TRANSFORMATIONS OF PHENOLIC ANTIOXIDANTS DURING THE INHIBITED OXIDATION OF POLYMERS

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ABSTRACT

During ageing and oxidative degradation of stabilized polymers, transformations of antioxidants take place as a result of reactions with radicals RO˙ and ROO˙, alkyl hydroperoxides and/or oxygen. Knowledge of these processes as well as of the properties of products thus formed is necessary for a complex evaluation of antioxidants. Data are given dealing with typical products of oxidative transformations of phenolic antioxidants prepared by independent syntheses, with model transformations under conditions simulating interactions in a stabilized organic substrate, with products identified under real conditions of oxidation of a stabilized substrate, and with influence of some transformation products on the course of oxidation of tetralin and polypropylene.

The oxidative radical degradation of polymers which takes place under most varied accompanying conditions during the atmospheric ageing or processing of polymers is limited by stabilization. The importance of the stabilization process and the theoretical interest devoted to it are an unequivocal consequence of the technical and commercial interests. The majority of the antioxidants technically used have an empirical basis. Complex requirements dealing with the properties of the stabilization systems have been gradually formulated. The data acquired so far about the stabilization processes and the chemical structure of the stabilizers have been summarized in a number of monographs[1-7]. Every year suggestions are also made concerning the use of new stabilization systems.

When choosing the antioxidants, one concentrates on attaining the maximum activity while preserving at the same time the optimum technical properties of the polymer. In the initiation stage of the degradation process, free radicals are formed from the oxidized polymer, RH

$$RH \xrightarrow[\text{X˙}]{\text{initiation}} R˙ \tag{1}$$
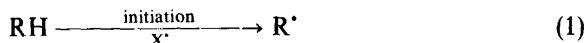
According to the generally accepted scheme of autoxidation, alkyl peroxyls and alkyl hydroperoxides are formed in the propagation step of the reaction; they are a source of further radicals which play their role in the degradation process

$$R˙ + O_2 \rightarrow ROO˙ \tag{2}$$

$$ROO˙ + RH \rightarrow ROOH \tag{3}$$

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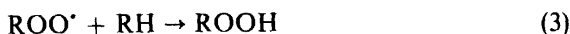
The stabilization of polymers against the oxidative degradation is based on a preventive protection against radical formation, on the deactivation of the peroxyls already formed, and on the non-radical decomposition of hydroperoxides. I shall consider here only compounds breaking the kinetic chain by their reaction with ROO˙. These compounds need not necessarily be free radicals themselves. However, they must be able to react comparatively readily with ROO˙ while giving rise to other radicals, so stable that they cannot initiate new kinetic chains. For this purpose, it has become a tradition to use a group of oxidation inhibitors (InH) containing a labilized hydrogen atom in their molecule. From the viewpoint of the polyolefins, phenolic compounds are those most important of all. The fundamentals about the relationships existing between the structure and the antioxidative activity have been defined[8], and any new development of the required construction of the molecule is already greatly restricted. No extraordinary novel results as to the antioxidative activity can be expected—the activity is determined by the mechanism of their action. However, the development leads to some partial modifications of the molecule of a phenolic antioxidant, to combinations with fragments containing heteroatoms and introducing into the molecule the ability of a polyfunctional action. Above all, these modifications provide activity at high temperatures of the oxidative degradation, when the phenols alone are quickly deactivated and therefore completely useless. For these compounds, the greatest potential development of types can be expected. They can be fully used up only under special conditions and at the processing temperatures. However, for the greatest part of the time of its practical applicability, the polymer is exposed to atmospheric temperatures, when just the monofunctional phenolic antioxidant is very useful. We possess a wide scale of information about the technical properties and toxicity of such compounds. For practical reasons, the terms discolouring and staining antioxidant have been introduced. It is just this property of the phenolic antioxidants, as well as a general survey of the transformations during the process of the inhibited oxidation leading to the consumption of the antioxidant, which are the subject of this lecture.

A phenolic antioxidant (InH) acts by breaking the kinetic chain of the autoxidation

$$InH + ROO˙ \rightarrow In˙ + ROOH \qquad (4)$$

During the process, a radical In˙, which can be primarily regarded as an aryloxyl, and a hydroperoxide are formed. An analogous aryloxyl arises by a reaction with alkoxyls RO˙

$$InH + RO˙ \rightarrow In˙ + ROH \qquad (5)$$

which are formed from alkyl peroxyls or alkyl hydroperoxides arising during the autoxidation. The aryloxyl In˙ is transformed into more stable products. From the viewpoint of an exact knowledge of the stabilization process, we are interested to know the structure of the products formed under the specific conditions of atmospheric ageing and thermo-oxidative degradation, and also the properties of the transformation products.

I shall first give the factors which can generally participate in the deactiva-

tion and transformation of an antioxidant in the process of inhibited oxidation during atmospheric ageing and thermo-oxidative degradation of polymers:

(a) Active radical species formed during autoxidation from the substrate RH (R˙, ROO˙, RO˙, HO˙) and the alkyl hydroperoxide ROOH appearing as the primary oxidation product in the chain reaction. A certain role in the process of deactivation can also be played by the secondary oxidation products of substrate (in the first place, compounds containing the hydroxyl and the carboxyl group) and by accumulating reactive transformation products of the antioxidant, aryloxyls in the first place.

(b) Air oxygen or traces of ozone and nitrogen oxides present in the air.

(c) The trace amounts of catalytically active impurities in the polymer, including the residues of the polymerization catalyst.

(d) Temperature of the process of the co-effect of radiation.

A mere general enumeration of factors points out the complicated character of the processes to be expected during the transformations. Besides chemical reactions and in spite of the low concentration of the antioxidant in the polymer there emerge possibilities of physical interactions causing changes in reactivity. These relationships are completely beyond the framework of this investigation.

It can be said, therefore, that an antioxidant of the InH type capable of breaking the kinetic autoxidation chains is transformed during the process, its original active form being consumed. It has been pointed out that at the end of the induction period the antioxidant added to the mixture is already mostly consumed by the inhibition reaction (active consumption), or that its concentration has fallen off to such a degree that it is no longer able to interfere in an active way with the propagation step of the autoxidation. As a rule, the consumption of the antioxidant in this step of the process is schematically represented by

$$In^˙ + ROO^˙ \rightarrow InOOR \qquad (6)$$

$$2In^˙ \rightarrow In\!-\!In \qquad (7)$$
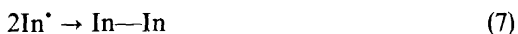
the overall process is often described as a formation of 'inactive products' from the antioxidant. As will be seen further, in no case is it possible to agree with this designation, as long as we do not know more exactly their character and the conditions of the degradation process. Thus, a complex characterization of the antioxidant under investigation requires—besides the knowledge of its activity—also the knowledge of the products arising therefrom during inhibited oxidation. An investigation of the formation of the transformation products of the antioxidants directly in the stabilized substrate is very difficult and must be preceded by a detailed study which can generally be divided into four stages:

(1) Obtaining a survey of the possible intermediates and oxidation products of the antioxidant under study. For this purpose, independent syntheses involving reagents leading to good yields of the individual well-defined products are used advantageously. The processes optimal from both the preparative and mechanistic viewpoints are chosen here, although they fre-

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quently differ from the processes which can be considered during inhibited oxidation. The products thus obtained are used as identification standards for the following model investigations, as well as for obtaining the necessary data about the chemical and physical properties under specific experimental conditions. The state of knowledge existing so far and the classification of information on the oxidative transformations of phenols allow a comparatively easy orientation, at least as to the main features of the problem studied here.

(2) Investigation of a model simulated reaction between an antioxidant and the ROO˙ or RO˙ radicals and a reaction with hydroperoxide and oxygen. It is only with great difficulty that one can perceive all reactions occurring during ageing in a real system. The results of a model investigation involving reactions with the above mentioned agents can give on the whole a real picture of the behaviour of an antioxidant during thermal oxidation. At a sufficient partial pressure of oxygen, the antioxidant terminates the kinetic chains by an interaction with alkylperoxyl. An interaction with the R˙ radicals need not be considered in a common case. However, such reaction can be taken into account in some special cases of the polymer oxidation, e.g. in the case of an insufficient access of the air oxygen. To identify the products of model reactions, standard compounds prepared as indicated sub (1) are used.

The model process more or less simulates interactions during the inhibited oxidation itself. The same partners take part in the model reaction, but it is carried out under different concentration, and very often also temperature, conditions. Although the results thus obtained are very illustrative for the transformations themselves and permit numerous conclusions about the course of the individual reactions, they nevertheless cannot be applied to the stabilization process proper without verifying them in a real inhibitive system.

(3) Oxidation of the stabilized substrates under conditions allowing an investigation of the changes in the structure of the antioxidant in various stages of the processes and under various conditions of oxidation. Preparation of products is extremely difficult owing to the necessity of isolating them from dilute solutions; as a rule, it is successful only for more stable compounds. The identification of the radical species is usually impossible; the mechanism of transformations can be considered only on the basis of knowledge of real analogies with the mechanisms of model investigations and of knowledge of the reactivity of the intermediates or primary reaction products.

(4) Determination of the effect of the transformation products of the antioxidant under investigation on the oxidized substrate under conditions for which their formation has been proved. The effect of the individual compounds and the mixtures thereof, or mixtures with the original antioxidant, must be known. Owing to the thermal sensitivity of some products or to their easy volatility, the effects on the autoxidation process should be followed even under mild conditions. Oxidation of low-molecular weight hydrocarbons instead of polymers, tetralin in the first place, has proved to be useful. The results can be extrapolated with a comparatively good accuracy also to the conditions of the oxidation of polyolefins.

The consideration concerning the formation of the transformation products of monohydric phenolic antioxidants allows us to take into account the formation and behaviour of the aryloxyl In⁺ which can arise during the inhibition process by reactions with oxyradicals 4 and 5 or by analogies thereof, by a reaction with the carbon radical R⁺

$$InH + R^{\cdot} \rightarrow In^{\cdot} + RH \tag{8}$$

or by oxidation with oxygen

$$InH + O_2 \rightarrow In^{\cdot} + HOO^{\cdot} \tag{9}$$
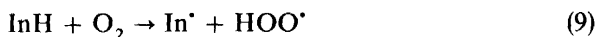
Neither is it possible to exclude the formation of an aryloxyl due to radiation

$$InH \rightarrow In^{\cdot} + H^{\cdot} \tag{10}$$

As to the reactions of the aryloxyl In⁺, we are interested in the first place in the products of oxidative coupling 7 which models the transformations of the antioxidant occurring without participation of alkoxyls or alkyl peroxyls, and the transformation products of reaction 6 or of its analogy with the RO⁺ or HOO⁺ radicals. With respect to the structure of the antioxidants and to the reactivity of the aryloxyls derived therefrom, we do not assume a reaction with the saturated hydrocarbon substrate RH

$$In^{\cdot} + RH \rightarrow InH + R^{\cdot} \tag{11}$$

However, the formation of addition products with hydrocarbons containing an activated C=C double bond cannot be excluded[9].

The generation and reactions of aryloxyls derived from monohydric phenols have been described in the literature[10, 11]. The aryloxyls react in their mesomeric forms as oxy- or carbon radicals. The charged mesomeric structures also contribute to their physical properties. For the aryloxyl to exist in a more stable form than a mere transient state during the reaction, its positions ortho and para must be substituted by groups causing resonance and steric stabilization. It is the same structural requirement which we know from the investigation of the relationships existing between the structure and activity of the phenolic antioxidants[8]. Aryloxyls are then able to exist also in the form of polyradicals[12]. However, they were not identified during the inhibited oxidation of polymers and their formation can be deduced only from the presence of more stable products.

The rate at which the primarily and transiently formed aryloxyls are transformed into further products is affected by their stability, by the momentary concentration of aryloxyls as well as radicals ROO⁺, and by reactivity of the surrounding medium. At different temperatures of inhibited oxidation, essential changes in the mechanism of their reactions must also be expected. Let us consider here typical reactions of the mono- and polynuclear aryloxyls derived from monohydric phenolic antioxidants which must be taken into account in the discussion of changes during ageing and thermo-oxidative degradation of polymers.

Oxidative coupling according to the general scheme 7 can lead in the case of mononuclear aryloxyls to the formation of new C—C and C—O bonds. The joining of two aryloxyls by the O—O bond is fully excluded. The reaction can occur repeatedly, with a mixture of primary and consequent products

having the character ranging from dimers to polymers as the result. The total result of the reaction is influenced by the structure of the original oxidized phenol. Simpler mixtures of products arise from sterically hindered phenols. The extent of the dimerization is determined by mesomeric and especially steric effects. The latter can completely suppress the dimerization[13]. Most of the sterically hindered aryloxyls undergo dimerization C—O. Quinol-ethers Ia, Ib are formed by this reaction. Such products arise from 2,4,6-trialkylphenols, 2,6-dialkyl-4-alkoxyphenols, or from 2,4-dialkyl-6-alkoxy-phenols, e.g. refs. 14–16.
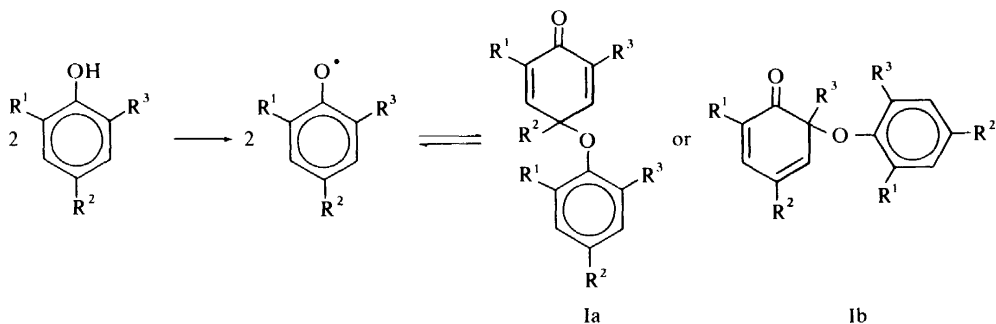
The position of the C—O bond formed is affected by the volume of the substituents in the position ortho or para to the phenolic hydroxyl. The steric factor also influences the equilibrium between aryloxyl and its dimer in solution; bulky substituents shift the equilibrium to aryloxyl.

From 2,6-dialkylphenols, products ranging as far as polymers are formed by route of a mechanism involving the disproportionation of quinolethers[19,20]. Intramolecular and intermolecular reactions of aryloxyls give rise to a mixture of products during the transformation of 1,1'-dinaphthyl-2,2'-diol[21].

The dimerization by means of a C—C bond occurring to positions 2 and 4 is typical for the di- and trialkylated phenols. Several cases have been described[10,14]; cyclohexadienoid (II) or diphenoquinoid (III) compounds are formed as the resulting products. In II, R^3 = H, a rapid rearrangement to bisphenol takes place. The dimerization by the C—C bond and the formation of a further intramolecular bond can occur during the oxidation of 2,4-dialkylphenols[17]. Similar changes were also observed for 2-tert-butyl-4-methoxyphenol[18], an important antioxidant. A spiro compound IV is formed.
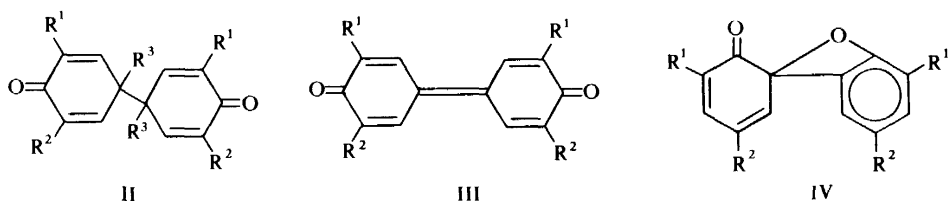

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In the case of an appropriate substitution of the ring, even a rearrangement of the radical can occur during the oxidative coupling of the mesomeric carbon radicals. Such a mechanism including formation of a benzyl radical was considered for the oxidation of 2,6-di-tert-butyl-4-methylphenol where a phenolic (V) and a quinoid (VI) dimer are formed[22]. However, there are no spectral proofs for the formation of the benzyl radical. A chemical proof of its transient formation in the course of the oxidation of 2,6-di-tert-butyl-4-methylphenol has been provided by the isolation of 2,6-di-tert-butyl-4-(3,5-di-tert-butyl-4-hydroxybenzyl)-4-methyl-2,5-cyclohexadienone[23](VII).

V   VI

VII
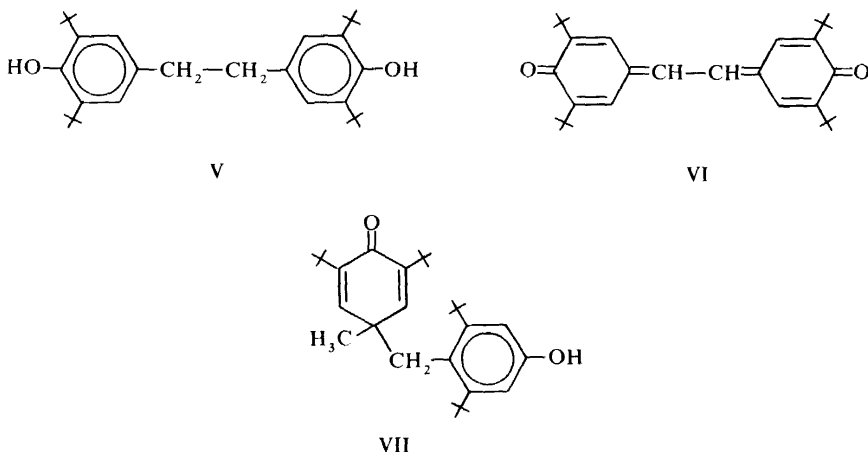
Aryloxyls derived from 2,4,6-trialkylphenols having α-hydrogen in their para-substituent undergo rather disproportionation than dimerization. This is accompanied by the formation of the original phenol and quinone methide, e.g. VIII, which is transformed further according to its stability[24, 25].
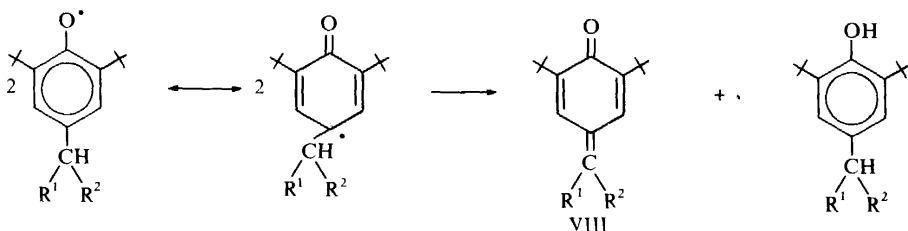
VIII

Quinone methide VIII having R^1, R^2 = H is very unstable and cannot be isolated. On this basis, the formation of compounds V and VI as oxidation products of 2,6-di-tert-butyl-4-methylphenol is interpreted[26]. (An alternative mechanism for the above dimerization of two benzyl radicals.) The stability

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of quinone methide is enhanced by the substitution of some of the α-hydrogens in the para substituent with an alkyl. For instance, quinone methide derived from 2,6-disubstituted para-isopropylphenol is stable for several days.

For phenol derivatives containing a methylene group at the position para, a slow oxidation to the carbonyl group[27] and the formation of a derivative of acetophenone IX can be expected.


IX
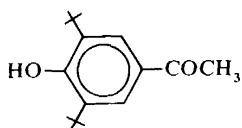
Aryloxyls are also formed from polynuclear phenols which belong to the technically important antioxidants. In radicals derived from the alkylidene- and thiobisphenols, the delocalization of the unpaired electron in the system of both six-membered rings is affected by the character of the bridge. More stable radicals are formed[28] from bisphenols having the bridge at positions 4,4'. One of the most stable radicals is the so-called galvinoxyl X derived from 4,4'-methylenebis(2,6-di-tert-butylphenol)[29]. Similar stable radicals, e.g. XI or XII, are formed from other alkylated polynuclear phenols[30, 31].
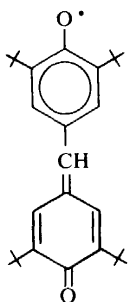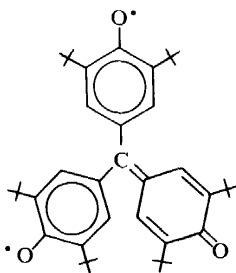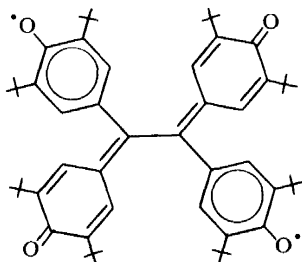

X   XI   XII

Such stable radicals can even participate in a transient way in the discolouration of the stabilized substrate during atmospheric ageing. In some cases, the aryloxyls derived from 4,4'-alkylidenebisphenols can undergo an intramolecular coupling with the formation of spirobisdienone. For instance, 4,4'-isopropylidene-bis-(2,6-di-tert-butylphenol)[32], which belongs to the group of nonstaining, but little active antioxidants, is oxidized in this way.

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The cyclohexadienone derivative thus obtained has the structure XIII. A transformation of another antioxidant of similar structure having ortho-methyl-substituents which improve its antioxidative activity, can lead[33] to a complex polymeric product (XIV).
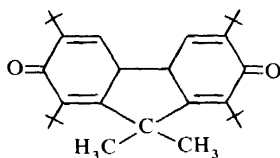

XIII
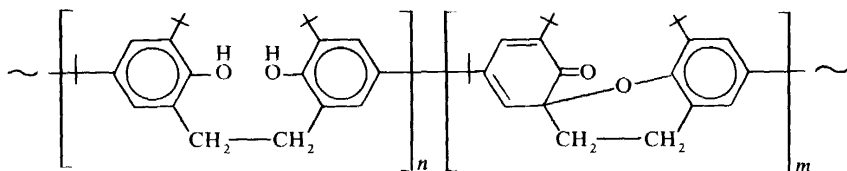
XIV

Oxidation of 4,4'-diphenyldiols gives rise to a biradical only transiently; diphenoquinones[34] (e.g. XV) are formed as the product.

From 2,2'-alkylidenebisphenols which belong to the group of important antioxidants, thermally stable cyclic quinolethers[35, 36] (XVI), can be formed in the case of an appropriate substitution of the aromatic ring which will not allow an intermolecular reaction.
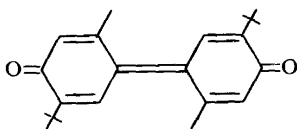

XV
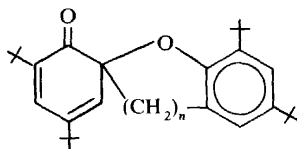
XVI

During the oxidation of binuclear phenols having their rings bonded by oxygen, sulphur or selenium atoms at positions 4,4', and tert-butylated at the positions ortho to the hydroxyl, the heteroatom is eliminated in the course of the oxidation reaction. 3,3',5,5'-Tetra-tert-butyl-4,4'-diphenoquinone (IV, R^1, R^2 = tert-butyl)[37, 38] appears here as the product. The oxidation of the sterically less hindered diphenyl ether proceeds with the formation of a more complex product[38].
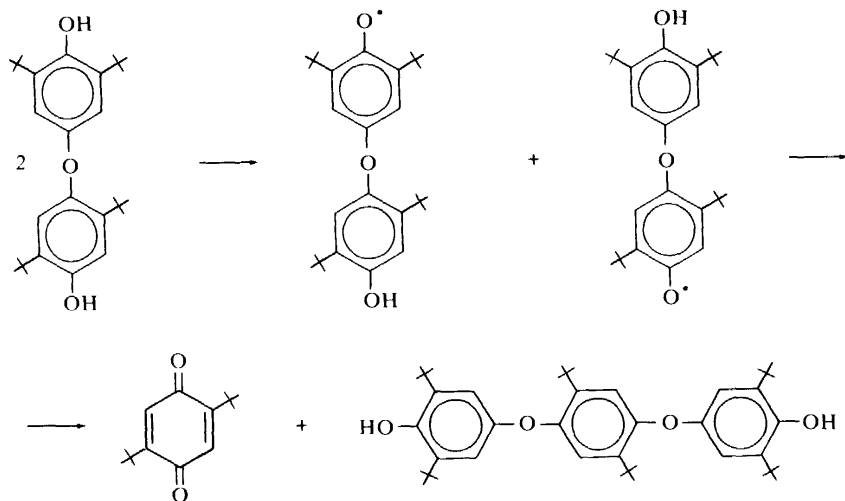
The examples given so far have been those of the transformations of the individual antioxidants. A more complicated interaction can occur in the mixture of phenols, giving rise—in the case of mononuclear phenols—to unsymmetrical cyclohexadienone ethers[39-41]. The structure of the product is determined by steric factors; the sterically more hindered residue is bonded in the cyclohexadienoid part of the molecule, e.g.
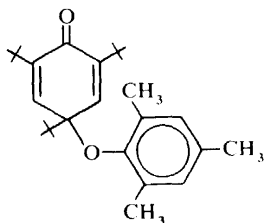
A number of such products have been described. The interaction between the sterically hindered and unhindered phenols and mixtures of aryloxyls and more stable products derived therefrom can serve as an explanation of the homosynergism of the phenolic antioxidants[42].

The process of inhibited oxidation can lead not only to the transformation of the phenolic antioxidants caused by their reaction with the ROO˙ radicals or with oxygen, but also—given adequate conditions—to products in which both these agents are chemically bonded. The reaction with alkyl peroxyls is a termination one, and is generally schematically represented by 6. Here, the aryloxyl reacts in one of its mesomeric forms, according to the steric effect of the substituents on the ring. The stability of products thus formed is

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affected by their structure; some peroxy derivatives do not decompose until at temperatures above 100°C, so that their formation during the ageing of the polymers is quite likely. The reaction products most frequently studied were those of the reaction with tert-butylperoxyl, which can be regarded as the simplest alkylperoxyl modelling tertiary hydroperoxyls arising during the autoxidation of polypropylene. A number of reactions have also been carried out with cumylhydroperoxyls or tetralylhydroperoxyls under conditions suitable for the modelling of the transformation process during inhibited oxidation. The ROO˙ radicals needed for the reaction are usually generated by a homolytic decomposition of hydroperoxide catalysed with the Co˙˙ ions[43, 44] or by the thermal decomposition of the readily splitting hydrocarbons or azo compounds in the presence of oxygen[43]. In both cases of the generation, the RO˙ radicals are also contained in the mixture. Their presence can be excluded by working in an excess of hydroperoxide, when the reaction

$$RO˙ + ROOH \rightarrow ROH + ROO˙ \qquad (12)$$

takes place. To investigate the reaction of the antioxidant with the RO˙ radicals (mostly tert-butoxyls), the necessary radicals can be unequivocally generated by the thermal decomposition of tert-butyl peroxide[45] or tert-butyl peroxalate[46].

I shall give here some typical products formed from the individual main types of phenolic antioxidants by their reaction with tert-butylperoxyl. 2.6-Dialkylphenols yield[47] 2,6-dialkyl-1,4-benzoquinone and diphenoquinone III. A varied mixture of products is obtained from 2,4-di-tert-butylphenol[48]. Apart from C—C and C—O dimerization products whose structures have been mentioned before, compounds XVII and XVIII are given as the examples of isolated peroxycyclohexadienones.
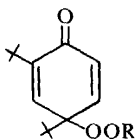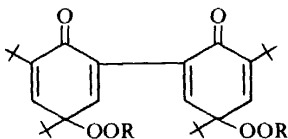

XVII   XVIII

Antioxidants having the structure of 2,4,6-trialkylphenols form 4-alkylperoxy-2,5-cyclohexadienones XIX or 2-alkylperoxy-3,5-cyclohexadienones (XX). The product formed from one of the phenolic mononuclear antioxidants most frequently used, namely, 2,6-di-tert-butyl-4-methylphenol[43, 49], belongs to the first type. It is reported[50] that thermal decomposition of alkylperoxycyclohexadienone XIX leads to 2,6-dialkyl-4-hydroxybenzaldehyde. Isomeric cyclohexadienones of type XX are formed from phenols containing a less bulky substituent R^2, e.g. from 2,4-di-tert-butyl-6-methylphenol.

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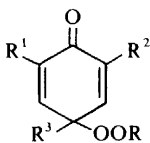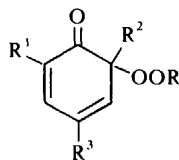
Compounds analogous to XIX and XX (R = H) are obtained by the autoxidation of trialkylphenols in an alkaline medium. For instance, from 2,4,6-tri-tert-butylphenol we obtain a mixture of the 2- and 4-cyclohexadienone hydroperoxides[51], while only the 4-isomer is formed from 2,6-di-tert-butyl-4-methylphenol[52].

The isolation of alkylperoxycyclohexadienones XIX or XX in the reaction of alkylperoxyl with mononuclear phenolic antioxidants is in accordance with the assumption that a mononuclear phenol is able to terminate two kinetic oxidation chains, which is expressed in a general form by reactions 4 and 6. This is a chemical contribution to the proof of the mechanism of the effect of the antioxidants breaking the autoxidation chains. Kinetic proof, and particularly the rate-determining step, have been for a long time an object of discussions. However, this problem also seems to have been solved satisfactorily by applying suitable experimental techniques.

Some products of the transformations of polynuclear antioxidants with the ROO˙ radicals have also been described. In our laboratory, alkylidenebisphenols have been studied in more detail. It has been found that some of the most active of them are transformed in polypropylene into deeply coloured products. In the series of 2,2′-alkylidenebisphenols, more active antioxidants were represented by compounds having hydrogen atoms on the carbon atom of the bridge and substituted in the benzene rings by a bulky alkyl at the position ortho to the hydroxyl and by the methyl group at the position para. Substitution of all hydrogens on the bridge with alkyls or replacement of methyl with the tertiary butyl group reduced the discolouration while at the same time also reducing the antioxidative activity. We have investigated in more detail the transformation products of a technically important antioxidant, namely, 2,2′-methylene-bis-(4-methyl-6-tert-butyl-phenol) which belongs to the most active alkylidenebisphenols for the stabilization of isotactic polypropylene. Although it is classified among the non-staining antioxidants, however, it substantially discolours polyolefins. It has been in use for a long time now, but nothing has been known about its transformation products. By using the reaction with tert-butylperoxyls, we prepared[53, 54] several products whose formation depends on the molar ratio of the reacting components. In a mixture in which the tert-butyl hydroperoxide used did not attain the equimolar ratio with respect to 2,2′-methylene-bis-(4-methyl-6-tert-butylphenol), dimer XXI, trimer XXII, and compounds having an intensive brown colour were formed as the main products.

Their amount increased with the increasing hydroperoxide content in the mixture. Compounds XXI and XXII were also obtained by the reaction of 2,2′-methylenebis(4-methyl-6-tert-butylphenol) with the tert-butoxyl radicals.

XXI
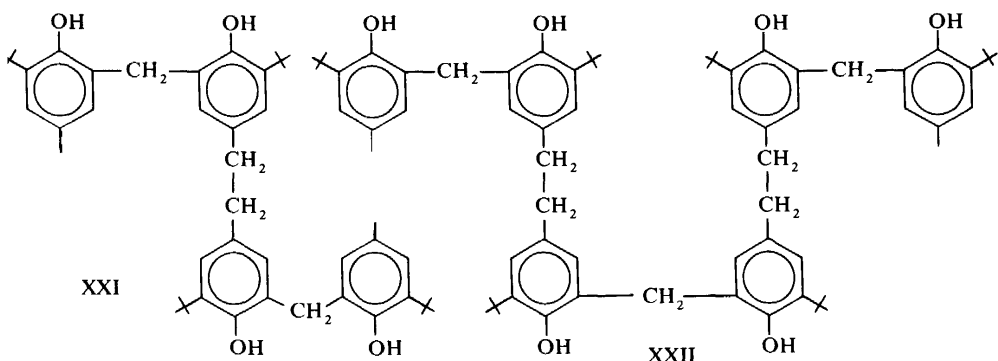
XXII

A large excess of tert-butyl hydroperoxide in the reaction mixture gave rise to the cyclohexadienone derivative XXIII and its isomer XXIV.

XXIII

XXIV
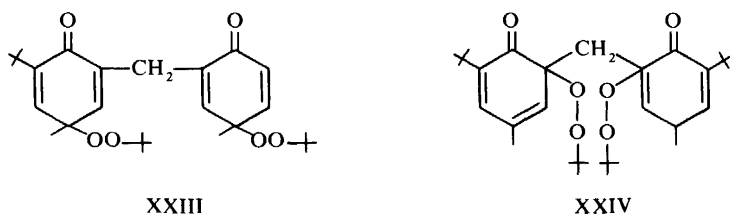
From a mixture of the coloured products formed, we succeeded in the identification[54] of dimer XXV and trimer XXVI and in the isolation of an analogous tetramer. The connection existing between the colourless oligomers XXI and XXII with the coloured oligomers XXV and XXVI has been proved. The compounds causing discolouration of the polymer lose their colour in a reaction with an excess of alkyl hydroperoxide; however, no products of type XXIII are formed in this case.

XXV

XXVI

219
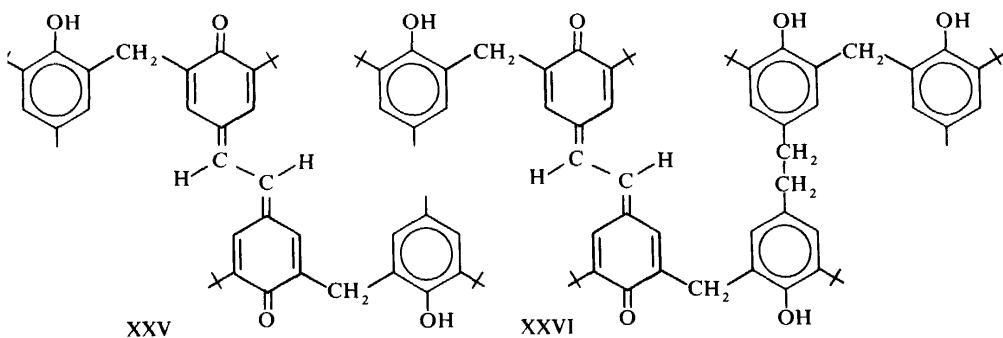
It has been found[55], by gel chromatographic investigation of the reaction mixture obtained by acting with tert-butyl hydroperoxide on 2,2'-methylene-bisphenols analogous to 2,2'-methylenebis(4-methyl-6-tert-butylphenol) that oligomeric products similar to XXI and XXII are probably also formed from a derivative having an ethyl group at the position para to the hydroxyl, while the derivative substituted with the tert-butyl group reacts quite differently (the formation of a compound of type XVI should rather be expected).

Cyclohexadienone XXVII is formed by oxidation of another technically important antioxidant, 1,3,5-trimethyl-2,4,6-tris-(3,5-di-tert-butyl-4-hydroxy-benzyl)benzene with tert-butylperoxyl[50]. The thermal stability of this compound is limited. At a temperature above 160°C, brown products and volatile compounds are formed therefrom; of these, acetone and 2,6-di-tert-butyl-1,4-benzoquinone could be identified, and the presence of the compounds of type XXVIII and XXIX is supposed on the basis of the mass spectra.

XXVII

XXVIII

XXIX
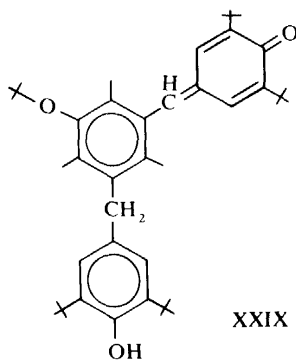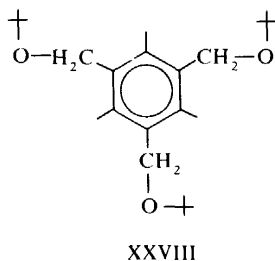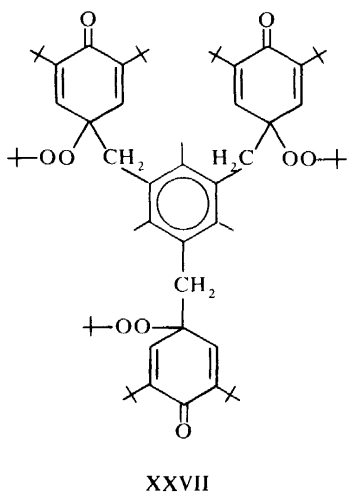
The results of the oxidation of polynuclear phenolic antioxidants indicate certain analogies with the process of transformation of the mononuclear phenols while at the same time explaining the sources of formation of the polymer-discolouring products.

During inhibited oxidation, particularly at high temperatures, it is possible to expect also an inactive consumption of the phenolic antioxidant by direct reaction with oxygen. The first step consists of a homolytic cleavage of the

H—O bond and of the formation of an aryloxyl. It is more likely, however, that this aryloxyl formation is due to a reaction with the ROO˙ radical, followed by a reaction with oxygen at a rate depending on the stability of aryloxyl[10,11,56]. For aryloxyls derived from the majority of mononuclear phenolic antioxidants the formation of cyclohexadienoneperoxyl (XXX) followed by the formation of cyclohexadienone peroxide (XXXI) can be assumed.

XXX   XXXI
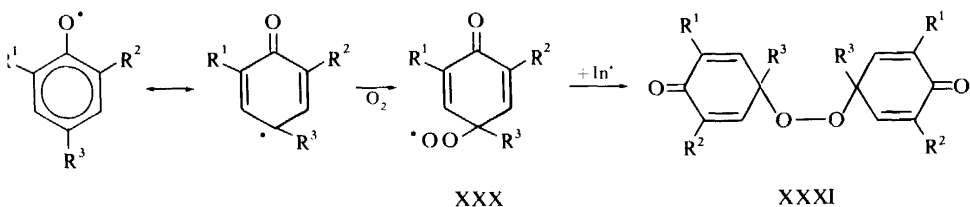
The peroxides of type XXXI are thermally and photochemically relatively unstable, slightly coloured compounds. It is therefore not possible to expect that they may be identified during the transformation of the antioxidants in the process of ageing of the polymers and particularly during thermo-oxidative degradation. However, their transient formation and the homolysis of the O—O bond can—similarly to the case of alkylperoxycyclohexadien-ones—explain the formation of some products of the oxidative transforma-tion. An example can be seen in the isolation of 2,6-di-tert-butyl-1,4-benzo-quinone as a product of the oxidation of 2,6-di-tert-butyl-4-alkoxyphenol[57,58]. A mixture of compounds has been formed[50] by the direct oxidation of 1,3,5-trimethyl-2,4,6-tris-(3,5-di-tert-butyl-4-hydroxyphenol)benzene with oxygen at 230°. In this mixture, besides mononuclear products probably due to the thermal cleavage of the cyclohexadienone derivative XXVII (i.e. 2,6-di-tert-butyl-1,4-benzoquinone and 3,5-di-tert-butyl-4-hydroxybenzalde-hyde), quinone methide XXXIII was identified by the mass spectrum.

XXXII
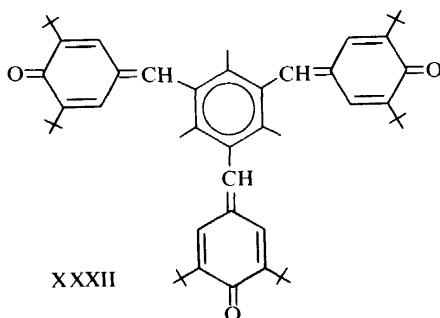
The examples given so far have been those of the transformations of the antioxidants from the group of the monohydric mono- or polynuclear phenols substituted with alkyls or alkoxyls. Dihydric phenols represent another

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group of active antioxidants. They are practically exclusively mono-tert.-alkylated derivatives of pyrocatechol and hydroquinone. Their transformation yields, in the first place, benzoquinoid (XXXIV, XXXV) and hydroxybenzoquinoid (XXXVI, XXXVII) compounds. The synthesis of both isomeric benzoquinones is easy[59]. Tertiary alkylated hydroxybenzoquinones were obtained by the oxidation of mono-tert-alkyl-pyrocatechols and hydroquinones with oxygen in an alkaline medium[60,61].
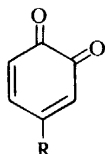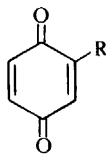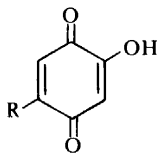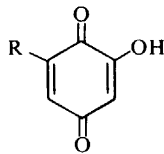
XXXIII   XXXIV   XXXV   XXXVI

By means of e.p.r., useful data on the mechanism of the autoxidation process were obtained[62]. Benzoquinones and hydroxybenzoquinones were also obtained by the reaction of 4-tert-butylpyrocatechol with tert-butylperoxyl, tert-butyl-hydroperoxide, and tetralylhydroperoxide; some further unidentified compounds were formed in this process.

From 2-tert-butylhydroquinone, only corresponding 2-tert-butyl-1,4-benzoquinone was formed[63]. Owing to the comparatively high thermal instability of benzoquinones, no simple quinoid products except for 2-tert-butyl-1,4-benzoquinone could be identified unambiguously between products formed by the oxidation of mono-tert-butylated pyrocatechol and hydroquinone with oxygen at 150°C in trichlorobenzene solution[64]. According to TLC, some other products due to both coupling and cleavage reactions are present in the mixture along with hydroxybenzoquinones. It has been deduced from the investigation of the transformations of dihydric phenolic antioxidants that the deactivation by oxidation with oxygen occurs at a measurable rate only at temperatures above 100°C. Therefore, such transformation does not appear during the atmospheric ageing of the polymers, but it must be considered at processing temperatures.

For the stabilization of both polymers and low-molecular weight hydrocarbons the antioxidants are used in low concentrations. This renders very difficult the isolation or identification of compounds formed therefrom during the inhibition process. As a rule the conditions of the oxidative degradation, such as would be studied for practical applications, are not the optimum ones for the preparation of compounds which have been obtained in a defined form by a model reaction or by an independent synthesis. Consequently, it must be borne in mind that in practice incomparable data are already obtained at small deviations under the process conditions.

Most results are based on the classical chemical and spectral analysis of laboriously isolated products. The application of chromatographic separation and identification techniques makes the task somewhat easier, but is by no means an absolute solution, as long as it cannot guarantee an uncom-

promisingly careful treatment of the concentrates of the transformation products, and if— and this is one of the main difficulties of the whole problem—there is not at our disposal a sufficient selection of standard compounds modelling the products of the primary transformation, as well as compounds obtained therefrom as secondary ones by further oxidation and by a thermal or photochemical process. An investigation of the transformations by means of standards is extremely labour-consuming, but it is the only one real approach to the solution of the problem.

So far, not many data have been reported about the transformation products of antioxidants isolated and identified during inhibited oxidation. Owing to high oxidation temperatures, in the first place more detailed data about the products formed during the oxidative degradation of polymers are missing. However, compounds detected in stabilized liquid hydrocarbon substrates oxidized in a temperature range to 100° are indicative for the process of the atmospheric ageing of polymers. Along with the knowledge of physical properties and reactivity of the identified compounds, they allow certain extrapolations for high-temperature degradation. A difficulty is caused by the formation of undefined 'tarlike' compounds, into which an essential part of the antioxidant is often transformed. Some data reported on the transformation products must be accepted with a certain reserve, since some of the compounds isolated may also be those formed only during the process of isolation.

Data were published dealing with the transformations of methylated phenols. Para-cresol and 2,4- and 2,6-xylenols present in autoxidized cumene changed[65] to products of the C—C dimerization. Diphenoquinone (III, R^1, R^2 = Me) was formed during the autoxidation of benzaldehyde stabilized with 2,6-xylenol[66].

The majority of papers published so far have been devoted to 2,6-di-tert-butyl-4-methylphenol, an antioxidant that is widely used in practice. The investigation is facilitated by good knowledge of the structure of the products formed by model reactions and by the generally unambiguous reactivity of this phenol. It was changed in oxidized cumene[27, 43, 67] into the dihydroxy-dibenzyl derivative (V) and stilbenequinone (VI). During the stabilization of a lubricating oil, the formation of an aldehyde, probably 3,5-di-tert-butyl-4-hydroxybenzaldehyde, was observed[68]. By means of a chromatographic analysis of the transformation products formed at the end of the induction period during the autoxidation of tetralin initiated with azobisisobutyronitrile, only the presence of peroxycyclohexadienones[47] (XIX, R^1, R^2 = t-Bu, R^3 = Me), obtained by a reaction with the ROO˙ radicals derived from the oxidized substrate and from the initiator was proved. No products having the stilbenequinoid structure have been observed in this case. The cyclo-hexadienones isolated in the latter case confirm the kinetic suggestions of the course of this inhibition reaction[69]. However, the data on the transformations of 2,6-di-tert-butyl-4-methylphenol in various substrates indicate that it is very difficult to outline a generally valid scheme of transformation also in the case of a very simple antioxidant used under relatively mild conditions.

There are not many chemical data about the transformations of phenols in polymers. It has been found[70] that during the oxidation of isotactic poly-propylene stabilized with 2,4,6-tri-tert-butylphenol, cyclohexadienone per-

oxide was obtained by a sequence of reactions which are assumed to proceed via the formation of aryloxyl, its interaction with polypropylene hydroperoxide, and further transformations. 4,4'-Methylene-bis-(2,6-di-tert-butyl-phenol) is believed to react in a similar way.

From 2,6-di-tert-butyl-4-methylphenol, used for the stabilization of isotactic polypropylene, some products were formed during the oxidation carried out at 200°, of which 3,5-di-tert-butyl-4-hydroxybenzaldehyde and 2,2',6,6'-tetra-tert-butyl-4,4'-stilbene-quinone[71] were identified.

The transformations of another important antioxidant, 2,2'-methylene-bis-(4-methyl-6-tert-butylphenol), during the polyolefin stabilization are assumed[72-76] on the basis of kinetic data. However, the chemical nature of the products was not proposed. According to ref. 77 a multicomponent system is formed. We used the TLC and GPC methods to investigate[54, 78, 79] the transformations of 2,2'-methylene-bis-(4-methyl-6-tert-butylphenol) during the oxidation of tetralin and polypropylene. Owing to the lower temperature of the tetralin oxidation (60°C), it was possible to prove the formation of a tetralyl analogue of alkylperoxycyclohexadienone XXIII in addition to the phenolic products of oxidative coupling (dimer XXI and trimer XXII) and of a mixture of brown-coloured products in which trimer XXVI was the main component. In the case of the oxidation of atactic (150°C) and isotactic (180°C) polypropylene, brown products are formed from the onset of the oxidation. However, their exact identification causes difficulties, especially in isotactic polypropylene, since owing to the confirmed thermal instability of oligomers with the stilbenequinoid structure they readily undergo further changes. Dimers XXI and XXV are proved[79] in atactic polypropylene by means of TLC. The presence of low amounts of phenolic oligomers XXI and XXII cannot be excluded in the oxidized isotactic polypropylene; these oligomers are rapidly consumed by an inhibition reaction[78] at 180°C, which is the reason why their momentary concentration is so low. If also the peroxidic derivative of cyclohexadienone is transiently formed at high oxidation temperatures, it undergoes thermal splitting and can be the source of compounds having a lower molecular weight than the original methylene bisphenol. Such compounds have been observed[80] by means of GPC in stabilized tetralin oxidized at temperatures above 100°C. Such compounds can also arise from products having the stilbenequinoid structure in the oxidation steps following the induction period, i.e. at a higher content of alkyl peroxyls or alkyl hydroperoxides and after consumption of the radical scavengers (either the methylenebisphenol originally present in the mixture or the products arising therefrom and exhibiting antioxidative activity). The benzoquinone derivatives may be present among these compounds, as has been demonstrated[81] by a model investigation with tetra-tert-butylstilbenequinone.

Interesting data on the structure of the products obtained by a transformation of the antioxidant during the oxidation of polypropylene stabilized with 1,3,5-tri-methyl-2,4,6-tris-(3,5-di-tert-butyl-4-hydroxybenzyl)benzene have been reported[71]. Owing to the fact that each of the hydroxybenzyl groups bound in this antioxidant to the central benzene ring can react independently, a very complex mixture of the oxidation products is formed; thirteen compounds have been identified by mass spectroscopy. They include
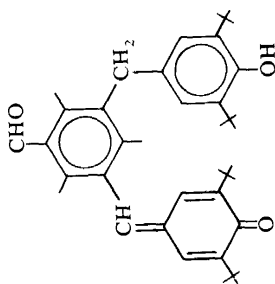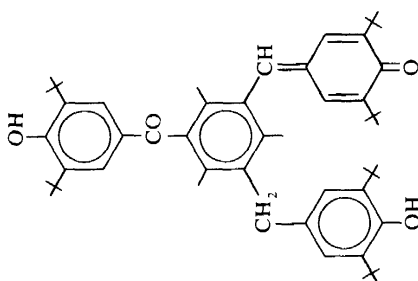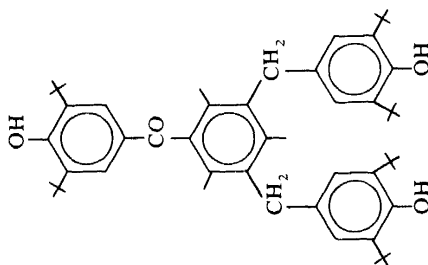
XL
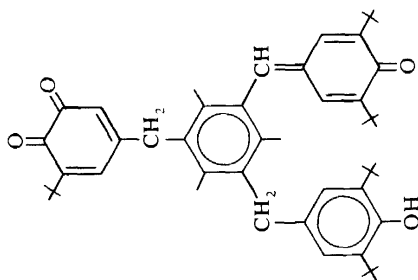
XXXIX

XXXVIII

XXXVII

compounds oxidized on the individual rings to a different degree. Some of the products contain the carbonyl groups, quinone methide or 1,2-benzoquinoid structures, as well as structures obtained by the oxidative splitting-off of the benzyl group, e.g. compounds XXXVII to XL.

However, 2,6-di-tert-butyl-1,4-benzoquinone was the main product of this transformation. It has been demonstrated[82], by using 1,3,5-trimethyl-2,4,6-tris-(3,5-di-tert-butyl-4-hydroxybenzyl)benzene labelled with ^{14}C, that a part of the oxidized molecule of the antioxidant is bonded to the polypropylene molecules. Structure XLI analogous to product XXVIII from the model reaction is considered here. However, the existence of compound XLI seems somewhat uncertain, owing to the steric requirements of such a molecule.

$$PP-O-H_2C \overset{\displaystyle|}{\bigcirc} CH_2-O-PP$$

$$CH_2-O-PP$$
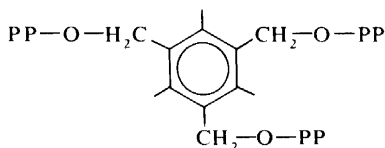
XLI

The data on the simulated transformations of the antioxidants indicate along with the data on some isolated products formed under real conditions of the inhibited oxidation how complex the whole process is. They point out the difficulty of determination of the real value of the stoichiometric factor giving the number of peroxyls deactivated by one molecule of a phenolic antioxidant based on the chemical analysis of the products. A more probable value of the stoichiometric factor determined on the basis of the products obtained can be approached only by using some antioxidants which are particularly suited for such study owing to their unequivocal reactivity. 2,6-Di-tert-butyl-4-methylphenol is such a compound. In the case of an investigation of the antioxidants which react in a more complex way while yielding compounds some of which undergo further oxidation immediately after their formation, the determination of the stoichiometric factor based on the products is rather illusory. This group of compounds includes polyhydric phenols and the majority of polynuclear phenolic antioxidants used for the stabilization of macromolecular compounds.

Also the value of the stoichiometric factor determined from the kinetic data should be regarded as informative only, since it is an integral fact involving the results of a whole complex of reactions occurring in varied ratio during the process of inhibition. These processes play their role in the kinetic evaluation as a complete set which is difficult to separate. However, the stoichiometric factor determined under comparable conditions for antioxidants for which the same mechanism of action can be considered is a useful qualitative tool indicating the effect of structural factors or the extent of the participation of the antioxidants being compared in the undesirable side reactions[84].

It can be said, consequently, that the knowledge of the transformations of the antioxidants somewhat restricts the general validity of a kinetic analysis of the stabilization process and puts the knowledge of the mechanism of

action of the antioxidants on a more realistic basis indicating more accurately the situation arising during atmospheric ageing and the degradation of polymers. At the same time, it allows information to be obtained about the participation of the transformation products in the individual processes occurring during ageing. A mere survey of the structures of compounds which can be formed under certain conditions from the originally present antioxidants in the stabilized polymer indicates that the compounds involved cannot always be inert in the further process of degradation. Their effect on the further course of oxidation is widely affected by the conditions of the process. I shall outline here the knowledge acquired so far about the influence of the individual types of transformation products on the process of autoxidation.

During the oxidation inhibited with monohydric mononuclear phenols[47] or polynuclear phenols[50, 53], alkylperoxycyclohexadienones are formed, if the temperature of oxidation does not exceed the temperature of their thermal decomposition. We investigated[85] the effect of the simplest compounds of this series having the structure
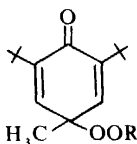

where R = tert-butyl, cumyl, α-tetralyl, or 2-cyanoisopropyl, in the course of the oxidation of tetralin. At 65°C, the presence of these alkylperoxycyclohexadienones has no influence on the rate of oxidation. However, an analogous alkylperoxycyclohexadienone XXIII derived from 2,2'-methylene-bis-(4-methyl-6-tert-butylphenol) had a weak retardative effect[78]. The homolysis of the O—O bond at an elevated temperature raises the effect of these compounds, and at 150° (i.e. above the point of incipient decomposition of all the compounds under investigation) there is a clear pro-oxidative effect. The ability of the RO· radicals produced by homolysis to initiate or propagate the autoxidative chains will play its role here. This process must be taken into account during processing or thermal treatment of polymers in which some alkylperoxycyclohexadienones were present as a result of transformations during preceding low-temperature oxidation. The products of a further thermal or oxidative transformation of these cyclohexadienones, 3,5-di-tert-butyl-4-hydroxybenzaldehyde or 2,6-di-tert-butyl-1,4-benzoquinone, have no antioxidative properties[82, 86, 87].

Benzoquinones and hydroxybenzoquinones have been proved to be products of transformations of pyrocatechol, and benzoquinones products of hydroquinone antioxidants[63]. They are effective inhibitors of polymerization[88]. They scavenge the R· radicals, and their presence can—in the first place—be reflected in the onset of oxidation, since their interference with the propagation step 2 can be assumed here, above all, at an insufficient pressure of oxygen. Kinetic treatment of the oxidation process indicates the possibility of such a retardative effect[66, 89–91]. We studied the behaviour of a series of

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isomeric mono-tert-alkylated benzoquinones and hydroxybenzoquinones XXXIII to XXXVI during initiated oxidation of tetralin[87] and found that with the exception of 2-tert-butyl-1,4-benzoquinone, the rate of the oxidation remained unaffected by any of the alkyl-1,4-benzoquinones and hydroxy-1,4-benzoquinones investigated. The same results were obtained when investigating the properties of (2-alkoxyalkyl)-1,4-benzoquinones[92]. However, 4-tert-alkyl-1,2-benzoquinones exhibited retardative activity. The different behaviour of isomeric benzoquinones and the semiquinones preceding them can also be one of the causes of the different antioxidative activity of the derivatives of the pyrocatechol and hydroquinone series.

Some changes in the action of the quinoid products can take place in the process of the atmospheric ageing of polymers as a consequence of the radiation co-effect. From inactive tert-alkyl-1,4-benzoquinones, (2-alkoxyalkyl)hydroquinones can be formed[93] in the presence of alcohols (which are found among the secondary oxidation products of hydrocarbons); for these (2-alkoxyalkyl)hydroquinones, a higher antioxidative activity has been proved during the stabilization of isotactic polypropylene and tetralin than that of tert-alkylated hydroquinones from which they are derived[92]. The transformation of 2-tert-butylhydroquinone is given as an example. 2,5- and 2,6-Di-tert-alkylhydroquinones also undergo gradual changes in a similar way.
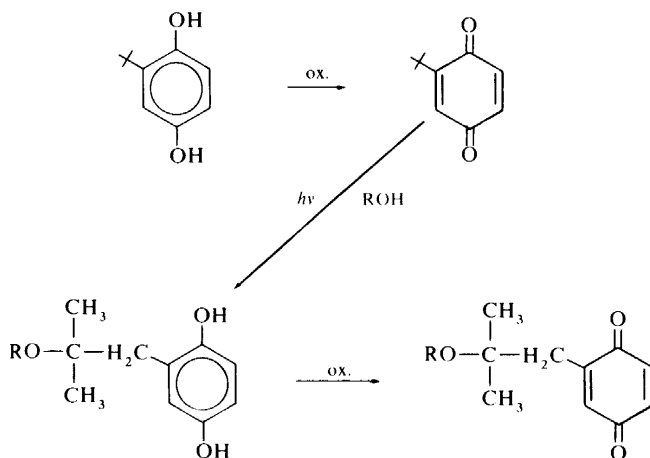
The oxidative transformations of 2,2′-methylene-bis-(4-methyl-6-tert-butylphenol) give rise to compounds with antioxidative activity. Their ability to stabilize to a certain degree various macromolecular substrates is indicated[76, 77, 94, 95] without any knowledge of their structure. However, the transformation of this antioxidant is also considered to be the source of free radicals, acting as initiators during the oxidation of polypropylene[96]. We have investigated in detail well-defined model compounds during the stabilization of isotactic polypropylene and tetralin and have demonstrated the antioxidative activity of the main individual transformation products

and of the synthetically prepared mixtures thereof[78]. At 60°C (tetralin oxidation), the antioxidative properties of the original methylene-bis-phenol and its dimer XXI did not differ, while trimer XXII was somewhat less active. Surprisingly, the mixture of the original methylene-bis-phenol and cyclo-hexadienone XXIII had a synergistic effect.

Good antioxidative properties—although lower than those of the original methylene-bis-phenol—have been found for phenolic products of the oxida-tive coupling (XXI and XXII) in the stabilization of isotactic polypropylene. The antioxidative activity gradually decreases when being recalculated to the same relative content of the hydroxyl groups from the monomeric phenol to the trimer. However, no synergism between the phenolic transformation products is observed in this case, similarly to tetralin. Owing to the presence of phenolic hydroxyls in the coloured transformation products, the latter also preserve a certain antioxidative activity. Alkylperoxycyclohexadienone XXIII added to polypropylene did not even reduce its induction period, although the oxidation proceeded above its decomposition temperature. However, this cyclohexadienone derivative has a distinctly negative effect in a mixture with the original 2,2′-methylene-bis-phenol.

I would also like to mention here the retardative activity of the transforma-tion products of phenolic antioxidants substituted with sulphur-containing groups and thiobis-phenols which appears in the step following the induction period[86, 97]. The retardative activity observed during the stabilization of polypropylene is explicitly a consequence of the presence of the sulphur atoms in the molecule. The character of the transformation products has not been exactly defined.

A complex knowledge of the properties of the transformation products of phenolic antioxidants allows us to evaluate more realistically the mechanism of the antioxidative effect under the conditions of polymer ageing. A large number of authors have contributed independently to the characterization of the products. Isolated products show that after the primary reaction between the antioxidant and the alkylperoxyl 4, further processes follow which are dependent on the conditions of degradation. These processes need not correspond to the course taking place under simulated model conditions; therefore, stoichiometry of the mutual interactions between the antioxidant and the species propagating the kinetic chain is not nearly so simple as could be assumed from pure kinetic studies. In the case of a practical application to the mechanism of action of the antioxidants during the ageing and thermal degradation of polymers, a whole complex of effects play their role in a ratio that is difficult to define, involving—apart from comparatively well-known oxidative and thermal transformations of the antioxidants—also the co-effect of the ions of metals present as impurities or as the residues of the poly-merization catalysts, radiation-induced photochemical reactions, as well as mechanical effects that cannot be neglected either. The products that are formed from the components of the stabilizing mixture in the complicated scheme of the parallel and consecutive reactions are accumulated in the stabilized polymer and affect its stability and appearance depending on their character. Therefore, a mere exact knowledge of the relationships between the structure and effectivity of the antioxidants is insufficient for a complex characterization of the applicability of the antioxidants to specific conditions,

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and the knowledge of the chemistry of transformations must necessarily become more effective. These transformations are valid not only for the region of the investigation of polymer stabilization, but also, with small modifications only, for the stabilization of further technically important organic substrates, such as gasolines, oils, and lipidic substrates in the first place. They also have a potential importance for the study of the interactions of rather complicated systems having the properties of the radical scavengers in the biological systems *in vivo*, especially in the investigation of the processes of biological ageing of humans. It is just for this region, where the synthetic polymers and biopolymers contact each other, that the investigation of the chemical transformations of antioxidants must be stimulated.

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