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This issue is devoted to the 70th anniversary of the birth of the outstanding Soviet scientist Academician Nikolai Markovich Emanuel' who directed the journal "Uspekhi Khimii" from 1972 until the last days of his life.

Emanuel"s scientific interests embraced many fields of science: the chemical physics of the liquid-phase oxidation of organic substances; elementary reactions and kinetics of processes in the condensed phase; the ageing and stabilisation of polymers; the kinetics of biological, mainly pathological, processes.

The issue includes articles by a number of the pupils of Academicain Emanuel'. They demonstrate the breadth of his thought and a surprising ability to foresee the scientific prospects for the development of particular branches of science.

Translated from *Uspekhi Khimii*, 54,1393-1419 (1985) U.D.C. 547.91.222

The Chemical Physics of the Ageing and Stabilisation of Elastomers

N.M.Emanuel' (deceased)

The ageing and stabilisation of elastomers are considered from the standpoint of chemical physics. A general method for the fitting to the kinetic curves of relations characterising the ageing of elastomers under the influence of oxygen, light, ozone, and mechanical stresses is discussed. Different principles and procedures for the stabilisation of elastomers are analysed. The bibliography includes 75 references.

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INTRODUCTION

Modern chemistry is concerned primarily with new materials for various branches of technology, agriculture, and ordinary life. Elastomers occupy one of the leading positions among such materials and the range of articles based on them is extremely wide.[1] The world production of different types of rubber in 1984 amounted to 14 million tonnes.[2]

The principal deficiency of the majority of elastomers is rapid ageing under operating conditions. Thus, when anticorrosion measures are taken, metals last for 15 and more years. Elastomers and articles prepared from them have in most cases a much shorter useful life.

Ageing is known to be a process which develops with time, i.e. the study of its mechanism is the subject to chemical kinetics. The knowledge of the mechanism of ageing makes it possible to solve rationally the problem of increasing the life of the articles and to predict their likely usefulness under various conditions.

Research into the kinetics and mechanism of the ageing and stabilisation of polymeric materials has developed in recent years on a broad front. A new field in the chemistry of macromolecular compounds, namely the chemical physics of the ageing and stabilisation of polymers, was initiated on the basis of these investigations.[3-5] It includes the study not only of the elementary reactions and macroscopic stages

in the ageing and stabilisation but also the role in these processes of the physical organisation of the polymer, the dynamics of molecular movements, and other physical factors which determine the operating properties of polymeric materials.

In the course of the processing, storage, and use elastomers are acted upon by numerous external factors which cause the initiation and development of chemical and physical processes leading to the alteration of the operating properties (Fig.1). At the present time it is possible to indicate which particular ageing factors act on particular articles containing elastomers (Fig.2). The principal elementary stages in the ageing process, the types of stabilisers, and the mode of their action are also known (Fig.3).

The aim of the present review is to describe the state of the principal trends in the chemical physics of the ageing and stabilisation of elastomers.

II. A GENERAL METHOD FOR THE FITTING OF EQUATIONS TO KINETIC CURVES

In the study of the ageing of elastomers under both natural and artificial conditions, various kinetic relations describing the variation of the parameters of the operating properties of materials or parameters indirectly related to these properties (for example, the absorption of oxygen in

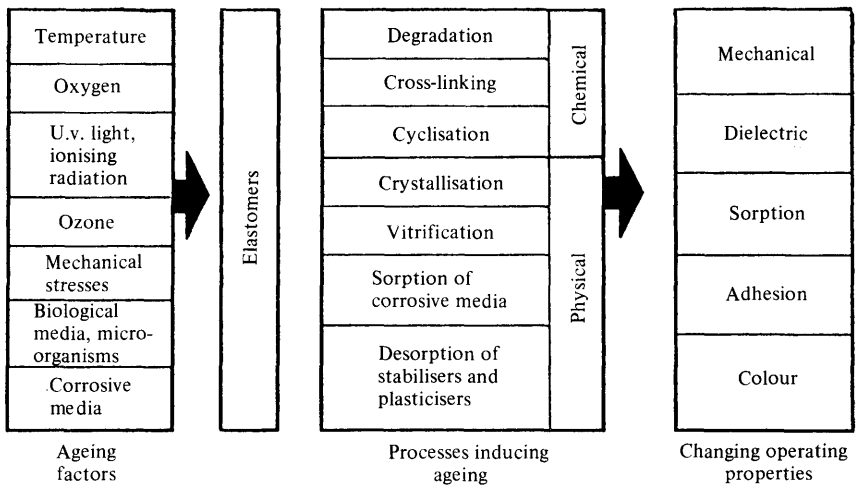


Figure 1. The effect of external factors and the changes in the operating properties of articles as a result of the ageing of elastomers.

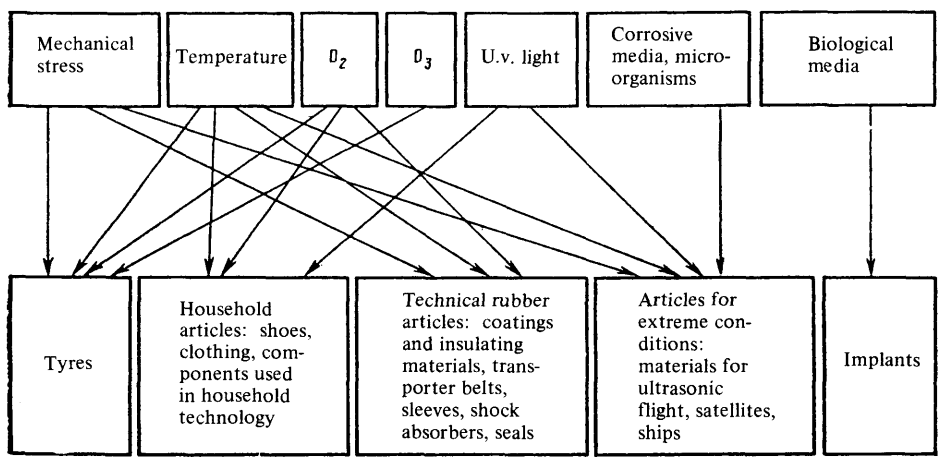


Figure 2. Principal types of articles based on elastomers and the external factors inducing their ageing.

thermo-oxidative ageing, the decrease of the mass of the specimen in thermal degradation, etc.) are obtained.

Extensive experimental data on the kinetics of the ageing of polymers, including elastomers, have now been accumulated. Various types of kinetic curves are known. As an illustration, Fig.4 presents several experimental curves for the ageing of various elastomers.[6-11] In a formal kinetic description of the ageing of polymers, it is of interest to obtain generalised kinetic curves which would make it possible, on the one hand, to classify a set of experimental data, and, on the other hand, would permit the solution of many problems of practical importance, for example the prediction of the behaviour of the operating properties during ageing.

Mathematical functions describing satisfactorily each of the above types of kinetic curves are known. A particular function can be chosen either on the basis of the known process mechanism or on the basis of analogies or an empirical selection by fitting equations to experimental data using the familiar methods of regression analysis.

A wide variety of chemical and physical processes take place in the polymeric material during ageing but under the real storage and operating conditions only some of them alter the operating properties. In many cases the changes in the operating properties can therefore be attributed to the occurrence of specific processes.

The decrease of the tensile strength σ in the high-temperature ageing of polymeric materials is mainly caused by degradation reactions and is described satisfactorily by the equation

$$\varphi = \exp(-\alpha t), \qquad (1)$$

where $\phi = (\sigma/\sigma_\infty - 1)(\sigma_0/\sigma_\infty - 1)^{-1}$, α is the transformation coefficient, and σ_0 and σ_∞ are the initial and limiting

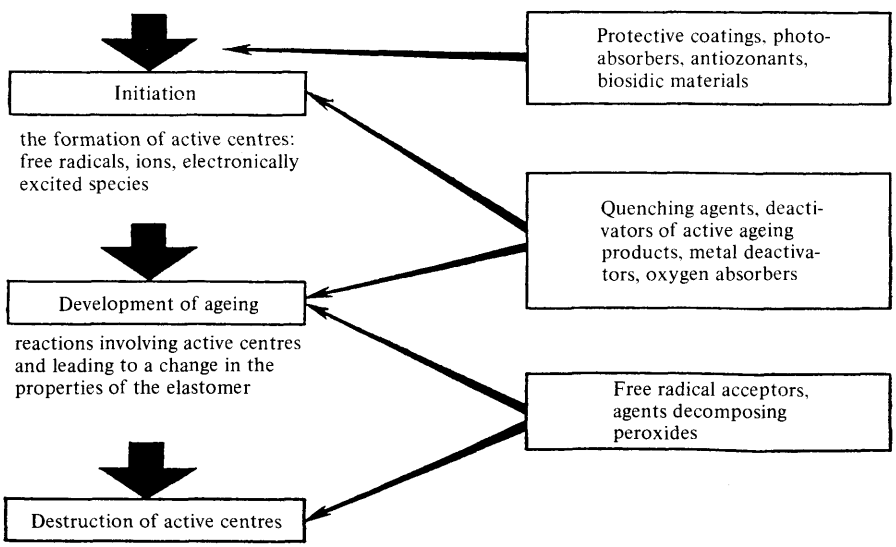


Figure 3. Principal elementary stages in the ageing of elastomers, the types of stabilisers, and the mode of their action.

stresses. Fig.5 presents a generalised kinetic curve for the decrease of ϕ in the ageing of various plastics and elastomers.[12] The deformation caused both by cross-linking and degradation reactions increases during the ageing of elastomers. The accumulation of the residual deformation ε is described by the equation

$$\psi = 1 - \exp(-\alpha t), \qquad (2)$$

where $\psi = (\varepsilon/\varepsilon_0 - 1)(\varepsilon_\infty/\varepsilon_0 - 1)^{-1}$. The generalised kinetic curve for a series of elastomers is illustrated in Fig.6.

III. THERMO-OXIDATIVE AGEING OF ELASTOMERS

A large set of data for the thermo-oxidative ageing of elastomers, some of which have been surveyed in monographs and reviews,[13-21] has now accumulated. The kinetics of the absorption of oxygen are most frequently studied in thermo-oxidative ageing.

1. Formal Kinetics of Thermo-oxidative Ageing

Analysis of the experimental data for the absorption of oxygen in the thermo-oxidative ageing of various polymers in both open and closed systems has shown that three main types of kinetic curves are encountered: curves of the autoaccelerating type, curves which decrease exponentially with time, and S-shaped kinetic curves.[22]

Kinetic curves of the first type are characteristic of the absorption of oxygen in the thermal oxidation of elastomers at temperatures below 200 °C; they are described by the equation

$$N_{O_2} = a(t - \tau)^2, \qquad (3)$$

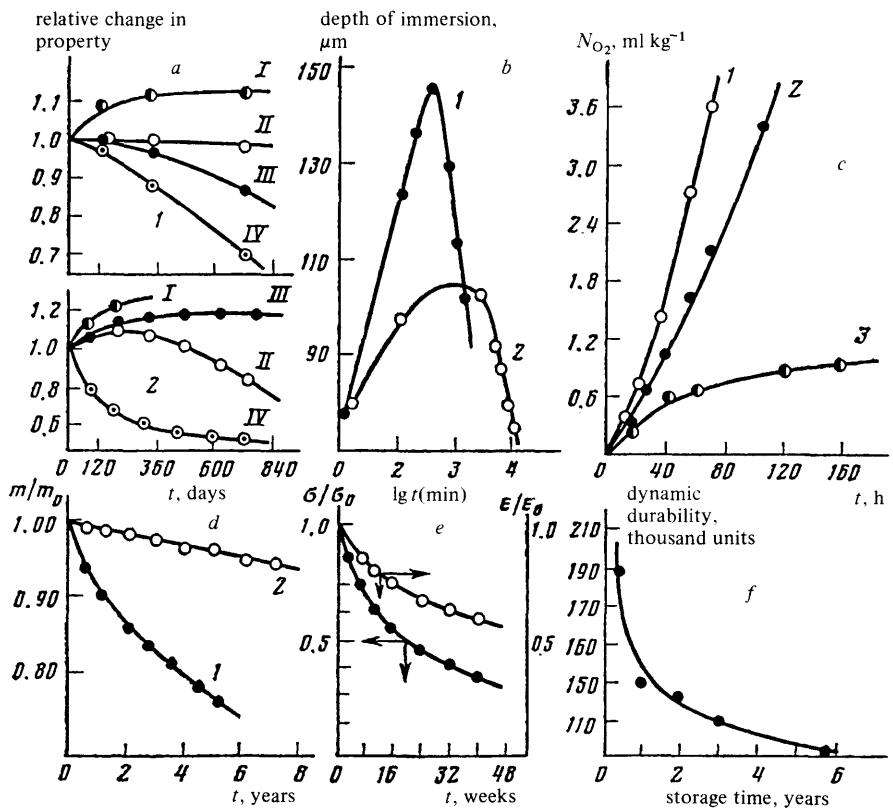


Figure 4. Kinetic relations obtained in the ageing of various elastomers: *a*) changes in the mechanical properties of raw rubber specimens during natural ageing in a climatic station: 1) butyl rubber; 2) butadiene-acrylonitrile rubber [I) Young's modulus; II) tensile strength; III) microhardness; IV) deformation on rupture]; *b*) changes in the microhardness of rubbers based on the raw butadiene-nitrile rubber in transformer oil during wear by rubbing: 1) 170 °C; 2) 120 °C; *c*) absorption of oxygen by the natural rubber latex containing 2% of 3,5-di-t-butyl-4-hydroxybenzyl acrylate at 70 °C: 1) without antioxidant; 2) antioxidant introduced mechanically; 3) antioxidant bound chemically to the raw rubber macromolecules; *d*) changes in the mass of polydimethylsiloxane (curve *1*) and segmented polyurethane (curve *2*) after implantation into a subcutaneous cell in rabbit; *e*) changes in the mechanical properties of specimens of a fluoro-silicone elastomer (Dow Corning, USA) at 200 °C; *f*) changes in the dynamic durability of protective rubber based on butadiene–styrene raw rubber during storage in an unheated space.

where N_{O_2} is the amount of oxygen absorbed by the polymer, a is a constant, and τ is the induction period. The parameters a and τ depend on the structure of the polymer, the oxygen pressure, and temperature. The equation is valid for low degrees of oxidation.

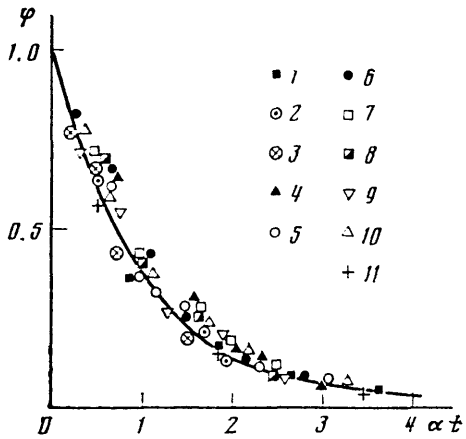
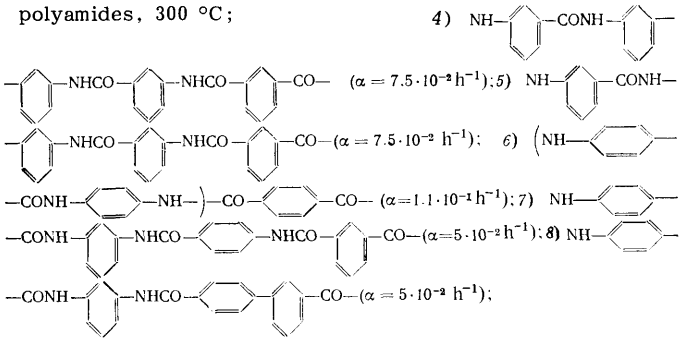


Figure 5. Generalised kinetic curve for the decrease of the tensile strength during the ageing of various plastics and elastomers: *1*) polyimide composite, 300 °C ($\alpha = 3.8 \times 10^{-3}$ h^{-1}); *2*) phenylon, 220–250 °C ($\alpha = 1.6 \times 10^{-3}$ h^{-1}); *3*) capton-H film, 300 °C ($\alpha = 2.6 \times 10^{-1}$ week^{-1}); aromatic polyamides, 300 °C;



rubbers based on different raw rubbers; *9*) butadiene–sytrene, 90 °C ($\alpha = 3.5 \times 10^{-3}$ h^{-1}); *10*) butadiene–nitrile, 20 °C ($\alpha = 0.1$ year^{-1}); *11*) isoprene, 100 °C ($\alpha = 2.8 \times 10^{-2}$ h^{-1}).

Fig.7 presents the generalised kinetic curve for the absorption of O_2 in the oxidation of various polymers, including elastomers, at 90–200 °C. Kinetic curves of an analogous type can be obtained for the thermal oxidation of vulcanised elastomers with different contents of technical carbon[23] and vulcanised elastomers with different structures of the main chain in the network,[24] and also kinetic curves recorded at different partial pressures of oxygen[25] and for vulcanised elastomers with different amounts of bound sulphur.[26]

An equation relating the change in the mechanical properties (tensile strength and elongation on rupture) to the absorption of oxygen and the accumulation of oxygen-containing groups in the polymer has been obtained for polyolefins.[27] Fig.8 presents analogous experimental data obtained in the thermal oxidation of vulcanised butadiene–styrene rubber.[21]

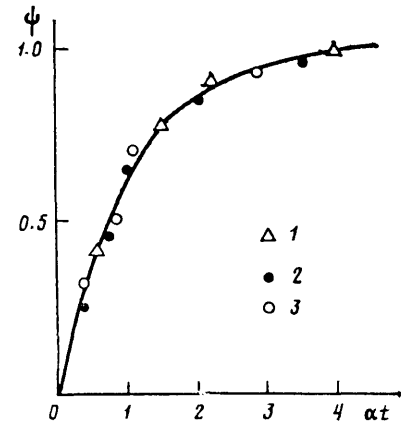


Figure 6. Generalised kinetic curve for the increase of the residual deformation during the ageing of various rubbers based on different polymers: *1*) butadiene–styrene, vacuum, 90 °C ($\alpha = 0.1$ day^{-1}); *2*) butadiene–styrene, 120 atm, 70 °C ($\alpha = 0.2$ day^{-1}); *3*) butadiene–acrylonitrile, SKI-18, ammonia, 20 °C ($\alpha = 3.5 \times 10^{-2}$ day^{-1}).

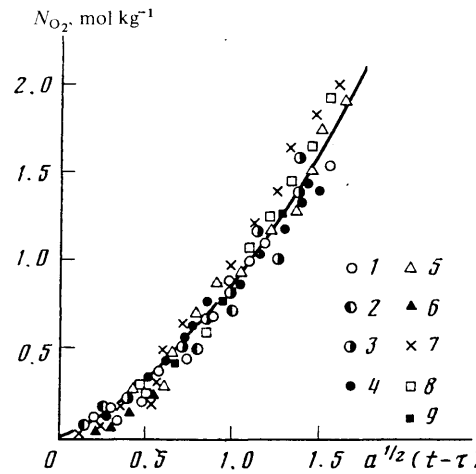


Figure 7. Generalised kinetic curve for the absorption of oxygen in the oxidation of various polymers: *1*) polyethylene (90 °C); *2*) polypropylene (130 °C); *3*) ethylene–propene copolymer (130 °C); *4*) poly-4-methylpent-1-ene (130 °C); *5*) vulcanised natural rubber (110 °C); *6*) polystyrene (160°); *7*) polyheptene (100 °C); *8*) polynon-1-ene (100 °C).

It has been suggested that the thermo-oxidative stability of polymers be characterised by the temperature at which 0.1 mol kg^{-1} of oxygen is absorbed in air in the course of 15 min[27] (Table 1). The values of 0.1 mol kg^{-1} was selected

because in the presence of this amount of absorbed oxygen the chemical and physical properties of polymers begin to change appreciably.

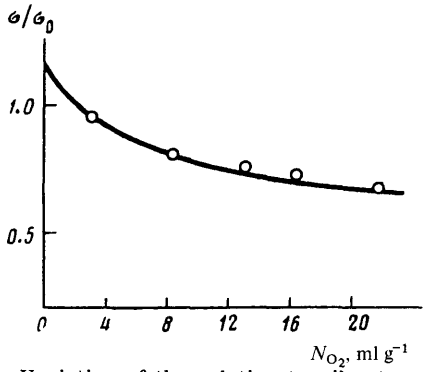


Figure 8. Variation of the relative tensile strength of vulcanised butadiene–styrene rubber as a function of the amount of oxygen absorbed at 110 °C and an oxygen pressure of 1 atm.

Table 1. The thermo-oxidative stability of carbochain polymers.

Polymer	T_{1h}*, °C	Polymer	T_{1h}*, °C
Polypropylene	135	Poly-4-methylpent-1-ene	165
Polyisoprene	135	Polyethylene	170
Polybutadiene	155	Polystyrene	205
Poly(methyl methacrylate)	160	Poly(vinyl chloride)	210

*The temperature corresponding to the absorption of 0.1 mol kg^{-1} of oxygen in 15 min.

2. Characteristic Features of the Solid-Phase Reactions in the Thermo-oxidative Ageing of Elastomers

Kinetic studies of the thermo-oxidative ageing of elastomers have always been based on the theoretical ideas concerning the liquid-phase oxidation reactions of hydrocarbons. Numerous investigations established that the liquid-phase oxidation of hydrocarbons is a degenerate-branched chain process.[4,28–30] However, the thermal oxidation of elastomers, like that of other polymers, shows many differences from the liquid-phase oxidation of hydrocarbons despite the similarity of the kinetics and the reaction products. Elastomers may contain domain structures—structurally similar groups segregated to form a microheterophase, while in filled elastomers there is a phase consisting of "hard" rubber adsorbed on the filler.[31,32] Such inhomogeneity of the physical structures of elastomers and the occurrence of solid-phase reactions give rise to the following characteristic features of the thermo-oxidative ageing of solid elastomers.

1. The inhomogeneity of the three-dimensional distribution of the active centres and reactants (oxygen, radicals, and stabilisers).

2. The structural-kinetic inhomogeneity, i.e. the distribution of regions differing in the frequencies and amplitudes of molecular movements, which influence the kinetics of radical processes.

3. Slow migration of segments of the macromolecules in polymers diminishes the rate of emergence of the radicals from the cage compared with a liquid and the probability of the radical recombination within the cage is greater in elastomers than in a liquid, i.e. the cage effect is more marked.

4. The slower diffusion of oxygen in polymers compared with liquid hydrocarbons is responsible for the specific features of the reactions of alkyl macroradicals which not only react with oxygen, as happens in hydrocarbons undergoing oxidation, but also enter into a whole series of other reactions: they isomerise, abstract hydrogen atoms from neighbouring C–H bonds, and react with hydroperoxides.[33]

5. In a liquid the R and RO_2 radicals migrate by diffusing; in solid polymers the diffusion of free-radical species is slow and other mechanisms of the migration of a free valence may operate—the relay migration and the transfer of the free valence by low-molecular-weight radicals and molecules.[1,34,35] The relative contributions of these mechanisms depend on the oxidation conditions and the structure of the elastomer.

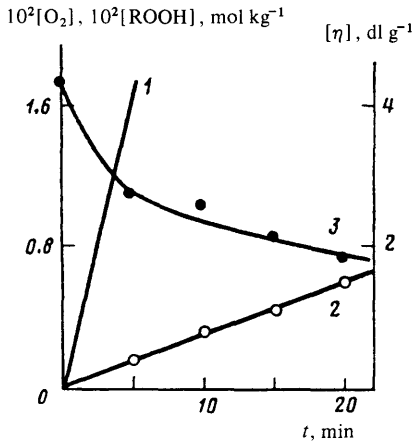
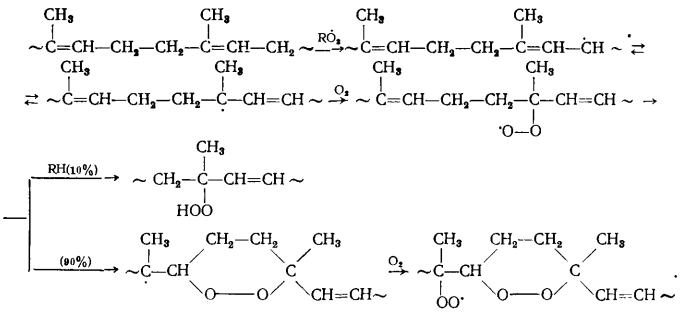


Figure 9. Kinetics of the absorption of oxygen (curve *1*), the accumulation of hydroperoxides (curve *2*), and the changes in the intrinsic viscosity of *cis*-1,4-polyisoprene (curve *3*) at 80 °C, $[DAC]_0 = 0.06$ M.

3. The Mechanism of the Thermo-oxidative Degradation of Polydienes

In the thermo-oxidative degradation of *cis*-1,4-polyisoprene only part of the absorbed oxygen is consumed in the formation of hydroperoxy-groups (Fig.9). This is associated with the propagation of the oxidation chain in two directions:[36,37] (a) via a reaction involving the intramolecular addition of the peroxy-radical to the double bond with formation of a cyclic peroxide with a rate constant k_p; (b) via the reaction involving the abstraction of a hydrogen atom from the α-methylene group with formation of a hydroperoxide (k_p'). The overall scheme includes the following

reactions:



The ratio $k_p'/k_p[RH] = 8.3$ for *cis*-1,4-polyisoprene.[37]

Oxidation results in the formation of peroxy-macroradicals in which peroxide bridges adjoin the free valence. Such structural fragments, which have been identified by NMR, are unstable and constitute centres for the degradation of polyisoprene via the scheme

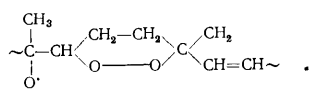
$$2R\dot{O}_2 \rightarrow 2R\dot{O},$$
$$R\dot{O} \rightarrow \text{degradation}.$$

According to this scheme, the rate of degradation is proportional to the rate of initiation;[37] the proportionality coefficient, measured in experiments on the initiated degradation of polyisoprene, is 15, i.e. the decomposition of the RO macroradicals formed is 15 times faster than the chain termination in the polyisoprene being oxidised.[37]

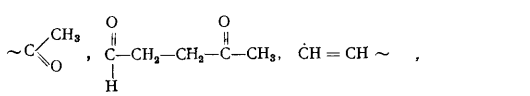
The kinetics of the oxidative degradation of polyisoprene in the presence of inhibitors have been investigated.[38] It was found that, in the presence of an inhibitor (phenol or aromatic amine), a new source of degradation appears, namely the reaction of the peroxy-macroradical with the inhibitor radical In:

$$R\dot{O}_2 + In \rightarrow ROOIn \rightarrow R\dot{O} + In\dot{O};$$
$$R\dot{O} \rightarrow \text{degradation}.$$

The radical $R\dot{O}$ has the structure



Its decomposition results in the formation of the groups



Together with the mechanism of the oxidative degradation described above, there is a possibility of another mechanism, according to which the polyisoprene degradation centres are the allyloxy-radicals formed on decomposition of the hydroperoxy-groups.[39]

4. Stabilisation of Elastomers

The stabilisation of elastomers has attracted continuous attention for many years and numerous studies have been devoted to the mechanism of the action of stabilisers. Two main types of antioxidants, which cause chain termination, are known: electron donors and proton donors. It has been shown by infrared spectroscopy that phenols and aromatic amines with bulky substituents are present in the matrices of polydiene elastomers as weak π-complexes with the double bonds.[40]

The mechanism of action of the antioxidant in the oxidation of elastomers depends on its concentration in the polymer. In the concentration range from 4.5×10^{-4} to 4.5×10^{-3} mol kg^{-1} the oxidation of *cis*-1,4-polyisoprene in the presence of sterically hindered phenols proceeds as a chain reaction with chain termination by the inhibitor molecules; the effectiveness of antioxidants in the polymer is close to that in hydrocarbon media (Table 2).[38]

Table 2. Kinetic parameters of the chain termination by phenolic antioxidants in the inhibited oxidation reactions of *cis*-1,4-polyisoprene (80 °C, $p_{O_2} = 10^5$ Pa).

Antioxidant	f	$k_2k_6^{-1/2}$, kg$^{1/2}$ mol$^{-1/2}$ s$^{1/2}$
2,6-Di-t-butyl-4-methylphenol	2.0	42.6±10.4
2,2-Methylenebis(6-t-butyl-4-methylphenol)	2.6	42.1±9.9
4,4-Methylenebis(2,6-di-t-butylphenol)	2.7	37.9±12.9
2,4,6-Tris(3,5-di-t-butyl-4-hydroxyphenyl)-1,3,5-trimethylbenzene	1.9	28.9±6.4
Ester of 3,5-di-t-butyl-4-hydroxyphenylpropionic acid and pentaerythritol	2.0	38.8±4 5

The rate of the inhibited chain oxidation is

$$W_{O_2} = \frac{k_2[RH]W_0}{fk_7[InH]_0}, \quad (4)$$

where W_0 is the rate of initiation and f the inhibition coefficient, i.e. the number of kinetic chains terminated by one antioxidant molecule.

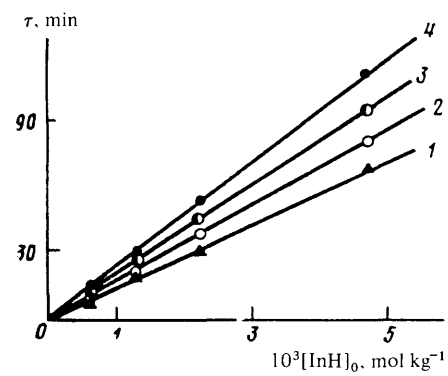


Figure 10. Dependence of the induction period in the oxidation of *cis*-1,4-polyisoprene on the initial concentration of antioxidants (80 °C, oxygen pressure 10^5 Pa): *1*) 1,3,5-trimethyl-2,4,6-tri(3,5-di-t-butyl-4-hydroxybenzyl)benzene; *2*) ester of 3,5-di-t-butyl-4-hydroxyphenylpropionic acid and pentaerythritol; *3*) 2,2-methylenebis(6-t-butyl-4-methylphenol); *4*) 4,4-methylenebis(2,6-di-t-butylphenol).

Figs.10 and 11 present the variation of the induction period of the oxidation reaction with the initial concentration of the antioxidants and of the inhibited oxidation chain length ν with the reciprocal of the concentration of the antioxidants.

In the concentration range from 4.5×10^{-3} to 4.5×10^{-2} mol kg^{-1} the rate of oxidation is[38]

$$W_{O_2} = \frac{aW_0}{[InH]_0} + bW_0, \quad (5)$$

where a and b are coefficients. The first term of Eqn.(5) reflects the occurrence of a chain oxidation process with chain propagation via the reaction of RO_2 and RH; the second term is associated with the involvement of the inhibitor radicals in chain propagation.

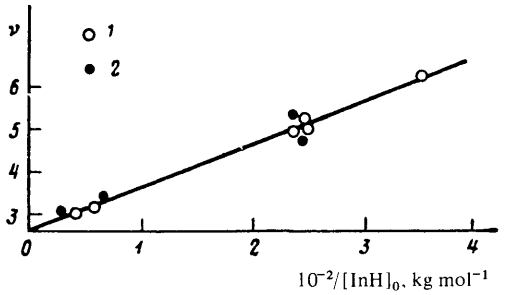
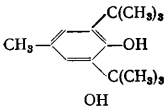
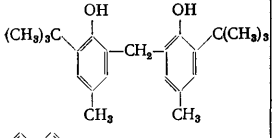
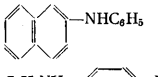
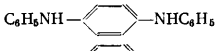
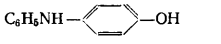
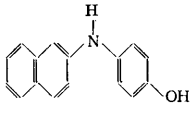


Figure 11. Dependence of the chain length ν of the inhibited oxidation of *cis*-1,4-polyisoprene on the reciprocal of the concentration of antioxidants (80 °C, oxygen pressure 10^5 Pa): *1*) 2,6-di-t-butyl-4-methylphenol; *2*) 2,2-methylenebis(6-t-butyl-4-methylphenol).

Table 3. Kinetic characteristics of the inhibitors of the oxidation and degradation of *cis*-1,4-polyisoprene (80 °C, $p_{O_2} = 10^5$ Pa).

Inhibitor	$k_7 k_6^{-1/2}$, kg$^{1/2}$ mol$^{-1/2}$ s$^{-1/2}$	$10^{-3}\frac{W_{degr}[InH]_0}{W_0^2}$, s
	43	5.5
	36	2.5
	52	2.1
	333	0.27
	3.9	1.4
	4.4	1.4

The rate of degradation of *cis*-1,4-polyisoprene depends on the rate of initiation and on the initial antioxidant concentration:

$$W_{degr} = k_{degr}\frac{cW_0^2}{fk_7[InH]_0}, \quad (6)$$

where k_{degr} is the degradation rate constant and c is a coefficient.

The coefficient of the proportionality between W_{degr} and $W_0^2/[InH]_0$ is a measure of the inhibition of the degradation process by the antioxidant. There is no parallel variation of $k_7(RO_2 + InH)$ and $W_{degr}[InH]_0/W_0^2$. Thus, in order to be able to select effective stabilisers it is important to know their ability to terminate kinetic chains and to suppress oxidative degradation.

Table 3 presents the kinetic characteristics of inhibitors of the phenolic and amine types in the oxidation and degradation of *cis*-1,4-polyisoprene.

Thermoanalytical methods [differential scanning calorimetry (DSC), differential thermal analysis (DTA), and thermogravimetric analysis (TCA)] have been used successfully in recent years for the determination of the efficiency of the action of stabilisers in elastomers.[41]

The thermo-oxidative stability of rubbers containing identical amounts of different antioxidants is estimated in terms of two parameters: the time corresponding to the appearance of the exothermic oxidation peak under isothermal conditions (the induction period τ) and the temperature at which this peak appears in the course of dynamic heating (T_0).

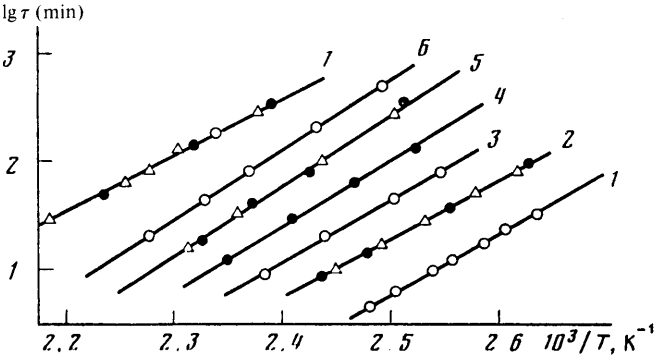


Figure 12. Relation between lg τ and $1/T$ for different compositions: *1*) polyisoprene; *2*) purified natural rubber (NR), NR + 2,6-di-t-butyl-*m*-cresol; *3*) NR + 1,7,10,16-tetrahydroxy-4,13-diazacyclo-octadecane; *4*) NR + *N*-phenyl-β-naphthylamine; *5*) NR + *N*-isopropyl-*N*-phenyl-*p*-phenylenediamine, NR + zinc diethyldithiocarbamate; *6*) raw NR; *7*) NR + *NN'*-diphenyl-*p*-phenylenediamine, NR + *p*-(*p*-toluenesulphanilamido)diphenylamine.

Fig.12 illustrates the linear relations between lg τ and the reciprocal of temperature, the straight lines obtained for different specimens being almost parallel. Analogous results have been obtained in another study.[42] A generalised lg τ – $1/(T + \Delta T)$ relation, where ΔT is a factor defined as the temperature difference $T_{st} - T_{sp}$, was derived from these data (Fig.13). The observed relations give rise to extensive possibilities not only for the estimation of the efficiency of the action of stabilisers but also for predicting the useful life of polymeric articles.

IV. PHOTO-OXIDATIVE AGEING OF ELASTOMERS

1. The Mechanism of Photo-oxidative Ageing

The photochemical oxidation of elastomers is a free-radical chain process with degenerate photobranching by hydroperoxides. This is confirmed by the form of the kinetic curve for the accumulation of the reaction products (ketones and alcohols), which are S-shaped, while the curve describing the variation of the concentration of the hydroperoxy-groups passes through an extremum, the maximum concentration of the hydroperoxides corresponding to the maximum rate of accumulation of the oxidation products (Fig.14).

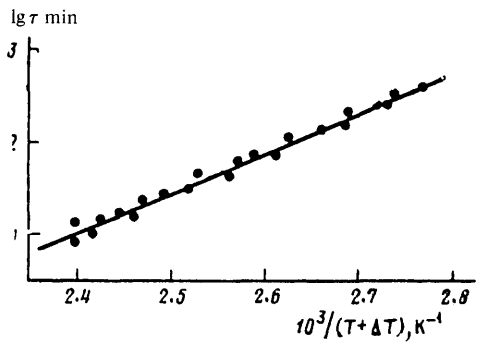


Figure 13. Generalised relation between lg τ and $1/(T + \Delta T)$, where $\Delta T = T_{st} - T_{sp}$ is the difference between the temperatures of the beginning of the exothermic peak for the standard and the specimen.

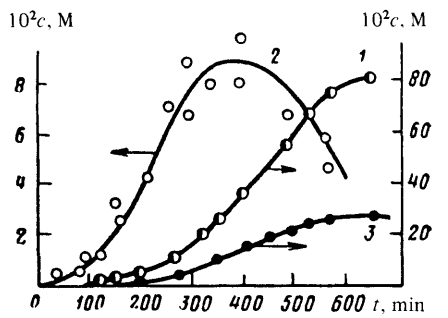


Figure 14. Kinetic curves for the accumulation of hydroxy-groups (curve *1*), carbonyl groups (curve *2*), and hydroperoxy-groups (curve *3*) on irradiation of 0.1 mm polyisoprene films with light having a wavelength $\lambda = 300$ nm.

The termination of the kinetic chain may be quadratic (for example, in polybutadiene) or linear (for example, in polyisoprene). This is manifested by the different character of the dependence of the rate of oxidation on the intensity of light (Fig.15). The chain length in the oxidation of polyisoprene is almost independent of the light intensity and amounts to ~100 units, whereas a decrease in the rate of initiation in polybutadiene, for example from 8×10^{-7} to 8×10^{-9} mol kg^{-1} s^{-1}, increases the chain length from 100 to 1000 units.[43]

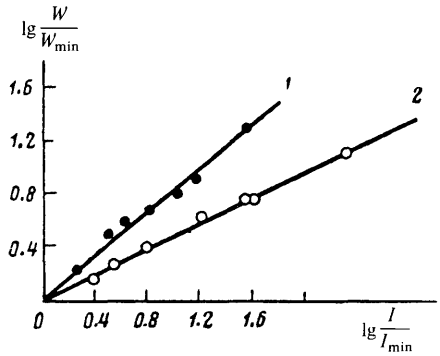


Figure 15. Dependence of the rate of oxidation on the light intensity I in the sensitised photochemical oxidation of polyisoprene (line *1*) and polybutadiene (line *2*); W_{min} and I_{min} are the minimum rate and intensity.

The linear chain termination in certain rubbers indicates that peroxy-radicals decompose with formation of low-molecular-weight radicals. In contrast to the widely familiar oxidation mechanism according to which chain termination takes place on direct interaction of macroradicals, in this case the mechanism is

$$\mathrm{RH} \xrightarrow{W_0/k_V} \dot{\mathrm{R}},$$
$$\dot{\mathrm{R}} + \mathrm{O_2} \xrightarrow{k_1} \mathrm{R\dot{O}_2},$$
$$\mathrm{R\dot{O}_2} + \mathrm{RH} \xrightarrow{k_2} \mathrm{ROOH} + \dot{\mathrm{R}},$$
$$\mathrm{R\dot{O}_2} \xrightarrow{k_{3.1}} \dot{r},$$
$$\mathrm{R\dot{O}_2} + \dot{r} \xrightarrow{k_{3.2}} \text{products},$$

where $\dot{r}$ is a low-molecular-weight radical. The expression for the rate of oxidation is

$$W = -\frac{d[O_2]}{dt} = \frac{d[ROOH]}{dt} = \frac{k_2[RH]}{k_{3.1}} W_0. \qquad (7)$$

In the general case, the dependence of the rates of oxidation on the rate of initiation (i.e. on the intensity of light) is complex, since at higher rates of initiation direct reactions of the macroradicals, leading to the appearance of a relation of the type $W \sim W_0^{1/2}$, compete with the radical decomposition process leading to linear chain termination. A change in the dependence of the rate of oxidation on the rate of initiation is observed, for example, in the photochemical oxidation of block and statistical butadiene–styrene copolymers.[44]

At room temperature the free radicals formed in the photochemical oxidation of polydienes are relatively unstable and the kinetics of their reaction have therefore been investigated at low temperatures.[45] Irradiation of raw rubbers with ultraviolet light leads to the appearance of EPR signals with a weak resolution (Fig.16), which have been attributed to terminal allyl radicals. On heating, they can be converted into allyl radicals and, in the presence of oxygen, into peroxy-radicals.[46]

The direct study of the nature of the radicals and of the kinetics of their reaction under conditions of photochemical oxidation showed that allyl radicals are the main free-radical species detected by EPR (Fig.17). The free valence in polybutadiene is destroyed on recombination of allyl and not peroxy-radicals, as usually happens in the oxidation of saturated polymers.[47] This feature must be taken into account when the stabilisation of elastomers is considered.

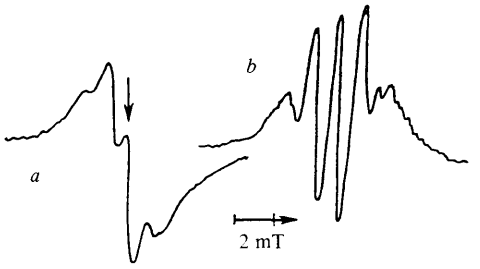


Figure 16. EPR spectra of *cis*-polybutadiene irradiated with ultraviolet light at 77 K: *a*) first derivative; *b*) second derivative; the arrow indicates the position of the DPPH signal.

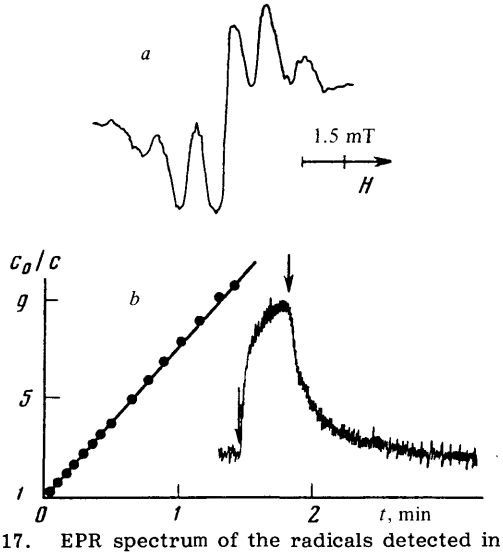
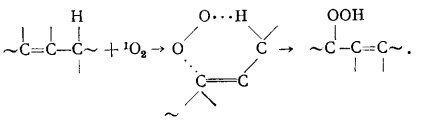


Figure 17. EPR spectrum of the radicals detected in the sensitised oxidation of polybutadiene (*a*) and the kinetics of their accumulation and destruction on switching on and switching off light (*b*); the instants when light is switched on and off are indicated by arrows.

The sensitised oxidation mechanism involving singlet oxygen ($^1O_2$, state $^1\Delta_g$), which has been discussed by a number of investigators[48] and which is an alternative to the free-radical mechanism examined above, proved to be ineffective. The widely current hypothesis of the key role of singlet oxygen in polymer photochemical oxidation processes is based on the postulate of a high reactivity of the double bond towards singlet oxygen in solutions:[49]



However, in elastomers the reactivity of double bonds proved to be much lower (by a factor of 10^2–10^3).[50] This is the main reason why the pathway involving $^1O_2$ cannot compete with the radical chain mechanism for the oxidation of materials based on polydienes.

2. Stabilisation of Elastomers to the Action of Light

The following main mechanisms of the action of photostabilisers of polymeric materials have now been established: (a) shielding (ability to absorb ultraviolet light); (b) quenching of the excited state of the polymer or additives; (c) deactivation of impurities; (d) decomposition of hydroperoxides; (e) interaction with free radicals.

The experimental data concerning the action of stabilisers in polydienes show that the most effective photostabilisers are photoresistant antioxidants (Table 4). Shielding also plays an important role.

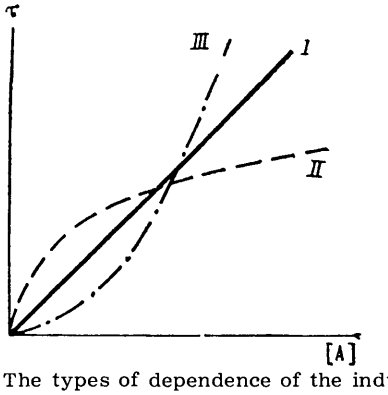


Figure 18. The types of dependence of the induction periods in the photochemical oxidation of elastomers on the concentration of photostabilisers [A].

As a result of the predominance of these two mechanisms, three types of concentration dependences of the induction periods in the photochemical oxidation of elastomers are characteristic of the majority of photostabilisers which are most effective for polydienes (Fig.18). In conformity with the theory of critical phenomena, in the inhibited oxidation[51] of the first type (Fig.18, curve *1*), a nearly linear variation of the induction period τ with the stabiliser concentration [A] is observed when the parameter k_{ROOH}/W_0, characterising the ratio of the rates of degenerate branching and initiation by impurities, does not exceed 10^7 litre mol^{-1}. Such variation is in fact characteristic of the relatively

photoresistant, weakly absorbing antioxidants of the class of stable nitroxy-radicals in polydienes (Fig.19) as a consequence of the high value of W_0.

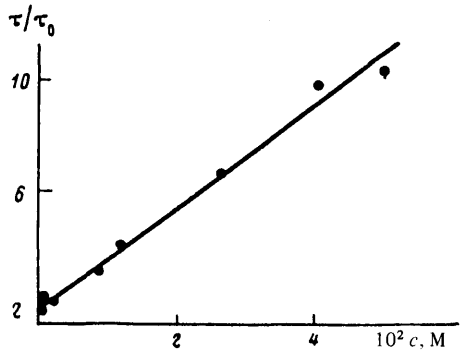


Figure 19. Dependence of the induction period in the photochemical oxidation of DSSK-30 butadiene–styrene rubber on the concentration of the 4-benzoyloxy-2,2,6,6-tetramethylpiperidin-1-yloxy-radical.

A second type of dependence of τ on [A] (with saturation, curve II in Fig.18) is observed when the stabiliser is photochemically unstable and can initiate photochemical oxidation:

$$\mathrm{RH} \xrightarrow{h\nu;\, W_0} \dot{\mathrm{R}},$$
$$\dot{\mathrm{R}} + \mathrm{O_2} \xrightarrow{k_1} \mathrm{R\dot{O}_2},$$
$$\mathrm{R\dot{O}_2} + \mathrm{RH} \xrightarrow{k_2} \mathrm{ROOH} + \dot{\mathrm{R}},$$
$$\mathrm{A} + f\mathrm{R\dot{O}_2} \xrightarrow{k_4} \text{products},$$
$$\mathrm{A} + \mathrm{RH} \xrightarrow[\mathrm{O_2}]{h\nu;\, k_5} \mathrm{R\dot{O}_2}.$$

In this case

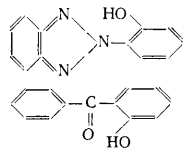
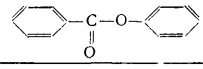
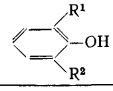
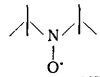
$$\tau = \frac{1}{k_5\,(1 + m/f)} \ln\left\{1 + \frac{k_5\,(1 + m/f)\,[\mathrm{A}]}{W_0}\right\}, \qquad (8)$$

where m is the number of radicals formed from the stabiliser A and f is the inhibition coefficient. An example of such a relation is presented in Fig.20.

A third type of such variation, to which curve III in Fig.18 corresponds, is characteristic of the case where the same substance behaves both as the antioxidant and as the absorber of ultraviolet light. The concentration variation of τ is described by the equation

$$\tau = \frac{2.3f\,[\mathrm{A}]^2 \varepsilon l}{W_0}, \qquad (9)$$

Table 4. Mechanisms of the photoprotective action of stabilisers.

Type of stabiliser	Main fragment	Effectiveness in polydienes	Main mechanism	Additional mechanism	Factor limiting effectiveness
Benzotriazoles and benzophenones		Low	Quenching	Shielding (large thicknesses)	—
Phenyl benzoates and phenyl salicylates		Low	Rearrangement to benzoates	Shielding (large thicknesses)	—
Aromatic amines	Ar—NH—Ar	Low	Interaction	—	Photostability
Sterically hindered phenols		Moderate	Interaction with radicals	—	Photostability
Sterically hindered amines		High	Oxidation with formation of inhibitors	—	Photostability of nitroxy-radicals
Stable nitroxy-radicals		High	Interaction with radicals	—	Photostability
Metal complexes (with dialkyldithiocarbamates)	ML_n, where $L = R_2N—\overset{\overset{S}{\|}}{C}—S—$	Moderate	Decomposition of hydroperoxides	Interaction with radicals; shielding	Low photostability
Azophenols and azoamines	Ar—N=N—Ar—X, where X=OH, NH_2	High	Interaction with radicals	Shielding (large thicknesses)	Low photostability

where ε is the extinction coefficient and l the thickness of the polymer film. The experimental curve corresponding to this type is illustrated in Fig.21.

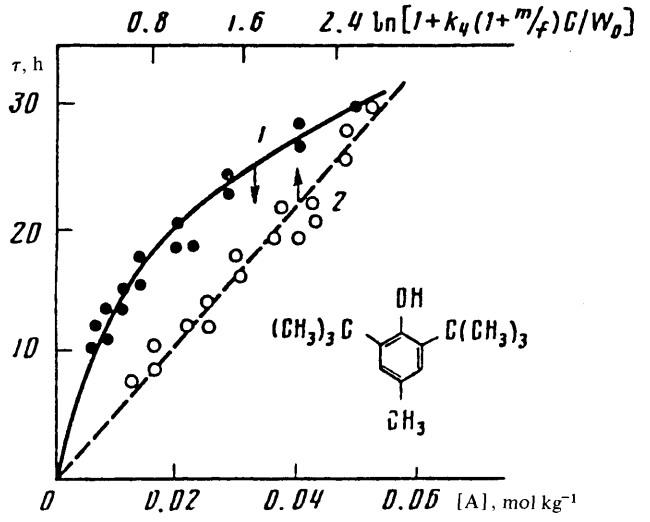


Figure 20. Dependence of the induction period in the photochemical oxidation of a film of IST-30 butadiene–styrene block copolymer on the concentration of 2,6-di-t-butyl-4-methylphenol (curve *1*) and its linear form in terms of the variables of Eqn.(8) (line *2*).

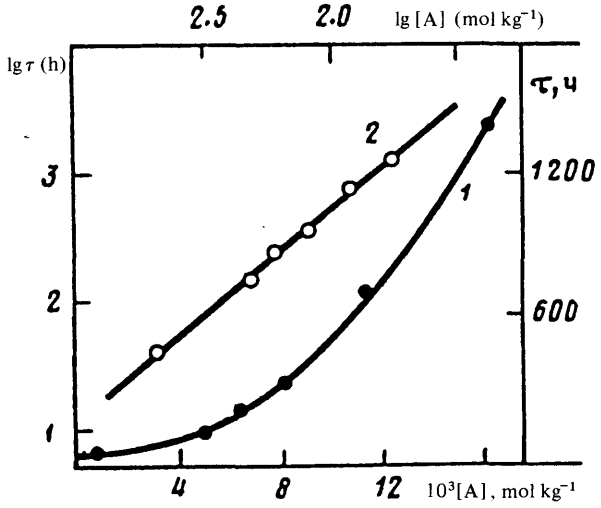
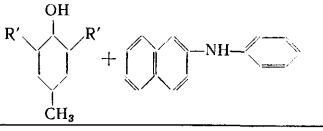
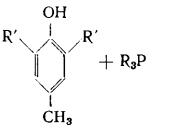
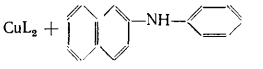
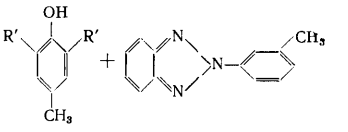
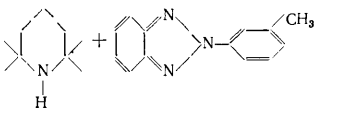


Figure 21. Dependence of the induction period in the photochemical oxidation of a film of the IST-30 butadiene–styrene block coploymer on the concentration of 4-hydroxy-3-methylphenylazo(azobenzene) (line *1*) and its logarithmic form (line *2*).

(a) *Synergism in the stabilisation of polymers towards the action of light.* Synergistic mixtures of stabilisers, whose classification as well as that of the mechanism of the synergism are given in Table 5, are widely used in practice for the stabilisation both of elastomers and of other polymeric materials.[52–57]

Table 5. The principal mechanism of the action of synergistic systems.

Mechanism	General mechanism of action of system	Example of system
Thermal oxidation		
Regeneration of active inhibitor	$A^1 \rightleftharpoons \dot{R}$ (+A^2)	
Decrease of critical inhibitor concentration	$RO_2 + RH \rightarrow ROOH + \dot{R}$ $ROOH \rightarrow RO_2$ $RO_2 + A^1 \rightarrow$ products $ROOH + A^2 \rightarrow$ products Tbl	
Formation of new stabiliser	$A^1 + A^2 \rightarrow A^3$	
Photochemical oxidation		
Quenching of excited states of antioxidant	$A \rightleftharpoons A^* \rightarrow$ products (Q)	
Diffusion of antioxidant from the volume protected by the u.v. ligh absorber to the surface layer undergoing photochemical oxidation	$[A]_{eff} = [A]_{av} L/l$	

Notation: L = thickness of specimen, l = thickness of surface layer, A* = excited state of photostabiliser, Q = quenching agent, and R′ = $C(CH_3)_3$.

In the photochemical oxidation of polymers systems acting according to two fundamental principles are capable of exhibiting synergism: with and without the interaction of the components. Among the possible mechanisms, the principal ones are the physical mechanisms involving the quenching of excited states of the antioxidants, the diffusion of the antioxidant from the volume protected by the ultraviolet light absorber to the surface layer undergoing oxidation, and the influence of additives on the distribution of stabilisers in polymers.

The diffusion mechanism of the synergism was analysed quantitatively for an antioxidant which does not absorb light and a strongly absorbing ultraviolet light absorber, both uniformly distributed throughout the thickness of the specimen.[55] The light intensity in the polymer film decreases as one moves away from the irradiated surface in proportion to $\exp(-\varepsilon c x)$, where x is the distance from the surface and c the concentration. The rate of photochemical processes varies in accordance with the same law within the thickness of the specimen and one can assume

that photoprocesses proceed mainly in a narrow surface zone whose width is $1/\varepsilon c$. The antioxidant present in the polymer is consumed in this zone at a much higher rate than in the deeper layers. The concentration gradient thus generated leads to the appearance of a diffusional flux of the antioxidant from the bulk of the specimen to the surface layer, the flux decreasing the rate of the photoprocess in the reaction zone, while the deep layers of the specimen serve as a "reservoir" of the antioxidant.

For an oxidation process described by the general scheme

$$\mathrm{RH} \xrightarrow{O_2;\ W_0} \mathrm{R\dot{O}_2},$$
$$\mathrm{R\dot{O}_2} + \mathrm{RH} \xrightarrow{k_1} \mathrm{ROOH} + \dot{\mathrm{R}},$$
$$\mathrm{R\dot{O}_2} + \mathrm{R\dot{O}_2} \xrightarrow{k_2} \text{products},$$
$$\mathrm{R\dot{O}_2} + \mathrm{A} \xrightarrow{k_3} \text{products},$$
$$\mathrm{ROOH} + \mathrm{A} \xrightarrow{k_4} \text{products},$$

the following system of equations has been obtained taking into account the diffusion of the antioxidant into the zone where oxidation takes place:

$$\frac{\partial [\mathrm{R\dot{O}_2}]}{\partial t} = W_0 \exp(-\varepsilon c x) - f_b k_3 [\mathrm{R\dot{O}_2}][\mathrm{A}] - 2k_2 [\mathrm{R\dot{O}_2}], \qquad (10)$$

$$\frac{\partial [\mathrm{A}]}{\partial t} = -k_4 [\mathrm{ROOH}][\mathrm{A}] - f_b k_3 [\mathrm{R\dot{O}_2}][\mathrm{A}] - \frac{\partial^2 [\mathrm{A}]}{\partial x^2} D, \qquad (11)$$

$$\frac{\partial [\mathrm{ROOH}]}{\partial t} = k_1 [\mathrm{RH}][\mathrm{R\dot{O}_2}] - f_h k_4 [\mathrm{ROOH}][\mathrm{A}], \qquad (12)$$

subject to the initial conditions

$$[\mathrm{A}]_{t=0} = [\mathrm{A}]_0;\ [\mathrm{R\dot{O}_2}]_{t=0} = 0;\ [\mathrm{ROOH}]_{t=0} = 0$$

and the boundary conditions

$$\left.\frac{\partial [\mathrm{A}]}{\partial x}\right|_{\substack{x=0,\\ x=l}} = 0;\ \left.\frac{\partial [\mathrm{R\dot{O}_2}]}{\partial x}\right|_{\substack{x=0,\\ x=l}} = 0;\ \left.\frac{\partial [\mathrm{ROOH}]}{\partial x}\right|_{\substack{x=0,\\ x=l}} = 0,$$

where l is the thickness of the film, D the diffusion coefficient of the antioxidant, ε and c are the extinction coefficient and the concentration of the ultraviolet light absorber, and f_b and f_h are the branching and inhibition coefficients.

The system in a general form can be solved numerically and, subject to a number of physically justified simplifying assumptions, also analytically. Two typical cases are of the greatest interest from the practical point of view.

1. Rapid diffusion regime, where the concentration of A is almost constant throughout the thickness of the specimen. For strongly absorbing specimens and when substances A reacting with free radicals are employed, we have

$$\tau = \left\{\frac{([\mathrm{A}]_0 - [\mathrm{A}])}{W_0}\right\} f_b \varepsilon c l. \qquad (13)$$

In the case of compounds A which react with peroxides, we obtain

$$\tau = \left\{\frac{([\mathrm{A}]_0 - [\mathrm{A}])}{(k_2 [\mathrm{RH}])}\right\} f_h \varepsilon c l \left(\frac{2k_3}{W_0}\right)^{1/2}. \qquad (14)$$

2. Diffusion-controlled regime. Diffusion results in an additional supply of the antioxidant to the surface layer, but this does not equalise the concentration of A throughout the thickness of the specimen. The corresponding expressions for τ assume the following form:

$$\tau = \pi D \{f_b \varepsilon c ([\mathrm{A}]_0 - [\mathrm{A}])/2W_0\}^2; \qquad (15)$$

$$\tau = [2\pi D k_3/W_0]\{f_h \varepsilon c ([\mathrm{A}]_0 - [\mathrm{A}])/(2k_3[\mathrm{RH}])\}^2. \qquad (16)$$

It follows from theoretical relations that the photostability of the specimen depends on the overall concentration of stabilisers, the component ratio (the 1:1 ratio is optimum), the thickness of the specimen, and, in the diffusion-controlled regime, also the light intensity. These relations have been tested experimentally. The results presented in Fig.22 show that there is a satisfactory agreement between theory and experiment.

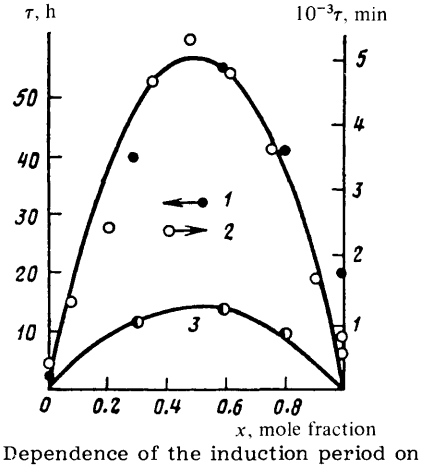


Figure 22. Dependence of the induction period on the mole fraction of the antioxidant in the photochemical oxidation of 60 μm (curve *1*) and 10 μm (curve *3*) polybutadiene films containing a mixture of 4-heptyloxy-2-hydroxybenzophenone and 2,6-di-t-butyl-4-methylphenol as well as films of polychloropropene containing a mixture of 2-hydroxy-4-octyloxybenzophenone and bis(3-t-butyl-2-hydroxy-5-methylphenyl)methane (curve *2*).

(b) *Synergism in the quenching of the excited states of the antioxidants by photostabilisers.* If the antioxidant is photochemically active, then synergism is possible when a photostabiliser capable of deactivating the excited states of the antioxidant is used as a second component. In the presence of a mixture of a quenching agent Q and an antioxidant A, the dependence of the induction period on the concentrations has the following form:

$$\frac{\tau}{\tau_0} = \ln(1 + \beta[\mathrm{A}]\eta)/\eta \ln(1 + \beta[\mathrm{A}]), \qquad (17)$$

where $\beta = k_5(1 + m/f)/W_0$, k_5 is the rate constant for the photochemical reaction of the antioxidant, and $\eta = [\mathrm{A}^*]_Q/[\mathrm{A}^*]$ a coefficient characterising the decrease of the rate constant for photochemical initiation involving A in the presence of Q. Fig.23 presents the dependence of the relative induction period in the photochemical oxidation of polybutadiene films on the relative concentration of the quenching agent, illustrating this mechanism of the synergism.

A new principle for the construction of synergistic systems involving the use of additives influencing the distribution of stabilisers in polymers has been proposed recently on the basis of a detailed study of the solubilities and distribution of additives in polymers. Such additives can be both chemically relatively inert substances (for example,

surfactants) and certain stabilisers. The highest efficiency of the synergistic mixture is then attained when photostabilisers are employed as the additional additives.[57]

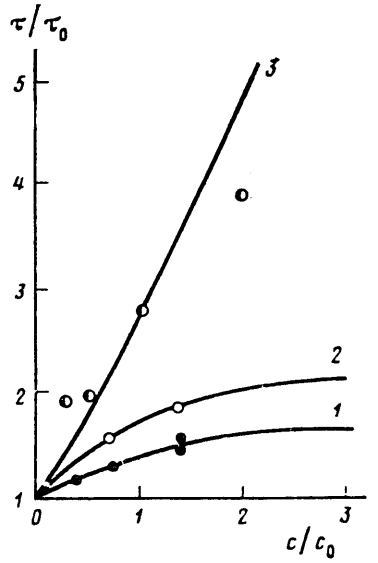


Figure 23. Dependence of the induction period on the concentration of the quenching agent. Curves—theoretical calculations for $\beta[A]_0 = 2$ (curve *1*), 4 (curve *2*), or 20 (curve *3*); circles—experimental data for mixtures of 2-(2-hydroxy-5-methylphenyl)benzotriazole and bis(3-t-butyl-2-hydroxy-5-methylphenyl)methane (curves *1* and *2*) or 2,6-di-t-butyl-4-phenylphenol (curve *3*).

(c) *The influence of the supermolecular structure on the efficiency of photostabilisers.* Thermoelastoplastics have now found extensive applications. These materials occupy an intermediate position, as regards their properties, between plastics and elastomers and consist of block copolymers. When the properties of the block differ appreciably, they form different phases with a fairly sharp interface.[58,59] Such materials include, for example, diene–styrene block copolymers. The kinetics of the photoprocesses are then influenced by the distribution of the stabilisers between the phases and their migration from one phase to another. For diene–styrene block copolymers, the difference between the reactivities of the additives to the "hard" and elastomeric phases is so significant that this property can be used to investigate the distribution and migration of additives.

For example, even after a brief irradiation with ultraviolet light of copolymer specimens containing stable nitroxy-radicals, the latter are almost fully consumed in the polydiene phase, whereas not more than 10% are consumed in the polystyrene phase (Fig.24, *a* and *b*). When the specimen is kept in the dark, the concentration of the nitroxy-radicals in the polystyrene phase falls, while that in the polydiene phase increases (Fig.24c), and after prolonged storage the initial distribution of the additive is restored. These data made it possible to estimate the distribution of the stabiliser between the phases and to determine the diffusion coefficient in the "hard" phase.

The photostability of the copolymer depends on the ratio of the volumes of the "hard" and elastomeric phases. Effective stabilisation requires the use of additives which are predominantly concentrated in the hard phase where they are more resistant to the action of light and hence can diffuse to the elastomeric phase being oxidised, ensuring its photostabilisation. The interfacial diffusion of the stabiliser must also be taken into account in selecting the conditions for accelerated tests of elastomers for photostability.

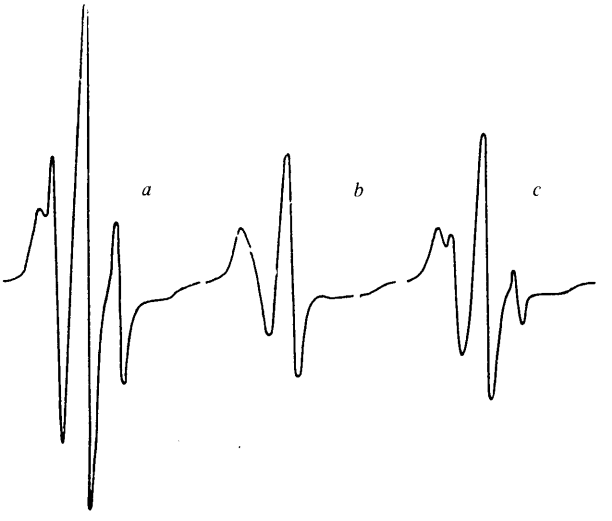


Figure 24. EPR spectra of the 4-hydroxy-2,2,6,6-tetramethylpiperidin-1-yloxy-radical before (*a*) and after (*b*) irradiation with ultraviolet light for 2.5 min and also after maintaining the irradiated specimen in the dark for 100 min (*c*).

V. OZONE-INDUCED AGEING OF ELASTOMERS

Ozone is an active species in the ageing of elastomers containing double bonds in the main chains of the macromolecules. Ozone is formed at sites where electric motors operate, electric welding is carried on, and sources of ultraviolet light are employed. Considerable amounts of corrosive gases, ejected with the exhaust gases of automobiles and with factory smoke, are formed in the air of large cities and industrial undertakings. Photochemical smog, one component of which is ozone, is formed from these gases under special meteorological and geographical conditions. The concentration of ozone in photochemical smog (up to 5×10^{-1} mg m^{-3}) is sufficient for the ageing of the majority of technical rubber articles.[60]

As ozone adds to the macromolecules of the elastomer, the formation and growth of surface cracks and the accumulation of oxygen-containing groups in the surface layer are observed. The absorption of ozone by stretched elastomer specimens differs significantly from that by undeformed specimens.[61] The rate of absorption of ozone by the specimens in the absence of stretching stresses diminishes after several minutes of exposure. The layer formed on the surface, on which the double bonds have reacted,

inhibits further absorption of ozone. The rate of absorption of ozone by stretched specimens remains close to the initial value, since the cracks formed under the influence of mechanical stresses open up and continually regenerate a fresh surface.

1. Kinetics and Mechanism of the Degradation of Polymers by Ozone

When polymers are acted upon by ozone, a decrease of the molecular weight and the accumulation of oxygen-containing functional groups (acids, ketones, peroxides, etc.) are observed.[62] Table 6 presents the effective rate constants for the reactions of ozone with the functional groups and the numbers of breaks in the chain per reaction step (n) in solution in carbon tetrachloride. The following trend has been observed for polymers: with increase in the rate constant for the reaction of ozone with the polymer, the number of breaks per reaction step diminishes.

Table 6. The rate constants for the reactions of ozone with various polymers k_{eff} and the numbers of chain breaks n per reaction step in solution in CCl_4 at 20 °C.[62]

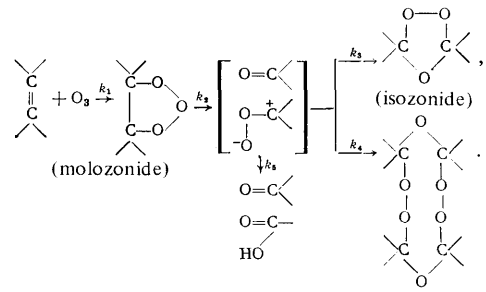
Polymer	k_{eff}, litre mol^{-1} s^{-1}	n
Polyphenyl	$5.0\cdot10^{-2}$	—
Polynaphthalene	$2.0\cdot10^{3}$	—
Polycarbonate	3,0	—
Polyisobutylene	$1.2\cdot10^{-2}$	0.05
Polyethylene	$4.6\cdot10^{-2}$	0.1
Ethylene-propylene copolymer	$6.0\cdot10^{-2}$	0.06
Polypropylene	$8.0\cdot10^{-2}$	0.1
Polystyrene	0,3	0.01
Polyvinylcyclohexane	0,8	—
Polyphenylacetylene	$1.4\cdot10^{3}$	—
Polybutadiene	$6.0\cdot10^{4}$	0.06
Polyisoprene	$4.4\cdot10^{5}$	0.002
Polychloroprene	$1.0\cdot10^{4}$	—

Table 7. The rate constants for the reactions of ozone with elastomers deposited on a fine-grained silica gel at 20 °C.

Elastomer	$10^{-4}\,k_{eff}$, kg mol^{-1} s^{-1}
Natural rubber	10.5
Polyisoprene	10.5
Polybutadiene	5.1
Butadiene-styrene copolymer (SKS-30 ARKP)	4.6
Polychloroprene	1.0
Butyl rubber	10.5

Table 7 presents the rate constants for the reactions of ozone with the elastomers deposited on a fine-grained silica gel in order to eliminate diffusion-dependent limitations. These rate constants are satisfactorily correlated with the rate constants for the corresponding polymers in solution (Fig.25). This makes it possible to predict the resistance of elastomeric materials to ozone with the aid of model experiments carried out in solution.

The degradation of elastomer fragments with unsaturated bonds proceeds via the formation of a molozonide and zwitter-ions in accordance with the scheme



The macromolecules are cleaved only as a result of the reaction with the rate constant k_5; the contribution of this reaction does not exceed 1–2%. The main reaction product is the isozonide.

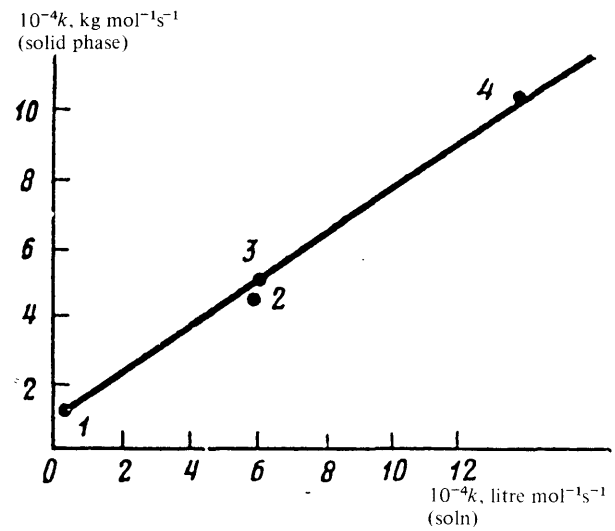


Figure 25. Correlation between the rate constants for the reactions of ozone with polydienes in solution and in the solid phase: *1*) polychloroprene; *2*) butadiene–styrene copolymer; *3*) *cis*-polybutadiene; *4*) *cis*-polyisoprene.

2. Protection of Polymeric Materials Against the Action of Ozone

Antiozonants and wax are used to protect elastomers against the action of ozone. Antiozonants include compounds of two classes: *p*-phenylenediamines and dihydroquinolines. There exist different explanations of the protective action of *p*-phenylenediamines in relation to ozone:

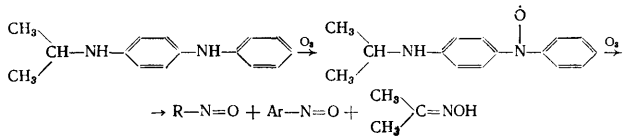
(a) The antiozonant reacts with ozone, diffusing to the surface of the article and forming a protective layer which constitutes a physical barrier.[63] This mechanism does not explain the effectiveness of antiozonants in elastomers subjected to a dynamic load, where the protective layer cannot remain continuous.

(b) The antiozonant reacts with the product of the addition of ozone to the polymer, preventing the decomposition of the resulting ozonides[64-66] or connecting the ends of the ruptured chains.[67,68] This hypothesis has not so far received convincing experimental confirmation.

(c) The antiozonant catalyses the decomposition of ozone on the surface of elastomers. This mechanism is inconsistent with the process kinetics.

(d) The antiozonant is a powerful competitor with the elastomer double bonds in the reaction with ozone. Despite its satisfactory agreement with many experimental data,[69] this mechanism cannot explain why other additives which actively react with ozone are ineffective.[70]

Ozone reacts with *p*-phenylenediamine to form nitroxyradicals, which are further converted into nitrosoalkyls, nitrosoallyls, and oximes:[71]



Dihydroquinones are less reactive than *p*-phenylenediamines but the antiozonants of these classes exhibit synergism in their influence on the resistance to ozone.[72]

Among the explanations of the protective action of antiozonants, the last has received the greatest amount of experimental confirmation: the antiozonant traps ozone on the surface of the elastomer. Fig.26 presents the logarithmic dependence of the relative time before the appearance of cracks on the relative rate constant for the interaction of ozone with the antiozonant in solution in carbon tetrachloride.[69]

The protective action of waxes is based on two effects:[73] the creation of a binary layer on the surface which diminishes the permeability of the polymer to ozone and interaction with ozone. For protective waxes, there is also a correlation between the time before the appearance of cracks and the rate constant for the reaction of ozone with the waxes (Table 8).

Table 8. The rate constants for the reactions of ozone with protective waxes in solution in CCl_4 at 23 °C on the time before the appearance of a crack on the SKI-3 elastomer during atmospheric ageing.[73]

Wax	$10^3 k$, litre $mol^{-1}s^{-1}$	τ, days	
		Batumi	Tashkent
Paraffin	4	30	32
MEV-1	42	54	60
MEV-2	60	180	90
MEV-4	70	100	65
Ceresite-80	6	119	59
MEVu-2	107	687	105

VI. THE INFLUENCE OF MECHANICAL STRESSES ON THE KINETICS OF THE REACTIONS OF ELASTOMERS

The influence of stress on the reactivity of elastomer macromolecules in reactions of various types has been observed and studied quantitatively. The stresses have accelerating, retarding, and neutral effects. The experimental data have been interpreted theoretically from the standpoint of transition state theory and conformational analysis.[74]

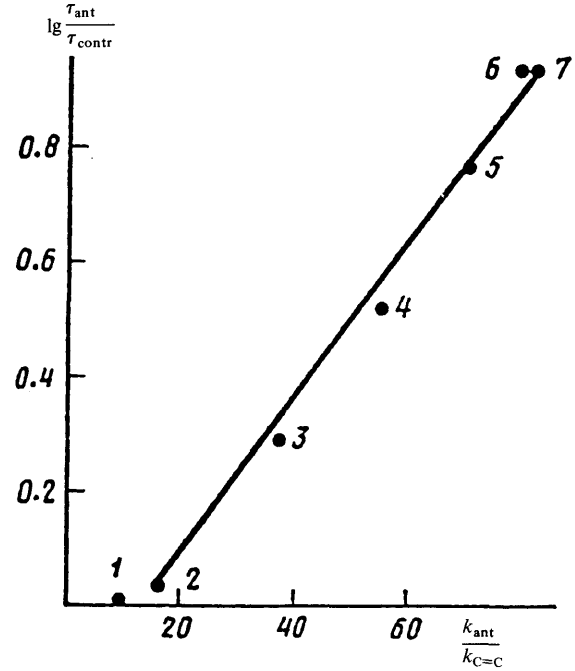
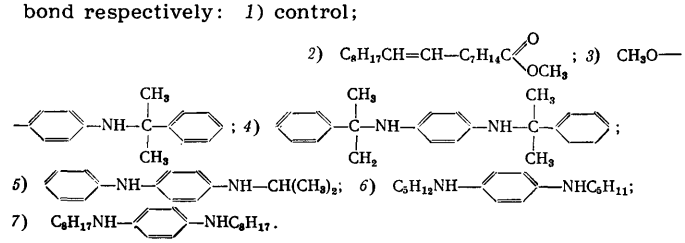


Figure 26. Logarithmic dependence of the optimum time τ_{ant} of the appearance of cracks on the relative rate constant for the interaction of ozone with antiozonants in solution in CCl_4; k_{ant} and $k_{C=C}$ are the rate constants for the reactions of ozone with the antiozonant and the double bond respectively: *1*) control;



In real articles excessive stresses can arise in the region of defects (for example, at the mouth of the crack) and the effects described above are in fact to be expected there.

One of the most dangerous reagents is atmospheric ozone, whose action is accompanied by the formation of microcracks and macrocracks. Fig.27 presents data concerning the influence of stretching stresses and deformations on the rate of growth of cracks, the lifespan, the degree of oxidation, and the chemical relaxation time of the elastomers. With increased load, the above parameters are found to increase in the initial stage up to ~20% deformation. After that, the degradation process slows down—the resistance to ozone-induced ageing increases with increasing stretching stress. This constitutes the fundamental difference from the familiar

dependence of the life of polymers on the load—an exponential decrease of the lifespan with increasing σ (Zhurkov's equation).

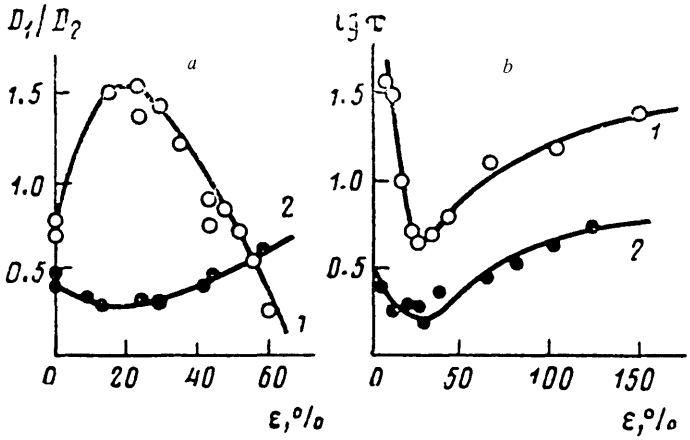
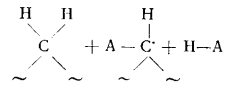


Figure 27. Variation of the optical density ratios D_{1720}/D_{1640} (curve *1*) and D_{1640}/D_{1375} (curve *2*) with the degree of deformation of *cis*-polyisoprene in its reaction with ozone; $[O_3] = 7 \times 10^{-8}$ M, 20 °C; *b*) variation of the chemical relaxation time of *cis*-polyisoprene with the degree of deformation in an atmosphere of ozone: *1*) $[O_3] = 2 \times 10^{-6}$ M; *2*) $[O_3] = 1 \times 10^{-5}$ M, 20 °C.

The phenomenon of "critical" deformation can be accounted for by a change of the reactivity of the double bond. This effect is caused by the competition of two opposed processes: the formation of cracks, which accelerate degradation, and a decreased reactivity of the double bond at the mouth of the crack. The first factor is manifested even for the smallest deformations. The contribution of the second is possible only when breaking stresses appear and therefore the first and second factors predominate respectively under the conditions of small and large deformations.[74]

The critical deformation is manifested most strikingly in elastomers with a *cis*-structure; in natural rubber and its synthetic analogue—polyisoprene as well as polybutadiene. In all these cases the stretching deformations do not increase the hardness of the elastomers and it is therefore impossible to account for the decreased rate of oxidative degradation with increasing deformation by a change in physical properties. The retarding influence of the physical factor can be shown only in systems where the molecular mobility diminishes with increasing stretch, as happens, for example, in the butadiene–styrene rubber with a *trans*-structure; however, the critical deformation in such systems is much less pronounced. This is apparently caused mainly by the fact that they have a *trans*-configuration of the monomer units, the reactivity of whose double bonds does not diminish under the influence of loads.

Many reactions of elastomers are accompanied by the rehybridisation of the carbon atoms in the main chain from the sp^2 to the sp^3 state. These can be both free-radical processes and reactions proceeding via S_N1 and S_N2 mechanisms. One of the commonest processes of this type is the abstraction of a hydrogen atom:



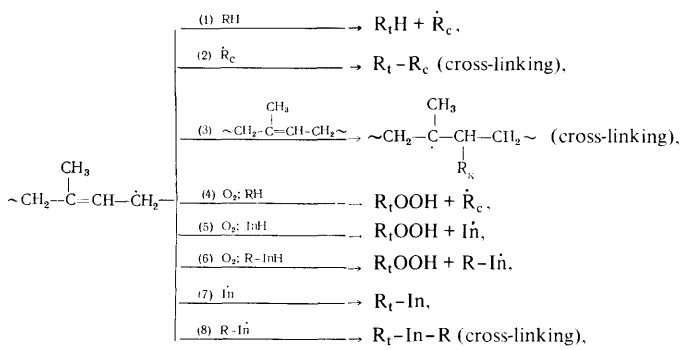
where A is a hydrogen acceptor (a molecule, a radical, or an atom, for example, O_3, O_2, RO_2, HO, CCl_3, Cl, Br, stable nitroxy-radicals, etc.). This reaction is extremely important in the thermo-oxidative degradation of elastomers (initiation, chain propagation, etc.). Recent studies have shown that the rates of reactions of the above class increase under the influence of external stretching stresses. A universal equation relating the rate of reaction to the load and temperature has been obtained:[74]

$$\ln\left(\frac{v_\sigma}{v_0}\right) = \frac{\alpha\sigma}{RT}, \qquad (18)$$

where ν is the rate of reaction, the subscripts σ and 0 refer to a polymer specimen with a load and without a load respectively, σ is the stress, and α a proportionality coefficient, which depends on the nature of the acceptor and the supermolecular structure of the specimen.

VII. THE ROLE OF RADICAL REACTIONS IN THE WEAR OF VULCANISED ELASTOMERS

Antioxidants exert a significant influence on the rate of wear of vulcanised elastomers with polysulphide cross-links under "rolling-up" conditions, low-molecular-weight antioxidants increasing the rate of the process and those linked to the network decreasing it.[75] These data can be accounted for by the following reaction scheme for the terminal macroradicals arising as a result of mechanical breaks in the vulcanisation network in the region of the rupture centre, which is produced when a strip is torn off and twisted in the "net".



where R_t and R_c are the terminal and central radicals respectively.

Reactions (2), (3), and (8) lead to the formation of new cross-links and thereby heal the network defects, which is the cause of the retardation of wear in the absence of low-molecular-weight antioxidants.

In the presence of low-molecular-weight antioxidants the terminal macroradicals in the region of the growing decomposition centre are stabilised in the reactions with the antioxidants and thereby prevent the processes leading to the healing of the network defects.[75]

The problem of the ageing and stabilisation of elastomers constitutes a major branch of polymer materials science—the science concerned with the creation of polymeric materials

and the preservation or regulation of their physical properties. Chemical processes alter the structure and physical properties of polymers, while the structural–physical properties of the polymer strongly influence in their turn the direction and rate of its chemical reactions.

Thus the physicochemical approach to problems of polymer materials science is best adapted to the specific features of this field, being concerned with a combination of the problems of the physics and chemistry of elastomeric materials, and creating new ways and principles for the control of their properties and stability.

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Institute of Chemical Physics,
USSR Academy of Sciences,
Moscow