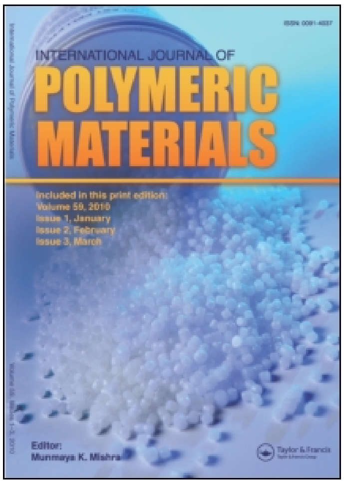

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Experimental Methods for Estimating Stabilizers' Efficiency

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Experimental Methods for Estimating Stabilizers' Efficiency

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Experimental methods for estimating the efficiency of stabilizers of various classes—phenols, amines, phosphites etc.—in various model systems both on the base of polymer and without polymer (low molecular) are described. The large experimental material considered is obtained with the help of various physicochemical methods: manometry, spectroscopy, DTA, calorimetry, chemiluminescence, viscosimetry, polarography etc. Determination of regularities in changes of efficiency of stabilizers characterized by various structures and reactivities allows us to choose the most promising ones for practical use and to look for new active stabilizers more reasonably and purposefully. The elaboration of a mathematical model of the oxidation process permits the creation of the base for semi-empirical forecast of the stabilizer properties.

KEY WORDS Stabilizers, efficiency, experimental methods.

INTRODUCTION

Model systems generally used for estimating stabilizers' efficiency may be divided into two groups: 1. model systems without polymer (reactions of stabilizers with hydroperoxides, radicals, oxygen etc. in solution), 2. polymer model systems.

There is a number of experimental methods for estimation of stabilizers efficiency for every group of model systems based on various physicochemical analyses.

Manometric methods, chromatography, spectrophotometry, chemiluminescence, polarography, ESR-spectroscopy are widely used for the first group of model systems.

Oxidation of solid phase polymeric systems has several specific features: stepped kinetics, levelling of stabilizers activity etc.

The investigation of these systems requires other physical and physicochemical methods (besides mentioned above): from DTA, TGA, DSC to PMR and IR-spectroscopy (carbonyl and hydroxyl indexes) etc.

The analysis of regularities in changes of efficiency of stabilizers characterized by various structures and reactivities allows us to look for new active stabilizers for polymers more rationally and more effectively.

One of the most important problems in chemistry and technology of polymers is the problem of stabilization of polymers.

In many studies[1-20] the destruction of polymers is investigated; various methods for physical and chemical stabilization of polymers are studied too.

One of the most important methods of stabilization of polymers is the chemical one—introduction of stabilizers (inhibitors against oxidation) into polymers.

Synthesis of stabilizers and study of their properties are the integral parts of the chemical method. The estimation of stabilizers efficiency is necessary for the correct choice of the most active stabilizers for practical use.

There are a number of methods for estimation of efficiency of stabilizers—compounds of various classes: phenols, amines, phosphites and others—in different model systems. These systems may include polymer or model low-molecular compound, for example, hydrocarbon.

Large experimental material described in this work is obtained with the help of various physicochemical methods—such as spectroscopy, calorimetry, manometry, viscosimetry, polarography, DTA, chemiluminescence etc.

Complex study of efficiency of stabilizers with various structures permits us to choose the most perspective ones for practical use from the compounds studied.

The results of the works on automation of testing of chemical compounds as stabilizers (with the help of PC for accumulation and treatment of experimental data) allow us to work out the mathematical model of process studied, to create the base for semi-empirical prediction of the stabilizers properties, to investigate their activity and mechanism of action.

1. METHODS FOR DETERMINATION OF STABILIZERS ACTIVITY IN MODEL SYSTEMS WITHOUT POLYMER

Methods for estimation of stabilizers efficiency may be divided into two groups: 1) methods for study of stabilizers reactivity and efficiency in model systems without polymer (oxidation of cumene, ethylbenzene, styrene and other hydrocarbons etc.); 2) methods based on the polymeric model systems.[21]

A number of physicochemical methods may be included in each of these groups allowing us to make conclusions relative to the structure, reactivity in reactions with radicals and molecules, and the influence of stabilizers on the oxidation process of monomeric and polymeric systems.[135-147]

One of the most known methods for kinetic study of liquid and solid state oxidation reactions in monomeric and polymeric systems is the manometrical one.[22]

In connection to the well known schemes of mechanism of oxidation as a radical chain reaction[8,23] the following values may be determined: the induction period of inhibited and non-inhibited oxidation τ, the inhibition constant k_7—the constant of the reaction of inhibitor with the peroxyradical

$$\mathrm{PhOH} + \mathrm{RO_2^{\cdot}} - \mathrm{PhO^{\cdot}} + \mathrm{RO_2H},$$

the inhibition coefficient f, which determines the quantity of chaines terminated by one inhibitor molecule and other kinetic characteristics of the process.

This method is described in detail in a number of articles and books[10,16,24] etc. This is one of the most simple methods. We can measure the quantity of the oxygen absorbed by the media (the rate of absorption of oxygen by the media oxidized). This method permits us to measure the rate of oxidation at the small extent of conversion.

In Table I some results of investigation of stabilizers activity in model reaction of inhibited oxidation of cumene are shown.[25]

As it is seen from the data of Table I, methylenebisphenol (N5) reacts with peroxyradicals more rapidly than 2,6-di-*tert*-butylphenol derivatives (NN 1–3). The rate of reaction of peroxyradicals with naphthol, hydroquinone, para-phenylenediamine derivatives is high too.

Many works on the inhibited oxidation showed that the use of the chemiluminescence method for the measurement of the concentration of peroxyradicals during the process permits us to obtain the quantitative information about kinetics and mechanism.[26]

It is known that the intensity of chemiluminescence, stipulated by the formation of electron-excited products (carbonyl compounds) from $RO_2^{\cdot}$ and deactivation of the latter in presence of the substances reacting with the peroxyradicals is reduced. The quantitative connection between the inhibitors activity and their ability to reduce chemiluminescence is found. The measurement of the dependence of chemiluminescence intensity on the inhibitor concentration during the reaction of initiated by asobisisobutironitrile oxidation of ethylbensene gave a row of relative activity of inhibitors. The data for this row are shown in Table II (the activity of phenol is a standard unit of activity).[33]

These values of relative activity characterize the radical activity of inhibitors,

TABLE I

Rate constants for reactions of peroxyradicals with inhibitors k_7 in model inhibited oxidation of cumene at 60°C[25]

NN	Inhibitor	$\lg K_7$
1.	4-methyl-2,6-di-tert-butylphenol (ionol)	4.34±.03
2.	2,4.6-tri-tert-butylphenol	4.33±.02
3.	Ester of 3,5-di-tert-butyl-4-oxyphenylpropanoic acid and pentaerythritol (irganox 1010)	4.17±.03
4.	Bis-(3,5-di-tert-butyl-4-oxybenzyl)sulfide	4.26±.03
5.	2,2'-methylene-bis-(4-methyl-6-tert-butylphenol)	5.60±.05
6.	α-naphthol	5.27±.04
7.	Hydroquinone	5.29±.09
8.	N,N'-diphenyl-para-phenylene-diamine	5.34±.09
9.	N-phenyl-N'-isopropyl-para-phenylene-diamine (4010 NA)	5.83±.05

TABLE II

Relative activities of inhibitors[53]

NN	Inhibitor	Relative aotivity
1.	α-naphthol	140
2.	β-naphthol	29
3.	4-methyl-2,6-di-tert-butylphenol	8
4.	o-kresol	9
5.	phenol	1
6.	p-nitrophenol	.055
7.	diphenylamine	15
8.	N-phenyl-β-naphthylamine (neozon D)	49

their ability to reduce the concentration of peroxyradicals during the oxidation. The chemiluminescence method is used in static or kinetic variant in connection with the extent of stabilizer activity.

Chemiluminescence and manometric methods give close values of k_7. Each of these methods has its own merits and deficiencies as well as its own limits. Chemiluminescence method is more precise, it may be used for the measurement of high values of $k_7 > 10^4$ L/M·s, when the rate of inhibited oxidation is quite small and cannot be measured by other methods. However, this method cannot be used in case of strong colored antioxidants, for the intensity of chemiluminescence may be reduced because of the absorption of chemiluminescence by antioxidant.

The use of method of chemiluminescence for the measurement of k_7 in solid polymers is quite limitted.

On the contrary manometric method permits to measure k_7 in solid state as well as to measure k_7 for strong colored substances. It is more simple in apparatus getting up.

Quite precise results of measurement of k_7 may be obtained with the help of impulsic methods.[28]

Under the action of light on the oxidized substance in solution in oxygen atmosphere peroxyradicals are formed. Their decay at low temperature in the presence of inhibitors is carried out mainly by the reaction with inhibitors. The value of k_7 may be obtained during the investigation of the kinetics of ruin of peroxyradicals by the ESR method.[16,29,30]

The ESR method permits us to study the kinetics of decay of inhibitors radicals,[31-33] whose stability causes the efficiency of stabilizers at the great extent. The data on the kinetics of phenoxyradicals (of ionol, santonox, irganox 1010, ethanox 330 etc.) decay—the values of the radicals life time—are in good correlation with the antioxidative activity in cispolyisoprene rubber, measured by the method of viscosimetry. The correlation is disturbed at the high temperature (>100°C) because of the volatility of compounds.

Authors[34,35] studied the stability of 4-R-2, 6-di-*tert*-butyl-phenoxyradicals (R –

CH_3, C_2H_5, CH_2OH, CH_2Br). The data on kinetics of the decay of radicals in benzene and the same data for 4-isopropyl-derivatives[36] are given in Table III. The values of rate constants of decay and the periods of semi-conversion for 4-R-2, 6-di-*tert*-butyl-phenoxyradicals from the Table III show that the stability of radicals raises in the following sequence of substituents:

$$CH_3 < C_2H_5 < \text{iso-}C_3H_7 < CH_2OH < CH_2Br \ll \textit{tert-}C_4H_9.$$

The radical 2,4,6-tri-*tert*-butyl-phenoxyl is stable, may exist in the absence of oxygen for a long time.

The causes of the high stability of phenoxyradicals studied are: 1. delocalization of non-twin electron in the π-bond system of phenolic ring and 2. space screening of the atom, which has formally non-twin electron, by the ortho-*tert*-butyl substituents.

Besides the interaction between inhibitors and radicals $RO_2^{\cdot}$, the reactions

$$PhOH + R^{\cdot} - PhO^{\cdot} + RH,$$

where R is alkyl radical, play the considerable role in the process of inhibited oxidation of polymers.

As in the reactions with the peroxyradicals, the bonds O—H (in the case of

TABLE III

Kinetic parameters for the ruin of 4-R-2,6-di-*tert*-butyl-phenoxyradicals[34–36]

NN	R	Temperature, °C	K_1*, sec^{-1}	K_2*, $M^{-1}.sec^{-1}$	$\tau_{1/2}$**, sec
1.	CH_3	25	$1.35.10^{-2}$	-	51
2.	C_2H_5	21	$2.50.10^{-2}$	-	139
		26	$.78.10^{-2}$	-	88
		47	-	25.4	24
3.	iso-C_3H_7	40	-	3.87	-
		50	-	5.1	-
4.	CH_2OH	50	$.89.10^{-2}$	-	-
5.	CH_2Br	50	$.10.10^{-2}$	-	-

Notes:

* K_1 and K_2 - rate constants of ruin of phenoxyradicals,

** $\tau_{1/2}$ - period of semi-conversion of phenoxyradicals.

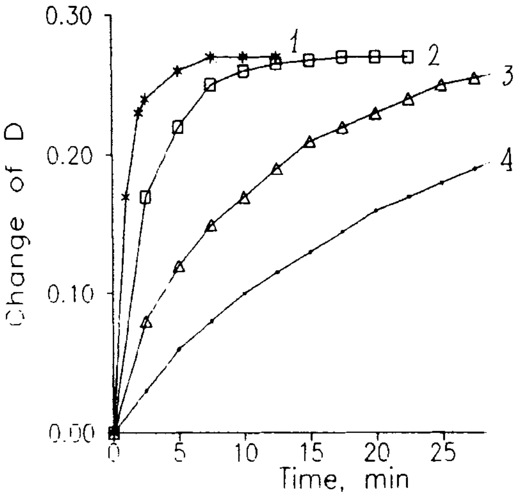


FIGURE 1 Kinetics of interaction of DPPH with bisphenols: 1—2,2′-methylene-bis-(4-methyl-6-*tert*-butylphenol), 2—2,2′-benzylydene-bis-(4-methyl-6-*tert*-butylphenol), 3—2,2′-methylene-bis-(4,6-di-*tert*-butylphenol), 4—2,2′-methylene-bis-(4-chlor-6-*tert*- butylphenol).[38]

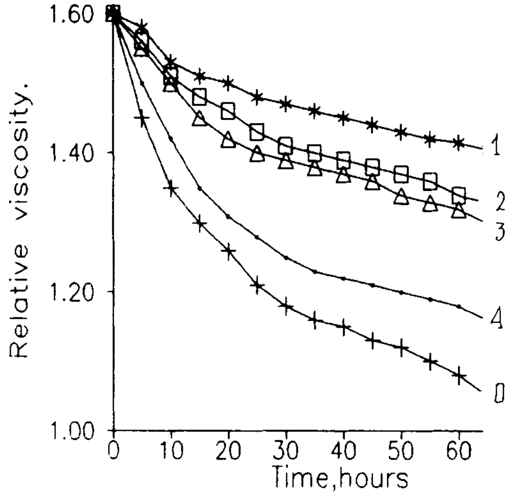


FIGURE 2 Relative viscosity of SKI-3 rubber solutions, containing stabilizers 1–4 (see legend to Figure 1, 0—without stabilizer), during thermooxidation at 100°C.[38]

phenolic inhibitors) and N—H (in the case of amines) are attacked.[16,21] The reactivity of inhibitors (phenols, amines) is determined by the easiness of the separation of the mobile atom H. The stronger is inhibitor, the easier is interaction of it with radicals. So inhibitors, active to alkyl radicals, are generally active to radicals $RO_2^{\cdot}$.

As a model reaction in this case inhibited polymerization of styrene is used. The rate of reaction is determined with the help of dilatometric method by the measurement of the reaction mixture volume during the process of polymerization.

This method was used in Reference 37 for the study of efficiency of para-phenylenediamine derivatives—active antioxidants for synthetic rubber.

The reaction of inhibitors with the radical diphenylpicrylhydrazyle (DPPH) is suitable model which permits us to receive the information about the easiness of separation of atom H from the molecules of phenols, amines and others.

DPPH is stable in solution having violet color. The change of its concentration in solution during the reaction with inhibitor is measured by spectrophotometry (electronic spectra of reaction mixture in the visible region).

Kinetic curves for reaction between DPPH and a number of bisphenols[38] are given in Figure 1.

The order of activity for bisphenols characterized by different structures (obtained on the base of these data) correlates with the order of efficiency of bisphenols during protection of the rubber SRI-3 solutions against thermooxidation (method of viscosimetry, Figure 2).[38] Rate constants for model radical reactions of mono-, bis- and thiobisphenols are given in Tables IV and V.[39,40]

As it is seen from these Tables, the nature of para- (Table IV) and ortho- (Table V) substituents influences on the reactivity of the compounds studied in the model reaction with radical DPPH. It was shown with the help of IR-spectroscopy method that there is good correlation between the radical reactivity of these compounds and efficiency of their antioxidative action in model polymeric systems (on the base of polypropylene and others).

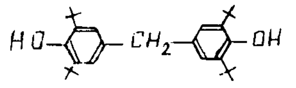
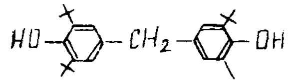
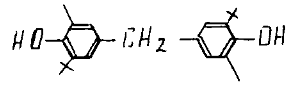
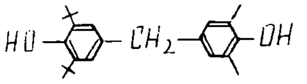
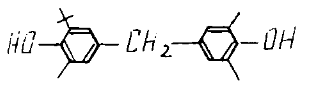
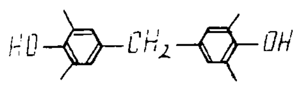
TABLE IV

Rate constants *K* for model reaction of DPPH with phenolic derivatives[39]

NN	Compound	K, $M^{-1}sec^{-1}$
1.	4-methyl-2-α-methylbenzylphenol	3.5
2.	4-ethyl-2-α-methylbenzylphenol	2.4
3.	4-iso-propyl-2-α-methylbenzylphenol	2.5
4.	4-sec-butyl-2-α-methylbenzylphenol	2.6
5.	4-chlor-2-α-methylbenzylphenol	.3
6.	2-α-methylbenzylphenol	.3
7.	2,2'-methylene-bis-(4-methyl-6-tert-butylphenol)	14.1
8.	2,2'-methylene-bis-(4-ethyl-6-tert-butylphenol)	9.6
9.	2,2'-methylene-bis-(4,6-di-tert-butylphenol)	7.3
10.	2,2'-methylene-bis-(6-tert-butylphenol)	3.2
11.	2,2'-methylene-bis-(4-chlor-6-tert-butylphenol)	3.6
12.	2,2'-methylene-bis-(4-brom-6-tert-butylphenol)	2.6
13.	2,2'-thio-bis-(4-methyl-6-tert-butylphenol)	25
14.	2,2'-thio-bis-(4,6-di-tert-butylphenol)	11
15.	2,2'-thio-bis-(4-chlor-6-tert-butylphenol)	10
16.	2,2'-thio-bis-(4-brom-6-tert-butylphenol)	6.5

TABLE V

Rate constants K for the reaction of DPPH with 4,4'-methylene-bis-phenols[40]

NN	Compound	K, $M^{-1}.sec^{-1}$
1.		.4
2.		2.7
3.		4.8
4.		7.1
5.		8.3
6.		20.5

One of the most important characteristics of stabilizers is their ability to decompose hydroperoxide nonradically. During the oxidation of various organic compounds hydroperoxides are the primary products of reaction. These products decompose slowly forming radicals which have the ability to give birth to oxidation chains. As a result the process of oxidation goes on with autoacceleration.

Stabilizer prevents the autoacceleration of the process by decomposition of hydroperoxides.

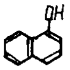
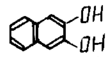
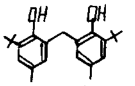
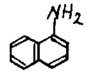
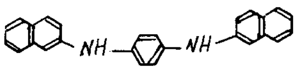
It is convenient to estimate the efficiency of stabilizers with the help of model reaction with various low molecular hydroperoxides (for example, of cumene, tetraline, *tert*-butyl etc.). The rate of hydroperoxide decomposition is determined by the measurement of the reduction of hydroperoxide concentration by means of iodometric titration.

In Table VI there are the rate constants for reactions of some phenols and aromatic amines with cumene hydroperoxide.[23]

The rate of decomposition of hydroperoxide and the time of semi-decomposition of hydroperoxide in the presence or absence of stabilizer are frequently measured. In addition, it is important to know the radical exit per one reacting hydroperoxide molecule.

TABLE VI

Rate constants K for reactions of phenols and aromatic amines with cumene hydroperoxide[23]

NN	Compound	K, $M^{-1}.sec^{-1}$
1.	2,6-$(CH_3O)_2C_6H_3OH$	$6.5.10^{-3}$
2.	4-(CH_3)-2,6-$(C_4H_9)_2C_6H_2OH$	$3.0.10^{-4}$
3.	2,4,6-$(C_4H_9)_3C_6H_2OH$	$7.8.10^{-5}$
4.		$6.7.10^{-4}$
5.		$4.5.10^{-3}$
6.		$4.2.10^{-4}$
7.		$1.4.10^{-4}$
8.		.14

The increase of decomposition rate needs to be accompanied by the decrease of radical exit—for effective inhibitor.

It is possible to use the "method of inhibitors" (by induction period)[6] or chemiluminescence method[26] for the determination of the rate of radical formation.

The kinetics is studied and the values of rate constants for the reactions of a number of aliphatic and aromatic phosphites of different structure with cumene hydroperoxide in solution of benzene are determined in the Reference.[41] The results obtained are shown in Table VII. Authors of this work used the polarographic method of reduction on the cathode for the determination of the hydroperoxide. As it is seen from the Table VII, aromatic phosphites have lower reactivity than aliphatic phosphites. The reason of this is probably the polar effect of substituents near the phosphorus atom.

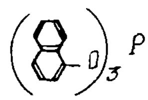
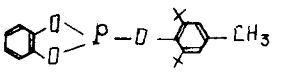
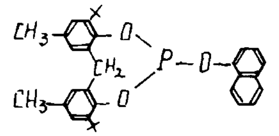
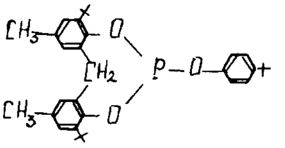
Polarographic method is used also for determination of potentials of one-electron oxidation of stabilizers. The values of these potentials may be the characteristics of stabilizers efficiency.[42–45] The electrochemical oxidation of various organic compounds is carried out generally on the graphite anode (polarograph with the potentiostate); comparative electrode is usually calomel.[46,47]

In Table VIII there are the values of potentials of electrochemical oxidation E for various bisphenols in standard acetate and borate buffer solutions.

The comparison of values E to the rate constants for the radical reactions and to the results of investigation of stabilizers efficiency in polymeric model systems shows that the oxidation potentials may be used with success for the estimation of inhibition activity of compounds.

TABLE VII

Rate constants for reactions of phosphites with cumene hydroperoxide in benzene[41]

NN	Compound	$K.10^3, M^{-1}sec^{-1}$
1.	$(n\text{-}C_4H_9O)_3P$	83.3
2.	$(C_6H_{11}O)_3P$	77.9
3.		5
4.		1.3
5.		.8
6.		.8

The study of electronodonor ability of various stabilizers in the reaction of complexation with tetracyanethylene and the comparison of the results to the antioxidative activity is of some interest.[48–50]

The linear dependence between the values of frequency of charge transfer band in UV-spectra and logarythm of rate constant for reaction of bensene and phenol derivatives with the peroxyradical is observed. The authors of this work propose to consider the charge transfer band frequency as one of indexes of antioxidative activity.

The oxidation of tetraline,[51] decaline and other hydrocarbons may be the model reaction. For example in Table IX[54] the data of relative antioxidative activity of haloid- and alkyl-cathechols obtained during the oxidation of tetraline at 65°C are shown. These data are in good correlation with the results of investigation of stabilizers efficiency at the oxidation of polypropylene.[52]

2. METHODS FOR ESTIMATION OF STABILIZERS EFFICIENCY IN POLYMERIC MODEL SYSTEMS

In spite of many common features of the model reactions in liquid phase and in solid polymers, it is necessary to estimate the stabilizer efficiency not only in liquid

TABLE VIII

Potentials of anodic oxidation *E* for bisphenols[46,47]

NN	Compound	E^0, V
1.	2,2'-methylene-bis-(4-methyl-6-tert-butylphenol)	.54
2.	2,2'-methylene-bis-(4-ethyl-6-tert-butylphenol)	.57
3.	2,2'-methylene-bis-(4,6-di-tert-butylphenol)	.59
4.	2,2'-methylene-bis-(6-tert-butylphenol)	.6
5.	2,2'-methylene-bis-(4-ohlor-6-tert-butylphenol)	.64
6.	2,2'-methylene-bis-(4-brom-6-tert-butylphenol)	.6
7.	1,1'-bis-(3-methyl-5-tert-butyl-6-oxybenzyl)ethane	.61
8.	2,2'-bis-(3-methyl-5-tert-butyl-6-oxybenxyl)propane	.64
9.	2,2'-benzylydene-bis-(4-methyl-6-tert-butylphenol)	.65
10.	2,2'-thio-bis-(4-methyl-6-tert-butylphenol)	.57
11.	2,2'-thio-bis-(4,6-di-tert-butylphenol)	.61
12.	2,2'-thio-bis-(4-chlor-6-tert-butylphenol)	.62
13.	2,2'-thio-bis-(4-brom-6-tert-butylphenol)	.63
14.	2,2'-thio-bis-(4-methyl-6-cumylphenol)	.66

phase model systems but also in solid phase ones—in polymers. The stabilizer efficiency in polymers is dependent on some specific factors—such as influence of solid phase on stabilizers reactivity, compatibility of stabilizer with polymer, solubility of stabilizer in polymer, chemical and physical stability of stabilizer against high temperatures during the treatment of polymer etc.

The investigation of stabilizers activity in polymers in natural conditions takes a lot of time, so accelerated methods are generally used. The acceleration of oxidation process is reached by raising of temperature or pressure of oxygen.[1]

For estimation of stabilizers efficiency in polymers some parameters, characterizing the properties of polymers containing stabilizers—such as viscosity, change of weight, heat effect, induction period of oxidation, durability (tensile strength), elasticity, elongation at break etc.—are used.

There is usually an analogy in these parameters change. So we can see such analogy in change of viscosity, elongation and absorption of oxygen during thermooxidation of polypropylene.[55]

Polyethylene, polypropylene, polyisoprene etc. are used as model polymers.

Among the reactions of oxidation of polymers in solid phase the reaction of initiated oxidation of polypropylene is the most fully studied. This reaction may be the test for the investigation of stabilizers ability to terminate oxidation chains during the process of oxidative destruction of polymers.

Oxidation rate is determined by the measurement of oxygen absorption on the

TABLE IX

Relative antioxidative activity of haloid- and alkyl-cathechols measured during the oxidation of tetraline at 65°C[54]

NN	Antioxidant	Relative Activity IP/IP_s *
1.	4-brom-cathehol	.65
2.	4,5-di-brom-cathehol	.706
3.	3,4,5-tri-brom-cathehol	.794
4.	Tetrabromocathehol	.95
5.	4-chlor-cathehol	.65
6.	4,5-di-chlor-cathehol	.725
7.	Tetrachlorocathehol	.962
8.	4-methyl-cathehol	1
9.	4-tert-butylcathehol	.962
10.	Tetrabrom-1,2-benzoquinone	.394
11.	4,4'-iso-propylydene-bis-(2,6-di-chlorphenol)	.297

* IP - induction period of oxidation;

IP_s - induction period of oxidation for standard
(standard - 4,4'-iso-propylydene-bis-phenol).

manometric unit (this operation is analogous to the same one for model reaction of liquid phase oxidation).[21]

During the investigation of the process of oxidation of polymers in solid phase the fact of levelling of the stabilizers reactivity was found. The decrease of the oxidation rate in solid phase in comparison to the liquid one and the decrease of the difference in the values of rate constants of oxidation in presence of antioxidants various in structure are observed.

In Table X[8] the rate constants for the reaction of oxidation chains termination by phenols at temperature 80°C in solid polypropylene k_{is} and liquid ethylbenzene k_{il} are shown. It appears from the Table X that the rate constants for liquid phase are higher than the solid phase constants. The value of k_{il} for para-methoxyphenol (compound N 1) is 70 times higher than the value of k_{il} for para-CN-phenol (compound N 10).

The value of k_{is} for compound N 1 is only 14 times higher than the value of k_{is} for compound N 10. So we see that in solid state there is a 5-fold decrease of stabilizers activity.

It is too difficult to explain this fact with the help of diffusion as a limiting step of reaction because the rate constants for diffusion limited reaction, calculated with the help of known coefficients of diffusion (for ionol as an example) is 3–4 times higher than the experimental values.

TABLE X

Rate constants for oxidation chains termination by phenols at 80°C in polypropylene K_{is} and ethylbenzene K_{il}[8]

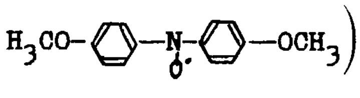
NN	Para-substituent in phenol	$K_{is} \cdot 10^{-3}$ kg/mole.sec	$K_{il} \cdot 10^{-4}$ kg/mole.sec	K_{is}/K_{il}
1.	OCH_3	8.1	20	25
2.	$OC(CH_3)_3$	3.9	8.3	21
3.	CH_3	3.5	3.5	10
4.	C_6H_5	1.8	3.3	18
5.	$C(CH_3)_3$	3.2	2.6	8
6.	Cl	2.7	1.4	5
7.	CHO	.6	.8	13
8.	$COCH_3$	.5	.4	8
9.	COC_6H_5	1	.3	3
10.	CN	.6	.3	5

However there is the correlation of rate constants to molecular mobility characterized by the frequency of rotation of para-magnetic sonde—nitroxyl radical.[56] These data may be explained with the help of model of hard polymeric cell.

The mutual orientation and rotation of particles in polymer are difficult because of the rigidness of polymer cell which does not change during the elementary act. The particles have to orient one to another in specific order to form the structure of activated complex. The more rigid the walls of polymer cell are, the more energy this process takes.

The increase of rigidity of polymer cell walls leads to decrease of rotation frequency for nitroxyl radical and so the correlation of rate constants of reactions in polymers to rotation frequency for nitroxyl radical is observed.

O. N. Karpukhin, T. V. Pokholok and V. Ya. Shlapintokh[57] have worked out the method for measurement of antioxidants efficiency in polymer for comparing the reactivities of antioxidants in liquid phase and in solid polymer. These authors have taken as a characteristic of antioxidative efficiency the value of the rate constant for the reaction between antioxidant and the radical. The latter is the decomposition product of initiator—dinitrile of asoisobutyric acid introduced in polymer together with the stable NO˙radical

(for example— )

and antioxidant studied. By means of the measurement of the reaction kinetics they have determined the relationship between the rate constant for interaction of inhibitor (k_2) and the stable radical (k_1) with the free radical of initiator. This was derived from the dependence of the rate of expenditure of NO$^{\cdot}$ radical on the concentration of antioxidant). This value characterizes the relative reactivity of antioxidant in the reaction with the free radical.

As it appears from the Table XI, the difference in values k_2/k_1[73] is not as large for antioxidants studied as is the difference in values of k_5 (the rate constant for the reaction of antioxidants with the peroxyradical of ethylbenzene in liquid phase).

Bisphenol N 7 (Table XI) is more than 100 times more active than phenol in liquid phase, but in polystyrene the difference between these two compounds is 17 times smaller.

In the work of E. V. Bystritskaya, O. N. Karpukhin and G. S. Karpovich[58] the relation between the rate constants for reactions in liquid k_1 and solid k_s phases is obtained on the basis of simple geometric model, the difference in life time for the pair of meeting reagents particles in solid and liquid phases and specifics of their mutual movement. The dependence obtained $k_s \sim \sqrt{k_1}$ has been examined with the help of experimental data for rate constants of reactions between antioxidants and peroxyradicals; good correlation is noted in many cases.

The relation mentioned above is of important theoretical and practical interest because one can estimate the antioxidant activity in polymer on the basis of the data on kinetics of liquid phase oxidation for model systems.

There is a lot of methods for estimation of stabilizers efficiency in polymer model systems: manometry, viscosimetry, chromatography-massspectrometry, HPLC, DTA, TGA, TVA, DSC, NMR-, UV- and IR-spectroscopy (FTIR, MDCIR and others) etc.[81-134]

The measurement of the reaction rate and induction period for oxidation of isotactic polypropylene is carried out at 114°C, initiator—cumene peroxide.

TABLE XI

Efficiency of antioxidants in solid polystyrene at 70°C[73]

NN	Compound	$K_2/K_1 \cdot 10^2$	$K_5 \cdot 10^{-4}$, M^{-1}, sec^{-1}
1.	Phenol	1	.3
2.	4,4'-methylene-bis-(2,6-di-tert-butyl-phenol)	5	2.6
3.	4-methyl-2,6-di-tert-butylphenol	5.6	2.5
4.	Ester of 3,5-di-tert-butyl-4-oxyphenyl-propionic acid and pentaerythritol	6.3	4.7
5.	α-naphthol	7.3	44
6.	2,2'-thio-bis-(4-methyl-6-tert-butyl-phenol)	12	18
7.	2,2'-methylene-bis-(4-methyl-6-tert-butylphenol)	17	48

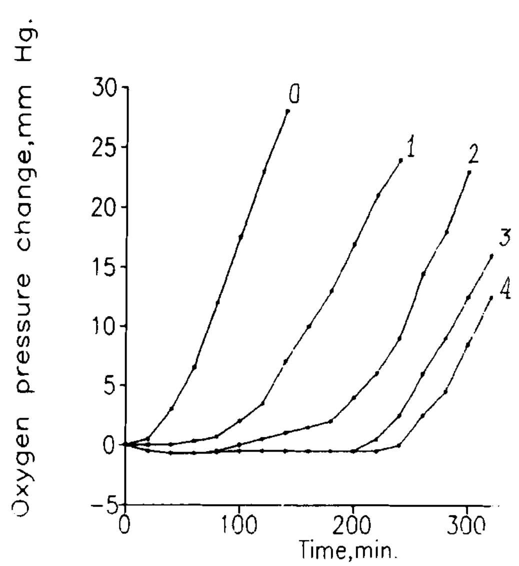


FIGURE 3 Kinetics of oxidation of polypropylene at 114°C in presence of 2,4-di-nonyl-6-(3',5'-di-*tert*-butyl-4'-oxybenzyl)phenol (1), 4-nonyl-2,6-di-(3',5'-di-*tert*-butyl-4'-oxybenzyl)phenol (2), 2,2'-methylene-bis-(4-methyl-6-*tert*-butylphenol) (3) and ester of 2,6-di-*tert*-butyl-4-*n*-butylphenol and maleic acid (4); 0—without stabilizer.

We see in Figure 3, for example, the kinetic curves for oxidation of polypropylene in presence of some stabilizers. It is seen that the induction periods of oxidation of polypropylene consist 100–200 minutes and depend on the efficiency of stabilizers studied.

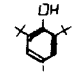
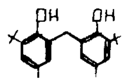
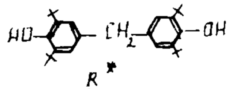
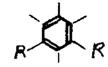
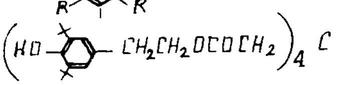
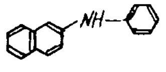
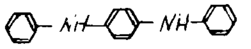
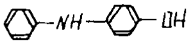
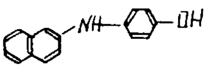
The oxidation of 1,4-*cis*-polyisoprene may be used as a model system for estimation of efficiency of stabilizers for elastomers. The kinetics of this process has been studied in References 59–64. There are some kinetic characteristics for the inhibitors of oxidation of 1,4-*cis*-polyisoprene (353 K, P_{O_2} = 10^5 Pa) in Table XII.[23,64]

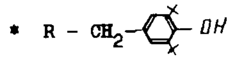
The rate of oxygen absorption by polyisoprene films in presence of different stabilizers is investigated in many studies[65,66] etc. There are the kinetic curves for oxidation of polyisoprene in presence of some stabilizers at 150°C in Figure 4. It is seen that the stabilizers based on 2,6-di-*tert*-butylphenol with unsaturated groups, which are able to join the polymer, have high values of induction periods. These values are close to the value of induction period for such active stabilizer as 2,2'-methylene-bis-(4-methyl-6-*tert*-butylphenol).

It is necesary to note that IR-spectroscopy is widely used for estimation of stabilizers efficiency in polymers. Efficiency characteristics—carbonyl and hydroxyl indexes—are obtained on the basis of kinetic study of the increase of intensity of the bands of valent vibrations of CO-groups (~1700 cm^{-1}) and OH-groups (~3600 cm^{-1}). This method is used, for example,[67–72] for the study of process of oxidation of elastomers. Some results of these investigations are shown in Figure 5.

TABLE XII

Kinetic characteristics for inhibitors of oxidation of 1,4-*cis*-polyisoprene (353 K, P_{O_2} = 10^5 Pa)[23,64]

NN	Inhibitor	$K_7(2K_t)^{-1/2}$, $(kg/mole.sec)^{1/2}$
1.		43
2.		42
3.		38
4.		32
5.		36
6.		52
7.		333
8.		3.9
9.		4.6



3. COMPLEX APPROACH TO ESTIMATION OF STABILIZERS EFFICIENCY

Complex study of stabilizers efficiency with the help of various methods gives very important results.

On the base of investigation of kinetics and mechanism of the chain processes, the complex of methods is worked out for the rapid quantitative testing of chemical compounds as stabilizers for polymers, whose destruction proceeds as a free radical process.[21,25]

This complex includes a number of methods for preliminary estimation of efficiency of chemicals with the help of model reactions of oxidation and polymerization of hydrocarbons and rapid testing in polymers.

The testing methods are used widely and successfully for investigation of activity of inhibitors of various types. The results of such complex study of efficiency of acids of phosphorus as stabilizers for polyethylene are given in Table XIII.[74] Data of DTA show that introduction of acids of phosphorus in polyethylene increases the temperature of beginning of oxidation from 196 to 257°C and reduces considerably the intensity of oxidation processes in polymer. As it appears from the Table XIII, the decrease of endothermic peak area for 60–90% in case of compounds

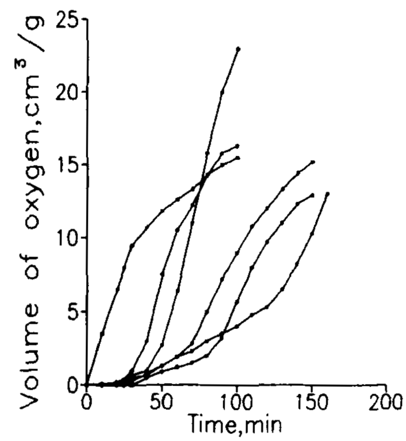


FIGURE 4 Kinetics of oxidation of polyisoprene in presence of phenolic stabilizers: 4-methyl-2,6-di-*tert*-butylphenol (1), ester of 4-*n*-propyl-2,6-di-*tert*-butylphenol and acrylic acid (2), ester of 4-methyl-2,6-di-*tert*-butylphenol and maleic acid (3), ester of 4-*n*-propyl-2,6-di-*tert*-butylphenol and maleic acid (4) and 2,2'-methylene-bis-(4-methyl-6-*tert*-butylphenol) (5); 0—without stabilizer.

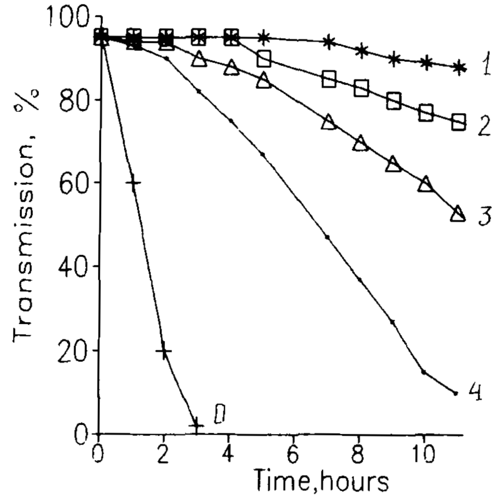


FIGURE 5 Change in intensities of CO-groups bands in IR-spectra of SKI-3 rubber films during thermooxidation in presense of bisphenols 1–4 (see legend to Figure 1; 0—without stabilizer).[38]

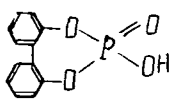
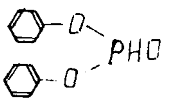
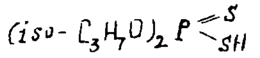
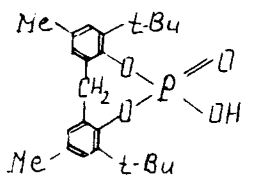
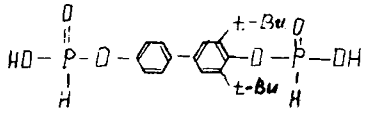
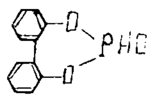
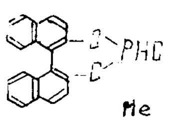
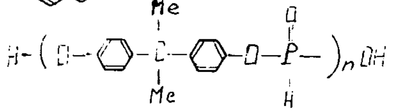
NN 7–10 is observed and these data correlate to the values of induction periods τ and to the results of measurement of tensile strength for samples of polyethylene of high density stabilized by acids of phosphorus.

Other examples of complex study of stabilizers efficiency are described in References 19, 25 etc.

The potentials E of the beginning of anodic oxidation of phenolic grafting stabilizers, induction periods of oxidation of polypropylene τ_{pp} and polyisoprene τ_{pi} in presence of these compounds are listed in Table XIV. As it is seen from this Table, the correlation exist between the values E and τ. The more active compounds have values τ close to τ of antioxidants as active as ionol (τ_{pp} = *100 min*, τ_{pi} = *10*

TABLE XIII

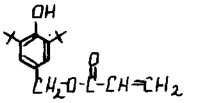
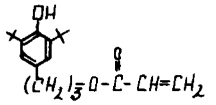
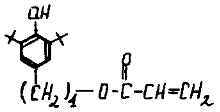
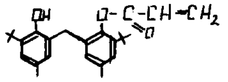
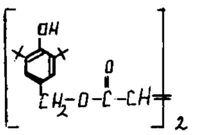
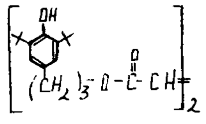
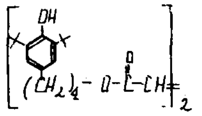
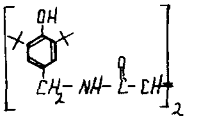
Results of the study of efficiency of acids of phosphorus as stabilizers for polyethylene of high density[74]

NN	Compound	Induction period of oxidation τ, min	Reduction of endothermic peak area, %	Time up to frailty,* hours
1	2	3	4	5
1.	**Without stabilizer**	20	-	1/84
2.	$(iso\text{-}C_8H_{17}O)_2PHO$	45	36	-
3.		80	45	-
4.		90	45	4/240
5.	 $(iso\text{-}C_3H_7O)_2P\genfrac{}{}{0pt}{}{=S}{-SH}$	130	-	5/340
6.		150	50	-
7.		210	68	7/30
8.		350	68	9/385
9.		370	66	10/400
10.		440	96	8/250

* numerator - thermo-mechanical testing at 160°C; denominator - static testing at 120°C.

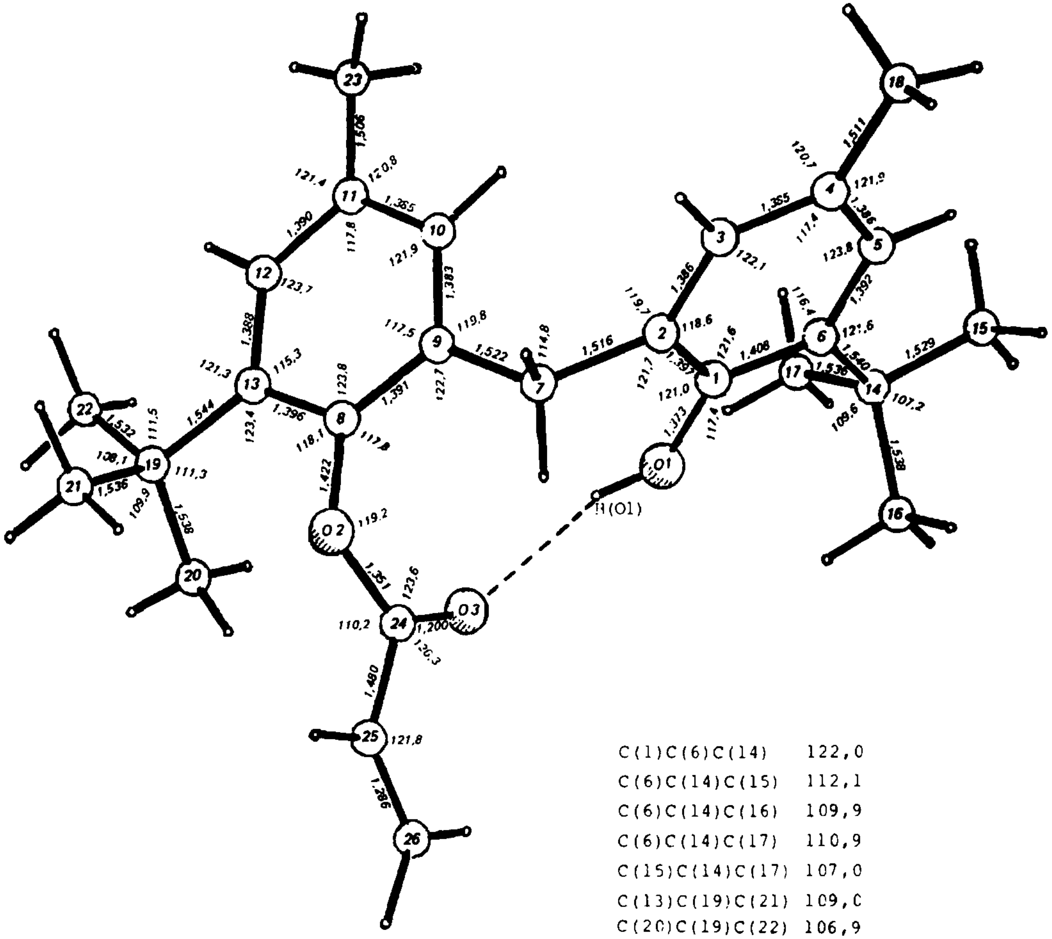
TABLE XIV

Antioxidative activity of grafting phenolic stabilizers

NN	Compound	E, mv	τ_{pp}, min	τ_{pi}, min
1	2	3	4	5
1.		224	160	-
2.		230	200	20
3.		239	150	-
4.		221	150	7
5.		-	220	22
6.		203	215	30
7.		212	240	18
8.		-	200	-

min) and antioxidant 2246 (τ_{pp} = 200, τ_{pi} = 25). It is possible to choose the most active grafting stabilizers for introduction into medicals on the basis of data given in Table XIV.

The investigation of the role of structural factors in antioxidative activity and efficiency leads to some important conclusions. So it was ascertained as a result of



C(1)C(6)C(14)	122,0
C(6)C(14)C(15)	112,1
C(6)C(14)C(16)	109,9
C(6)C(14)C(17)	110,9
C(15)C(14)C(17)	107,0
C(13)C(19)C(21)	109,0
C(20)C(19)C(22)	106,9

FIGURE 6 Molecular structure of ester of 2,2′-methylene-bis-(4-methyl-6-*tert*-butylphenol) and acrylic acid (x-ray diffraction analysis).[75]

study of molecular structure of several bisphenols, that the stabilizers whose molecules have *cis*-conformation (both OH-groups are arranged on one side of the plane passing through the bridge carbon atom and two carbon atoms of aromatic nuclei linked to it—see Figure 6[75]) are more active stabilizers than those with *trans*-conformation.

In recent years the results of studies[76–78] on automation of kinetic investigations of oxidation process permit us to study in detail the kinetic dependence of oxidation process and its mechanism. The comparison of results of the complex study lead to a mathematical model of reaction, which describes the process quantitatively,[79,90] and allows us to link the structure of molecules and mechanism of their oxidation. This in turn provides the basis for semi-empirical methods for predicting the ability of compounds to undergo oxidation and study the antioxidative activity and mechanism of inhibitors action.

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