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New aspects of the problem of the ageing and stabilisation of polymers

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Abstract. The results of the most recent studies in the field of the ageing and stabilisation of polymers are presented. The review deals with the questions of the photo-ozone and radiation induced ageing of polymers, and thermo-oxidative degradation and stabilisation of elastomers, various aspects of the interaction of polymers with corrosive media, the problems of the synthesis and efficiency of natural and synthetic stabilisers, and various applications of polymers and polymer blends. New approaches and methods for the investigation of the degradation of polymers are described. The bibliography includes 78 references.

I. Introduction

The regulation of the lifetime of polymer articles is not only a chemical but also a social problem of current interest. On the one hand, prolongation of the duration of use and of storage life is equivalent to an increase in the output of polymeric articles and an improvement in their quality.[1] On the other hand, the accumulation of polymer waste brings to the fore problems of the protection of the environment and of the utilisation of polymeric products.[2] The search for a new method for the modification of polymeric articles in order to improve their operational characteristics (in the first place, in order to modify the properties of their surface) and for the synthesis of polymers with a controllable lifetime has not lost its interest.[3]

Studies on the diffusion, sorption, and desorption of low-molecular-mass compounds in a polymer phase are of interest. This is associated not only with the problem of the protection of polymeric materials against the loss of stabilisers but also with the use of polymers in medicine and the creation of new polymeric long-acting medicinal systems.

The present review deals with problems of regulating the duration of the use and storage and the ageing and stabilisation of polymers as well as the search for ways of prolonging and shortening the lifetime of polymeric articles within the framework of studies carried out in our country during recent years. The review includes also information concerning the prediction of a reliable operating lifetime, which will permit a fuller use of polymeric articles without risk of their premature breakdown.

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II. Thermodynamic and kinetic aspects of the photo- and radiation-induced ageing and photostabilisation of polymers

1. Photo-ozone ageing of polymers

The ageing of polymers under natural conditions takes place under the simultaneous influence of many factors (light, ozone, heat, etc.). Ivanov and Shlyapintokh[4] showed recently that synergism may be observed in photo-ozone ageing. Thus it was observed in a study of the ageing of rubbers based on polydieneurethanes that, under the simultaneous influence of ozone and light, cracks arise much faster than on exposure to ozone alone, while exposure to light alone does not lead to the formation of cracks during the period of observation (Fig. 1*a*).

The synergistic effect of light and ozone is also manifested on non-stabilised resins and resins containing antiozonants and photostabilisers. The mechanisms of the action of these influences are then different. Fig. 1*b* shows that an antiozonant of the class of *p*-phenylenediamine, which protects the polymer against ozone quite effectively, becomes inactivated when acted upon by light and ozone simultaneously. On the other hand, a photostabiliser of the class of azo-compounds actually accelerates the ozone-induced ageing process, which is apparently due to its catalytic properties. At the same time, when one uses a mixture of this photostabiliser with an antiozonant acting in accordance with a physical mechanism, a synergistic enhancement of the protective effect is observed. Thus, during the photoozone-induced ageing of a polymer, synergistic phenomena of two types are manifested: the synergistic effect of UV light and ozone; the mutual synergistic influence of antiozonants and photostabilisers.

2. A special type of kinetics in the photochemical oxidation of polyamides

A series of independent tests confirmed[5] the hypothesis, put forward by Postnikov, of the ketoimide mechanism of the oxidation of aliphatic polyamides (PA). An unusual type of kinetics, for which there are as yet no analogues in the photochemical oxidation of other polymers, of the variation of the concentrations of the principal intermediates, i.e. the ketoimide fragment of the macromolecule ($\sim CONHCOCOCH_2 \sim$) and the structurally similar unsaturated ketone, correspond to this new mechanism. Both products have dual functions: under the influence of light, they behave as photoinitiators of the oxidation chains and at the same time, regardless of the influence of light, they participate in kinetic chain transfer with dissociation of the macromolecule accompanied by the alternation of radicals of two types.

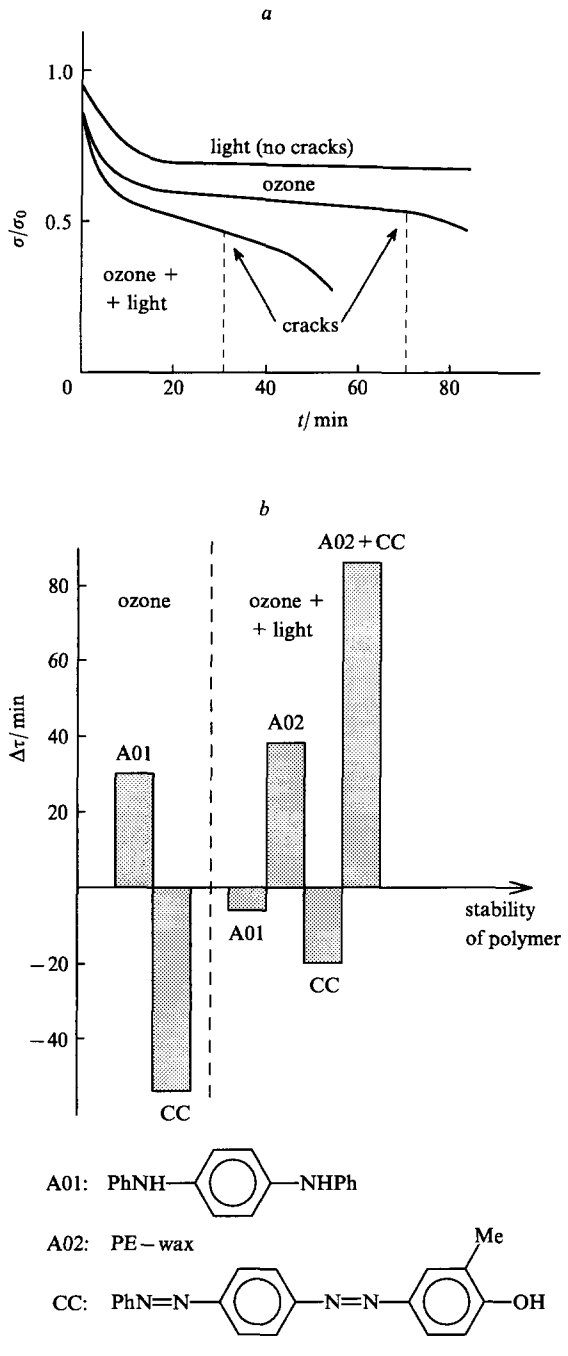


Figure 1. The synergistic effect of UV light and ozone in the ageing of polydieneurethanes: (*a*) kinetics of the relaxation of stresses; (*b*) kinetics of the formation of cracks.

Under any conditions of the photochemical oxidation of polyamides the stationary concentrations of these products are established after a time and for deliberate regulation of the process it is necessary to discover the quantitative parameters which determine both the stationary concentrations themselves and the kinetics of their attainment. The ketone mechanism explained for the first time the known kinetics of the photochemical oxidation of polyamides under all irradiation conditions of practical interest.

The kinetics of the approach to a stationary regime in the case where a polyamide is acted upon by the longest-wavelength light still capable of inducing photooxidative degradation may serve as a clear example of the importance of the above findings. Under such conditions, the kinetic chain is transferred by intermediates (K and K′), but the photoinitiator is only one of them (the ketoimide K). The kinetics of the variation of their concentrations from the initial (K_0 and K'_0) to the stationary (K_{st} and K'_{st}) values are then described by the following functions:

$$K = K_{st}\left[\coth\left(\frac{F+Gt}{2}\right)\right]^2,$$

$$K' = K_{st} - (K'_{st} - K'_0)\times$$

$$\times\left[\left(\sinh\left(\frac{F+Gt}{2}\right)\right)^{Ak'_5/G} \Big/ \sinh\left(\frac{F}{2}\right)\right],$$

where F, G, A, and k'_5 are familiar parameters with a known physical significance:

$$F = \ln\left|\frac{(K_0)^{1/2} - (K_{st})^{1/2}}{(K'_0)^{1/2} - (K'_{st})^{1/2}}\right|,$$

$$G = -\left[\frac{k_7}{k_5}I_0\left(\frac{k_7}{k_5}I_0 + 4\frac{k_2}{k_6}\right)\right]^{1/2}\frac{k_5}{2},$$

$$A = 2\frac{k_2}{k_3}\left(\frac{k_3k_7I_0}{k_6k_2}K_{st}\right)^{1/2},$$

$$PO_2 + PA \xrightarrow{+O_2} POOH + PO_2^{\cdot}, \quad (1)$$

$$PO_2^{\cdot} \longrightarrow A + r^{\cdot}, \quad (2)$$

$$PO_2^{\cdot} \longrightarrow B + r^{\cdot}, \quad (2')$$

$$r^{\cdot} + PA \xrightarrow{+O_2} rH + PO_2^{\cdot}, \quad (3)$$

$$A \xrightarrow{+2O_2} K, \quad (4)$$

$$A \xrightarrow{+2O_2} K', \quad (4')$$

$$K + r \longrightarrow PO_2 + S, \quad (5)$$

$$K' + r \longrightarrow PO_2 + S, \quad (5')$$

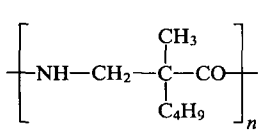
$$PO_2 + r \xrightarrow{-O_2} S, \quad (6)$$

$$K \xrightarrow{+I_0+2O_2} 2PO_2 + S. \quad (7)$$

Here k_i is the rate constant, the subscript i corresponding to the ordinal number of the reaction in the mechanism, I_0 is the light intensity, P is a polymer radical, PO_2 are the peroxide macroradicals $\sim CH_2CONHCH(OO^{\cdot})CH_2\sim$, r are low-molecular-mass radicals $HO_2^{\cdot}$ or O_2^{-}, A, K, and K′ are intermediate molecular products, B is the final product, and S denotes the dissociation of the macromolecule.

Functional relations of this type have not so far been considered in the kinetics of the photodegradation of polymers. Such relations help in the rational selection of photostabilisers. Previously stabilisers were selected without taking into account the actual mechanism of the photochemical oxidation of polyamides.

The observed mechanism is valid for different industrially manufactured aliphatic polyamides regardless of the number of CH_2 units. However, it ceases to operate in the absence of hydrogen atoms attached to the α- or β-carbon atom, for example, when they are substituted by alkyl groups, because the formation of the ketoimides

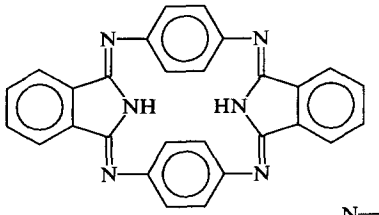


becomes impossible. As a result of this, the photochemical oxidation of poly(3-butyl-3-methylazetidine) follows completely different kinetics.

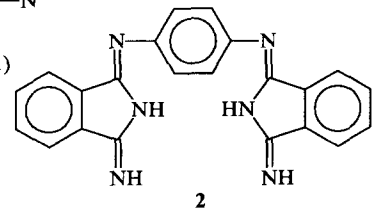
3. A new class of photostabiliser

Cellulose acetates (CA) are widely used nowadays in different branches of industry, but, owing to their inadequate photostability, the operating characteristics of articles made from this material become strongly impaired after a time. Therefore, despite the great variety of cellulose acetate stabilisers, the search for effective photostabilisers is still a timely problem.[6, 7]

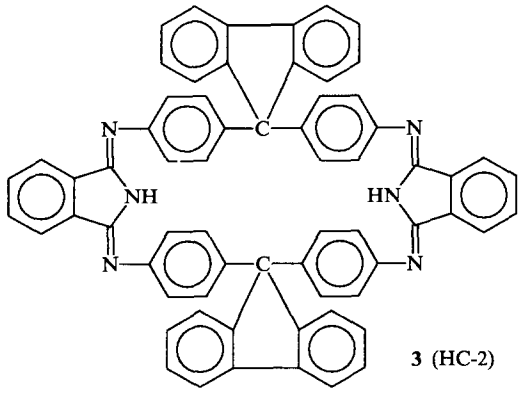
A new class of photostabilisers based on macroheterocyclic substances — hexaazacyclanes (HC) — has been developed.[8] Among different derivatives of hexaazacyclanes, phthalonitrile and its derivatives comprising *p*-phenylenediamine (a conjugated substance — compound **1** or HC-1) and 9,9-bis(4-dianilino)fluorene (a non-conjugated substance — compound **3** or HC-2) were selected for study. In order to determine the influence of the structure of the macrocyclic stabiliser on its properties, the product of the linear condensation of phthalonitrile and *p*-phenylenediamine (compound **2**) was also investigated. All the substances are powders with different colours (depending on the structure) ranging from yellow to brown. They are fairly compatible with cellulose acetate and do not impair the operating properties of the latter at concentrations in the range 5–7.5 mass%.



1 (HC-1)



2



3 (HC-2)

The proposed photostabiliser can act simultaneously via several mechanisms, among which the most important involve shielding from UV light, inhibition, and photosensitivity. The contribution of UV shielding to the overall effect of the stabiliser is calculated using the formula proposed by the present authors:[4]

$$i_p = \frac{D_{d+st}(1 - 10^{-D_d})}{D_d(1 - 10^{-D_{d+st}})},$$

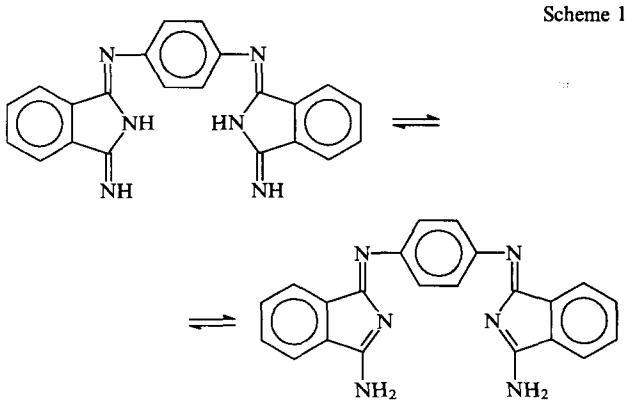
where D_d and D_{d+st} are the optical densities of the non-stabilised and stabilised films respectively. The coefficient i_p characterises the quantitative decrease in light absorption by the polymer owing to the presence of the stabiliser. Thus, if the effect of the stabiliser is limited to the absorption of UV light, then the rate of degradation falls by factor i_p relative to the amount of absorbed light.

The principal product of the degradation of cellulose acetate by UV radiation is acetic acid, the rate of formation of which characterises the photostability of the material. The overall effect of the increase in stability (A) is determined by the ratio of the rates of formation of acetic acid without stabiliser (W_0) and in its presence (W_{st}):

$$A = \frac{i_p W_0}{W_{st}}.$$

Data concerning the influence of the structure of the photostabiliser on the overall increase in the photostability of the composition are presented in Table 1. For all stabilisers, $A < 1$. Consequently these stabilisers not only provide a shield against UV light but they also operate as photosensitive elements.[9] The highest photosensitivity is shown by compound **2**. The point is that this substance has two resonance states (see Scheme 1 below), one of which contains amino-groups. Evidently these amino-groups act as photostabilisers in relation to the photodegradation of cellulose acetate, in agreement with the present authors data.[4]

Scheme 1



In terms of its photostabilising properties, HC-2 is superior to compound **2** but is inferior to HC-1. This is probably associated with the shorter length of the conjugated chain and the smaller number of aromatic groups in the structure of HC-2.

HC-1 is the most effective stabiliser. Its effective photostabilising properties could be accounted for by the simultaneous shielding and inhibiting activities. In order to estimate the possible contribution of the inhibition mechanism to the overall effect of HC-1, measurements were made of the kinetic parameters of the photochemical oxidation of unstabilised cellulose acetate and cellulose acetate stabilised by HC-1. These parameters are the chain oxidation parameters $k_p[PH]k_t^{-1/2}$ and the photoinitiation quantum yield P_i.

The results are presented in Table 2. The HC-1 stabiliser does not influence the cellulose acetate chain oxidation parameter or, in other words, it is not an inhibitor interacting with polymer radicals. On the other hand, the photoinitiation quantum yield P_i diminishes sharply in the presence of HC-1. This means that transition from the pure to the stabilised cellulose acetate alters the initiation mechanism, i.e. the stabiliser becomes the initiator instead of cellulose acetate. However, the significant decrease in P_i in the presence of HC-1 is also responsible for the overall protection against light. Thus HC-1 introduced into cellulose

Table 1. Dependence of the overall increase in photostability on the stabiliser structure.

Stabiliser[a]	A
1	0.40
2	0.21
3	0.31

[a] The stabiliser concentration in cellulose acetate was 5 mass%.

Table 2. Kinetic parameters of the photochemical oxidation of cellulose acetate at 25 °C in dry air.

Specimen	$10^{-4}k_p[PH]k_t^{-1/2}$/mol litre^{-1} s^{-1}	P_i
CA without stabiliser	2.2 ± 0.2	0.100
CA stabilised with HC-1 (concentration 5 mass%)	2.4	0.004

acetate acts both as a screen against UV light and as a photosensitive element.

The stabilising properties of HC-1 have been confirmed by comparative data, presented in Table 3, and the decrease in the viscosity of cellulose acetate solutions in acetone after the UV irradiation of films stabilised by HC-1 and one of the most effective stabilisers—carbazole-5,10,12-trisulfonamide (CTS). The stabilising properties of HC-1 are significantly more effective than those of CTS. The protective effect of HC-1 begins to be manifested at its relatively low concentrations (0.5 mass%), the maximum effect being attained at a concentration of 3 mass%. The high stabilising effect under the conditions of prolonged irradiation is also remarkable.

The photostabilising properties of polyhexaazacyclanes (PHC) have been investigated in cellulose acetate and polycaproamide (PA). The photostabilising activity of PHC was estimated from the change in the viscosity of a 5% solution of cellulose acetate in dimethylformamide (DMF) and a solution of polycaproamide in formic acid. Comparative data on the photostability of cellulose acetate and polycaproamide films stabilised by PHC over a period of 24 h are presented in Table 4. They show that PHC is a stabiliser in relation to the photooxidative degradation of both cellulose acetate and polycaproamide, its photostabilising properties in relation to cellulose acetate being more effective than those in relation to polycaproamide. Comparison of the data presented in Tables 3 and 4 demonstrates that the photostabilising properties of HC-1 are significantly more effective than the analogous properties of PHC.

A further search for new effective stabilisers for cellulose acetate and polycaproamide should be continued among macrocyclic aromatic substances with an extensive conjugated chain and a nearly planar structure. A characteristic feature of all macrocyclic stabilisers is their ability to colour textiles yellow, red, and brown depending on the nature and amount of the stabiliser.

Table 3. Changes in the viscosity of a 0.5% cellulose acetate solution after UV irradiation for different irradiation times t_r (%).

Stabiliser	Concentration (mass%)	t_r = 24 h	t_r = 48 h
Without stabiliser	0.0	13	7
TSC	0.5	25	–
	2.0	79	–
	5.0	70	–
HC-1	0.5	79	–
	2.0	92	–
	3.0	94	66
	5.0	93	–

Table 4. Changes in the viscosity of 0.5% solutions after irradiation (%).

Stabiliser	Solution of CA in DMF	Solution of PA in HCOOH
Without stabiliser	13	64
PHC-1	25	73
PHC-2	76	76
PGC-3	47	80

4. Certain problems of the photodegradation and photostabilisation of polymers

Mel'nikov et al.[10] showed in relation to the photooxidative ageing of polystyrene that the photochemical reactions of the peroxyl radicals formed from the central macroradicals

$$\sim CH_2\underset{\displaystyle C_6H_5}{\overset{|}{C}}(O\dot{O})CH_2\sim$$

lead to the disruption of the main polymer chain. The spectroscopic characteristics of this reaction are presented in Fig. 2. The quantum yield of the reaction, accompanied by the formation of low-molecular-weight transfer agents (OH· radicals), is 10^{-3} at 77 K. The photochemical reactions of radicals of other types—cyclohexadienyl radicals, central macroradicals, peroxyl radicals obtained from cyclohexadienyl radicals—have quantum yields ranging from 10^{-1} to 2×10^{-5}; they lead to the migration of the free valence and the formation of low-molecular-mass products without involving the main chain.

The photochemical reactions of radical-anions and polymers such as poly(vinyl acetate), polyacetals, and aliphatic polyurethanes do not exert any significant influence on the molecular mass distribution of the polymers indicated.[11]

In the study of the mechanisms of the photochemical reactions of peroxyl radicals of different types grafted to the surface of chemically activated silicon dioxide, it was possible to show[12] that the primary step in the photolysis involves dissociation at the O–O bond (Table 5).

$$R\dot{O}_2 \longrightarrow [R\dot{O} + O] .$$

The subsequent course of the process is determined by the behaviour of the [RO· + O] pair formed. In particular, the energy evolved in the reverse reaction (250 kJ mol^{-1}) exceeds the energy of the C–O bonds in the peroxyl radicals and hence the vibrationally excited radical may decompose:

$$[R\dot{O} + O] \longrightarrow [RO_2] \longrightarrow \dot{R} + O_2 .$$

The extent of the reaction should be correlated with the strength of the C–O bond in the peroxyl radicals. These results are important for the interpretation of many data on the photooxidative ageing of polymers.

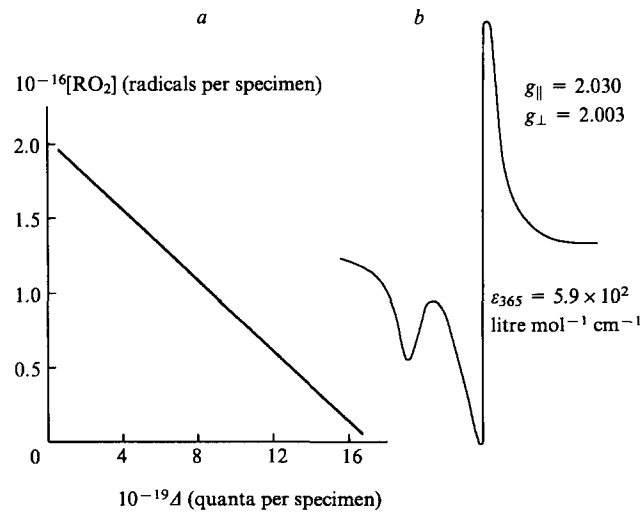


Figure 2. Dependence of the concentration of the RO_2 radicals on the irradiation dose (*a*) and the absorption spectrum at a wavelength of 365 nm (*b*).

Table 5. Photochemical reactions of peroxyl radicals stabilised on the RSi surface at 77 K.

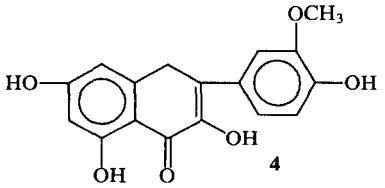
Radical	Detected paramagnetic products[a]	Suggested mode of reaction
$\geqslant SiO\dot{O}$	$\geqslant Si\dot{O}$ (0.8 ± 0.1)	$\geqslant SiO\dot{O} \xrightarrow{h\nu} \geqslant Si\dot{O} + O$
$\geqslant Si(OH)CH_2O\dot{O}$	$>Si(OH)O\dot{C}H_2$ (0.3 ± 0.1)	$>SiOHCH_2O\dot{O} \xrightarrow{h\nu} \geqslant SiOHCH_2\dot{O} + O$, $>SiOHCH_2\dot{O} \longrightarrow >SiOHO\dot{C}H_2$, $>SiOHCH_2\dot{O} \longrightarrow >Si\dot{O}H + CH_2O$
	$>Si\dot{O}H$ (0.6 ± 0.1)	
$\geqslant SiOCH_2O\dot{O}$	$>Si\dot{O}$ (0.5 ± 0.1)	$\geqslant SiOCH_2O\dot{O} \xrightarrow{h\nu} \geqslant SiOCH_2\dot{O} + O$, $\geqslant SiOCH_2\dot{O} \longrightarrow \geqslant Si\dot{O} + CH_2O$, $\geqslant SiOCH_2\dot{O} \longrightarrow \geqslant SiOCHO + H$, $>Si: + H \longrightarrow Si\dot{H}$
	$>Si\dot{H}$ (0.5 ± 0.1)	
$\geqslant SiCH=CHO\dot{O}$	$\geqslant Si\dot{C}HCHO$ (0.7 ± 0.1)	$\geqslant SiCHCHO\dot{O} \xrightarrow{h\nu} \geqslant SiCHCH\dot{O} + O$, $\geqslant SiCHCH\dot{O} \longrightarrow \geqslant Si\dot{C}HCHO$
$\geqslant SiCH_2CH_2C(=O)O\dot{O}$	$\geqslant SiCH_2\dot{C}H_2$ (0.7 ± 0.1)	$\geqslant SiCH_2CH_2CO(O\dot{O}) \xrightarrow{h\nu} \geqslant SiCH_2CH_2CO\dot{O} + \cdot O$, $\geqslant SiCH_2CH_2CO\dot{O} \longrightarrow \geqslant SiCH_2\dot{C}H_2 + CO_2$
$\geqslant SiOCH_2CH_2C(=O)O\dot{O}$	$\geqslant SiOCH_2\dot{C}H_2$ (0.5 ± 0.1)	$\geqslant SiOCH_2CH_2CO(O\dot{O}) \xrightarrow{h\nu} \geqslant SiOCH_2CH_2CO\dot{O} + O$, $\geqslant SiOCH_2CH_2CO\dot{O} \longrightarrow \geqslant SiOCH_2\dot{C}H_2 + CO_2$
$\geqslant SiCH_2CH_2O\dot{O}$	$\geqslant SiOCH_2\dot{C}H_2$ (0.8 ± 0.1)	$\geqslant SiCH_2CH_2O\dot{O} \xrightarrow{h\nu} \geqslant SiCH_2CH_2\dot{O} + O$, $\geqslant SiCH_2CH_2\dot{O} \longrightarrow \geqslant SiOCH_2\dot{C}H_2$
$\geqslant SiOCH_2CH_2O\dot{O}$	$\geqslant SiO\dot{C}H_2$ (0.7 ± 0.1)	$\geqslant SiOCH_2CH_2O\dot{O} \xrightarrow{h\nu} \geqslant SiOCH_2CH_2\dot{O} + O$, $\geqslant SiOCH_2CH_2\dot{O} \longrightarrow \geqslant SiO\dot{C}H_2 + CH_2O$
$\geqslant SiCH_2CH=CHCH_2O\dot{O}$	$\geqslant Si\dot{C}H_2$ (0.75 ± 0.1)	$\geqslant SiCH_2CHCHCH_2O\dot{O} \xrightarrow{h\nu} \geqslant SiCH_2CHCHCH_2\dot{O} + O$, $\geqslant SiCH_2CHCHCH_2\dot{O} \longrightarrow \geqslant SiCH_2CHCHCHO + H$, $>Si: + H \longrightarrow Si^{\cdot}H$
$\geqslant SiCH_2CH(O\dot{O})CH=CH_2$	$>Si\dot{H}$ (0.15 ± 0.1)	$\geqslant SiCH_2CH(O\dot{O})CHCH_2 \xrightarrow{h\nu} \geqslant SiCH_2CH(O^{\cdot})CHCH_2 + O$, $\geqslant SiCH_2CH(O^{\cdot})CHCH_2 \longrightarrow \geqslant Si\dot{C}H_2 + CH_2=CHCHO$
$\geqslant SiC_6H_4O\dot{O}$	$\geqslant Si\dot{}$ (0.3 ± 0.1)	$\geqslant SiC_6H_4O\dot{O} \xrightarrow{h\nu} \geqslant SiC_6H_4\dot{O} + O$, $\geqslant SiC_6H_4\dot{O} \longrightarrow \geqslant Si\dot{} + C_6H_4O$
	$>Si(OH)\dot{O}$ (0.5 ± 0.1)	
$\geqslant SiOC_6H_4O\dot{O}$	$>Si\dot{H}$ (0.5 ± 0.1)	$\geqslant SiOC_6H_4O\dot{O} \xrightarrow{h\nu} \geqslant SiOC_6H_4\dot{O} + O$, $>SiOC_6H_4\dot{O} \longrightarrow \geqslant Si\dot{O} + C_6H_4O$
	$\geqslant Si(OH)\dot{O}$ (0.5 ± 0.1)	

[a] The fraction of the corresponding paramagnetic products of the photolysis of the peroxyl radicals is indicated in brackets.

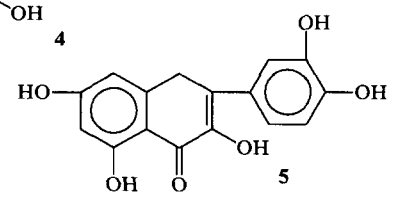
5. Photostabilisation of cellulose diacetate and cellulose paper by natural products

The problem of the photostabilisation of cellulose diacetate (CDA) and cellulose paper (CP) by compounds of natural origin has become of primary importance, since it is directly associated with the protection of the environment and the utilisation of waste.

Studies of the use as stabilisers of flavanoids (isorhamnetin **4** and quercetin **5**) as well as extracts of the walnut, henna, and the total dyes of the polypore (bracken fungus) (TDP) have been carried out by Kalontarov, Niyazi, and coworkers.[13] The walnut extracts contain 25% of juglone and the henna extracts contain 1.85% – 2.23% of lawsone.

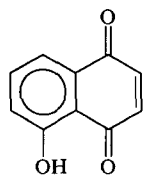


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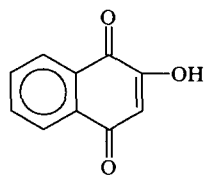


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These natural products are coloured antioxidants. This permits their use as dyes and photostabilisers for cellulose and its acetates.



juglone



lawsone

It is known that, during the photoageing of cellulose materials, the degree of their polymerisation (DP) diminishes, the concentration of >C=O groups increases, and their physicochemical properties are impaired.[14] The results of certain tests are presented in Table 6. The introduction of such additives retards the decrease in the degree of polymerisation and the formation of

Table 6. The influence of additives on the photostability of paper after UV irradiation for 20 h.

Dye[a]	Content of carboxy-groups (%)		Content of aldehyde groups (%)		Average DP	
	I	II	I	II	I	II
Without dye	0.048	0.123	0.061	0.028	970	390
Quercetin, 1:1000	0.096	0.167	0.012	0.230	990	415
Walnut, 1:10	0.051	0.118	0.065	0.230	990	420
Henna, 1:10	0.056	0.117	0.064	0.215	985	425
TPD, 1.5 mass%	0.049	0.119	0.063	0.226	995	420

[a] The concentration of the dye or its dilution is quoted.

Note. The following notation has been adopted here and in Table 7: (I) before irradiation; (II) after irradiation.

carboxy- and aldehyde groups. The stabilising effect of the additives is manifested to the greatest extent in the case of quercetin.

In order to investigate the mechanism of action of the additives, transparent films of cellulose diacetate into which these additives had been introduced were obtained. The results of tests on the retention of viscosity are presented in Table 7.

Table 7 shows that all the additives promote the retention of viscosity after irradiation for 24 h. The best result has been achieved with isorhamnetin (78%). After UV irradiation of cellulose diacetate films containing isorhamnetin, a change in is colour is observed — decolorisation as a consequence of the consumption of the dye. The rate constant for the consumption of isorhamnetin was determined from the initial portion of the kinetic optical density curve. Since this relation is linear in terms of logarithmic variables (Fig. 3), the rate constant was calculated from the equation for a first order reaction.[15]

Fig. 3 shows that the rate of consumption of isorhamnetin is inversely proportional to the concentration of the additive. Isorhamnetin is consumed at the lowest experimentally determined rate when its concentration is 3 mass%. These data agree with the literature.[13, 14] According to Kalontarov, at low concentrations the molecules of the additive are distributed in the polymer, forming a monolayer. With increase in the isorhamnetin concentration, the forces of the interaction between the additive and the polymer are overcome and ultimately the isorhamnetin molecules are converted into aggregates, which are decolorised more slowly as a consequence of the effect of the concentration-induced quenching.[16]

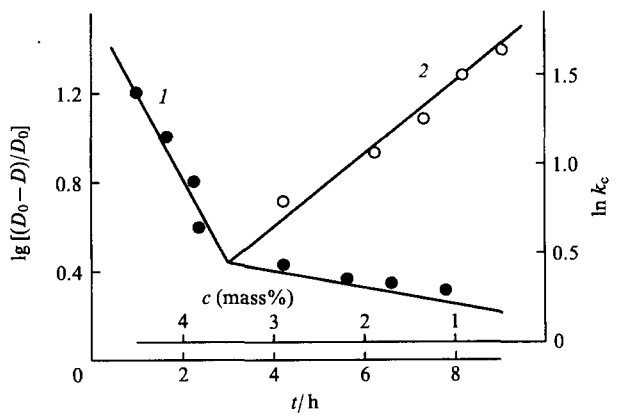


Figure 3. Kinetics of the consumption of isorhamnetin under UV irradiation: (*1*) $\lg[D_0-D)/D_0] = f(t)$; (*2*) $\ln k_c = f(c)$; k_c is the consumption rate constant, D_0 and D are the initial and current optical densities, and c is the concentration of the additive.

Table 7. Changes in the relative viscosity of CDA solutions during UV irradiation.

Additive	Concentration (mass%)	Relative viscosity		Degree of retention of viscosity (%)
		I	II	
Without additive	0	1.12	0.08	6.8
Isorhamnetin	3	1.30	1.02	78.0
Quercetin	3	1.04	0.74	71.5
Walnut	3	1.14	0.74	64.6
Henna	3	1.17	0.73	61.9
TPD	1	1.02	0.59	58.8

6. Laser-induced degradation of polymers

Kalontarov and Marupov investigated in recent years[17–21] the degradation of certain materials — poly(vinyl alcohol) (PVA), polyacrylonitrile (PAN), and polyimide (PI) — by the continuous radiation from an argon laser (514.5 nm). It was shown that the laser-induced degradation process is determined by the kinetics of the accumulation of the products of the thermal decomposition of the macromolecules. Typical dependences of the absorbances of the polymer films on the duration of the laser irradiation are illustrated in Fig. 4. The figure shows that the laser-induced degradation process has two stages: the activation stage (for the duration t_a) and the stage involving a sharp increase in absorption (for the duration t_b), which is completed by the breakdown of the film. The avalanche-like nature of the decomposition is due to the establishment of a positive feedback between the heating of the polymer and the absorption of radiation in the degradation zone. The phenomenon of the sharp increase in absorption and temperature on laser decomposition of polymers has been called photothermochemical instability (PTCI). The first and second stages of the laser-induced degradation (Fig. 4) are therefore called respectively the activation phase and the PTCI development phase. The duration of both phases (t_a and t_b) depends on the power of the absorbed radiation.

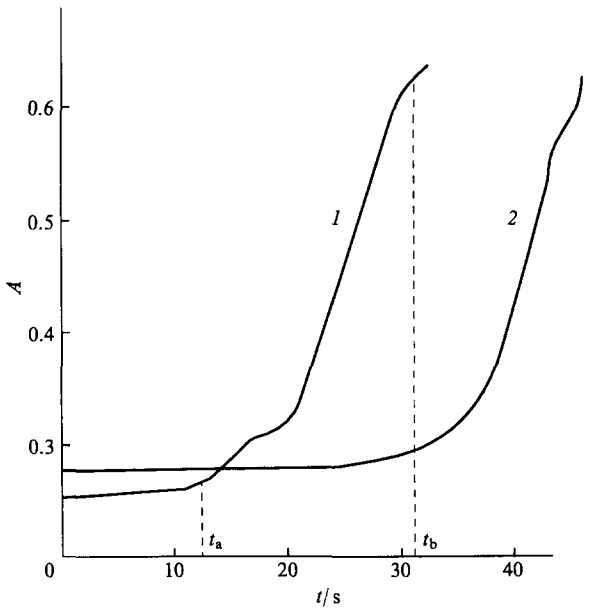


Figure 4. Kinetics of the variation of the absorbance of dyed PVA during laser irradiation for a solid solution of the dye (curve *1*) and for the dye bound chemically to the polymer (curve *2*).

A model of PTCI based on the non-stationary approximation has been constructed[17] and the temperature variation of t_a has been obtained:

$$t_a = \left(\frac{2T_0}{\alpha\gamma}\right)^{1/2} \exp\frac{\alpha}{2}, \quad (8)$$

where $T_0 = \mu P + T_a$ is the temperature of the specimen in the field of the irradiation before the development of the PTCI, P = the power of the incident radiation, T_a the ambient temperature, μ a coefficient, $\alpha = E/RT_0$, $\gamma = (P\varepsilon v)/(\rho C_p S)$, E and v are the activation energy and the pre-exponential factor for the rate of accumulation of the thermal degradation products, C_p is the heat capacity of the polymer film, and ε the extinction coefficient. It has been shown[17] that the activation times calculated by Eqn (8) agree with data for the laser-induced degradation of PVA (Fig. 5).

It has been observed[19, 20] that the duration of the second phase is determined by the rate of development of the PTCI and obeys the following empirical relation:

$$t_b = \tau_0 \exp(-\beta T_0), \quad (9)$$

where τ_0 and β are constants.

The difference between the $t_b(T_0)$ and $t_a(T_0)$ relations is of greatest interest. Eqn (8) was derived on the hypothesis that the Arrhenius equation holds for the chemical reaction rate constant. The fact that the experimental values of t_a are described satisfactorily by Eqn (8) confirms the validity of the Arrhenius equation for the initial stage of the laser-induced degradation when the changes in the temperature and concentration of the degradation products are still small. The qualitative PTCI model shows[20] that the process involving the development of instability is significantly non-stationary. Under these conditions, the Arrhenius kinetics break down, which is reflected in its turn in the dependence of the time of the development of the PTCI on the temperature T_0 [Eqn (9)].

The non-linear thermochemical processes in polymers under the conditions of the thermal effect of the laser radiation have been investigated.[21, 22] The effect involving the self-stabilisation of the laser-induced dehydration of PVA, the propagation of travelling degradation waves, and the vibrational and random dynamics of the evolution of volatile products during the laser-induced decomposition of polymers have been observed.

The effect of the radiation of a Nd:YAG continuous wave laser (1064 nm) on the colour of the PVA film has been investigated.[23, 24] It has been established by mass-spectrometric analysis[23] that the qualitative composition of the volatile products on thermal and laser decomposition is virtually the same, but the relative contributions of the individual components can differ significantly. It was concluded that the laser-induced decomposition of polymers takes place on the whole via a thermal mechanism, although the dynamics of the laser-induced processes differ from the dynamics of the usual thermal degradation. It has been shown[24] that the laser stability of the coloured PVA depends both on the type of the dye introduced and on the way in which the dye is bonded to the polymer. It has also been observed that the resonance effect of the radiation decomposes polymers much more effectively than the non-resonance effect.

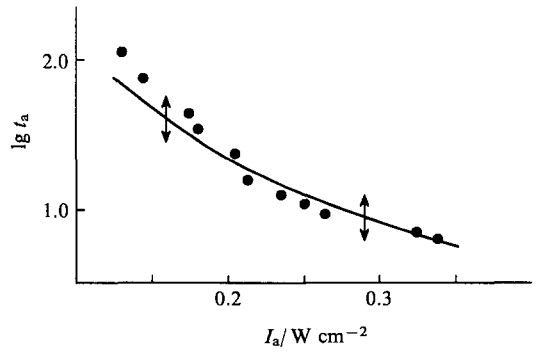


Figure 5. Dependence of the thermochemical instability activation time on the initial intensity of the absorbed radiation: circles — experimental data; continuous line — calculations; C_p = 2.0 kJ kg^{-1} K^{-1}; ρ = 1.2 g cm^{-3}.

III. Stability of elastomers and water-soluble polymers. Their applications in medicine and petrochemistry

1. A new method for estimating the thermal and radiation stabilities of elastomers

The existing methods for the determination of the lifetime (τ) of elastomers, widely used in practice and based on thermal ageing, take a long time, consume a large amount of materials, and are unsuitable for high temperatures. A new method, developed by Prokopchuk et al.,[25] is free from these disadvantages and makes it possible to estimate the contributions of different factors in the external medium to the decrease in the lifetime of rubbers. A distinctive feature of the new method involves the thermooxidative degradation of elastomers in a field of a tensile mechanical stress. The method is based on a single relation (Fig. 6) between the lifetime and the activation energy U_0, established on the basis of extensive experimental data obtained by the existing thermal ageing method. It includes also a high-speed method for the estimation of the values of U_0 from the temperature variation of the breaking stress when the thermooxidative degradation takes place with the specimen being acted upon simultaneously by heat, atmospheric oxygen, and a mechanical tensile stress, i.e. is accelerated by the applied field of mechanical forces.

The lifetimes of 20 types of rubbers, based on different polymers and having different compositions, have been determined by the above method.[25] The results agree with data obtained by the existing method in parallel experiments.

In order to estimate the contribution of ionising radiation to the decrease in the lifetime of rubbers based on butadienenitrile (SKN-18SM) and chloroprene (nairit M) raw rubbers,[26] their specimens were irradiated with ^{60}Co γ-rays. The radiation dose was 500 kGy (50 Mrad) and the dose rate was 4 Gy s^{-1} (400 rad s^{-1}). The results of the investigation are presented in Table 8.

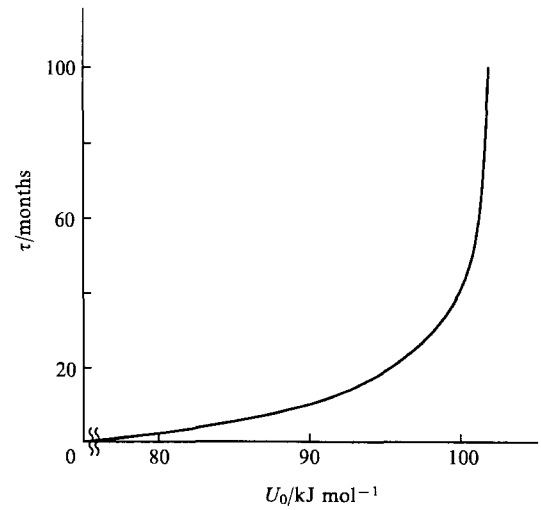


Figure 6. Dependence of the lifetime of rubbers in air at 25 °C on the activation energy for their thermal ageing.

Table 8. Changes in the properties of rubbers under the influence of ionising radiation.

Polymer	Initial specimen			Specimen after irradiation		
	$\sigma(1+\varepsilon)$/ MPA	U_0/ kJ mol^{-1}	τ^a/ months	$\sigma(1+\varepsilon)$/ MPA	U_0/ kJ mol^{-1}	τ^a/ months
SKN-18SM	30	109	190	14.2	102	68
Nairit M	75	121	1103	22.2	105	106

[a] Lifetime at 25 °C.

It follows from the above table that the breaking stress $\sigma(1 + \varepsilon)$ is reduced on irradiation by a factor of 2.1 for the SKN-18SM specimens and by a factor of 3.4 for the nairit M specimens, the activation energies for the thermooxidative degradation U_0 being reduced by 7 and 16 kJ mol^{-1} respectively. The quantity U_0 is a critical parameter for the determination of the lifetimes of rubbers.[25] The influence of γ-radiation on the lifetimes of rubbers with a different polymer base varies: the value of t for irradiated SKN-18SM specimens is 35% of the values for the initial specimens, while for nairit M it is only 9.6%. However, the lifetimes of both rubbers are fairly long after irradiation with a dose of 500 KGy and they meet fully the technical requirements for rubbers serving as components of different technological objects.[25]

2. Elastomers in medicine

Highly elastic materials employed in the manufacture of articles for medical purposes play an important role among polymers. In the first place, these are elastomers based on *cis*-1,4-polyisoprene and obtained mainly from natural rubber (NR) and natural latex (NL). Apart from their natural origin, one may include among their advantages a unique set of properties associated with strength and elasticity. The latex technology based on the natural latex ensures an ecologically safe manufacture of articles for mass consumption and makes it possible to obtain articles with a specified thickness and with a complex configuration.

However, owing to their low resistance to different types of ageing and the risk of toxic effects of different low-molecular-mass substances used for the vulcanisation of polyisoprene, the materials based on it have come to be regarded as undesirable or unsuitable for prolonged contact with living tissues. Nevertheless, because of the lack of systematic studies, existing ideas about the biocompatibility of these materials are fairly contradictory.

Khodzhaeva et al.[27] investigated in recent years the influence of prolonged contact between polyisoprene and a biologically active medium (blood serum). The structure and properties of the polyisoprene, vulcanised polyisoprenes, and latex materials were studied. The relative contributions of several factors influencing the above materials were estimated in parallel experiments: water, salt (isotonic) solution, proteins, at the temperature of living tissues (~40 °C).

The following results of the above study are of greatest interest and importance.

It was established that the biological medium does not exert a specific disruptive influence on natural rubber. Water and the protein components of the blood serum, adsorbed on the polymer surface, protect it against the thermooxidative degradation gradually developing at 40 °C. After being kept in blood serum for 2 years, polyisoprene retains a high molecular mass, while in air the latter diminishes (Fig. 7).

Biologically stable highly elastic materials can be obtained from natural rubbers. For this purpose, it is essential that the vulcanisation network should be resistant to thermooxidation at 40 °C and that the composition of the material should ensure a minimal level of sorption of the components of the medium. The cross-linking density of natural rubbers changed little in the course two years of contact with different media and they retained a high strength and elasticity (Table 9).

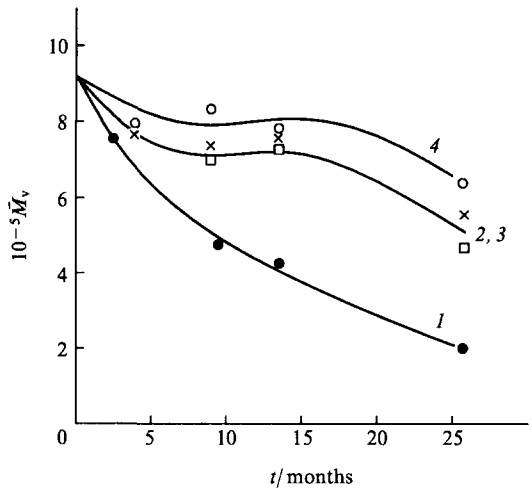


Figure 7. Variation of the molecular mass of *cis*-1,4-polyisoprene under conditions of prolonged contact at 40 °C with air (curve *1*), water (curve *2*), isotonic solution (curve *3*), and blood serum (curve *4*).

For latex materials, which are on the whole inferior to vulcanised block polyisoprene as regards resistance to thermooxidation, the most active disruptive factors during prolonged contact with a biological medium are the absorption of water and the effect of temperature. The negative effect of these factors can be to a large extent abolished by the specific regulation of the microstructure and composition of the material.[28] The application of these principles made it possible to obtain from natural latexes thin-walled film articles which retain highly effective properties during contact with aqueous and biological media in the course of a year.

Table 9. Changes in the properties of vulcanised natural rubbers on exposure to air, in isotonic solution, and in blood serum at 40 °C.

Time/months	$10^5(1/M_s)$/mol cm^{-3}	f_{700}/ MPa	f_r/ MPa	ε(%)
	Initial specimen			
0	12.9	17.5	32.8	880
	Specimen maintained in air			
12.0	16.1	24.6	35.0	820
22.2	12.5	24.2	29.8	750
	Specimen maintained in isotonic solution			
12.0	12.2	12.1	34.9	920
22.2	13.3	14.9	29.8	810
	Specimen maintained in blood serum			
12.0	14.8	13.8	30.7	850
22.2	15.6	13.4	29.8	890

Note. $1/M_s$ = density of cross-linking; f_{700} = modulus of elasticity; f_r = tensile strength; ε = relative elongation on rupture.

Materials and articles for medical purposes with thromboresistant properties have been developed on the basis of natural latexes; the characteristics of the structure of the latex gel and the presence in the latter of protein components served as a basis for the improvement of the method of ionic-covalent immobilisation of heparin.[29-31]

In order to increase the biological compatibility of latex articles and to impart to the latter new functional properties, procedures have been developed for the preparation of composite materials based on the combination of a natural latex with an aqueous dispersion of a high-molecular-mass polyorganosiloxane[32] and on the surface modification by coatings consisting of segmented polyesterurethanes.[33]

The present state of the problem of the biological compatibility of highly elastic materials based on *cis*-1,4-polyisoprene and also the advances in the field of their preparation and application have been surveyed in a review.[34]

3. Stabilisation of coatings in biochemically active media

The problem of the stabilisation of the protective properties of coatings used in biochemically active media is of great theoretical and practical importance.

The complexity of the solution of the problem arises from the fact that the protective properties of coatings depend on many physicochemical factors: the adhesion strength of the bond between the coating and the support; the magnitude and the kinetics of the growth of internal stresses, arising during their formation and use, which are comparable to the adhesion and cohesion strengths; the barrier properties of coatings; the ability of polymers to inhibit electrochemical processes at the interface; the resistance of polymers to the effect of the microflora in undertakings for the food industry.

In order to stabilise the structures and properties of protective coatings used in biochemically active media, Rozantsev[36] developed structure-forming additives for the industrially produced compositions based on organoelement and other compounds with an aromatic conjugation system, which promote the creation in the coatings of an ordered structure of the mesomorphic type. The influence of these additives on the specific features of the structure formation during the production of epoxide coatings as well as the internal stresses and the physicomechanical protective properties of the coatings have been investigated.

It has been shown by the NMR method and electron microscopy that the introduction of these additives in small amounts (1–2 mass%) promotes the formation of structures of the nematic type made up of uncoiled macromolecules with a coplanar orientation in the plane of the support. The mesomorphic level of order in the structure ensures a kinetically convenient order for the involvement of the functional groups in the adhesion and cohesion interactions.

Table 10 presents data concerning the influence of an organosilicon additive on the stability of the properties of epoxide coatings in corrosive media. Modifying agents based on derivatives of the piperidinoxyl (PPO) radical have been developed for the stabilisation of the properties of the coatings in acid media.[36] It was shown that they are capable of retarding strongly the rates of oxidation processes at the interface and in the bulk of the polymer.

Table 10. The mechanical and adhesive properties of polymeric coatings.

Properties	Without additive	With additive
Internal stress/ MPa	4.0	1.5
Adhesion scale points		
initial	1	1
after ageing		
in 3% lactic acid solution	4	2
in 1.5% NaOH solution	2	1
Impact strength/ N m		
initial	5	5
after ageing		
in 3% lactic acid solution	1	3.5
in 1.5% NaOH solution	1.5	4
Lifetime/days		
in 3% lactic acid solution	7	350
in 1.5% NaOH solution	34	400

The introduction of small amounts of the PPO into the corrosive medium increases the corrosion stability of the material as a result of the adsorption of the inhibitor molecules on the surface and a change in the kinetics of the electrochemical reactions (Table 11). The effectiveness of the inhibitor (W) is estimated from the formula

$$W = \frac{i_k - i_k''}{i_k},$$

where i_k and i_k'' are the corrosion currents without and with the inhibitor.

Table 11 shows that the introduction of PPO into electrolyte solutions in an amount of 0.5–2 mass% shifts the stationary potential in the positive direction by 100–120 mV, lowers the maximum dissolution currents by a factor of 8, and increases the degree of protection to 80%–85%.

Similar features have been observed after the introduction of PPO in an amount of 0.5–1 mass% into perphthalic, perchlorovinyl, and epoxide coatings. The modified coatings have already found practical applications for the protection of equipment in the food industry.

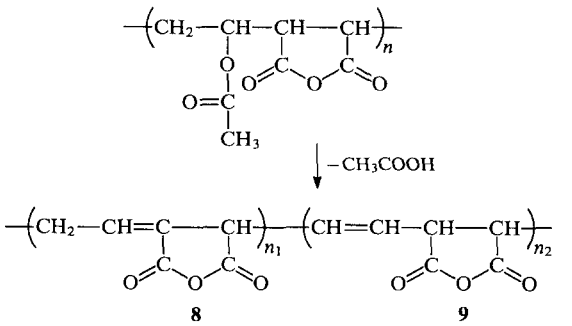
Table 11. The influence of piperidine oxide on the electrochemical characteristics of steel (ST-3).

PPO content (%)	Stationary potential/mV		Maximum dissolution current/mA cm^{-2}		Degree of protection (%)	
	I	II	I	II	I	II
0	−500	−600	16.7	80.0	0	0
0.5	500	−600	10.0	62.0	39	25
1.0	−450	−570	2.2	43.0	80	50
1.5	−450	−500	3.0	15.0	66	80
2.5	−450	−480	4.4	10.0	66	85
3.0	−550	−530	25.0	80.0	–	0

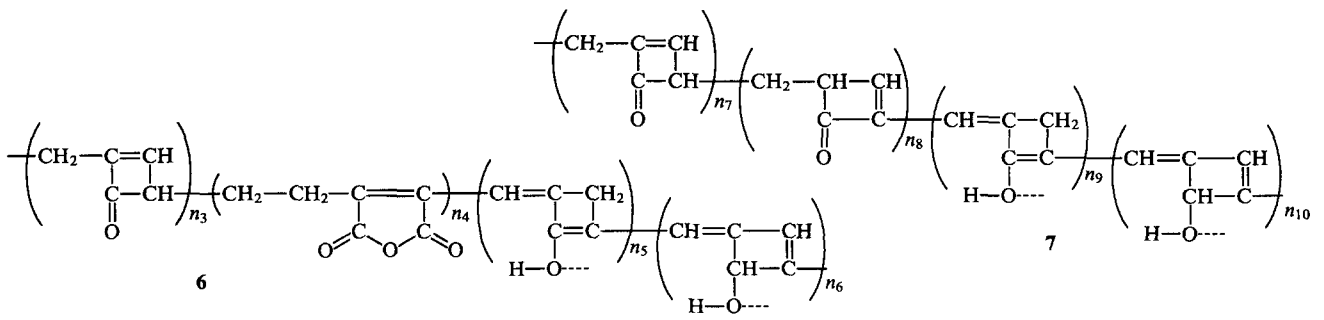
Note. Electrolyte: (I) 0.5 N Na_2SO_4; (II) 5% HCl.

4. Regulation of the liberation of medicinal preparations by the controlled degradation of polymers

Among various applications of the degradation of polymers, yet another has been discovered in the study of the copolymer of maleic anhydride and vinyl acetate (MA/VA). The present authors investigated the thermal degradation of this copolymer jointly with McNeill using his method for the thermal analysis of the volatile degradation products (TV/ATVA).[37, 38] The results showed that the first stage of the isothermal degradation at 205 °C can be represented in the form



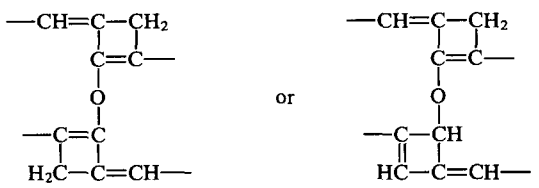
8 9



6 7

The next stage involves rearrangements of structures **8** and **9** without the evolution of carbon dioxide or as a result of such evolution, which leads to structure **6**†. The last stage of the isothermal degradation involves the decomposition of the anhydride ring, which leads to structure **7**.

The quantities *n* in the above structures can vary and we have no adequate grounds for attributing any definite values to them. The appearance of a cyclic structure in the side chain diminishes the mobility of the latter and is one of the causes of the decrease in solubility. Another cause may be the cross-linking of the polymer as a result of the dehydration of the hydroxy-groups. This explanation has been confirmed by the liberation of water as a consequence of isothermal degradation. This type of reaction may lead to the cross-linking of individual units.



Conclusions concerning the presence of the above structures were based on data obtained by UV, IR, and NMR spectroscopic and mass-spectrometric methods and also by gas chromatography.

Apart from thermal degradation, the behaviour of the polymer in the presence of water was also investigated. In the first place, the question to what extent the sorption of the polymer can be regulated by its controlled degradation was elucidated.

The first stage of the interaction of water vapour with the polymer involved reversible sorption up to an equilibrium value. The increase in the activity of water vapour induced its irreversible binding accompanied by the rupture of the chemical bonds in the copolymer chain with subsequent dissolution. The critical concentration for hydrolysis was attained only for an activity of water vapour close to unity (liquid phase). The general characteristics of the sorption of water by partly degraded polymers are the same as for the initial material and the observed differences are associated with the degree of structural rearrangement as a consequence of the equilibrium sorption. The specimens obtained after degradation for 10 and 20 min are insoluble in water, although their partial hydrolysis was observed. After degradation for 30 min, a swollen polymer was obtained for which the irreversible sorption stage was limited.

The change in the hydrophilicity of the copolymer as a result of the different degrees of its degradation has been used to create a system where it was necessary to regulate the hydrophilic-hydrophobic balance in the polymer matrix, namely a system for the controlled liberation of medicinal preparations.[39]

We investigated a multicomponent system incorporating polyamide coated by a mixture of the MA/VA copolymer with furacilin. The redistribution of the drug between the two polymers controls the multistage process involving is liberation, which includes desorption from the moderately hydrophilic polyamide and subsequent transfer in the swollen or dissolving copolymer.

The retardation of the liberation of the medicinal preparation as a result of the partial degradation of the polymer is illustrated in Fig. 8, which describes the kinetics of the liberation of furacilin from the above system containing the initial or degraded copolymer.

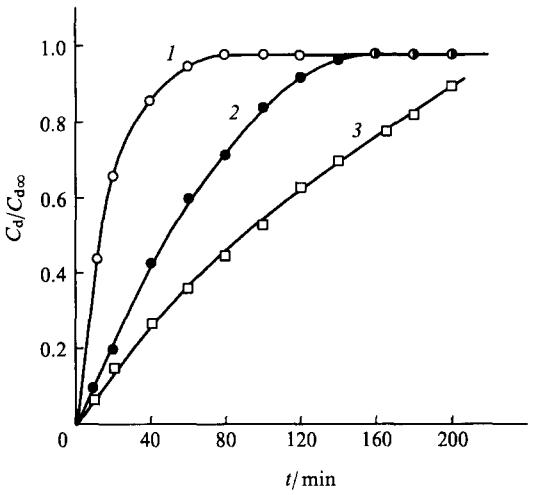


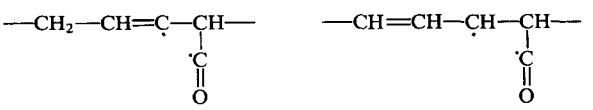
Figure 8. Kinetics of the liberation of furacilin from polyamide coated by the initial (curve *1*) and partially degraded copolymer of maleic anhydride and vinyl acetate. Thermodegradation time (min): (*2*) 10; (*3*) 20.

Following the appearance of the possibility of the simultaneous monitoring of the polymer structure and of its transport properties, good prospects have arisen for the development of new systems in which it will be possible to regulate the rate of liberation of medicinal drugs.

5. Regulation of the stability of water-soluble polymers

Studies by Golubev and coworkers[40, 41] on the regulation of the stability of water-soluble polymers have been published recently. These investigations were undertaken because of the expanding use of such substances in the petroleum industry to make good the non-uniformities in the productive stratum and to increase its coverage when it is flooded. Polymers based on acrylamide are used widely for this purpose. The employment of polyacrylamide

† In the last case, one can postulate the following intermediate states of the chain fragments:



The 1755 cm^{-1} absorption band in the IR spectrum of the partly degraded polymer as well as the appearance of signals at 3.0 and 23 ppm in its ^1H and ^{13}C NMR spectra respectively allow the assumption that the structure of a four-membered ring ketone is more probable than that of other ketones and aldehydes. On this hypothesis, we obtain structure **6**.

(PAA) to increase the extraction of petroleum from the strata has a number of advantages, but at the same time it suffers from a series of important disadvantages. The principal disadvantage is the degradation of PAA under the conditions of joint exposure to elevated temperatures and pressures, shear stresses, as well as metal salts, oxygen, and hydrogen sulfide dissolved in the water within the strata.

Studies on numerous commercial PAA specimens showed that, even when the polymer contains traditional stabilisers, a sharp impairment of the viscous characteristics of aqueous PAA solutions is observed in the presence of iron ions and hydrogen sulfide, especially at elevated temperatures.

The decrease in the viscosity of PAA solutions under the conditions in the strata is associated not only with the degradation of the polymer molecules as such, accompanied by a decrease in the molecular mass, but also with a series of more complex intramolecular and intermolecular processes, cross-links, and conformational changes, which diminish the volume of the macromolecular coil with retention and even an increase in the molecular mass. This has been confirmed by independent methods of measurement, such as viscometry, light scattering, and sedimentation (Table 12).

Table 12. The molecular mass characteristics of polyacrylamide.

Type of influence		Molecular mass/ 10^6 M			
T/ °C	$[Fe^{3+}]$/mg litre^{-1}	M_η	M_w	M_s	$M_{s\eta}$
20	–	8.5 (0)	7.4 (0)	8.3 (0)	8.5 (0)
45	–	1.1 (28)	8.84 (28)	0.91 (28)	0.96 (28)
20	10	3.2 (16)	8.92 (10)	10.8 (16)	8.65 (16)
45	10	3.6 (12)	5.43 (12)	8.52 (45)	10.14 (45)

Note. The molecular mass characteristics were determined for a zero degree of hydrolysis at a PAA concentration of 0.005 mass%; the subscripts to M correspond to the methods used: η = viscometry, w = light scattering; s = sedimentation; the numbers in brackets denote time in days.

Different classes of new PAA stabilisers and metal deactivators, the joint application of which makes it possible to improve significantly the viscous characteristics of aqueous PAA solutions under the conditions of the saturation of the polymer with water, have been investigated.[41]

The copolymers of acrylamide with cationic monomers (dialkyldiallylammonium halides, aminoesters) possess effective flocculating properties. This permits their use in the extraction of petroleum to restrict the inflow of water and also to solve ecological problems, for example, that of the purification of petroleum-containing waste waters. However, it has been established that, during processing in storage, these polymers can lose their solubility in water, probably as a consequence of structure formation in them or they can be degraded, which diminishes their molecular mass.

A study was therefore made of the influence of a series of additives on the stability of polymers in the course of their processing. It was found that mercaptobenz-imidazole and thiourea exhibit a high stabilising activity. Polymers containing 0.3 mass% of these additives do not lose their solubility in water during processing and storage. The intrinsic viscosity of solutions of these polymers is higher than that for polymers processed in the absence of stabilisers.

IV. New approaches to the fundamental investigation and practical application of polymer degradation and stabilisation processes

1. A new approach to the estimation of the physical and thermal parameters of polymers

Askadskii developed in recent years an approach to the estimation of the physical and thermal characteristics of polymers based on the chemical structure of the repeating unit.[42-46] According to this approach, the repeating unit of the polymer consists of a set of anharmonic oscillators each of which consists of a pair of interacting atoms. In order to estimate properties such as the glass and melting points and the coefficient of volume expansion, intermolecular interactions at different levels have been considered: weak (dispersion) and strong (dipole–dipole interaction, hydrogen bonds) due to the presence of polar groups. The temperature corresponding to the loss of stability of such an oscillator characterises the glass and melting points of the polymer.

In order to estimate the temperatures of the onset of the intense thermal degradation of the polymer, when the loss of stability by the set of anharmonic oscillators is due to the dissociation of chemical bonds, chemical reactions are considered. As a result, it is possible to calculate on the basis of the chemical structure of the repeating unit of the polymer, apart from the temperature of the onset of the intense thermal degradation, chemical characteristics such as the glass and melting points as well as a number of other properties—density, refractive index, dielectric constant, the coefficient of the optical sensitivity to stress, the Hildebrand solubility parameter, and the criterion of the solubility of polymers.

In the case of thermal degradation, there is a possibility of estimating by means of the proposed approach the influence of the end groups on the thermal stability of the polymer as well as the influence of other 'weak points' in the composition of the repeating unit.

The possibility, in principle, of synthesising polymers with glass points which are much higher than the temperature of the onset of the intense thermal degradation has been demonstrated.

Askadskii's ideas have been successfully applied to the prediction of the properties of polymer networks, particularly for highly cross-linked polymers, which constitute the basis of many polymeric building materials. In the case of a dense network, the thermal stability of the network nodes themselves and not only the internodal fragments begins to play a major role.

The application of this approach made it possible, in particular, to predict the possibility of obtaining highly cross-linked polymers with extremely unusual properties. Networks containing massive nodes and very short flexible linear fragments between them can have any prespecified modulus of elasticity in the range from 3 MPa to 3 GPa. Despite the fact that these values of the modulus of elasticity are in the intermediate range between those characterising the vitreous and viscoelastic states, such materials have elastic properties and not viscoelastic properties like the majority of polymers.

2. The influence of organic acids on the effectiveness of phenolic inhibitors of the oxidation of polymers

Higher organic acids may be present in the polymer for various reasons: they may be the products of the oxidation of the polymer and can also be present in mixtures of antioxidants. Unfortunately, the contribution of higher organic acids to the effectiveness of the inhibition of the oxidation of polymers has not yet been adequately described in the literature.

The studies of Shlyapnikov and coworkers[47, 48] were devoted to the influence of stearic acid on the effectiveness of antioxidants—2,2′-methylenebis(6-*tert*-butyl-4-methylphenol) (MBP) and the ester of 3,5-di-*tert*-butyl-4-hydroxyphenylpropyldiethyleneglycolic acid (fenozan 28)—in the oxidation of fused isotactic polypropylene (PP).

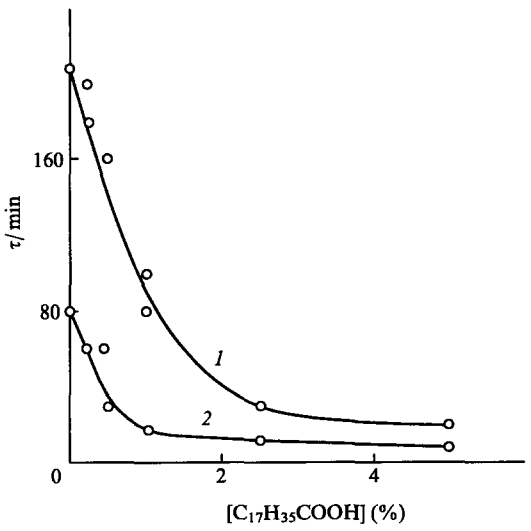


Figure 9. Dependence of the induction period in the oxidation of polypropylene on the concentration of stearic acid in the presence of 0.015 mol kg^{-1} MBP (*curve 1*) and fenozan 28 (*curve 2*); T = 200 °C; P = 300 torr.

At the same initial concentration of the antioxidant, the induction period in the oxidation of PP diminishes appreciably with increase in the concentration of the acid, the action of the latter on the oxidation process being opposed to that of the antioxidant (Fig. 9).

The dependence of the induction period on the initial concentration of MBP is characterised by the fact that in the initial stage at low concentrations of the antioxidant and MBP the latter slightly retards the oxidation reaction and, after the attainment of a definite critical MBP concentration, the induction period increases (Fig. 10). The critical MBP concentration depends on the amount of acid and increases from 0.0012 mol kg^{-1} (in the absence of the acid) to 0.0053 mol kg^{-1} (at a stearic acid concentration of 0.06 mol kg^{-1}). It is suggested that the acid binds the antioxidant into complexes which do not retard the oxidation process. This leads in its turn to an increase in the critical concentration.

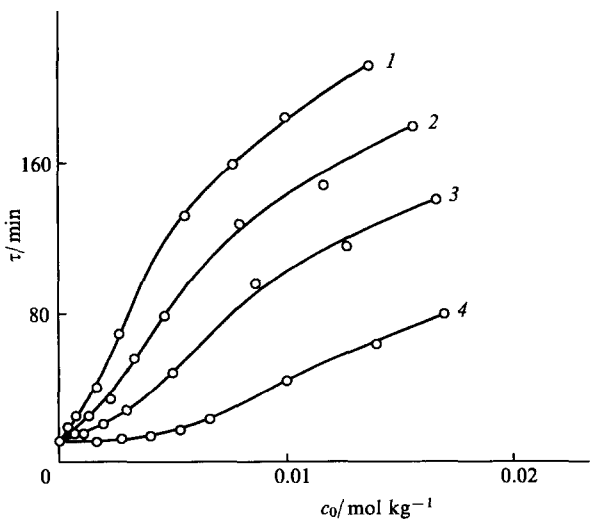


Figure 10. Dependence of the induction period in the oxidation of polypropylene on the MBP concentration in the absence (curve *1*) and in the presence of stearic acid at different concentrations (mol kg^{-1}): (*2*) 0.015; (*3*) 0.03; (*4*) 0.06.

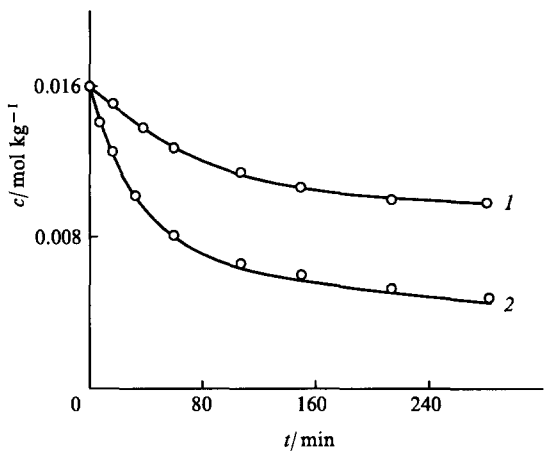


Figure 11. Kinetics of the consumption of MBP in the course of its reaction with stearic acid in polypropylene at 200 °C; initial stearic acid concentration (mol kg^{-1}): (*1*) 0.03; (*2*) 0.06.

Another cause of the observed effect may be the esterification of phenol by stearic acid. In order to confirm the latter hypothesis, specimens of PP containing phenol and stearic acid were heated under a nitrogen atmosphere to 200 °C. In the presence of stearic acid, a slight consumption of phenol was observed, its rate increasing with increase in the initial acid concentration (Fig. 11). A sharp decrease in the induction period and in the critical antioxidant concentration was not observed.

The above phenomena may be explained by the formation of complexes between phenol and the acid and also by the slow reaction between these substances. This leads to the synthesis of the ester, the contribution of which becomes significant only in later stages of the process.

The formation of phenol–acid complexes has been confirmed by the IR spectra of solutions of these substances in CCl_4. A mixture of MBP with stearic acid is characterised by absorption bands at 3840 cm^{-1} (isolated OH groups) and 3520 cm^{-1} (bound OH groups). The absorption of bound OH groups diminishes on complex formation, whilst the absorption band due to isolated hydroxy-groups shifts to (3540 cm^{-1}).

3. Estimation of the effectiveness of antioxidants

The estimation of the effectiveness of antioxidants in polymer systems is a problem the solution of which is of considerable interest from both theoretical and practical points of view. The attempts to find a unique parameter determining the activity of the antioxidant, such as, for example, the oxidation-reduction potential or the rate constant for the reaction of the inhibitor with the peroxyl radical derived from the substrate, have not yielded positive results. The reason for this is primarily the fact that the process involving the consumption of the antioxidant is complex and includes a whole series of reactions involving the antioxidant itself as well as radical and molecular products of its conversion.

According to Shanina,[49, 50] the effectiveness of the antioxidant can be estimated by studying the kinetics of its consumption. The kinetic curves reflect the entire wide variety of the processes occurring in the polymer containing the antioxidant. Comparison of the results obtained at different initial concentrations of the antioxidant makes it possible to estimate the contribution of side reactions, whilst comparison of the kinetic curves for its consumption in the polymer and in an inert medium permits the estimation of the contribution of the inhibitor oxidation process (apparently the main one among side processes which significantly reduce the effectiveness of the antioxidants).

We shall consider two examples of the kinetics of the consumption of phenolic antioxidants in polymer systems.

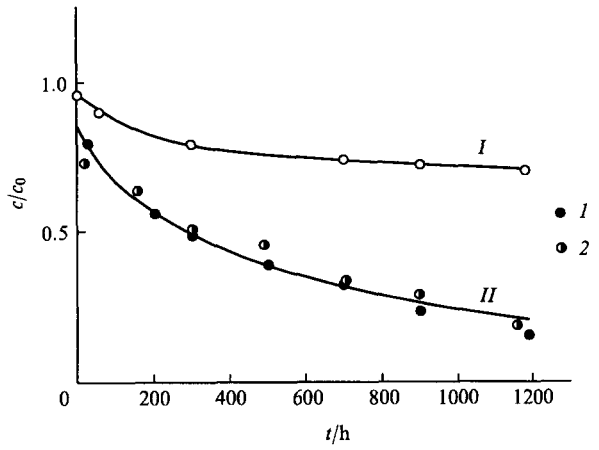


Figure 12. Kinetics of the consumption of antioxidants in isotactic polypropylene (I) Irganox 1076; (II) Topanol CA; concentration (mol kg^{-1}): (*1*) 10^{-2}; (*2*) 2×10^{-3}.

Fig. 12 presents kinetic curves for the consumption in isotactic polypropylene of two industrial antioxidants produced by the Himont Company. Evidently, under experimental conditions in air at 130 °C, the Irganox 1076 stabiliser is consumed much more slowly than Topanol CA. The lower effectiveness of the latter can apparently be accounted for by its slightly sterically hindered structure, which is known to facilitate the occurrence of side reactions. Experimental data confirm this hypothesis. Points corresponding to an initial concentration of 2×10^{-3} mol kg^{-1} were plotted on the curve for the consumption of Topanol CA, obtained at an initial stabiliser concentration of 10^{-2} mol kg^{-1} (relative concentrations of the stabilisers were plotted along the ordinate axis). Despite the fact that the initial concentrations differ by a factor of 5, these points fit satisfactorily on a single curve, i.e. the initial sections of the consumption curves virtually coincide. This shows that an appreciable proportion of the stabiliser is consumed in side processes.

Fig. 13 presents kinetic curves for the consumption of the Nonox WSP stabiliser in the polyethylene–polypropylene (PE/PP) composition at different temperatures. This composition is used in the cable industry for the insulation of optical cable. It is important to note that in the PE/PP blend the antioxidant is consumed at a higher rate than in each of its constituent polymers, which may indicate a higher rate of oxidation of the blend compared with its components.

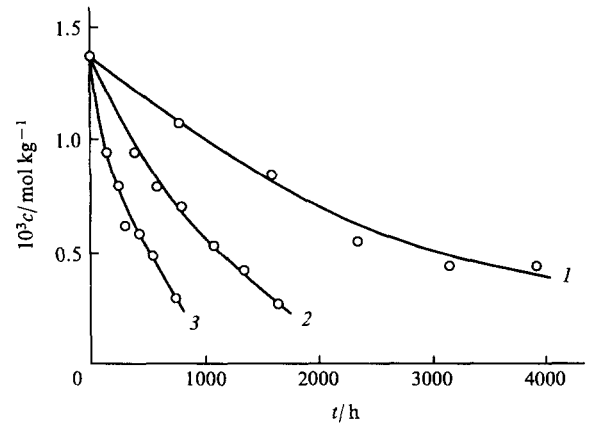


Figure 13. The influence of temperature on the kinetics of the consumption of the antioxidant Nonox WSP in the PE/PP blend; T (°C): (*1*) 60; (*2*) 80; (*3*) 105.

The results permit the estimation of the time required for the consumption of the antioxidant until the attainment of the critical concentration. The accuracy of such an estimate is not very high, but it can serve as a guide in determining the operating stability of the material. Furthermore, the knowledge of the temperature dependence of the rate of consumption makes it possible to extrapolate these rates to any temperatures corresponding to the real operating conditions.

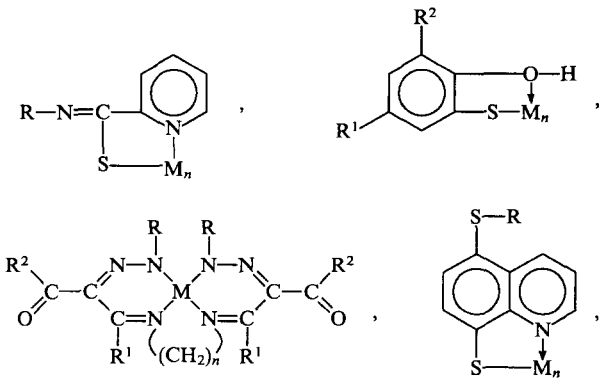
4. The inhibiting properties of heavy metal chelates

Studies on the inhibiting properties of heavy metal chelates have been prosecuted in the course of a number of years by Vinogradova and coworkers.[51–53]

A range of problems associated with the deactivation of alkyl and peroxyl radicals by metal chelate complexes of different classes have ben investigated. Chelates differing in the composition and structure of the chelate units as well as in the nature of the substituents in the ligands and their reactions of the type

$$RO_2^{\cdot} + ML_x \longrightarrow \text{termination},$$
$$R^{\cdot} + ML_x \longrightarrow \text{termination},$$

were investigated. The reactivities of both well known compounds (dithiocarbamates and salicylideneamine complexes) as well as new compounds with N,N-, S,N-, and S,O-containing chelate units, for example



were studied.

The influence of added chelates was investigated in two types of model autoxidation systems: in the oxidation of solutions of polyoxyethylene and its low-molecular-mass analogues, hydrocarbons, and ethers, and in the polymerisation of styrene in solution.

It was shown that the inhibiting activity of the chelates is determined by the composition and hence the properties of the radicals propagating the oxidation chain. The inhibiting activity is different for different oxidation substrates: in ethers and hydrocarbons, only chelates containing sulfur (or selenium) atoms in the chelate units are active, some of them (the copper and antimony chelates) being characterised by a high activity, which is independent of the nature of the substrate. In the oxidation of polyoxyethylenes having different molecular masses, a high inhibiting activity was shown, apart from the sulfur-containing chelates, by compounds with N,N-units. For sulfur-containing chelates in such systems, there is a sharp increase (by more than an order of magnitude) in the inhibiting activity of the chelates. Data have been obtained indicating the possibility of the repeated termination of the oxidation chains of polyoxyethylene involving copper and cobalt chelates and/or their reaction products.

The structure of the ligands of the majority of the chelates investigated contains no functional groups capable of the classical hydrogen atom transfer reaction, which deactivates the peroxyl radicals $RO_2^{\cdot}$ (the OH an NH atoms in phenols and amides). Inhibition is due to the redox mechanism of the interaction between the peroxyl radicals and the chelate units of the complexes.

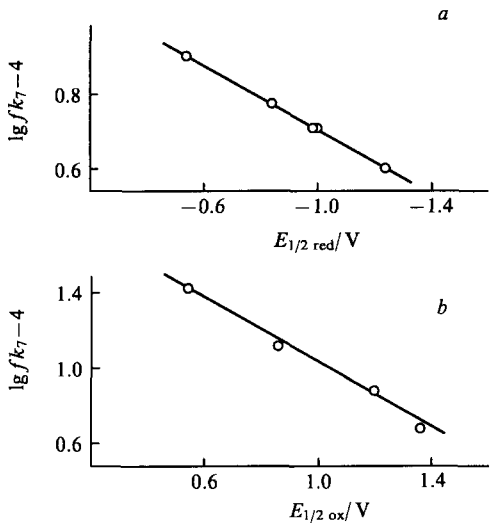


Figure 14. Dependence of the chain termination rate constant on the reduction potentials of copper complexes (*a*) and the oxidation potentials of cobalt complexes (*b*).

Comparison of the rate constants for the chain termination in the interaction of the $RO_2^{\cdot}$ radical derived from polyoxyethylene with chelates and of the half-wave potentials for the electrochemical oxidation and reduction of the chelates demonstrates the presence of a relation between the 'antiradical' activity of the chelates and the oxidation and reduction potentials of the metal complexes (Fig. 14). This correlation indicates that the peroxyl radicals responsible for the oxidation of polyoxyethylene have dual, i.e. oxidising and reducing, properties.

In the interaction with arylalkyl radical R$^{\cdot}$ (in the polymerisation of styrene), the highest reactivity is manifested by the sulfur-containing copper(II) and iron(III) chelates. The inhibiting properties are also characteristic of the cobalt analogues of the above chelate complexes. Copper chelates with nitrogen and oxygen atoms in the chelate unit exhibit catalytic properties.

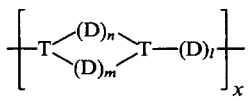
Comparison of the oxidation-reduction properties of chelates and their activities in the inhibition of the polymerisation of styrene showed that in this instance two mechanisms of the interaction of the chelates with the R$^{\cdot}$ radicals operate — a redox mechanism accompanied by the reduction of copper(II) to copper(I) and a mechanism involving the transfer of a hydrogen atom from the activated ligand in the chelate.

5. Stabilisation of polydimethylsiloxanes by the introduction of cyclic fragments into the linear chain

The stabilisation of linear polyorganosiloxanes by the introduction of cyclic fragments both into the chain and into the side groups has been the subject of the latest studies by Khananashvili and coworkers.

It is known that the introduction of various cyclic fragments into the linear dimethylsiloxane chain leads to the decomposition of the helical structure of the polymers and hence alters their physicochemical properties. The glass point can be varied within a wide range by merely altering the organic groups attached to the silicon atoms in the linear macromolecules. As a result of the extensive possibilities for the structural modification of polysiloxane chains by the introduction into the latter of polyfunctional branching centres, mono- and poly-cyclic fragments having a different structure [spirocycles and condensed rings (for example sections corresponding to a 'ladder' structure)], and others, polysiloxanes occupy an exceptional position as excellent model systems for the creation of polymeric materials with a set of physicochemical properties capable of being varied over a wide range.

The influence of the introduction into the dimethylsiloxane chain of organocyclotetrasiloxanes, organocyclopentasiloxanes, and organocyclohexasiloxane with a 1,5- and 1,7-disposition of the organocyclohexasiloxane fragments in a chain of the following composition has been demonstrated:



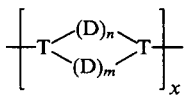
$n, m = 1, 2, 3; n \neq m,$
$l = 2-50$

where D are siloxane units and T are silsesquioxane units.

The principal process leading to the degradation of such copolymers begins at a temperature higher by 80–100 °C than for linear polydimethylsiloxanes.[54–56] A similar result was achieved by introducing cyclocarbosiloxanes and bissiloxaindan fragments into the dimethylsiloxane chain.[57, 58]

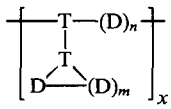
When cyclic fragments are introduced into the linear dimethylsiloxane chain, the copolymers are stabilised, since the cyclic fragments prevent, during depolymerisation, the chain transfer, which proceeds with formation of type D organocyclosiloxanes.

The synthesis of a new class of copolymers, occupying an intermediate position between linear and ladder polymers, has been described.[59, 60] The ratio of the D and T units can be varied in such copolymers. It was shown that, by varying the ratio of the D and T units in the atactic polymer, it is possible to vary the properties of copolymers having the following composition:



$n, m = 1, 2; n \neq m.$

Studies have also been carried out on the synthesis of new copolymers in which the branching segments are organocyclosiloxanes distributed regularly in the side chain.[61, 62]



$m = 1, 2, 3;$
$n = 2-30.$

It has been shown that, with increase in the bulk of the cyclic fragments, the thermooxidative stability of the copolymers diminishes. In addition it has been demonstrated that copolymers with cyclic fragments in a side chain behave in the same way as copolymers with cyclic fragments within the main chain.

6. The ageing of the ABS plastic under atmospheric conditions

In the latest studies by Seitablaev and Kalontarov[63, 64] the influence of climatic factors on the physicomechanical, electrical, and structural properties of acrylonitrilebutadienestyrene (ABS) plastic of type 2020 S were investigated under the conditions of prolonged exposure to the atmosphere in various regions of Tajikistan at different heights above sea level: in the mountain settlement Gissar, 800 m, non-industrial zone; in Dushanbe, 890 m, industrial zone; in the mountain gorge Varzob, 1 700 m; on the mountain pass Anzob, 3 372 m.

It was established experimentally that, during the initial period of the climatic tests on the ABS plastic specimens, the degradation processes predominate greatly over structure formation processes. During the first 1.5–2 months of atmospheric ageing, the decrease in the breaking stress (σ_r) is 28% – 30% and the relative deformation leading to rupture (ε_d) is reduced to 80%. This is followed over the three years by slow ageing processes, whilst towards the fourth year an increase in σ_d is observed. IR spectroscopic studies showed that, during the first 100–200 h of atmospheric ageing, the formation of C=O groups takes place most vigorously (the 1720 cm^{-1} band). After the saturation of

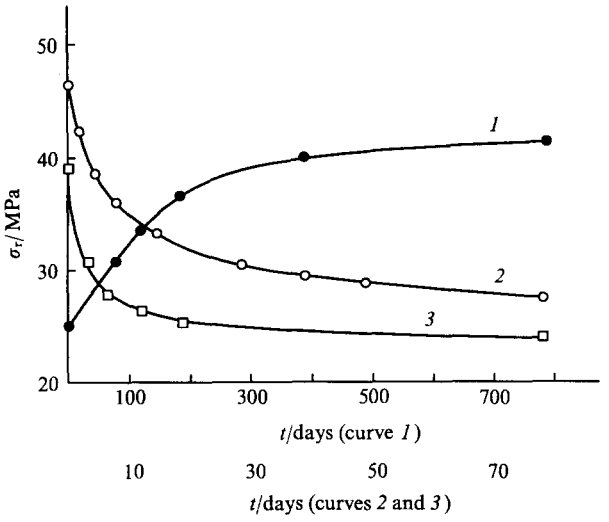


Figure 15. Dependence of the breaking stress (σ_r) for the ABS plastic on the exposure time in an enclosed space (curve *1*) and in open areas (curves *2* and *3*).

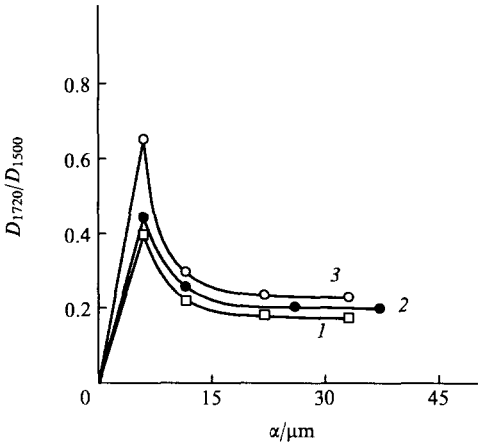


Figure 16. Dependence of the ratios of the optical densities on the thickness of the layer of the ABS plastic undergoing degradation in tests in the Dushanbe climatic area in the course of different periods (days): (*1*) 4; (*2*) 7; (*3*) 13.

surface layers by oxygen-containing products and the closure of the so called channels for the free access of oxygen into the deeper layers of the plastic, a monotonic decrease in σ_d is observed. Under the conditions of prolonged 'oxygen starvation', dark reactions begin to be manifested. Their occurrence is indicated by the increase in σ_d after ageing for 3 years on open areas exposed to the atmosphere. A similar situation has been observed also in specimens stored for a long time under laboratory conditions after climatic tests.

Thus under the conditions of natural ageing of the plastic, dark reactions are manifested towards the fourth year of exposure, whilst under conditions where the influence of atmospheric factors has ceased they become apparent towards the beginning of the 'rest' period. The tensile strength of the plastic after a year's 'rest' is restored to 87% of its initial value, i.e. an increase in σ_d by 34% is observed (Fig. 15).

A considerable accumulation of defects in the first stage of the ageing process is known to be associated with the intense degradation processes in the surface layers of the plastic. It has been established experimentally that, as the surface layer of specimens aged for a short time (2–3 months) is removed, both the strength and viscous properties are restored. On the other hand, in the specimens subjected to prolonged climatic influences (for a year and more), this is not observed and subsequently quasi-brittle decomposition takes place. This finding is explained by the predominance in the bulk of the plastic of cross-linking reactions over degradation processes, which has been confirmed by studies on gel formation. During the first 12 months of ageing, the content of the gel fraction diminishes by 10%–30%, while after an increase in the ageing period from 12 to 48 months, the content of the insoluble fraction rises by 30%–40%. Furthermore, in the specimens aged in the Dushanbe climatic area the degree of gel formation is higher than in the specimens aged in other areas. The high degree of contamination of the atmosphere and the increased temperature of the air probably have an effect here. IR spectroscopic studies on different layers of the plastics showed that the dependence of the ratio of the optical densities D_{1720}/D_{1500} on the thickness of the degraded layer is exponential and, furthermore, with increase in the duration of the exposure during the initial ageing period the degradation processes proceed most vigorously in a surface layer having a depth up to 10 μm, where the C=O groups mainly accumulate (Fig. 16).

Fractographic analysis of the specimens after natural climatic ageing showed that the structure of the surface of the plastic has undergone appreciable changes — microcracks appeared. This is characteristic of all the regions where the specimens were tested. With increase in the ageing period, the number of microcracks and their density also increase.

Thus it has been established that the nature of the decomposition of the ABS plastic under different climatic conditions is determined by processes leading to the degradation of the surface layers and structure formation in the bulk of the material.

7. Radical processes in filled polymers

In filled polymers, boundary layers, the properties of which differ appreciably from the polymer bulk phase, are formed near the surface of the filler particles. It has been shown that the structural features of the boundary layers affect the kinetics of the elementary radical reactions. Thus a dependence of the effectiveness of the thermal reaction of the radical-cations generated at 77 K by the photochemical reduction of iron(III) chloride in polyvinylpyrrolidinone (PVP) on the content of the aerosil filler has been observed.[65, 66]

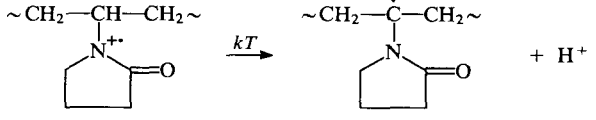
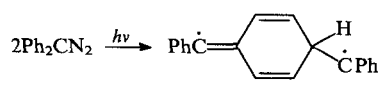


Fig. 17 presents the relative concentrations of macroradicals during the thermal reaction of the radical-cation in PVP without a filler and with 15 and 50 mass% of aerosil. The maximum relative amounts of the macroradicals characterise the fraction of their precursors stabilised at 77 K during the reduction of iron(III) chloride. It was found that in the highly filled specimens (~50% of aerosil) only 10% of the radical-cations are stabilised at 77 K, whereas in the unfilled specimens approximately 70% are stabilised.

In solid polymers [polycarbonate, poly(methyl methacrylate)], the dimerisation of diphenylcarbenes in the quasi-clusters of the added diphenyldiazomethane (DDM), accompanied by the formation of biradicals in which the distance between the unpaired electrons is $r \simeq 5$ Å, was observed.



The relative yield of the biradicals, recorded by the EPR method, serves as a quantitative characteristic of the non-uniformity of the distribution of the low-molecular-mass additive.

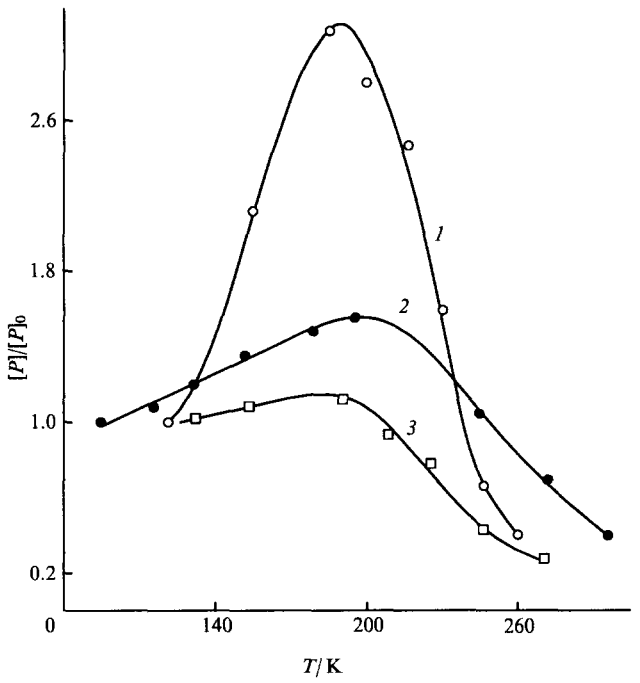


Figure 17. Variation of the concentration of macroradicals during the heating of PVP with $FeCl_3$ irradiated at 77 K: (*1*) without filler; (*2*) 15 mass% of aerosil; (*3*) 50 mass% of aerosil.

Fig. 18 presents the dependence of the yield of the biradicals in the polymer on the additive concentration. At fairly high concentrations (~0.1 M), biradicals with $r \simeq 10$ Å were detected. They are formed in larger quasi-clusters. The study of the dependence of the yield of the biradicals made it possible to estimate the non-uniformity of the distribution of various low-molecular-mass additives whose structures is similar to that of diphenyldiazomethane, for example, photostabilisers, antioxidants, and photosensitisers (salicylates, bisphenols, and benzophenones).

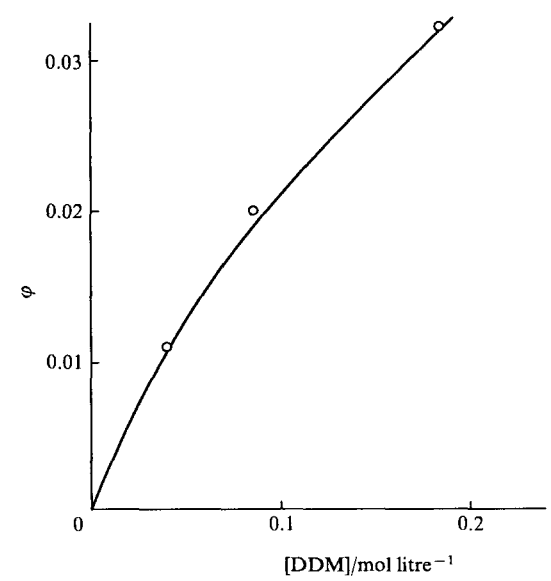


Figure 18. Dependence of the yield of biradicals on the concentration of diphenyldiazomethane in polycarbonate.

8. The inhibiting capacity of natural phenols in radical reactions

Askarov and Saidov[67] estimated the reactivities of a series of natural phenols such as vanillin, guaiacol, eugenol, and gossypol in the model cumene oxidation reaction. Their approach makes it possible to estimate rapidly and quantitatively the ability of various additives to inhibit radical reactions and to reach thereby a preliminary conclusion about the usefulness of the further employment of such substances as stabilisers for polymeric materials. These compounds are also interesting because they can be obtained from reproducible sources—plants and seeds.

In the initiated chain reaction involving the oxidation of cumene (isopropylbenzene), the inhibiting capacity of the additive is estimated in terms of the rate of constant k_7 in the classical oxidation mechanism. For this purpose, the induction period is determined in a preliminary step from the slope of the kinetic oxidation curve under the conditions of fairly long chains:

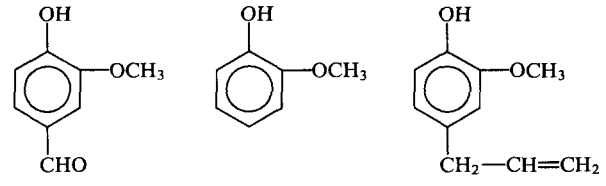
$$\tau = f_n \frac{[\mathrm{InH}]}{W_i},$$

where n is the number of inhibiting groups in the inhibitor molecule, f the inhibition coefficient for one group, [InH] the initial inhibitor concentration, and W_i the rate of initiation.

The inhibition rate constant k_7 is then determined from the relation

$$\frac{[\mathrm{O_2}]}{[\mathrm{RH}]} = -\frac{k_3}{k_7} \ln\left(1 - \frac{t}{\tau}\right),$$

where $[O_2]$ is the amount of absorbed oxygen (mol litre^{-1}), [RH] the amount of cumene taken for the reaction (mol litre^{-1}), and k_3 the chain propagation rate constant (for cumene at 60 °C, k_3 = 1.75 litre mol^{-1} s^{-1}).

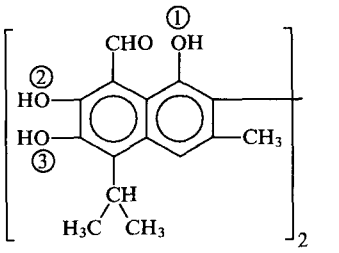


vanillin $k_7 = 3.6 \times 10^{-3}$, guaiacol $k_7 = 5 \times 10^{-3}$, eugenol $k_7 = 1 \times 10^{-4}$.

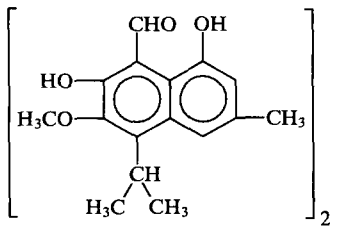
A typical initiated and inhibited cumene oxidation curve as well as its logarithmic form are presented in Fig. 19. The ratio k_3/k_7 is determined from the slope of the logarithmic plot and then k_7 is found. The corresponding calculations yielded the following inhibition rate constants (litre mol^{-1} s^{-1}):

These data make it possible to reach a conclusion about the nature of the influence of the substituent in the *para*-position (with the inevitable presence of a methoxy-group in the *ortho*-position). The transition from the electron-accepting aldehyde group to the electron-donating allyl group leads to a successive increase in k_7. This provides grounds for the assumption that the role of the substituents must always be taken into account in predicting the subsequent application of substances as inhibitors. The Hammett constant of the substituent permits a preliminary conclusion about the usefulness of the antioxidant for the inhibition of the oxidation of particular polymers.

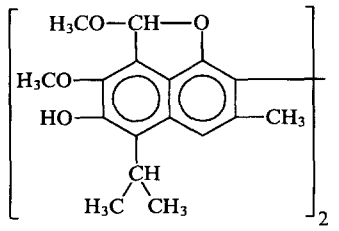
The study of gossypol and its derivatives concerned mainly the determination of their physiological properties. The use of gossypol as an antioxidant in the oxidation of various classes of substances, including polymers, appears promising. In the first place, this is associated with the enormous renewable raw materials base for its preparation. For a detailed estimation of the reactivity of each of the numbered hydroxy-groups, a series of derivatives of the methyl ethers of gossypol were obtained.



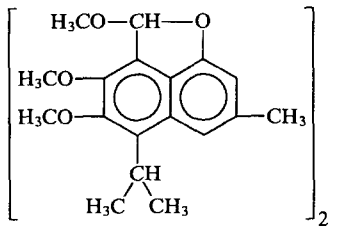
Gossypol
T_m = 282–284 °C ,



Dimethylgossypol
T_m = 168–170 °C ,



Tetramethylgossypol
T_m = 205–207 °C ,



Hexamethylgossypol
T_m = 210–215 °C .

It is noteworthy that hexamethylgossypol does not exhibit an inhibiting effect on the initiated oxidation of cumene.

The subsequent study of the role of the hydroxy-groups responsible for the inhibition of the oxidation reaction can be conveniently begun with tetramethylgossypol. Calculation based on the results presented in Fig. 19 yielded $k_7 = (0.83 \pm 0.03) \times 10^{-4}$ litre mol^{-1} s^{-1} for this compound. When cumene is oxidised in the presence of dimethylgossypol, we are apparently dealing with hydroxy-groups differing in their reactivity. This conclusion was reached on the grounds that a break point is clearly observed on the logarithmic form of the curve (Fig. 20). This shows that, after the consumption of the 'stronger' hydroxy-groups during the induction period, the 'weaker' groups begin to be consumed. From the slope of the logarithmic curve, we obtain respectively for the initial and final sections of the kinetic curve

$$k_7 = (5 \pm 0.04) \times 10^{-4} \text{ litre mol}^{-1} \text{ s}^{-1} ,$$

$$k_7 = (0.85 \pm 0.04) \times 10^{-4} \text{ litre mol}^{-1} \text{ s}^{-1} .$$

There is also only one point of inflection on the logarithmic form of the cumene oxidation curve in the presence of gossypol. This justifies the conclusion that one pair of hydroxy-groups have approximately the same reactivity. If all three types of hydroxy-groups had different reactivities, two points of inflections with three sections of the logarithmic plot would have appeared. Calculation of k_7 for gossypol yielded the following values:

$$(5.2 \pm 0.05) \times 10^{-4} \text{ and } (0.8 \pm 0.04) \times 10^{-4} \text{ litre mol}^{-1} \text{ s}^{-1} .$$

It appears logical to assume that the hydroxy-groups in the 2- and 3-positions have the same reactivities.

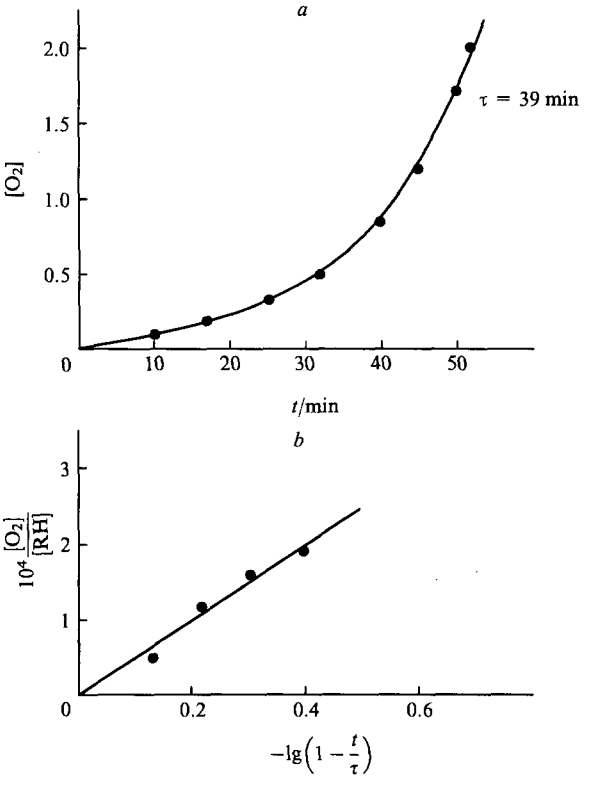


Figure 19. Curve for the initiated oxidation of cumene in the presence of tetramethylgossypol (*a*) and its logarithmic form (*b*); [InH] = 10^{-5} M; $W_i = 1.26 \times 10^{-8}$ mol litre^{-1} s^{-1}.

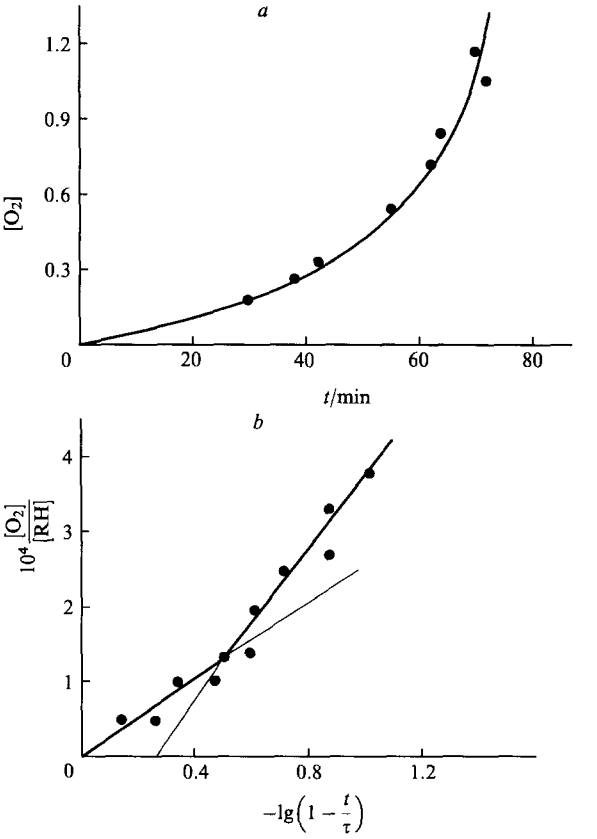


Figure 20. Curve for the initiated oxidation of cumene in the presence of dimethylgossypol (*a*) and its logarithmic form (*b*); [InH] = 1.2×10^{-1} M; $W_i = 5.44 \times 10^{-8}$ mol litre^{-1} s^{-1}.

Since $k_7 = (0.83 \pm 0.03) \times 10^{-4}$ litre mol^{-1} s^{-1} for the OH group in the 3-position (tetramethylgossypol), it is difficult to postulate that $k_7 = (5 \pm 0.04) \times 10^{-4}$ litre mol^{-1} s^{-1} can be assigned to the hydroxy-group in the 2-position. This becomes particularly evident if the constants k_7 for gossypol and its derivatives are compared with the corresponding values for vanillin, guaiacol, and eugenol taking into account the nature of the substituents in the corresponding positions relative to the hydroxy-group. Therefore $k_7 = (5.2 \pm 0.05) \times 10^{-4}$ litre mol^{-1} s^{-1} should be assigned to the hydroxy-group in the 1-position.

In contrast to synthetic sterically hindered phenols, for the majority of which the inhibition rate constant (of the order of 10^{-4} litre mol^{-1} s^{-1}) depends little on the nature of the substituents (provided that they are not highly polar), in the case of sterically unhindered phenols the role of substituents is more pronounced. If the chemical formula of a potential stabiliser (antioxidant) of radical processes is known, then, taking into account the nature and positions of the substituents, it is possible to predict the behaviour of the compound. It must be emphasised that the estimates are preliminary. The final conclusion about the usefulness of a particular compound as a stabiliser can be reached only taking into account the results of technological tests.

9. Structural model of the autoxidation of polypropylene

The autoxidation model proposed by Mikheev and coworkers[68-71] includes heterophase-coupled reaction chains distributed among non-uniform structural zones of the polymer being oxidised. The operation of the heterophase mechanism had been demonstrated previously in relation to the modification of polymers by benzoyl peroxide.

The autoxidation of PP has a number of characteristic features which cannot be explained within the framework of the traditional mechanism of the homogeneous oxidation of hydrocarbons. Some of these features have become the subject of acute controversy in the literature, whilst others remained unnoticed. The latter include the presence of kinetic macroscopic stages due to the change in the reaction order with respect to the hydroperoxide (HP). It is possible to distinguish three stages.[72]

In the first stage, which is of average duration (induction period), the oxidation proceeds via an unbranched chain reaction and the accumulating hydroperoxide does not catalyse the process. The hydroperoxide becomes a catalyst (branching agent) in the second stage. To date theoretical studies have been concentrated on the second stage. It is brief and the degree of oxidation during this period is small. This period is convenient for the conservative employment of the established oxidation mechanism for liquid hydrocarbons.

The third stage of the oxidation of PP is prolonged and is characterised by a zero reaction order with respect to the hydroperoxide. The latter is the principal process initiator in this stage. A similar situation had been observed earlier for the oxidation of poly(ethylene oxide) and was accounted for by a heterophase mechanism.[73, 74]

Furthermore, the oxidation of PP exhibits a specific dependence of the rate on the oxygen pressure P. The dependence is different for the initial and subsequent stages. Namely, during the induction period the rate of oxidation increases gradually over a very large range of values of P but it reaches saturation rapidly as a function of P in the subsequent stages. This property has not been explained.

The problem of the mechanism of the degradation of macromolecules in the oxidation process also remained unsolved. It was established that the rate of degradation in the initiated process is directly proportional to the rate of initiation (macroradicals are destroyed). A mechanism was proposed for the degradation of polymer chains in the oxidation chain with quadratic termination steps. However, this mechanism does not explain the effect of inhibitors. Degradation is known to occur even when the inhibitor fully suppresses the oxidation chains.

The above features agree with the heterophase mechanism based on the micellar-cellular model of the supermolecular structure of the non-crystalline polymer (the oxidation reaction involves primarily the non-crystalline PP phase).[75, 76]

The model is based on the consideration of two structural zones within the polymer globules made up a large number of macromolecules. The point is that the polymer chains encapsulated in the globule form a conglomerate of micropores. The surface forces operating in this conglomerate compress the internal micropores (the v-zone) but at the same time stretch and increase the size of other micropores adjoining the rigid envelope of the globules (the s-zone). This alters in its turn the reactivity of the reactants belonging to different micropores and is the cause of the kinetic polychromaticity. In particular, the narrow v-micropores suppress the reactivity as regards dissociation of the hydroperoxide and the impurity initiator. Dissociation takes place in the spacious s-micropores. Furthermore, elastic mechanical forces suppress the macroradical decomposition steps in the compressed v-zone but promote degradation in the extended sections of the chains of the s-zone.

The primary formation reactions of macroradicals as well as their degradation and destruction take place in the micropores of the s-zone. The s-mechanism should not include the hydroperoxide formation reaction. The latter occurs in another reaction chain, in the v-zone, by virtue of the interzonal s–v transfer of the free valence.

$$PH_s + O_{2s} \xrightarrow{k_{0s}} \delta_1 P_s^{\bullet}, \qquad P_s^{\bullet} \longrightarrow R_s^{\bullet}\text{(degradation)},$$

$$R_s^{\bullet} \xrightarrow{k_{1s}} R_{1s}^{\bullet}\text{(isomerisation)}, \qquad R_s^{\bullet} + R_{1s}^{\bullet} \longrightarrow \text{(products)}.$$

The mechanism of the s–v transfer includes steps (which occur with a low probability) involving the transfer to the thermal $R_s^{\bullet}$ radicals from the lattice structure of the s-micropore and conversely as well as the oxidation of $R_m^{\bullet}$ within the volume of the micropore and the ejection of HO$^{\bullet}$.

$$R_s^{\bullet} \underset{k_{-m}}{\overset{k_m}{\rightleftharpoons}} R_m^{\bullet},$$

$$R_m^{\bullet} + O_{2s} \xrightarrow{k_{tr}} RO_{2m}^{\bullet} \longrightarrow HO_m^{\bullet}.$$

The light hydroxyl penetrating into the v-zone initiates the oxidation chains

$$HO_m^{\bullet} \longrightarrow HO^{\bullet} \xrightarrow{PH} P^{\bullet}, \qquad P^{\bullet} + O_2 \xrightarrow{k_1} PO_2^{\bullet},$$

$$PO_2^{\bullet} + PH \xrightarrow{k_2} POOH + P^{\bullet}, \qquad 2PO_2^{\bullet} \xrightarrow{k_3} \text{termination}.$$

As it accumulates, the hydroperoxide begins to pass from the v-zone to the s-zone, i.e.

$$HP_v \xrightarrow{k_{vs}} HP_s,$$

as a consequence of which steps involving the generation of the radicals HP_5, i.e.

$$HP_s \xrightarrow{k_{0s}} \delta P_s^{\bullet},$$

and the heterogeneous non-radical bimolecular reaction

$$HP_v + HP_s \xrightarrow{k''} \text{molecular products},$$

are included in the process. The latter reaction limits the rate of generation of the radicals and ensures the attainment of a stationary rate of the oxidation process in a zero order reaction with respect to the hydroperoxide.

The above mechanism reproduces the principle of the heterophase conjugation of the s- and v-reaction chains and entails the non-equivalent involvement in the chains of the oxygen dissolved in the polymer. The O_2 molecules (like those of other low molecular mass compounds) are localised within the micropores under the influence of surface forces. This results in steric hindrance to the oxidation reaction, which promotes within the micropores of the s-zone the destructive pathway competing with the oxidation reaction and involving the conversion of alkyl macroradicals into $P_s^{\cdot}$. On the other hand, in the v-zone the destruction of the $P^{\cdot}$ radicals is suppressed by the change in structure and the radicals are oxidised.

In the initial stage of the heterophase reaction, oxygen participates twice in the stages determining the rate of the process: in the radical generation steps with participation of CH_2 groups and in the s–v free valence transfer steps. As a consequence of such 'double initiation', the rate of oxidation is initially

$$W^{(1)} = k_2[\mathrm{PH}][\mathrm{PO}_2^{\cdot}]_1 = \frac{aP}{\sqrt{b+P}} \simeq \tau_{\mathrm{ind}}^{-1},$$

where a and b are constants subject to the condition that the microporous structure does not change in the course of the oxidation reaction.

As a result of the migration of the hydroperoxide into the s-zone, the hydroperoxide becomes the main source of radicals and after a time increases the rate of reaction as a result of the increase in the rate of initiation:

$$W^{(2)} = \frac{\delta k_{0s} k_{vs} g}{(k_{0s} + k'' g)} \gg \delta_1 k'_{0s}[\mathrm{PH_s}][\mathrm{O_{2s}}],$$

where g is the hydroperoxide concentration, but after a short autoaccelerated stage, the maximum rate of initiation is established for a long period:

$$W_i^{(3)} = \frac{\delta k_{0s} k_{vs}}{k_{0s}}.$$

It is independent of the overall hydroperoxide content. In stages (2) and (3), the role of oxygen in the generation of radicals is negligible, but it retains its influence as a participant in the interzonal transfer of radicals.

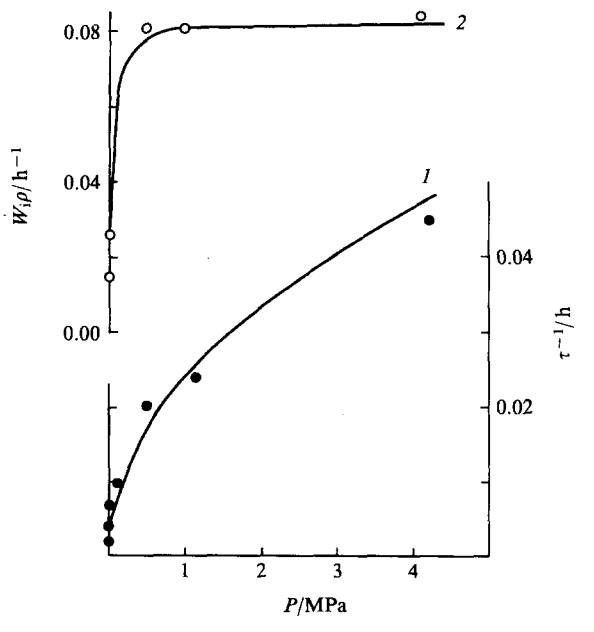


Figure 21. Dependence of the induction period (curve *1*) and of the maximum rate of oxidation of polypropylene (curve *2*) on the oxygen pressure; T = 90 °C.

The rate of oxidation is now described by the expressions

$$W^{(2)} \simeq \left(\frac{P_0}{b+P}\right)^{0.5} \left(\frac{\delta k_{0s} k_{vs}}{c+g}\right)^{0.5},$$

$$W^{(3)} \simeq \left(\frac{P}{b+P}\right)^{0.5},$$

where b and c are constants and $W^{(2)}$ and $W^{(3)}$ differ from $W^{(1)}$ by faster saturation as a function of P.

The calculated $W^{(1)}(P)$ and $W^{(3)}(P)$ curves for PP and polyethylene (PE) oxidation are presented in Figs 21 and 22. Experimental data have been obtained for PP films[77] and for a PE melt.[78] The unique mechanism of the oxidation in all stages of the process is confirmed by the finding that the expressions for $W^{(2)}$ and $W^{(3)}$ include the same value of b: 0.1 MPa for PP and 10, 50, and 200 torr for PE at 141 °C, 157 °C, and 165 °C respectively.

The observed correspondence between the calculated curves and the experimental points permits the conclusion that the heterophase mechanism predominates over the traditional homogeneous oxidation mechanism in relation to a hydrocarbon polymer, which differs fundamentally from a homogeneous liquid by its supermolecular organisation.

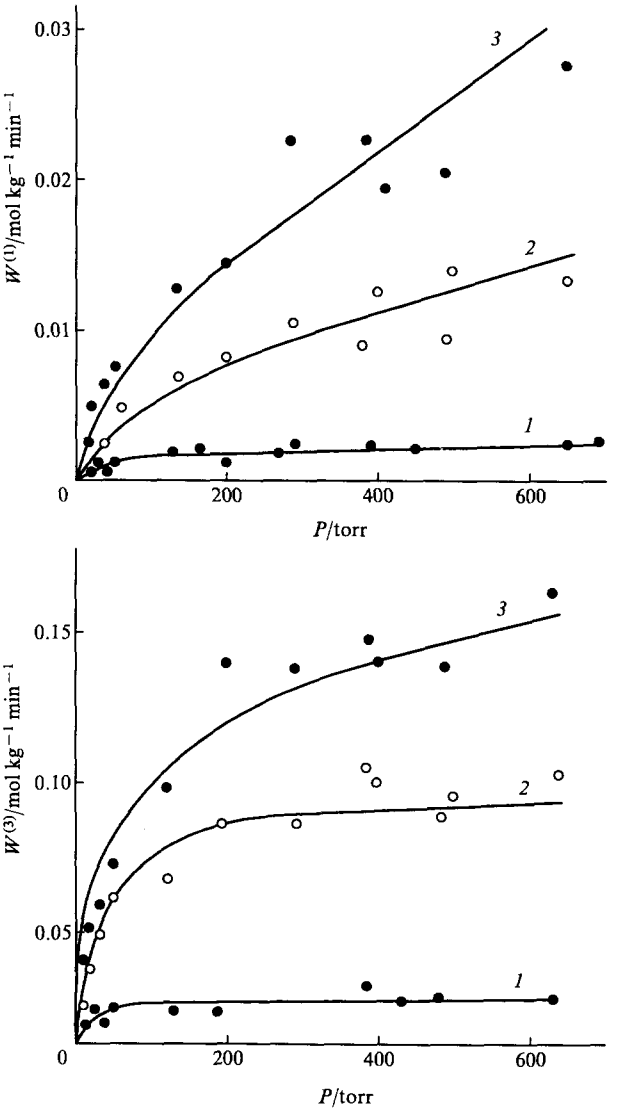


Figure 22. Dependence of the rate of oxidation of polyethylene on the oxygen pressure; T(°C): (*1*) 141; (*2*) 157; (*3*) 165.

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