inhibitor at twice its concentration. Consequently this mechanism of the action of a mixture shows no synergistic effect. The mechanism shows that the concentration of the strong inhibitor component in the mixture should not alter in the oxidation process as long as the weaker inhibitor is not completely consumed.

Indeed, it has been shown[63] in the sensitised oxidation of ethylbenzene, that in the presence of β-naphthylphenylamine and 2,6-di-t-butylphenol at 60°C the concentration of the first compound remains constant and begins to fall only after the phenol has been completely consumed. It has also been shown[63] that the induction period is higher than the additive value, but does not exceed the value corresponding to the amine at the total inhibitor concentration.

Thus at a low oxidation temperature in the absence of chain branching, the interaction of inhibitors with the peroxide and of the inhibitor radicals with the hydrocarbon, i.e. in the absence of chain propagation reactions, the enhanced activity of the inhibitors is caused only by the transfer of hydrogen from the phenol to the amine.

In the oxidation of ethylbenzene at 120°C and in the presence of the same inhibitor, the authors observed a synergistic effect: the induction period for the mixture proved to be longer than that corresponding to the amine at the total inhibitor concentration[64]. At this temperature, the termination of peroxy-radicals by the inhibitor and the transfer of hydrogen from the phenol to the inhibitor radical may be accompanied by the decomposition of the hydroperoxide and chain propagation due to the reaction of the radical derived from the inhibitor (amine) with ethylbenzene: $\dot{In} + RH \rightarrow InH + \dot{R}$.

However, in the presence of the phenol, the chain propagation reaction is suppressed because of the lower activation energy for the reaction of the inhibitor radical with the phenol ($\dot{In} + PhOH \rightarrow InH + Ph\dot{O}$) than with ethylbenzene. Since chain propagation by the inhibitor radical sharply reduces the effectiveness of the inhibitor, suppression of this reaction does greatly enhance the effectiveness of the mixture. To establish the influence of the chain propagation reaction on the effectiveness of the mixture, a kinetic calculation was made on the branched chain mechanism of inhibited oxidation in the absence of the chain propagation reaction. The computer calculation showed that the suppression of the chain propagation reaction leads to the appearance of a synergistic effect. Nevertheless, it has been noted[6] that this effect can appear also due to the interaction of the hydroperoxide with the amine, evidently as a result of the suppression of chain branching.

According to published work, many mixtures of free radical process inhibitors are more effective than would be expected from additivity, but until the publication of the studies described above a synergistic effect was not observed in any of the investigations.

The experimental observation of the synergistic effect and the theoretical explanation of its mechanism in mixtures of inhibitors of free radical processes opens up new prospects in the search for synergistic compositions.

The synergistic effect observed in the oxidation of alimentary fats and oils between phenols and certain organic and inorganic acids, which, while lacking antioxidant properties, nevertheless increased the effectiveness of the phenols, can also be accounted for by the hydrogen transfer reaction from the acid to the phenoxy-radical[65-67]. However, fairly strong acids such as phosphoric, succinic, and citric can decompose hydroperoxides catalytically without the formation of free radicals and thus suppress chain branching[68].

In a study of the combined action of phenols and dialkyl phosphites in the oxidation of a mineral oil it was shown that the effectiveness of phenols greatly increases although the activity of dialkyl phosphites is very low[69].

According to the authors, the enhancement of the activity of phenols is due to the reduction of the phenoxy-radical by the hydrogen of the phosphonic acid ester produced by the isomerisation of the dialkyl phosphite:

$$\dot{In} + (RO)_2\underset{\underset{H}{|}}{P}O \rightarrow InH + (RO)_2\dot{P}O .$$

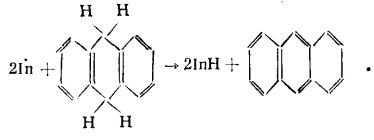
This involves the formation of quadrivalent phosphorus. However, phosphites are known to decompose hydroperoxides and thereby suppress chain branching so that the synergistic effect of this mixture may be a consequence of both hydrogen transfer from the phosphonate ester to the phenoxy-radical and the suppression of chain branching. The reduction of the phenoxy-radical by the hydrogen of diethyl phosphite has been demonstrated using the ESR method[70]. It was also shown[70] that the concentration of phenoxy-radicals diminishes with increase in the concentration of diethyl phosphite. However, when the diethyl phosphite concentration is raised further, that of the radicals does not change, probably because of the formation of a phosphonate ester dimer.

A synergistic effect was also observed in the oxidation of a polyamide stabilised by naphthol and a diaryl phosphite[71] and in the oxidation of polypropylene in the presence of tri-t-butylphenol and *o*-phenylenephosphorous acid[37]. Thus, the synergistic effect observed in the oxidation of mineral oil, polyamide, and polypropylene in the presence of phenols and phosphonate esters is probably due to the

hydrogen transfer reaction[70] and evidently the suppression of chain branching[46].

Apart from the mechanisms of the synergistic effect examined above, there can be yet another mechanism, which has been little investigated but which is important for the increased effectiveness of inhibitors and their mixtures at elevated temperatures.

The inhibitor radicals formed in the high-temperature inhibited oxidation initiate a new reaction chain by reacting with the substrate[64,72,73]; therefore, for example at temperatures above 250°C, inhibitors of free radical processes (phenols and amines) have only a weak inhibiting effect on the oxidation process. Initiation by the inhibitor radical may be sharply reduced, by adding to normal inhibitors or their synergistic compositions, compounds capable of combining with inhibitor free radicals, for example aromatic polymers with a system of conjugated bonds[24,74,75]. For this purpose, one can also use condensed aromatic compounds such as dihydroanthracene, which reacts with the inhibitor radical as follows:



The inhibitor radical is then reduced to the inhibitor molecule and dihydroanthracene is converted into anthracene, which is probably also capable of forming complexes with the radicals and thereby reducing their reactivity. However, dihydroanthracene may be oxidised by oxygen with formation of anthracene and $H\dot{O}_2$ radicals, which propagate the oxidation chain. Therefore the greatest effect should be shown by additives with a system of conjugated bonds, which do not initiate the oxidation reaction but are capable of inhibiting the chain propagation reaction. The study of inhibitors and their mixtures to which substances capable of binding inhibitor radicals have been added is probably important in solving the problem of stabilising polymers at a high temperature[74].

The effectiveness of a mixture of inhibitors changes when two components form a complex. Then the rate of reaction of the peroxy-radical with the complex may prove to be greater or smaller than that with any of the components. Moreover, in the reaction of the complex with the hydroperoxide there is a possibility of a decreased yield of free radicals. Thus the formation of complexes from the components may lead to either an increase and a decrease of their effectiveness. However, this mechanism of the action of mixtures has not been investigated. The effectiveness of inhibitor mixtures also changes when the components form a new chemical compound. It has been shown[76,77] that the oxidation of polyoxymethylene in the presence of α-naphthol and β-naphthylamine involves the interaction of the components with the formaldehyde formed, which leads to the formation of a new compound—1-(2-hydroxynaphthyl)-1-(2-aminonaphthyl)methane. It has been shown experimentally that this compound is more effective than any component present at the overall mixture concentration.

Table 2 lists the mechanisms of the action of inhibitor compositions examined together with their possible antioxidant effects. These effects of the mixtures evidently change when the components participate in processes other than the reactions quoted.

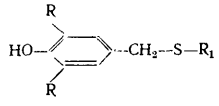
4. Polyfunctional Stabilisers (PFS)

Polyfunctional stabilisers contain in their molecules several reactive groups capable of terminating chains and suppressing chain branching, i.e. capable of inhibiting individual elementary steps in a branched chain oxidation reaction. The application of polyfunctional stabilisers has a number of advantages compared with synergistic compositions, which usually consist of two components, one of which terminates the chain and the other decomposes the hydroperoxide with formation of stable molecules. Moreover, photostabilisers and deactivators of metals are introduced into these mixtures. In order to obtain the maximum synergistic effect, it is necessary to combine the components in appropriate proportions and mix them uniformly with the polymers, which requires complicated and laborious preliminary operations. Nor can one exclude the possibility of chemical interaction between the individual mixture components in the course of the high-temperature processing of the polymer, which may change their antioxidant activity.

Table 2. Mechanism of the action of inhibitor compositions in the oxidation process in the presence of the reaction $In_1H + R\dot{O}_2 \rightarrow ROOH + \dot{In}_1$.

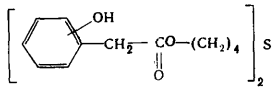
Type	Mechanism of action	Possible antioxidant effect	Refs.
Free-radical process inhibitor	$R\dot{O}_2 + In_2H \rightarrow \dot{In}_2 + ROOH$	additive effect	
Hydroperoxide decomposing agent	$ROOH + R'XR'' \rightarrow ROH + R'X(O)R''$	mutual enhancement of effectiveness by inhibitors (synergism)	15, 33, 46, 52, 53, 54
Hydrogen donor	$\dot{In}_1 + In_2H \rightarrow In_1H + \dot{In}_2$	enhancement of effectiveness (weak synergism)	63, 64
Radical acceptors. Polymers with conjugated bonds, condensed aromatic compounds	$\dot{In}_1 + A \rightarrow In_1 - A$	enhancement of effectiveness	24, 74
Complexones	$In_1H + In_2H \rightarrow In_1H - In_2H$	enhancement or decrease of effectiveness	
Chemical interaction between components	formation of a new compound	enhancement or decrease of effectiveness	76, 77

All these disadvantages may be removed by employing universal polyfunctional stabilisers capable of inhibiting all the elementary steps in the oxidation and photodegradation. In recent years chemists have endeavoured to synthesise such ideal polyfunctional stabilisers. Among the known inhibitors, thiobisphenols should have polyfunctional properties (owing to the presence of the OH group and the sulphur atom), but their sulphur atoms are relatively inactive and therefore when they are mixed with sulphides they exhibit a synergistic effect[54]. Thioethers with the structure



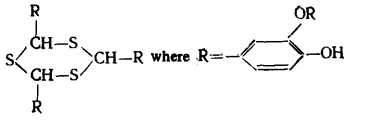
are regarded as the simplest polyfunctional stabilisers. Their effectiveness is higher than that of the corresponding phenols, but lower than that of the bisphenols[78,79].

Thioethers of aromatic hydroxy-carboxylic acids have a higher stabilising effect, for example:



and also mixed esters of two carboxylic acids containing sulphur or phosphorus atoms in the molecule[80].

Various heterocyclic compounds containing sulphur atoms in the ring are effective antioxidants for polyolefins, for example 2,4,6-tri(hydroxyphenyl)-1,3,5-trithianes[81-83]:



These compounds protect the polymer from oxidation and reduce the catalytic effect of multivalent metals. The effectiveness of aromatic derivatives of 1,3,5-trithianes is much higher than that of phenolic antioxidants and depends strongly on the substituents in the benzene ring. Trithianes with an alkoxy-group attached to the ring in the *ortho*-position relative to the hydroxyl show the best antioxidant properties. The addition of a sulphide is stated not to increase the antioxidant effectiveness of trithianes[83], but this needs to be verified.

In recent years reports have appeared on polyfunctional stabilisers which are active thermo- and photo-stabilisers. These data show that the most effective photo- and thermo-stabilisers are phosphorodithioic acid salts of various multivalent metals[84]. Complex chelate quinoxaline compounds appear to be particularly effective photostabilisers[85]. The study of the mechanism and effectiveness of the action of polyfunctional stabilisers constitutes a new field and, as shown by the first results, may lead to the discovery of more effective inhibitors than those known at present.

In conclusion we may note that the stabilisation of polymers at high temperatures still remains an unsolved problem. Possibly one of the ways for its solution will be the application of polyfunctional stabilisers resistant to oxidation by oxygen and capable of chain termination and suppression of chain branching.

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