Some Peculiarities of Phenolic Stabilizers' Consumption and the Role of their Transformation Products in the Oxidation Process

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Some Peculiarities of Phenolic Stabilizers' Consumption and the Role of their Transformation Products in the Oxidation Process

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Problems of kinetics of phenol antioxidants consumption and the role of their transformation in inhibited oxidation process are reviewed. Problems of the choice of the best stabilizer for a specific case are outlined and the method to solve this problem is presented. The main body of the paper, however, concerns the inhibited oxidation of polyolefins.

Keywords: Polyolefins; stabilization; antioxidants; phenols; hindered phenols; side reactions; kinetics of antioxidant consumption

INTRODUCTION

The rapid increase in polymer consumption inevitably leads to the tasks to make these systems stable in service for prolonged periods of time. In addition, it is also required to protect polymers during processing and storage. That is why the right choice of stabilizer is very important.

The most usual type of stabilizers are substances that are able to react with peroxy radicals of substrate, transforming them into some inactive species which are incapable to propagate the chain. For this purpose the substituted phenols are most frequently used. The number of phenolic stabilizers is rather large, but the most effective are the hindered phenols with bulky substituents in the ortho position (1, 2).
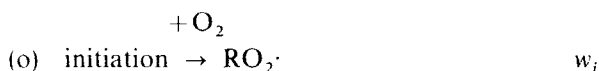
Considering, on one hand, the large number of stabilizers and the other, large variations in exposure conditions and requirements for specific polymeric systems and their applications, it is easy to grasp why is the choice of the optimal stabilizer for a specific case becomes a very difficult problem. In principle this is a problem of selecting an inhibitor with the following properties
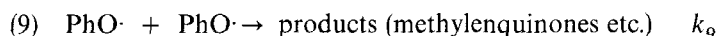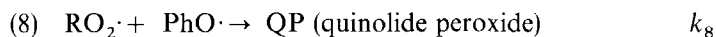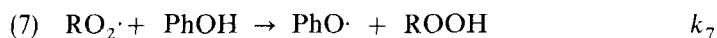
a) full compatibility with the polymer,
b) rather slow consumption rate, which provides sufficient stability during processing and exploitation.

High consumption rate does not always indicate low inhibiting activity, sometimes it is a result of physical losses, but frequently is an indication of inhibitor participation in the side chemical reactions. The complex nature of inhibitor consumption in the polymer prevents the characterization of its efficiency with a single parameter. For the same reason a far extrapolation of results, obtained in the narrow temperature region, can lead to wrong conclusions. Prognosis is further complicated also by the activity of products of inhibitor transformation. Therefore, the kinetic curve of inhibitor consumption, reflecting all processes in the oxidising system, is the only reliable base for evaluation of its efficiency. Some problems connected with kinetics of phenol antioxidants consumption and role of their transformation products in this process are taking into consideration in this paper. The available kinetic information is concerned predominantly with inhibited oxidation of polyolefins. Therefore, all above mentioned problems are considered only for this class of polymers. Sometimes for comparison data for liquid hydrocarbons are given.

KINETIC SCHEME OF INHIBITED WITH PHENOLS OXIDATION

At sufficiently high oxygen pressures the oxidation of polyolefins inhibited with phenols can be described with following main reactions:

$$
\text{(o)} \quad \text{initiation} \xrightarrow{\;+\,O_2\;} RO_2 \cdot \qquad\qquad w_i
$$

$$\text{(2)} \quad RO_2{\cdot} + RH \xrightarrow{+O_2} ROOH + RO_2{\cdot} \qquad k_2$$

$$\text{(3)} \quad ROOH \xrightarrow{+O_2} 2\delta\, RO_2{\cdot} + \text{ products} \qquad k_3$$

$$\text{(7)} \quad RO_2{\cdot} + PhOH \rightarrow PhO{\cdot} + ROOH \qquad k_7$$

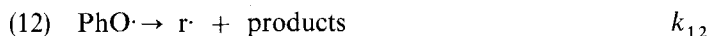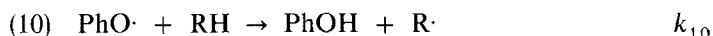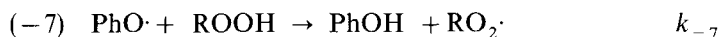$$\text{(8)} \quad RO_2{\cdot} + PhO{\cdot} \rightarrow QP \text{ (quinolide peroxide)} \qquad k_8$$

$$\text{(9)} \quad PhO{\cdot} + PhO{\cdot} \rightarrow \text{ products (methylenquinones etc.)} \qquad k_9$$
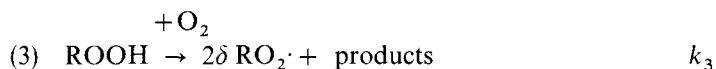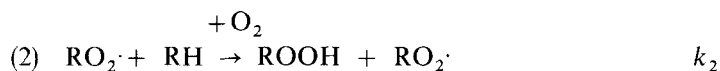
In the more complete variant this scheme can be supplemented with reactions

$$\text{(}-7\text{)} \quad PhO{\cdot} + ROOH \rightarrow PhOH + RO_2{\cdot} \qquad k_{-7}$$

$$\text{(10)} \quad PhO{\cdot} + RH \rightarrow PhOH + R{\cdot} \qquad k_{10}$$

$$\text{(12)} \quad PhO{\cdot} \rightarrow r{\cdot} + \text{ products} \qquad k_{12}$$

$$\text{(13)} \quad PhOH + ROOH \rightarrow PhO{\cdot} + RO_2{\cdot} + \text{ products} \qquad k_{13}$$

In this simplified scheme reactions of alkyl radicals are not taken into the consideration despite the fact that in solid polymer unlike in the liquid hydrocarbons radical concentrations ratio $[R]/[RO_2]$ can be rather high even at the relatively high oxygen pressure [3, 4]. The concentration of alkyl radicals higher, than in the liquid phase, leads under certain conditions to the inhibiting activity of such substances as quinones and methylenequinones in the solid polymer.

In the reaction scheme of direct oxidation of phenol with atmospheric oxygen is also absent. Over a number of years this reaction was considered as one to be taken into account only at the higher temperatures, essentially higher than 200 °C. However during last years data were obtained, which indicated the necessity of consideration of this reaction also at lower temperatures. Among this data are our results of comparison of three phenols consumption in solid polypropylene and in the inert solvent. It was shown, that initial consumption rates for

each phenol in both media are practically equal. So, at 130° inhibitor consumption rate is controlled predominantly by oxidation of phenol itself [5]. Results, obtained in other experiments showed, that even at the much lower temperatures oxidation of inhibitor in the blend PE-PP is to be taken into account [6].

Conclusion about possibility to ignore reaction of phenol oxidation is usually based on the thermochemical calculation for the simple reaction

$$PhOH + O_2 \rightarrow PhO\cdot + HO_2\cdot$$
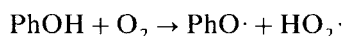
This reaction is strongly endothermic. Its thermal effect can be calculated using the equation

$$q_1 = D_{OH}(HO_2\cdot) - D_{OH}(PhOH)$$

where $D_{OH}(HO_2\cdot)$ and $D_{OH}(PhOH)$ are the energies of O — H bonds in the $HO_2\cdot$ radical and in the molecule of phenol. Rate constant can be estimated taking into account that activation energy can not be lower than value of $-q$, and supposing that preexponential factor has normal value $\approx 10^9$ l/mole sec. Such estimation results in the value of the rate constant which is a few orders lower than that experimentally observed. This discrepancy indicates the complex nature of phenol oxidation process, which most likely proceeds via stages of phenoxy radical formation and its reaction with oxygen. At least such scheme works in the case of model substance-2,6-di-tert-butyl-p-quinone oxidation with oxygen [7].

Above written reactions can be regarded as some upper part of the large complex of chemical processes which is called inhibited auto-oxidation. These reactions describe behaviour of reactions of initial inhibitor or its radical. But as another step it is necessary to take into account also reactions of molecular products arising as a result of this first group of reactions and first of all reactions of substances with pro- or antioxidative activity: quinones, methylenequinones, quinolide peroxides. These three groups of substances are rather well investigated and their properties are known.

However such step by step expansion of the taking into account reactions set makes kinetic description of process difficult or even

impossible, besides such expansion is endless. That is why it is necessary to limit the set of reactions in the each concrete case in order to simplify calculations.

Nevertheless it is necessary to understand clearly how serious can be consequences of such simplification and exclusion of some reactions out of the consideration.

In the accessible reviews [7–10] quantitative data which could characterise activity of the above mentioned products are practically absent. We decided to analyse some of such data, first of all dealing with three types of products of phenols transformation-quinones, methylenequinones and quinolide peroxides.

QUINOLIDE PEROXIDES

During with phenols inhibited oxidation quinolide peroxides (QP) can be formed as a result of reactions of phenoxy radicals with oxygen or with peroxy radicals. In the first case so called symmetric QP of I, II types are formed (for simplicity here are shown QP of ionol), in the second case the asymmetric QP III and IV are formed.

I   II   III   IV
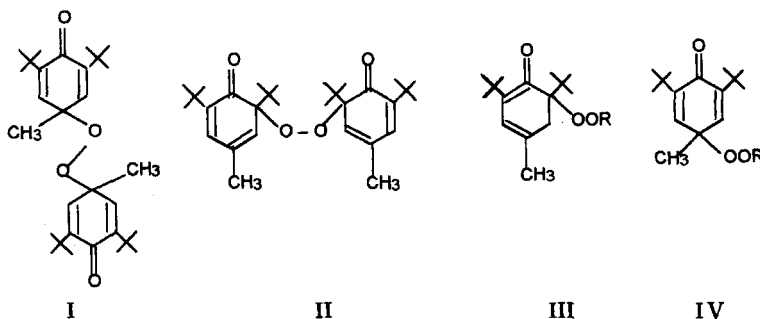
Taking into consideration the simple scheme of inhibited oxidation (initiation and reactions (7), (8) and (9)) the probability of QP formation can be found from equation (1) [11]

$$\alpha^2(1 + \alpha) - A(1 - \alpha)/k_o = 0$$

where

$$A = \frac{k_8^2 W_i}{k_7^2 [\text{PhOH}]^2} \qquad (1)$$

This probability depends on the phenol structure and on the conditions of process. For the very stable 2,4,6-tri-tert-butylphenoxy radicals this probability is practically always equal to 1. The numerical solutions of (1) at different values of parameter A are shown on the Figure 1 [12].

Since as other peroxide substances QP are capable of O — O bond rupture, their decomposition process may lead to two active radicals formation. Thus QP have to influence oxidation process at least under certain conditions.

The decomposition kinetics of QP formed from tri-tert-butylphenol (TTBP) was studied in [13] by two different methods: ESR-stable
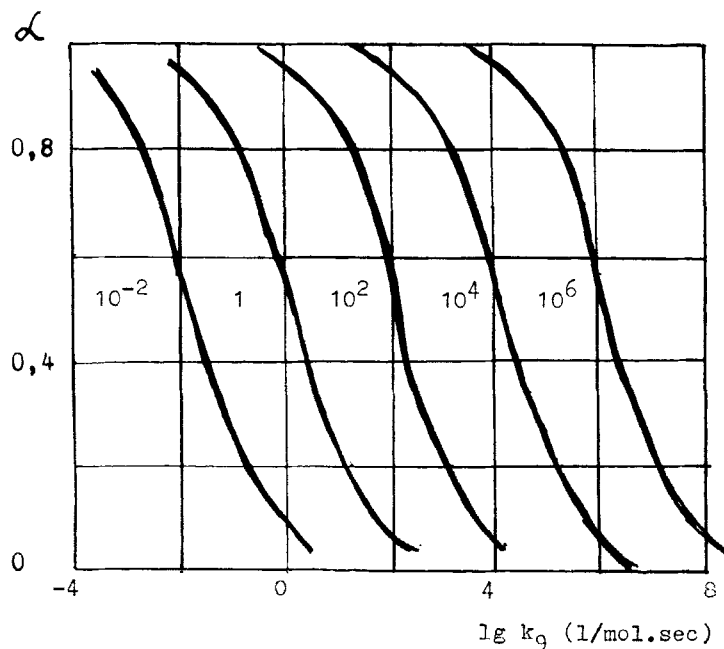

FIGURE 1   Dependence of k_9 on α for different values of parameter A (Values of A are given in the Fig.).

nitroxyl radical consumption rate measurement, and spectropho-tometry-measurement of QP consumption rate. First of these two methods gave information about the initiation rate and second-about the rate of dissociation. It was shown, that QP decomposition fol-lowed the first order kinetics law.

Activation energies values were 29–35 kcal/mole. Some of kinetic parameters of QP decomposition process are given in Table I. From

TABLE I   Kinetic Parameters of QP Decomposition [11]
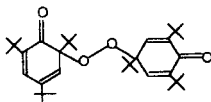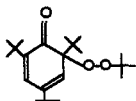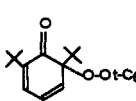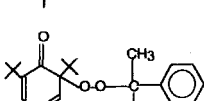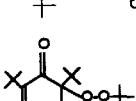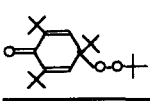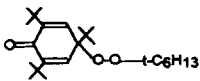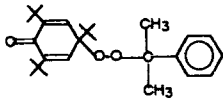
Substance	Solvent	Preexponent, sec^{-1}	Activation energy, kcal/mole	Lg k (90°)	Method[1]
	n-decane	15,4	32,2±1,0	−3,85	A
	solid PP	–	–	−3,54±0,1(102°)	B
	–"–	16,65	35,5±1,5	−4,54	A
	n-decane	14,05	30,5±1,0	−4,18	A,B
	n-decane	14,07	30,6±1,0	−4,2	A,B
	n-decane	15,53	32,2±1,0	−3,72	A
	n-decane	–	–	−3,83±0,5	B
	n-decane	14,55	32,2±1,0	−4,77	A,B
	chloro-benzene	–	–	−3,05±0,2(115°C)	
	cumene	13,46	29,5±1,0	−3,48	
	solid PP	–	–	−6,24	A
	n-decane	13,99	33,0±2,0	−5,74	A

TABLE I   (Continued)

Substance	Solvent	Preex-ponent, sec^{-1}	Activa-tion energy, kcal/mole	Lg k (90°)	Method[1]
	n-decane	13.52	35.4 ± 2.0	−5.73	A
	n-decane	15.69	35.0 ± 2.0	−5.17	A
	n-decane	13.58	33.0 ± 2.0	−6.18	A
	n-decane	12.81	29.0 ± 2.0	−4.6	A
	n-decane	14.4	31.5 ± 2.0	−4.45	A
QPPP	solid PP	–	–	−4.5(115°)	B

[1]A–measurements of active radicals generation (ESR).
B–measurements of QP consumption rate (spectrophotometry).

these data it can be seen, that thermal stability of QP is practically independent on the nature of tert-alkyl substituent bonded with the cyclohexadiene fragment by O—O bridge. Decompositio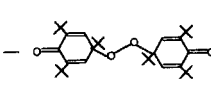n rate constants of p-QP depend on the nature of α-substituent and are much lower then for corresponding o-isomers. Decomposition rate constants of different QP are practically undependent on concentration. Oxygen does not influence decomposition rate but changes the products assortment.

Comparison of two set of data-decomposition rate and initiation rate constants-made possible to calculate values of initiation efficiency (cage effect). In the liquid phase this values are close to 1, in the polymer matrix (polypropylene) they are essentially lower[1].

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[1]Low molecular peroxide was added to the polymer and its consumption rate was studied.

It is important to note, that QP decomposition constants, especially the ones of o-isomers, are much higher then the rate constants of hydroperoxide decomposition.

QP bonded to polymer chain were also synthesized [11]. Authors proved, using different methods, that cyclohexadiene fragment was really bonded to the polymer. Thermal decomposition of this QP was studied and the main product of this process-quinone was registered.

In the other work [14] ionol was added to the oxidised PP, hydroperoxide acted as initiator and as a result QP was formed. Bonding was proved using UV and ESR spectroscopy.

Calculations made for oxidation of PP inhibited with TTBP showed that for three initiation rates-W_1 for hydroperoxide, W_2 for o-QP and W_3 for p-QP the following dependence holds

$$W_1 : W_3 : W_2 = 1 : 0,3 : 3,5 \quad (90\,^\circ C)$$

Decomposition of bonded to polymer QP leads to destruction of polymer chain. For example, after 96 hours of photooxidation tensile strength of the IPP film, containing QP, was twofold lower then of free of QP film [11].

It is obvious, that QP can act as initiator, but sometimes situation becomes more complicated, because in the process of QP decomposition rather strong inhibitors can be formed. For example as a result of QP V decomposition two phenols are formed: 2,6-di-tert-butyl-1,4-benzoquinone VI and 4-tert-butoxy-2,6-di-tert-butylphenol VII [2].

| V | VI | VII | VIII | IX |
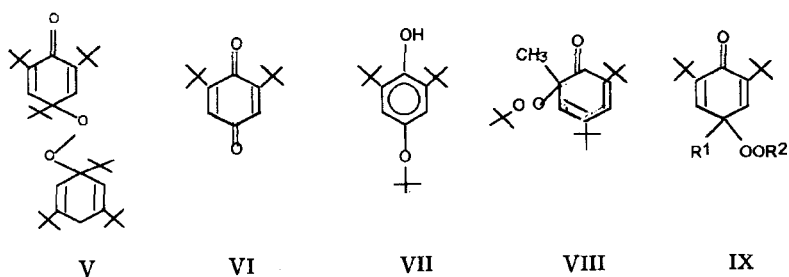
a) R^1 = Me, R^2 = tert-Bu

b) R^1 = R^2 = tert-Bu

c) R^1 = Me, R^2 = H

Formation of inhibitors from QP explains some pecularities of oxidation process. In [15] influence of some nonsymmetrical QP (VIII and IX) on the oxidation of atactic PP (APP) at $120°$ was studied.

Of these substances the most noticeable accelerating effect gives QP VIII, addition of 2×10^{-3} mole/kg of this QP led to oxidation of polymer with constant rate without induction period. At the same time IX a, b and c acted as inhibitors of APP oxidation and inhibiting effect of IXb was stronger than of IXa but the strongest inhibitor was IXc. Induction period of oxidation of APP with 5×10^{-4} mole/kg of QP IXc was 6,6 times longer than for pure polymer. This result most probably is connected with formation of such strong inhibitor as ionol from QP IXc.

Some differences in behaviour of QP in the processes of polymers and liquid hydrocarbons oxidation were observed in [11] and [15]. For example, QP IXc inhibits APP oxidation but accelerates oxidation of tetralin, the same behaviour was observed for QP IXa, but efficiency of the last is lower in the both substrates [15]. The authors explained the observed effect by different oxidation rates of the polymer and hydrocarbon. But in our opinion more probable cause is a different cage effect and as result-different yield of molecular products of decomposition per one leaving cage radical. Besides, if quinone is formed as a product, its inhibition activity may be much higher in the polymer because of higher concentration of alkyl radicals. Another possible cause could be in different products of QP decomposition in different media. It was shown, for example, that decomposition of QP Y in the melt in the absence of solvents does not lead predominantly to phenol formation as in the liquid phase, in the melt both products-phenol and quinone-are formed in the practically equal quantities [16].

METHYLENEQUINONES

Formation of the methylenequinones (MQ) is possible in the process of inhibited with phenol oxidation as a result of reaction between two phenoxy radicals. The key condition of their formation is existance of at least one hydrogen atom at the carbon atom of o- or p-position towards OH-group. Structure of these substances is similar to those of quinones but one of the oxygen atoms is substituted with methylene

group. For MQ formed from hindered phenols the following structures are possible:

I (o-MQ)   II (p-MQ)
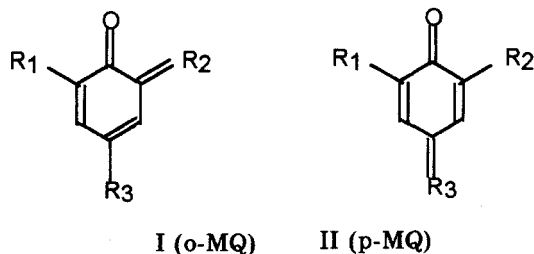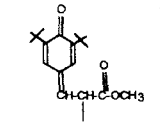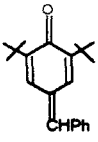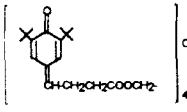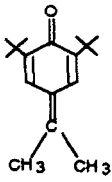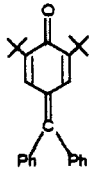
Methylenequinones have high chemical activity. For example, formed from ionol MQ spontaneously dimerises with formation of stilbenequinone and bis-dihydroxyphenylethane even in dilute solutions [17]. Nevertheless some reactions of this MQ were studied. In particular it was shown that it inhibits decane oxidation [18].

Similar to other substances of quinones class MQ effectively react with alkyl radicals. Parameters of this process were measured [19] and some of them are given in the Table II. Alkyl radicals react with double bond of MQ and this mechanism was confirmed by the absence of activity in the case of MQ III. This substance does not inhibit styrene polymerisation even in concentration 10^{-2} mole/l ($60°$, initiation rate $2,5 \times 10^{-7}$ mole/l.sec). Having strongly hindered double bond substance IV is also inactive in this process.

III   IV
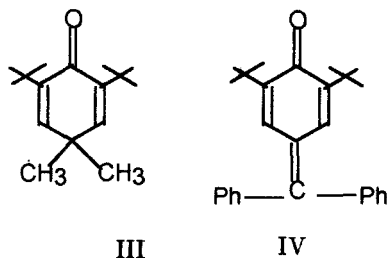
Significant feature of MQ is their ability to react not only with alkyl, but also with peroxy radicals. For example all MQs (except α,α-disubstituted) studied in [20] inhibited cumene oxidation. Termination of almost all chains took place on the molecules of inhibitor. Independence on the oxygen pressure also was a proof of reaction with peroxy radicals. Mechanism of termination seems to be the same

TABLE II   Rate constants of some methylenequinones in the reactions with Alkyl (k_a) and Peroxy (k_7) radicals [19, 20]

Substance	$k_a \times 10^5$ l/mole.sec	$k_7 \times 10^4$ l/mole.sec	k_a/k_7	Method
(structure, n=2)	1.3	0.14	93	A
	0.9	0.058	150	B
(structure, CHPh)	0.18	2.0	0.9	A
(structure, c, n=4)	0.08	0.018	45	A
	0.03	0.018	17	B
(structure, C(CH3)2)	–	1.6	–	A
(structure, C(Ph)2)	doesn't inhibit styrene polymerisation	doesn't inhibit cumene oxidation	–	

A–styrene polymerisation.
B–cumene oxidation.

as for alkyl radicals-addition to the double bond. This mechanism is in agreement with experimental data about nonreactivity of substance without double bond outside the ring. This substance doesn't inhibit cumene oxidation similar to IV with strongly hindered double bond. Absence of phenols in all these experiments was proved by special experiments.

In a number of cases k_7 values for phenol and corresponding MQ are rather close one to another but stoichiometric coefficient of inhibition is lower for MQ and equal to 1 [2]. Measured value of k_7 does not depend on the concentration of MQ in the wide range of concentration values, this fact is evidence of low activity of the from MQ formed radicals. Also it was shown that phenoxy radical formed as a result of reaction between MQ and peroxy radical was inactive in the chain propagation process.
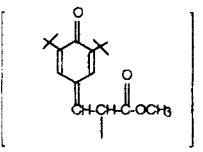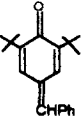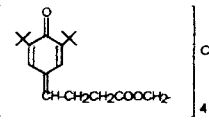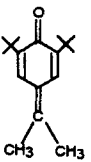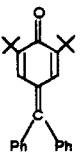
Certain advantage of MQ as inhibitors in comparison with phenols is absence of hydroperoxide-chain branching product-among the products of reaction with peroxy radicals. Rate constants of MQ reactions with peroxy radicals usually are 1–2 orders of magnitude lower, than with alkyl radicals (See Tab. II), but some MQ exhibit equal activity for both types of radicals (for example, V) [19].

Such activity towards both alkyl and peroxy radicals ensure high efficiency of MQ as stabilisers. For example, transformation products of Irganox 1010 and silanophenol inhibit thermooxidative destruction of PP almost just as strong as starting phenols [21]. Quantitative data about some MQ ad PP oxidation inhibitors are given in the Table III [22]. In the solid polymer concentration of alkyl radicals is higher than in the liquid phase, and activity of MQ is determined with combination of reactions with both types of radicals. Simultaneous proceeding of these two reactions leads to dependence of effective k_7 value on oxygen pressure, for example it can be seen for MQ VIII. This MQ has 20–40 times higher rate constant in the reaction with alkyl radicals in comparison to peroxy. For MQ VI such dependence of stoichiometric coefficient of inhibition on O_2 pressure does not exist, because this MQ efficiently terminates kinetic chains via reaction with peroxy radicals.

V   VI
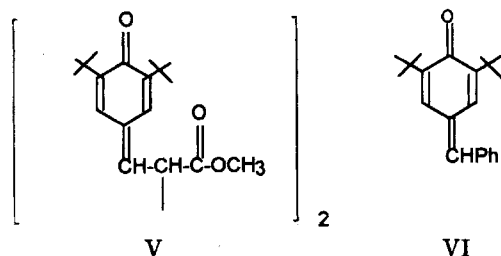
[2] These measurements were made in the presence of initiator. For auto-oxidation term "stoichiometric coefficient of inhibition" is rather senseless.

TABLE III   Stoichiometric coefficients of inhibition and k_7/k_2 values for MQ in the process of with dicumene peroxide initiated polypropylene oxidation [22]

Substance	Gaseous phase	$k_7/k_2 \times 10^3$	f^1_{02}
	oxygen	1,6	0,9
	air	1,6	0,9
	oxygen	0,73	1,8
	air	0,44	2,4
	oxygen	14,0	1,3
	air	9,0	2,1
	oxygen	1,8	3,0
	air	1,8	3,0
	does not inhibit oxidation process		

[1]These values were found from equation $f = w_i \tau_{ind}/[MQ]_0$.

For the most of methylenequinones stoichiometric coefficients of inhibition in the air are higher than in the oxygen. This fact can be explained with the following reaction [22]

$$MQ \xrightarrow{+R\cdot} PhO\cdot \rightarrow PhOH$$
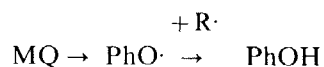
Dependence of antioxidative activity of MQ with the following structure

VII

$$R=CH_3; \quad C_{18}H_{37}$$
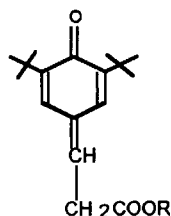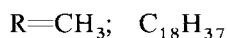
on temperature in the process of tetralin oxidation initiated with azobis-isobutironitrile was observed in [23]. At 65 °C in the chlorobenzene (initiator concentration-5 × 10^{-3} mole/l) both methylenequinones slightly decelerated oxidation, but without initiator at 120 °C (autoxidation of tetralin in the trichlorobenzene solution) they behaved as initiators. It is interesting to note the same behaviour of the non-identified product of ionol transformation in PP (130 °C, air) [24]. In the initiated process of PP oxidation it acted as inhibitor (80 °C), but did not inhibit autoxidation of this polymer at 100 °C.

MQ VIII efficiently stabilises PP melt [25]. Its activity stays the same even after double extrusion. According to authors opinion, MQ of such structure has to have volatility close to the one of ionol and preservation of its activity can be an argument for chemical bonding of this MQ to the polymer chains. Formation of products IX and X in the model reaction of MQ VIII with ethyl radicals demonstrates successful competition of this MQ with O$_2$ for these radicals and confirms high activity of MQ towards alkyl radicals.
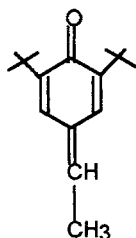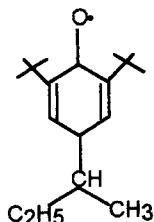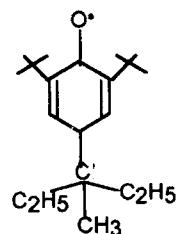
VIII   **IX**   **X**

It is necessary to mention also that besides their own activity in the radical processes MQ are intermediate products in the processes of formation of other compounds with inhibitor ability. For example, dimerization of MQ XI can be considered as possible mechanism of formation of four-nuclear derivative of 2,2-methylenebis-(4-methyl-6-tertbutylphenol) [26]:
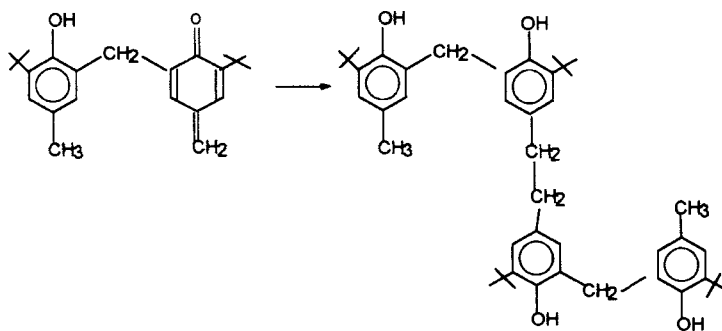
XI

It is necessary to mention however that this dimer can also be the product of benzyl radical XII dimerization:
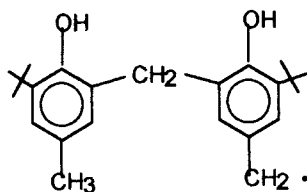
XII

Hypothesis about possible rearrangement of aryloxyradical to the benzyl one was stated in a number of papers, but direct evidences of such process was not obtained till now. As a result of dimerization of methylenequinone-ionol radicals disproportionation product-stilbene-quinone is formed, but inhibiting activity of this compound is rather low [27].

One of the products of Phenol XIII transformation is MQ XIV (hydrogalvinoxyl)-very active inhibitor comparable with ionol. This MQ gives very stable radical product-galvinoxyl XV.
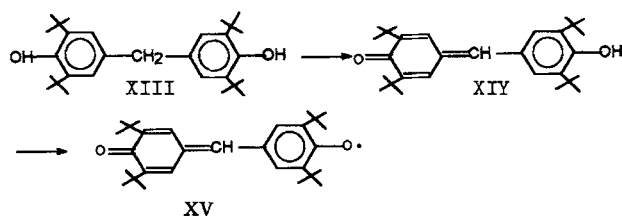
Galvinoxyl is an effective stabiliser of PP melt under conditions of limited oxygen access, when competition with oxygen for alkyl radical is not possible [28, 29]. In this process regeneration cycle arises, because galvinoxyl gives hydrogalvinoxyl that again gives radical. Relative concentrations of galvinoxyl and hydrogalvinoxyl depend on the ratio of alkyl and peroxy radicals concentrations [28].

Transformations of Phenol XIII can be used as an illustration of some sequence of formation of substances with pro- and antioxidative activity during inhibited process. For example, galvinoxyl is able to stabilise the melt in the absence of oxygen, but galvinoxyl is rather easily oxidzed with oxygen, giving quinolide peroxide-initiator, accelerating oxidation of galvinoxyl itself [30] as well as oxidation of polymer. At the same time among galvinoxyl transformation products are phenol and quinone capable to inhibit oxidation and stabilise polymer. Such transformation sequences are typical for phenol antioxidants and can be responsible for different efficiency of phenol antioxidants depending on process conditions (temperature, initiation rate etc.).

QUINONES

Formation of quinones as the products of different phenol antioxidants transformation in the inhibited oxidation process is rather usual. These substances are able to efficiently bonding of alkyl radicals with π-bond system. Usually quinones do not react with peroxy radicals. For example, in decane in the presence of initiator (50 °C, quinone concentration$-10^{-6}-5 \times 10^{-5}$ mole/l, initiator-dicyclohexylperoxydicarbonate) quinones I–IV [3] are being consumed only in the absence of oxygen

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[3] Namely these quinones were chosen because they were transformation products of corresponding 2,6-di-tert-butyl- and 2,6-diphenylphenoles when these phenols were used as inhibitors.

[31]. p-Benzoquinone decelerates initiated oxidation of isooctane at $60°C$ only if its concentration is higher, than 3×10^{-2} mole/l [32].

$$\text{I} \qquad \text{II} \qquad \text{III} \qquad \text{IV}$$
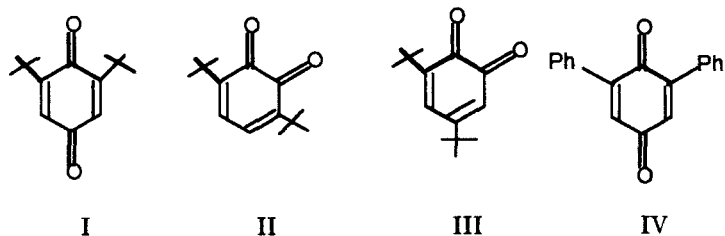
Nevertheless in some cases for example during oxidation of isopropanol [33] quinones can react with peroxy radicals, it was shown that such reaction is possible if corresponding radicals possess reducing power. Reaction with such radicals in solid polymer enables quinone regeneration in the inhibited process. In more details this question will be considered below.

The roles of quinone I and stylbenequinone V in the APP oxidation were investigated in [14]:

$$\text{V}$$
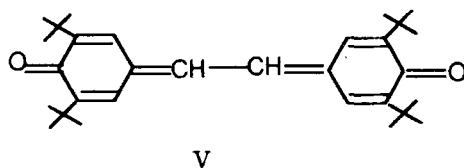
At $120°C$ both substances quinone I and stylbenequinone II inhibited APP oxidation, addition of each of them to polymer in 5×10^{-4} mole/kg concentration led to respective increases in induction period corresponding to 2,2 and 3,4 times. In the solid polymer ratio of alkyl to peroxy radicals concentrations is higher than in the liquid phase as a sequence of diffusion limitations, and some substances that do not behave as stabilisers in the liquid phase can manifest such properties in the solid polymer. The higher are diffusion limitations the higher has to be inhibiting activity of such substances.
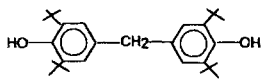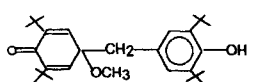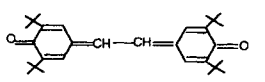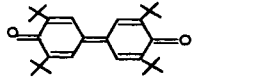
Interesting data dealing with inhibitor regeneration were obtained during investigation IPPoxidation inhibited with bisphenols [34, 35]. It was shown that bisphenols VI and VII terminate chains with typical for such phenols stoichiometric inhibition coefficients (2,5 - 3,6) if benzoyl peroxide was used as initator. If preliminary accumulated

polymer hydroperoxide was used as initiator on the same conditions stoichiometric inhibition coefficients became several times higher.

| VI | VII |
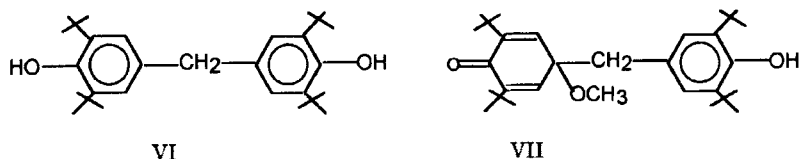
Authors of this work related this effect to formation of quinones in the oxidation process and studied their activity in the process of PE and IPP oxidation. Values of stoichiometric inhibition coefficients for some of investigated quinones are given in the Table IV. As it can be seen from these data, a repeated termination takes place by phenols as well as by quinones addition to polymer. Experiments showed that necessary condition of regeneration process is building of block hydroperoxide. This phenomenon is characteristic for PP oxidation. In the oxidized PE where predominantly isolated hydroperoxide groups are formed regeneration is impossible. Regeneration did not occur also if in PP isolated hydroperoxide groups were formed artificially (during

TABLE IV Inhibition parameters for some phenols and quinones in the reactions of inhibited oxidation of PE and IPP (93 °C) [34, 35]

Substance	Polymer	Initiator	f	$(2k_7/k_2) \times 10^3$	$2K_A/K_P$
	IPP	Benzoyl peroxide	2,5	–	–
	HDPE	Benzoyl peroxide	2,6	–	–
	HDPE	POOH	2,9	–	–
	IPP	POOH	27	–	–
	HDPE	Benzoyl peroxide	1,8	–	–
	IPP	POOH	33	–	–
	IPP	Benzoyl proxide	–	0,5	0,093
	IPP	POOH		5,0	0,68
	IPP	Benzoyl peroxide	–	0,38	0,018
	IPP	POOH		1,0	0,2

[1] Ratio of constants of reactions with alkyl and peroxy radicals.

conjugate oxidation of polymer and cumene). It was also shown that in the containing block hydroperoxides IPP chain termination on the quinone molecules proceeds more intensively and not only in reaction with alkyl radicals but also with peroxy ones. As was already mentioned quinones can react with peroxy radicals possessing reducing power. In this case such radical is $HO_2\cdot$ which formation is a result of hydrogen peroxide decomposition. Hydrogen peroxide can be formed in the process of polymer oxidation during hydroperoxide decomposition. Interaction of $HO_2\cdot$ radical with quinone can lead to inhibitor regeneration. For example:

$$Q + HO_2\cdot \rightarrow PhO\cdot + O_2$$

$$PhO\cdot + RO_2\cdot \rightarrow ROOH + Q$$
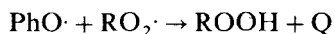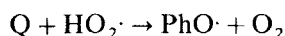
Purposely made experiments with added to PP-chlorobenzene system hydrogen peroxide confirmed validity of hypothesis about $HO_2\cdot$ radical part in the quinones regeneration process. In this case repeated termination also took place. In total, the regeneration cycle can be described as a sequence of reactions:

$$\qquad RO_2\cdot \qquad Q \qquad\quad RO_2\cdot \ \ HO_2\cdot$$

$$ROOH \ \rightarrow \ H_2O_2 \ \rightarrow \ HO_2\cdot \ \rightarrow \ QH \ \rightarrow \ Q \ \rightarrow \ QH \text{ and so forth.}$$
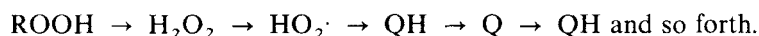
It is necessary to note that from the standpoint of polyolefin stabilisation this result is not very useful, because all these effects arise in the rather deeply oxidised polymer, contained significant concentrations of hydroperoxide. But it is possible that these data could be useful for choice of stabilising composition for the polymers of more complex chemical structure.

Interesting results were obtained during investigation of oxidation ($130°C$, air) inhibited with 4,4'-bis(2,6-di-tert.butylphenol) [36]. Product of this phenol transformation-quinone-shows synergy effect with parent phenol. As it can be seen on the kinetic curves (Fig. 2) from the certain moment phenol consumption becomes slower and concentration of quinone reaches maximum and then begins to fall. Thus, quinone behave as typical intermediate that takes part in the process. Experiments with specially made mixtures of phenol and quinone confirmed existence of synergy effect. One of possible reactions able to explain this
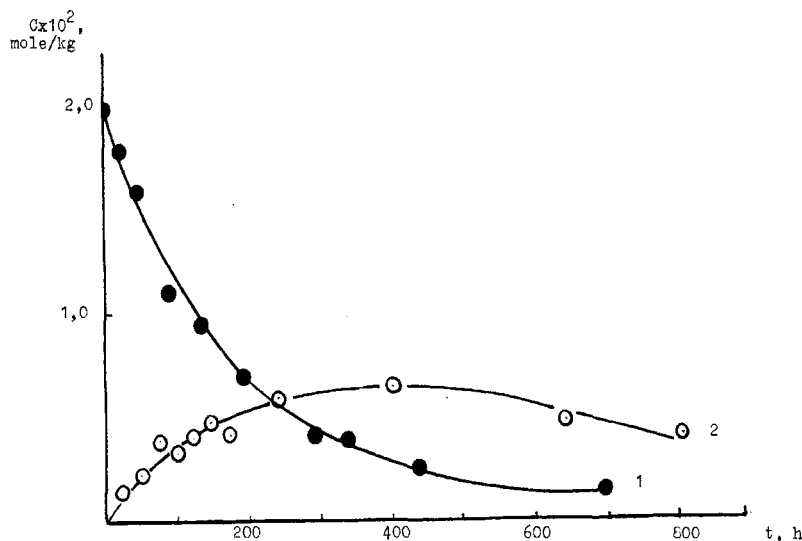
FIGURE 2   The kinetics of bisphenol consumption (1) and diphenoquinone accumulation (2) in the oxidizing polypropylene (130°, air).

effect is reaction between phenol and quinone with formation of active phenoxy radicals:

$$PhOH + Q \rightarrow PhO\cdot$$
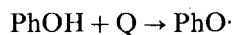
In the process of autoxidation where values of stoichiometric inhibition coefficients are very far from theoretical values, this reaction can give synergy effect.

INHIBITORS CONSUMPTION IN THE OXIDISING POLYMER

All processes of inhibitor consumption can roughly be divided into two groups. The first one-inhibition as such, the second-side reactions. In the absence of these side reactions inhibitor consumption would proceed during some time with constant rate and than consumption rate would decrease sharply till the end of IP. In such situation value of IP would be proportional to initial inhibitor concentration. But such ideal case is very seldom (if at all) realized in the autoxidation

process. Only in the initiated process with rather high initiation rate, the side reactions can be suppressed and it is possible to obtain linear dependence of IP on the concentration of inhibitor and constant consumption rate (equal to initiation rate)[4].

Such effect was observed, for example, in the oxidised PP (PP hydroperoxide acted as initiator) inhibited with TTBP [37].

Among physical processes, leading to the losses of inhibitor, evaporation is the most important one. If consumption of inhibitor is connected with its evaporation, concentration is changing proportionally to the square root of time, the rate of the process is controlled by the rate of inhibitor diffusion towards the surface. If the diffusion does not control the process, it can be described with the first order kinetic law.

Among most important side chemical processes of phenol inhibitor consumption, it is necessary to mention oxidation with oxygen. Partially this problem was considered above, but because of great importance of this process it is useful to return to this subject. Our data show, that oxidation of inhibitor with air oxygen influences its consumption kinetics even at rather low temperatures. This process is especially important at the high inhibitor concentrations. Of the many phenolic inhibitors the lowest oxidation rate (experiments with chlorobenzene solution of inhibitor) has Irganox 1010 (tetrakis [methylene(3,5-di-tert-butyl-4-hydroxyhydrocinnamate] methane). It is interesting to note that unlike the other inhibitors studied by us, the consumption of this inhibitor proceeds at least in the interval of concentration $2 \times 10^{-3} - 10^{-2}$ with constant rate (2×10^{-9} mole/kg sec at $140°$)[5].

As a rule, the kinetic curves of inhibitors consumption are of very complicated appearance, which reflects variety of reactions in this process. Accumulation and consumption of different active products of phenol transformation and hydroperoxide formation is the cause of their contribution to the process.

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[4]In the most common case when side reactions are suppressed τ_{ind} depends on the inhibitor concentration C_0 linearly

$$\tau_{ind} = k\,C_0 + \tau'$$

where τ'–independent on C_0 time, corresponding to the transient period from inhibited to uninhibited oxidation. At the high initiation rates this term can be omitted and proportional dependence can be obtained as in [37].

[5]As was reported in [38] at $120°$ and initial concentration 8.5×10^{-4} mole/kg sec consumption rate for this inhibitor is 7×10^{-11} mole/kg sec.

Some examples of inhibitor consumption curves are given in Figure 3. Variant (a) is a variant for an "ideal" inhibitor with constant consumption rate and distinct transient region. Different intermediate maximums and minimums on the consumption curves (b) usually are due to formation of different products and sometimes maybe to regeneration of inhibitor. Such curves are usual for polymer melts, where concentration is high and contribution of side reactions is especially
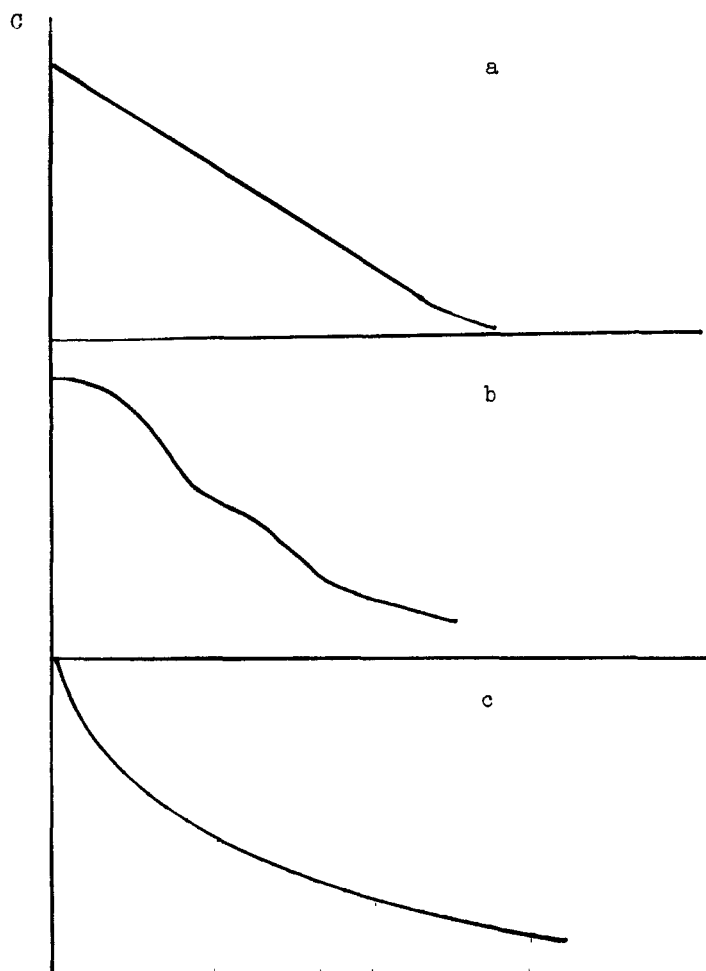
FIGURE 3 Different types of phenols consumption curves in the oxidizing polymer.

significant [39]. First order kinetics of inhibitor consumption (c) can be a result of evaporation as was noted above as well as oxidation. Experiments with three different hindered phenols gave evidence, that oxidation of all of them in the liquid phase (chlorobenzene solution) proceeds in accordance to this kinetic law [5]. Measured effective constants of this process were 8.0×10^{-7} (TTBP), 4.86×10^{-6} (ionol), 5.81×10^{-7} (bis-phenol 2246) $\sec^{-1}$. In PP only consumption of TTBP follows first order kinetics with rate constant 1.15×10^{-6} $\sec^{-1}$.[6] Comparison of consumption processes in liquid phase and polymer showed that initial parts of corresponding curves practically coincide. This fact indicates the primary role of phenol oxidation, at least in the beginning of the process when concentrations are rather high. At the deeper conversions inhibitors consumption rates in PP become faster than in chlorobenzene because besides oxidation of phenol itself, the inhibition process proceeds.

It is possible to evaluate at least approximately the contribution of inhibitor oxidation to the total rate of consumption. For example, the initial rate of TTBP consumption in PP at 130° is about 10^{-8} mole/kg sec [5]. Assuming that the consumption of Irganox 1010 in the same polymer is controlled only by "useful" processes and taking value 4×10^{-10} mole/kg sec for its consumption rate (interpolation between above given values for 120 and 140°), it is possible to come to the corresponding for TTBP as 1.6×10^{-9} mole/kg sec (taking into account difference between stoichiometric coefficients of inhibition for this two phenols). Then "useful" value for TTBP is only 16% of the total consumption rate. This is a very rough evaluation note that it is also necessary to take into account that contribution of the oxidation rate has to be significantly lower at lower inhibitor concentration, and that this contribution has to depend on temperature.

Phenol oxidation undoubtedely proceeds as radical process and can contribute to initiation process, for example as a result of $HO_2\cdot$ radical formation. In its turn this process has to accelerate inhibitor consumption. Lately we studied oxidation of 2,6-di-tert-butyl hydroquinone in the liquid phase and successfully described this pro-

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[6]Phenoxy radical from TTBP does not enter the disproportionating reaction, may be because of this reason such simple kinetics is possible.

cess with scheme in which reaction of phenoxy radical with oxygen as a key reaction was included [7].

Among other side reactions the following one

$$PhOH + ROOH \rightarrow PhO\cdot + RO_2\cdot$$

is to be mentioned. Its contribution can be noticeable at high inhibitor concentrations.

Problem of side reactions in the inhibited oxidation and criteria of taking these reactions into consideration is analyzed in detail in [1].

Formation of new inhibitors in the process of initial inhibitor consumption develops in the appearance of so called secondary IP after removal of starting inhibitor from polymer. For example after removal of ionol from PP oxidized at 200° and oxygen pressure 300 mm secondary IP was observed [44], and authors came to conclusion that new inhibitor is more active than the starting one. It was shown also [24], that after extraction of low molecular substances from the polymer oxidized with ionol (oxidation at 130°, air, initial ionol concentration 10^{-2} mole/kg), besides ionol at least one more inhibitor is present in solution. Rate constant of reaction with peroxy radical of cumene for this inhibitor is $2,7 \times 10^3$ l/mole sec (60°), for the ionol corresponding value is $1,48 \times 10^4$ l/mole sec.

Secondary IP were observed also after elimination of non-reacted inhibitor 2246 in a number of polymers: polyethylene (PE), PP, polyisobutylene (PIB), butyl rubber (BR) [40]. The longest values were observed in PE and PIB, the shortest-in PP. In all polymers value of IP went over the maximum, especially sharp for BR. All results were qualitatively similar, any correlation with polymers oxidability was absent. In the inhibitor consumption process at least two directions of the active products formation exist-inhibited oxidation itself and oxidation of inhibitor. The second unlike the first one seems to be practically independent on the nature of polymer. Proportion of products for every polymer is different even if set of such products is the same in every polymer. The search of a correlation with some property of polymer appears to be hopeless.

Secondary IPs were observed also after washout of low molecular products from PP oxidized at 130° [24]. Polymer was thoroughly washed with benzene but even after this operation some inhibitor

stayed in it. This fact permitted to think that inhibitor which gave this secondary IP was bound to the polymer chain. Such chemically bound inhibitors were observed also be others, for example in [41]. A number of facts give reason for hypothesis of quinomethide structure of these inhibitors bound to polymer chain. It is interesting to note, that similar supposition was made in [41], but authors of that work supposed that bounding proceeds via reaction with hydroperoxide group of polymer. It is necessary to mention that in the case of polynuclear phenols, formation of products with rather high molecular weight is possible. These products elimination is very difficult problem even in the washout process and even more in the evaporation. Therefore, the final evidences of chemical bonding have to be obtained with independent methods.

It is interesting to note that addition of synergistic-hydroperoxide decomposer-di-laurythiodipropionate did not influence consumption rate of three phenolic antioxidants, studied in [23]. This fact indicates that the stationary concentration of PP hydroperoxide in the induction period is low and coincides with calculations, made in [1]. In this connection it is useful to return to the data about synergistic influence on the induction periods of PP oxidation for two antioxidants-Irganox 1010 and EC 63 (octadecyl 3-(3,5-di-phenyl-4-hydroxyphenyl)-propionate) [36]. From these data it is well seen that addition of a synergist significantly increases situation for EC 63 and only slightly for Irganox 1010, as a result the efficiency of both inhibitors becomes comparable. Thus, the influence of synergist is noticeable only for bad inhibitor which can not maintain stationary character of process.

In conclusion it is necessary to analyse one more problem, the problem of inhibitor concentration measurement. Most often for this purpose spectrophotometry is used, usually after elimination of inhibitor from the polymer. For measurements the bond at 270–280 nm is usually used with extinction coefficient $\varepsilon \cong 2 \times 10^3$ l/mole cm. But it is necessary to take into account that adsorption bond of these phenols transformation products lie usually in the same region. For example, in accordance to data given in [17] the characteristic absorption bond for methylenequinones lies in slightly more long-wave region, for different MQ-270–310 nm[7], but the extinction coefficients for MQ are practically an order of magnitude higher, than for phenols. Position of

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[7]For ionol λ_{max} = 278 nm and for corresponding MQ-285 nm [2].

adsorption maximums for QP depend on their structure, for o-peroxides λ_{max} is near to 315 nm ($\varepsilon \cong 3 \times 10^4$l/mole cm), for p-peroxides–230–240 nm ($\varepsilon = (1-2) \times 10^4$ l/mole cm). Thus it is possible to make mistake in measurement of phenol concentration because together with phenol its products can be eliminated. Molecular weights of these products are close to these of phenols and during *in vacuo* evaporation volatilites of these compounds are similar. Besides, some phenols with more than one phenol ring in molecule can give products with partially quinoid and partially phenolic structure. It is rather difficult to consider this fact studying UV spectra. Of course all this difficulties become negligible if conversion of starting phenol is low.

Results of kinetic method of phenols concentration measurements also can be attributed to the starting phenol only at low conversions. This method includes the following operations: extraction of phenol with chlorobenzene, adding of this extract to the mixture of cumene (substrate) and initiator-azo-bis-isobutironitrile, measurement of induction period of cumene oxidation in standard conditions and calculation of phenol concentration using known values of initiation rate and stoichiometric coefficient of inhibition [5]. Possible source of mistake in this case are the phenol transformation products which inhibit or initiate cumene oxidation. But a number of products which distort the result in this case is less than for spectrophotometry. Besides sometimes it is necessary to find total inhibiting potential of system, in such case obtaining result conforms to this requirement.

In theory the ideal method of following the inhibitor concentration is liquid chromatography. But in the process of inhibited oxidation the number of products is high, and this is especially true for the stabilisers with more than one phenolic *nucleus*. But sometimes combination of liquid chromatography with above mentioned methods gives reliable results.

Recently some other methods were proposed for this purpose, but for the present they have not wide application. It seems, that optimal results can be obtained by using a combination of different methods.

CONCLUSIONS

In conclusion some deductions from above considered peculiarities of sterically hindered phenols consumption in the oxidising polymers will be considered.

In the most cases only part of inhibitor, is efficiently consumed. Even if physical losses are absent, a significant decrease of anti-oxidative activity of inhibitor takes place as a result of its participation in the side reactions. This involves primarily in the reaction with oxygen. Depending on the phenol structure othe directions of its non-effective consumption can exist.

Phenol transformation products, mainly methylenequinones, quinolide peroxides are able to contribute to the process of inhibited oxidation. Sequences of influence of each product depends on properties of this product as well as on oxidation conditions. For example among products of QP decomposition, inhibitors can be formed and these inhibitors can balance initiating effect of peroxides and even lead to the inhibition of process. Yield and products ratio depend on conditions and it is the reason of dependence of observed regularities on oxidation temperature and on the substrate type [14,42,43].

The same difficulties arise in the evaluation of MQ role, their behaviour can be different depending on oxidation conditions [22]. As a result of reaction with R· or RO_2· radicals, MQs transform to phenoxy radicals with rather poorly known properties. It is known that these radicals do not participate in chain propagation reactions and, apparently do not react with peroxy radicals, because stoichiometric inhibition coefficients for MQs are close to 1 [19]. This fact indicates low activity of such phenoxy radicals, but it is not enough for conclusion about their absolute inertness. The behaviour of these radicals may influence the final results observed during consumption of methylenequinones in the oxidizing system. In addition, it is necessary to take into account the ability of methylenequinones to dimerize, which can lead to formation of phenols with significant inhibiting effect.

All the above gives evidence that despite rather vast information about behaviour of phenols transformation products it is rather difficult to evaluate their contribution to the phenol consumption in the oxidising system. Further data about hindered phenols consumption kinetics and transformation mechanisms and about properties of products are required to allow us to come closer to the final goal. Namely, which is the best inhibitor for given conditions and substrate.

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