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The Mechanisms of the Stabilisation of Thermostable Polymers

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New data on the stabilisation of thermostable polymers are presented, attention being concentrated on quantitative data and reaction mechanisms. The theoretically feasible polymer stabilisation pathways at temperatures exceeding 250°C are briefly analysed, various methods for the inhibition of thermo-oxidative and thermal degradation of polymer systems are considered, and experimental results concerning the kinetics and mechanisms of these processes are described.
One of the general polymer stabilisation pathways, based on non-chain inhibition reactions, is analysed in detail; procedures for the generation of highly active stabilisers directly in polymeric materials or during their processing and employment are considered, new approaches are proposed to the solution of the problem of the stabilisation of thermostable polymers, and certain experimental data are quoted.
The bibliography includes 203 references.

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I. INTRODUCTION

Studies on the stabilisation of thermostable polymers constitute an independent branch of the science of the ageing of polymers, since in this field one cannot use the general procedures which have become common in the stabilisation of non-thermostable polymer materials. The considerable interest in the problem of the stabilisation of thermostable polymers is indicated by the abundance of monographs, reviews, and experimental studies on this problem[1-44] published in recent years. Unfortunately, most of these are concerned solely with the influence of particular additives on the ageing of polymers or with the problem of stabilisation when the usual antioxidants and inhibitors of thermal degradation, effective at temperatures not exceeding 200–250°C, are used.

Among highly thermostable polymers†, organosilicon, organofluorine, and other polymers derived from organic derivatives of the elements, phenyl ether resins, polyimides, etc. are of greatest interest[45,46]. The available literature information about the mechanisms of the stabilisation of these polymers is contradictory[28,45-58]. In a number of studies, conclusions have been reached without taking into account the experimental conditions. For example, some workers investigated the relevant processes under conditions where the rate of the latter is limited by the diffusion of oxygen or of the degradation products and yet this factor was not taken into account in the determination of the mechanism.

The most interesting studies dealt with the stabilisation of polymeric liquids[55-57], but the conclusions reached in such investigations concerning the process mechanisms cannot always be extended to solid polymeric systems[59,60].

Several general approaches have been formulated in recent years and new mechanisms of the stabilisation of thermostable polymers have been proposed[4,19,20,35-38]. Although the theory of high-temperature stabilisation is not complete and only a few theoretical studies have been made as yet, important data have accumulated and can be usefully considered.

This review deals with the mechanisms of the stabilisation of thermostable polymers which are experimentally and theoretically justified and also with certain empirical data taken from studies on the stabilisation of thermostable polymers published in 1969–1975. Studies which are of practical interest alone, the references to which may be found in a number of monographs[5-7,14,15,17,18,43] and reviews[21,29,31,32-35], are not discussed.

II. GENERAL APPROACHES TO THE PROBLEM OF THE STABILISATION OF POLYMERS

It has come to be assumed that polymers may be stabilised in two ways: by the introduction of special additives (stabilisers) or by modification using different procedures. The first method is most widely used. Stabilisers are normally involved in the following reactions:

1. Interaction with free radicals leading to the deactivation of active centres and chain termination.
2. Interaction with the molecular degradation products involved in [further] reactions and leading to the decomposition of the polymer.
3. Interaction with active agents penetrating the polymer from an external medium[4,37].
4. The blocking (deactivation) of the reactive centres of macromolecules (weak bonds).
5. Deactivation of impurities by the binding of the latter into stable complexes.

† Polymers which can be used at temperatures above 200–250°C will henceforth be referred to for brevity as thermostable.

From the thermodynamic standpoint, the hypothesis that the chemical reactions leading to stabilisation should result in the formation of stronger bonds compared with those whose presence in the polymer is responsible for its thermodynamic instability under the given conditions is frequently valid[4]. It can be shown that this principle holds also from the kinetic standpoint, since the chemical bond energy is both a thermodynamic and a kinetic criterion of the occurrence of bond dissociation processes under the influence of heat and chemical agents. Knowing the detailed polymer decomposition mechanism, one can therefore select stabilisers for thermostable polymers on the basis of the chemical bond strengths.

Inhibited processes can be divided into two groups: those involving chain and non-chain inhibition[19,20]. Chain inhibition presupposes the deactivation of the active centres for the chain process, i.e. their conversion into inactive products from the standpoint of chain propagation. Non-chain inhibition is associated with the deactivation of a substance involved in any reactions leading to the degradation of the polymer. In chain polymer degradation processes, non-chain inhibition is associated with the deactivation of the substances initiating the chains or involved in the chain propagation reactions. In non-chain polymer degradation processes, non-chain inhibition presupposes the deactivation of the active centres responsible for the degradation.

Thus, there are two general ways of inhibiting the polymer degradation processes.

1. Inhibition of the chain processes by the introduction into the system of substances leading to chain termination.
2. The removal from the system of chemical agents (present in the polymer composition or formed as a result of ageing), weak bonds, etc.

A rigorous kinetic criterion of non-chain inhibition, associated with the deactivation of a particular compound, is a zero rate of initiation (reaction) with participation of the given substance X′ during the ageing of the polymer:

$$w_{X'} = 0$$

Quantitative criteria of the efficiency of non-chain inhibition can be readily obtained from the following ratios:

$$w_{Z+X'}/w,$$

where $w_{Z+X'}$ and w are the rates of the non-chain inhibition and the overall rate of the process in the absence of the stabiliser Z.

Chain processes are inhibited by inhibitors of thermal (thermostabilisers) or oxidative (antioxidants) degradation of polymers. The inhibition of the decomposition of the polymer is associated with chain termination, which can be represented by elementary reactions of the following type:

$$R^{\cdot} + InH \rightarrow RH + In^{\cdot}$$
$$R^{\cdot} + In^{\cdot} \rightarrow RIn$$
$$RO_2^{\cdot} + InH \rightarrow ROOH + In^{\cdot}$$
$$RO_2^{\cdot} + In^{\cdot} \rightarrow \text{inactive products},$$
$$2In^{\cdot} \rightarrow In - In$$
$$R^{\cdot}, R_2^{\cdot} + X \rightarrow \text{inert products, etc.},$$

where R· is the active radical propagating the chain, InH the inhibitor molecule, X a stable radical or molecule containing a short [multiple?] bond, etc.

The assortment of stabilisers effective below 200–250°C is fairly extensive[5,14–18,27,31,61]. However, at higher temperatures the mechanism of the degradation of polymers changes and the "low-temperature" stabilisers such as phenols, amines, etc. frequently vaporise or are themselves converted into initiating agents. The assortment of suitable stabilisers under these conditions is therefore restricted. Inhibiting activity is shown at elevated temperatures by compounds such as certain phosphites[26,35], inorganic acids[62–66], alkalies[67,68], metals and their compounds[35,69–87], and polyconjugated systems[21,77].

Furthermore, at high temperatures the method involving the generation of radicals directly in polymer compositions is effective. Such acceptors must be themselves firmly stable and must not participate in chain initiation and chain transfer processes[4].

The procedures for the elimination of active degradation products have been used for a long time in polymer chemistry[5]. On the other hand, methods for the removal of weak bonds and other initiating components from systems have been inadequately studied. Although it has been known for a long time that oxygen acceptors inhibit oxidation, the lack of knowledge about the mechanism as a whole precluded the determination of the optimum conditions for the application of these substances, led to contradictory data, etc. This approach became very promising only after it had been shown theoretically[4,19,20,37,38] that the oxidative ageing of polymers can be fully suppressed by using appropriate oxygen acceptors. The essential feature of the elementary interaction of O_2 (as well as other agents causing the degradation of polymers) with the acceptor, called non-chain inhibition[19,20], is that, under conditions of a fairly high reactivity and concentration of the stabiliser Z, oxygen is not involved in initiation reactions of the type

$$RH + O_2 \rightarrow R^{\cdot} + HOO^{\cdot}$$
$$2RH + O_2 \rightarrow 2R^{\cdot} + H_2O_2, \text{etc.}$$

and is fully absorbed in the reaction with the stabiliser:

$$nZ + \frac{m}{2}O_2 \rightarrow Z_nO_m \text{ (inert product).}$$

Table 1. Schematic description of polymer stabilisation pathways.

Type of initiation of degradation	Stabilisation method	Substances involved in reactions (examples)
1. Dissociation of main macromolecular chains, scission of side (terminal) groups: $R_m-R_n \rightarrow R_m^{\cdot} + R_n^{\cdot}$; $R_m-YX_2-R_n \rightarrow R_m-YX-R_n + X^{\cdot}$	(a) chain inhibition: $R^{\cdot} + YR' \rightarrow RY + R'^{\cdot}$; $R'^{\cdot} \longrightarrow R'R$; $R^{\cdot} + Z'^{\cdot} \rightarrow RZ'$; R′R and RZ′ are inert products.	YR′–InH–antioxidant, thermostabiliser; Z′·—stable radical
	(b) non-chain inhibition, structural stabilisation	substances forming clathrate compounds
2. Reactions with chemical agents: $R_m-YX_2-R_n \xrightarrow{X'} R_m-YX-R_n + X'X^{\cdot}$ (or active ionic forms)	(a) chain inhibition: $R'^{\cdot} + Z'^{\cdot} \rightarrow$ inert products	Z′·—radical acceptor; X′—chemical agent (O_2, O_3, H_2O, HCl, etc.) Z—acceptor X′ (metal, metal oxide, sulphide, etc.)
	(b) non-chain inhibition: $X' + Z \rightarrow$ inert product	
3. Reaction of weak bonds and active impurity groups: $R_m-Y-Y-R_n \rightarrow R_mY^{\cdot} + R_nY^{\cdot}$; $R_m-X_1-R_n \xrightarrow{Y_2} R'^{\cdot} + \text{products}$ (where $X_1 = >C=C<$, $-C\equiv C$, etc.)	(a) chain inhibition: $R'^{\cdot} + Z'^{\cdot} \rightarrow$ inert products	Z′—stabiliser (InH, stable radical)
	(b) non-chain inhibition: $R_m-X_1-R_n \xrightarrow{Z_1}$ inert product; $Y_2 + Z_2 \rightarrow$ inert product	Z_1–chemical agent (H_2, F_2, etc.); Z_2—acceptor of chemical agent; Y_2—chemical agent

The employment of non-chain inhibition in combination with the generation of highly active oxygen acceptors directly in polymeric systems made it possible to increase

significantly the lifetime of certain thermostable materials[4,37,38]. A number of chemical processes permitting the generation of highly active stabilisers of different types[37,75] in polymer compositions virtually in any specified temperature range have been proposed recently (Section IV). Thus the non-chain inhibition method has been extended to various types of ageing.

Table 1 summarises the possible polymer stabilisation pathways. The methods listed in Table 1 are applicable to the stabilisation of not only thermostable, but, in principle, any polymers undergoing decomposition via different mechanisms.

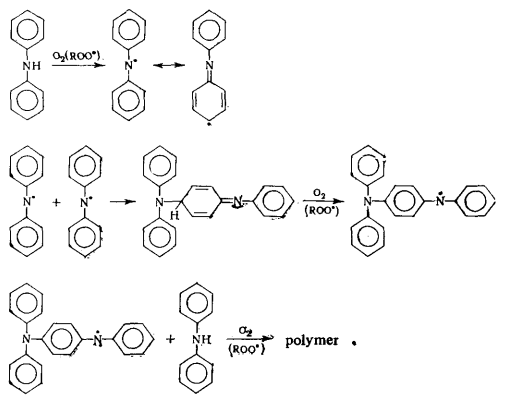
Methods for increasing the stability of polymers based on their modification[1,16,88-95] and structural stabilisation[19,96-98] and the structural-chemical stabilisation of chemical agents and stabiliers[4,19], etc. are also known. These procedures, involving the employment of the cage effect[45,99-101], the reduction of the rate of diffusion of active agents in polymers[5,102,103], etc. are not considered in detail in the present review. Special stabilisation methods[104,105] used in light- and radiation-induced ageing processes[1,106,107] are not analysed either.

III. THE MECHANISMS OF THE STABILISATION OF THERMOSTABLE POLYMERS

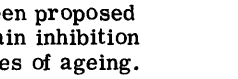
As already stated above, a number of inhibiting systems retarding the chain degradation of polymers at elevated temperatures are known. Stabilisation methods can be based on both chain and non-chain inhibition procedures. Since the stabilisation of many polymer compositions involves the application of both these procedures, it is useful to consider the mechanisms of the inhibition of degradation on the basis of the nature of the stabiliser.

Berlin, who investigated the inhibiting properties of various polyconjugated systems, showed that they are frequently effective inhibitors of high-temperature chain processes[21,77].

Many polyconjugated systems, including those formed in consequence of chemical transformations of antioxidants and substrates, exhibit a high inhibiting activity. Thus, polydiphenylamines, with a higher inhibiting activity than the initial amines, are formed in the oxidative dehydropolymerisation of secondary aromatic amines[21]. One of the hypothetical mechanisms of the formation of these polymers may be as follows:



Stemniski et al.[84] pointed out the possibility of inhibiting the thermal degradation of polyphenyl ethers at 420–440°C and their thermo-oxidative degradation at 250–300°C by organic derivatives of variable-valence metals (Co, Cu, Ti, Al, Mn, Ni, Fe, Be, and Cr) and proposed a mechanism for their action. Thus they showed that the decomposition of a polyether involves, on the one hand, the formation of relatively stable free radicals of the type



or their derivatives. On the other hand, variable-valence metal compounds interact with hydroperoxides in the following way:

$$M^{n+} + ROOH \rightarrow M(\dot{O}H)^{2+} + RO^{\cdot} ,$$
$$M(\dot{O}H)^{2+} + ROOH \rightarrow M^{n+} + HOH + ROO^{\cdot} .$$

Archer and Bozer[87] suggest that the stabilisation of polyphenyl ethers by organic cobalt salts is associated with the interaction of the metal ions and active radicals:

$$Co^{3+} + R^{\cdot} \rightarrow Co^{2+} + R^{+} . \qquad (1)$$

One may postulate that analogous processes occur also in the reactions of RO$^{\cdot}$, ROO$^{\cdot}$, etc. radicals. There is reason to believe[57] that the efficiency of reaction (1) is not very high when inorganic salts are used.

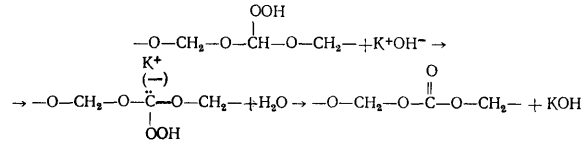
According to Ravner et al.[57], the high-temperature stabilisation in the presence of alkalies, for example KOH, is associated with the occurrence of the following reactions:

$$\text{I. } ROO^{\cdot} + KOH \rightarrow ROH + KOO^{\cdot} ,$$
$$KOO^{\cdot} + R'O^{\cdot} \rightarrow KOR' + {}^{\cdot}OO^{\cdot}(=O_2) ,$$
$$KOR' + H_2O \rightarrow KOH + R'OH ,$$
$$\text{II. } 4KOH + 3O_2 \rightarrow 4KOO^{\cdot} + 2H_2O ;$$
$$KOO^{\cdot} + ROO^{\cdot} \rightarrow KOOR + O_2 ,$$
$$KOOR + R'O^{\cdot} \rightarrow ROR' + KOO^{\cdot} .$$

Peroxides of the type ROOM can be generated similarly from basic salts of other alkali metals. However, the details of this interesting mechanism require experimental tests.

The stabilisation probably involves mechanism (I) when the decomposition of peroxy-radicals is base-catalysed; in other cases, mechanism (II) may obtain. It is noteworthy that there is a correlation between the stabilising activity of alkali metal [and alkaline earth] hydroxides and the ability of the alkali metals to form peroxides; calcium and strontium hydroxides are exceptions.

Alkali metal hydroxides are also effective stabilisers of trioxan–dioxolan copolymers[48]. It is suggested that alkalies decompose hydroperoxides without breaking macromolecular bonds. Thus the secondary hydroperoxy-groups present in the polymer can react with KOH via the following mechanism:



It is noteworthy that an inhibiting activity of KOH is observed at comparatively low temperatures in the thermal decomposition of polyethylene[67,68]. This involves a decrease of the branching of the polymer, lowers the concentration of "weak" sites in the macromolecules, and prevents the formation of fragments with unsaturated terminal groups[68].

Nielsen[55,56] used iron and cerium compounds as stabilisers in the study of the oxidation of liquid siloxanes. It was found that below 150°C iron(III) compounds accelerate the thermo-oxidative degradation. At higher temperatures the same compounds have a stabilising effect, a definite Fe^{3+} concentration, ensuring the minimum rate

of oxidation, corresponding to each temperature. The author believes that the following reactions occur in the degradation of liquid siloxanes.

Initiation:

$$\equiv SiCH_3 + O_2 \rightarrow \equiv SiCH_2^{\cdot} + {}^{\cdot}OOH \text{ and (or)}$$
$$\equiv SiCH_3 + O_2 \rightarrow [\equiv SiCH_2OOH] \rightarrow \equiv Si^{\cdot} + {}^{\cdot}OH + CH_2O \quad .$$

Chain propagation:

$$\equiv SiCH_2^{\cdot} + O_2 \rightarrow \equiv SiCH_2OO^{\cdot} \quad ;$$
$$\equiv SiCH_2OO^{\cdot} \rightarrow \equiv SiO^{\cdot} + CH_2O \quad ;$$
$$\equiv SiO^{\cdot} + O_2 \rightarrow \equiv SiOO^{\cdot} + O \quad ;$$
$$\equiv SiCH_3 + \equiv SiO^{\cdot} \rightarrow \equiv SiOH + \equiv SiCH_2^{\cdot} \quad .$$

Chain branching:

$$\equiv SiCH_2OOH \rightarrow \equiv Si^{\cdot} + {}^{\cdot}OH + CH_2O \quad ;$$
$$\equiv SiOOH \rightarrow \equiv SiO^{\cdot} + {}^{\cdot}OH \text{ or } \equiv Si^{\cdot} + {}^{\cdot}OOH \quad ;$$
$$HOOH \rightarrow 2{}^{\cdot}OH \quad ;$$
$$CH_2O + O_2 \rightarrow {}^{\cdot}CHO + {}^{\cdot}OOH \quad .$$

Chain termination:

$$\equiv Si^{\cdot} + {}^{\cdot}OH \rightarrow \equiv SiOH \quad ;$$
$$\equiv Si^{\cdot} + {}^{\cdot}OSi \equiv \rightarrow \equiv Si{-}O{-}Si \equiv \quad ,$$

etc.

It is suggested that free radicals are destroyed as a result of the reduction of the metal ion:

$$M^{x+1} + {}^{\cdot}R \rightarrow M^x + R^+ \text{ (where } R^{\cdot} \equiv Si^{\cdot} \text{ or } \equiv SiCH_2^{\cdot}) \quad , \qquad (2)$$

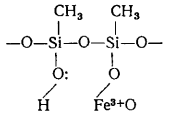
and that at a fairly high oxygen concentration there is a possibility of the regeneration of the metal ion M^{x+1} via the reaction

$$M^x + O_2 \rightarrow M^{x+1} + O_2^- \quad . \qquad (3)$$

Further studies[56] suggested also the occurrence of non-radical processes of the type $\equiv SiCH_3 + Fe^{3+}O$ complex $\rightarrow \equiv SiOH + Fe^{2+}$ complex followed by oxidation of the product and regeneration of the initial compound:

$$Fe^{2+} \text{ complex} + O_2 \rightarrow Fe^{3+}O \text{ complex.}$$

It is suggested that the stabilisation of liquid dimethylsiloxane by iron octoate [octanoate?] involves the formation of a chelate structure of the type



There have been a number of other studies on stabilisation in the presence of metal ions. However, the majority of the results refer to low temperatures. Nevertheless, some of them are important in the consideration of high-temperature processes. We may mention a study[74] where the influence of variable-valence metals on the resistance of polyurethanes to thermo-oxidation was investigated. It was shown that, when the system contains hydroperoxides (120°C), its stabilisation is associated with the following reactions:

$$ROOH + M^{3+} \rightarrow M^{3+} + OH^- + RO^{\cdot} \quad ;$$
$$ROOH + M^{3+} \rightarrow RO_2^{\cdot} + H^+ + M^{2+} \quad .$$

Presumably the oxidation of certain thermostable polymers at temperatures not exceeding 200–250°C in the presence of complex inhibitors can be described in terms of the scheme for the inhibited oxidation of hydrocarbons[74,108,109]:

$$\gamma \rightarrow r^{\cdot} \quad ;$$
$$r^{\cdot} + \text{polymer} + O_2 \xrightarrow{w_i} RO_2^{\cdot} \quad ;$$
$$RO_2^{\cdot} + RO_2^{\cdot} \xrightarrow{\eta k_6} \text{products} + h\nu \quad ;$$
$$MA_2 + L \underset{}{\overset{K_p}{\rightleftarrows}} ML \quad ;$$
$$RO_2^{\cdot} + ML \xrightarrow{k_7} \text{inactive product} \quad ;$$
$$RO_2^{\cdot} + L \xrightarrow{k_7'} \text{inactive product} \quad ,$$

where γ is the initiator decomposing at a rate w_i, $r^{\cdot}$ the radical initiator, L the ligand (for example urethane) molecule, MA_2 the variable-valence metal salt, ML the molecule of the complex, η the overall chemiluminescence yield, and the constants k with the appropriate subscripts are the rate constants for the elementary reactions.

When the concentration of peroxy-radicals corresponds to a steady state and $[M] \gg [L]$, the following expression holds:

$$\frac{I_0 - I}{\sqrt{I_0 I}} = \frac{[MA_2]_0}{\sqrt{w_i k_6}} \left[\frac{k_7 \cdot K_p [L]_0}{1 + K_p [MA_2]_0} + k_7 \right] \quad , \qquad (4)$$

where I_0 and I are the initial and final intensities of illumination and K_p is the equilibrium constant. Eqn. (4) holds satisfactorily in many instances, which confirms the above stabilisation mechanism.

It has been noted[42] that, at temperatures of the order of 350°C and above, the mechanism of the stabilisation of polyorganosiloxanes in the presence of metal-phthalocyanines can be attributed not only to the interaction of the paramagnetic species with the radicals but also to trans-coordination accompanied by the formation of complicated chelate compounds.

The stabilising action of metals and their oxides at high temperatures is attributed by some workers[42,47,51,75,86] to the orienting effect of the dispersed particles, which serve as centres for the formation of secondary structures, or to the formation on degradation of new polymers with metal heteroatoms in the chain. These mechanisms do indeed occur, but they are not always decisive. There is no doubt that in a number of cases the stabilising action of many metals at high temperatures is largely associated with a non-chain inhibition reaction or with oxidation–reduction processes.

Analysis of a number of studies[29,51,56,74,75] has shown that the influence of metals and many inorganic compounds on the ageing of polymers cannot always be accounted for unambiguously. Thus it has been stated that iron and tin[74] salts, aluminium, chromium, zinc, phosphorus, and boron[76] oxides, and metallic lead and cadmium[51] accelerate the oxidation process under certain conditions. On the other hand, it has been noted in other investigations[5,75] that these compound have an inhibiting effect. Cobalt, copper, and cerium[74] salts and iron, magnesium, and other oxides[80] usually stabilise thermostable materials at temperatures in the range 300–390°C; at low temperatures or at 400°C and above, they do not inhibit or actually accelerate polymer decomposition processes[56,76,80]. Many apparent contradictions in the interpretation of the action of a wide variety of stabilisers used in the high-temperature ageing of polymers can be readily explained by taking into account the conditions under which the studies were carried out and also the characteristics of the methods, which are sometimes imperfect.

Examination of Table 1 in the preceding section shows that the use of non-chain inhibition processes leads to new possibilities for the solution of the problem of the stabilisation of thermostable polymers. This approach attracted the attention of investigators only in recent years[36,110-112] after the determination of the mechanism of stabilisation in the presence of oxygen acceptors, generated in polymer compositions or articles[4,19,20,38,113]. Subsequently Shustova showed that the application of a non-chain inhibition method can be sometimes effective in the stabilisation of thermostable materials, losing many of their useful properties under the influence of various chemical agents[37,111,186].

We shall now examine the characteristics of the mechanism of non-chain inhibition[4,37,112,114]. The oxygen acceptors generated in polymer compositions or acceptors introduced into the polymer during its processing may serve as highly effective inhibitors, preventing oxidative degradation via a non-chain inhibition mechanism. Acceptors of the first group exhibit a high activity already at room temperature and for technical reasons cannot therefore be introduced in the usual way. On the other hand, acceptors of the second type exhibit a low activity under these conditions, but become fairly effective at high temperatures.

We shall now consider the general kinetic scheme (A) for the oxidative degradation of polymers containing mobile hydrogen atoms involved in initiation processes[4,20].

I. Initiation:

$$\begin{aligned}
&\text{weak bond} \xrightarrow{k_{in}} 2R^{\cdot}_{pri}\ ; \quad \text{(a)}\\
&R^{\cdot}_{pri} + RH \xrightarrow{k'_{in}} R^{\cdot} + R_{pri}H\ ; \quad \text{(b)}\\
&RH + O_2 \xrightarrow{k_0} R^{\cdot} + HO^{\cdot}_2\ ; \quad \text{(c)}\\
&2RH + O_2 \xrightarrow{k'_0} 2R^{\cdot} + H_2O_2\ . \quad \text{(d)}
\end{aligned} \qquad \text{(A)}$$

II. Chain propagation:

$$R^{\cdot} + O_2 \xrightarrow{k_1} RO^{\cdot}_2\ ; \quad \text{(a)}$$

$$RO^{\cdot}_2 + RH \xrightarrow{k_2} R^{\cdot} + ROOH \xrightarrow{k_3} \text{inert products;} \quad \text{(b)}$$

$$\text{branching } \downarrow k_3$$

$$\text{products} \rightarrow 2R'^{\cdot}\ .$$

III. Chain termination:

$$R^{\cdot} + R^{\cdot} \xrightarrow{k_4} R{-}R$$

$$RO^{\cdot}_2 + R^{\cdot} \xrightarrow{k_5} ROOR$$

$$RO^{\cdot}_2 + RO^{\cdot}_2 \xrightarrow{k_6} \text{products.}$$

IV. Non-chain inhibition:

$$Z + O_2 \xrightarrow{k_Z} \text{inert products.}$$

If k_Z is fairly high, it is possible to select conditions such that the oxygen reacts virtually only with Z and is not involved in other elementary reactions.

On the basis of published data[109,115,116], we shall adopt the following rate constants for the elementary reactions (Ic), (Id), and (IIa) and the concentrations of the components (250–350°C):

$$k_0 = 10^{-2} - 1 \text{ litre mole}^{-1}\text{ s}^{-1};\ k'_0 = 10^{-3} - 10^{-1} \text{ litre}^2 \text{ mole}^{-2}\text{ s}^{-1};$$
$$k_1 = 10^8 \text{ litre mole}^{-1}\text{ s}^{-1}$$
$$[RH] = 10\ \text{M};\ [O_2] = 10^{-4}\ \text{M};$$
$$[R^{\cdot}] = 10^{-8} - 10^{-7}\ \text{M}.$$

The rates of the corresponding elementary processes involving oxygen are:

$$w_{RH+O_2} = k_0[RH]\cdot[O_2] = 10^{-5} - 10^{-3} \text{ mole litre}^{-1}\text{s}^{-1};$$
$$w_{2RH+O_2} = k'_0[RH]^2\cdot[O_2] = 10^{-5} - 10^{-3} \text{ mole litre}^{-1}\text{ s}^{-1};$$
$$w_{R^{\cdot}+O_2} = k_1[R^{\cdot}]\cdot[O_2] = 10^{-4} - 10^{-3} \text{ mole litre}^{-1}\text{s}^{-1}.$$

Next we assume that $w_{Z+O_2} = 10^{-2}$ mole litre^{-1} s^{-1}. After recalculation for a heterogeneous process, these values correspond to the real case of the stabilisation at 350°C of siloxane elastomers by pyrophoric iron generated in the polymer on decomposition of iron oxalate[37,113] (iron concentration 5 wt.%; surface area $S \simeq 10$ m^2 g^{-1}; oxidation rate constant $k_{Fe} = 10^{-14}$ g^2 cm^{-4} s^{-1}).

Thus we have the following relation for a number of systems:

$$w_{Z+O_2} \gg w_{R^{\cdot}+O_2},\ w_{RH+O_2},\ w_{2RH+O_2}.$$

Bearing in mind that the equilibrium concentration of O_2 in polymers is low, it can be easily shown that, as long as Z does not react with oxygen, reactions (Ic), (Id), and (IIa) hardly play an appreciable role.

It is noteworthy that the above estimate is based on unduly low values of S and k_{Fe}. In real systems, it is possible to obtain pyrophoric metals with surface areas of 100 m^2 g^{-1} and more[117,118]. Furthermore, the oxidation rate constant may be greater than 10^{-14} g^2 cm^{-4} s^{-1}. Thus, in the presence of copper 350–400°C, we have $k \simeq 10^{-8}$ g^2 cm^{-4} s^{-1} and the rate of the reaction $Cu + O_2 \rightarrow Cu_2O \xrightarrow{O_2} CuO$ should reach 10^2 mole litre^{-1} s^{-1}.

When the mechanism of the oxidative degradation of polymers is known, it is easy to obtain quantitative criteria of the efficiency of the stabilisers Z. Thus, at low temperatures, when the oxidation of the polymer[109] proceeds in accordance with the classical mechanism A, one can usefully consider three cases.

If the oxygen concentration in the polymer is low and the reaction rate $-d[O_2]/dt$ is directly proportional to the oxygen pressure p_{O_2}, effective inhibition is observed when the following condition is fulfilled:

$$fk'_Z[Z] \gg \frac{k_1 w_{in}^{1/2}}{k_4^{1/2}},$$

where f is the number of oxygen molecules interacting with one stabiliser molecule ($fk'_Z \equiv k_Z$) and w_{in} is the rate of initiation.

At a high oxygen concentration in the polymer, when the rate of oxidation is independent of p_{O_2}, effective inhibition should be observed provided that

$$fk'_Z[Z] \gg \frac{k_2 w_{in}^{1/2}}{k_6^{1/2}}\frac{[RH]}{[O_2]}.$$

In the intermediate case, where chain termination in the absence of stabilisers proceeds via reactions (4)–(6), effective inhibition requires that

$$fk'_Z[Z] \gg \frac{k_2 w_{in}^{1/2}}{k_6^{1/2}}\frac{[RH]}{[O_2]}\gamma,$$

where

$$\gamma = f([O_2], [RH]).$$

As oxygen diffuses into the specimen, the stabiliser Z is consumed via reaction (IV), while the lifetime of the article is determined by the rate of diffusion of oxygen. Calculations have shown[4] that, even for polymers whose oxygen permeability coefficients are high and amount to approximately 10^{-6} cm^3/cm^2/s.cm/atm [cm^2 s^{-1} atm^{-1} ?],[4,119-122] the lifetime of specimens 0.1–1 cm thick can reach many tens and hundreds of hours in the temperature range 300–400°C.

As an example, we shall consider the specific instance where the entire oxygen diffusing into the system interacts with the active stabiliser Z and the lifetime of the specimen is determined by the rate of diffusion of oxygen[37,38]. We assume that the lifetime of the polymer τ is equal to the time during which the specimen decomposes to the extent of 80% ($t_{80\%}$). If the specimen is a plate, oxygen diffuses from both sides and the two fronts of the reaction

$$Z + O_2 \rightarrow \text{inert product}$$

move at right angles to the surfaces of the plate towards the centre (there is no countercurrent diffusion of Z).

The following equation holds in this case:

$$P = -D_{O_2}(\partial c/\partial x), \tag{5}$$

where P is the permeability (the amount of substance transferred per unit time, per unit area, and per unit thickness at the normal concentration or pressure difference), D_{O_2} the diffusion coefficient, and $\partial c/\partial x$ the concentration gradient. Next, one can write

$$P = D_{O_2}\frac{[O_2]_0 - [O_2]_x}{x}, \tag{6}$$

where $[O_2]_0$ is the concentration of oxygen at the interface (mole cm^{-3}) and $[O_2]_x$ the concentration in the specimen at a depth x.

Having denoted by w' the specific rate of reaction between Z and O_2 (equal to the number of moles of Z which have reacted per unit time and per unit area in the reaction zone), we obtain

$$w' = [Z]\frac{dx}{dt}, \tag{7}$$

where [Z] is the concentration of the substance (mole cm^{-3}), x the distance (cm), and t the time (s).

Since the rate of reaction (assuming that one mole O_2 reacts with one mole of Z) is equal to the flux of oxygen in the reaction zone and $[O_2]_0 \gg [O_2]_x$, one can write

$$w' = [Z]\frac{dx}{dt} = \frac{D_{O_2}[O_2]_0}{x}, \tag{8}$$

$$x\,dx = \frac{D_{O_2}[O_2]_0}{[Z]}\,dt. \tag{9}$$

Integration of Eqn. (9) yields

$$\frac{x^2}{2} = \frac{D_{O_2}[O_2]_0}{[Z]}t.$$

Thus the movement of the reaction front in the specimen is described by a parabolic law.

Next we obtain

$$t_{80\%} \equiv \tau = \frac{x^2}{2}\cdot\frac{[Z]}{D_{O_2}\cdot[O_2]_0} \simeq k_0\frac{l^2[Z]}{D_{O_2}[O_2]_0}, \tag{10}$$

where l is the thickness of the specimen and k is a coefficient equal to approximately 0.1 and determined by the stoichiometry of reaction (IV) and the assumptions made.

Taking into account the temperature variation of D_{O_2} and $[O_2]$, we have

$$\tau = \frac{kl^2[Z]}{D_0 e^{-E_D/RT}\cdot\sigma_0'\cdot e^{-\Delta H/RT}},$$

where E_D is the activation energy for diffusion, ΔH the heat of solution of the gas, and D_0 and σ_0' are the corresponding pre-exponential factors.

However, ΔH is small for many polymers (between −2 and +2 kcal $mole^{-1}$), and one can therefore assume that

$$\tau = k\frac{l^2[Z]}{D_0 e^{-E_0/RT}[O_2]_0}. \tag{11}$$

Since the diffusion coefficients in polymer compositions may be low, of the order of 10^{-8} and even 10^{-9} $cm^2\ s^{-1}$, the lifetimes of polymeric materials can reach many thousands of hours.

Eqns. (10) and (11) have been obtained on the assumption that, in the absence of a stabiliser Z, the polymer decomposes almost at once. In the general case, the following expression is valid:

$$\tau = k\frac{l^2[Z]}{D_{O_2}[O_2]_0} + \tau' = k'l^2[Z] + \tau', \tag{12}$$

where τ' is a quantity comparable to the lifetime of the non-stabilised specimen.

Eqn. (12) has been obtained for the case where there is no diffusion of the stabiliser and the changes in the concentration of oxygen owing to its reaction with a polymer may be neglected. A detailed mathematical model without allowance for these limitations has been examined[39,110] and it has proved possible to explain theoretically the causes of the appreciable deviations from Eqn. (12) for fairly large thicknesses of the polymeric specimens. It has also been shown that τ' may be set equal to the lifetime of the non-stabilised specimen only for highly efficient stabilisers such that $\tau' \ll \tau$. If the stabilisation effects are small, one must bear in mind that

$$\tau' = t_p + (2t_p t_D^{(1)}\alpha)^{1/2},$$

where t_p is the polymer decomposition time subject to the condition that the concentration of oxygen is $[O_2]_0$ at all points in the polymer, $t_D^{(1)} = l^2/D_{O_2}$ is the time required by oxygen to diffuse into the specimen, and $\alpha = [Z]_0/\nu[O_2]_0$, ν being the stoichiometric coefficient of non-chain inhibition (the number of stabiliser molecules which have reacted with one oxygen molecule).

If the stabiliser Z inhibits not only oxidative but also thermol degradation and interacts with the primary radicals forming stable compounds of the type RZ (chain inhibition), then a simplified kinetic mechanism (B) of inhibited degradation is valid in the simplest instance:

$$\text{I. weak bond} \xrightarrow{k_{in}} R^{\cdot}_{pri};$$

$$\text{II. } R^{\cdot}_{pri} + Z \xrightarrow{k'_Z} R_{pri}Z;$$

$$\text{III. } O_2 + Z \xrightarrow{k_Z} \text{inert products.}$$

The mechanisms (A) and (B) described above do not take into account the possibility of chain-transfer processes via the stabiliser ($R_1R_2 + Z^{\cdot} \rightarrow R_1^{\cdot} + ZR_2$) and certain other elementary reactions. However, the satisfactory agreement of the calculations with the experimental results shows that the mechanism of the stabilisation processes considered here can operate[37,38].

We shall now consider certain reactions of the type $Z + O_2 \rightarrow$ inert products which may be important for the stabilisation of polymers. It has been mentioned in the literature that the oxidation of organic compounds is inhibited by inorganic substances such as sulphides, phosphorus compounds, arsenic, antimony, bismuth, boron, silicon, tin, lead, sulphur, and others[123]. However, the mechanisms of these reactions have not been studied in detail and some of the above substances have not been used at all to stabilise polymeric materials[5].

Demonstration of the possibility of inhibition via a non-chain mechanism[4,37] necessitates the study of the rates of interaction of the above inhibitors with oxygen in order to find the optimum conditions for their utilisation as stabilisers. Together with classical data, quantitative studies published in recent years are considered below.

The kinetics of the oxidation of cobalt sulphide have been investigated[124] and it has been shown that, at temperatures of the order of 500°C, the process is described satisfactorily by the equation

$$\frac{d\alpha}{dt} = K(1-\alpha)^n,$$

where α is the degree of oxidation, $K = f(T,\ P_{O_2},\ S_0)$ and n are constants, P_{O_2} is the oxygen pressure, and S_0 the surface area of the specimen.

It has been established[125] that Co_9S_8 is vigorously oxidised at 200°C with formation of the complex $Co_9S_8O_8$. The temperatures of the maximum rates of oxidation of the sulphides Sb_2S_3, AlFeS, FeS, Cu_3FeS_3, $CuFeS_2$, Fe_7S_8, MoS_2, ZnS, PbS, Cu_2S_3, CdS, and others, have been determined in a number of studies[126], and the reaction mechanisms have been established[127]. Thus it has been shown that chalcopyrite is oxidised via the mechanism

$$n\,CuFeS_2 + 4O_2 = 2\,FeO + Cu_2S\,(n-2)\,CuFeS_2 + 3SO_2 \quad ;$$
$$3\,FeO + \frac{1}{2}\,O_2 = Fe_3O_4 \quad ;$$
$$2\,Fe_3O_4 + \frac{1}{2}\,O_2 = 3\,Fe_2O_3,$$

and that the mechanism of the oxidation of iron and copper sulphides is[128]:

$$2\,FeS \xrightarrow{O_2} [2FeSO \xrightarrow{O_2} 2\,FeSO_2 \rightarrow Fe_2SO_3 \cdot 2SO_2] \xrightarrow{-2SO_2} Fe_2O_3 \quad ;$$
$$Cu_2S \xrightarrow{O_2} [Cu_2SO \xrightarrow{O_2} Cu_2SO_2 \xrightarrow{O_2} Cu_2SO_3 \xrightarrow{-SO_2} Cu_2O \cdot SO_2] \xrightarrow{O_2} Cu_2O \rightarrow 2CuO \quad .$$

We may note that many sulphides are also effective synergistic agents, decomposing peroxides via a molecular mechanism[129,130]. Thus it has been shown[130] that WS_2 appreciably reduces the yield of radicals in the decomposition of hydroperoxides, while increasing its rate.

Antimony is slowly oxidised below 350°C, while at 500°C the process is rapid and involves the formation of Sb_2O_3 and then Sb_2O_4.[131] Vigorous oxidation of silicon and lead is observed above 400°C.[132-134]

The oxidation of a number of variable-valence metal hydroxides has been thoroughly studied, namely the oxidation of $Fe(OH)_2$, $Co(OH)_2$, $Mn(OH)_2$, etc. Manganese(II) hydroxide absorbs oxygen vigorously even at low temperatures[135]:

$$Mn(OH)_2 + \frac{1}{2}\,O_2 \rightarrow MnO_2 + H_2O \quad .$$

Certain variable-valence metal oxides are also effective oxygen acceptors[136-138]. For example, the kinetics of the oxidation of CoO in accordance with the equation

$$3\,CoO + \frac{1}{2}\,O_2 \rightarrow Co_3O_4$$

can be described by the equation

$$1-(1-\alpha)^{1/3} = kt \quad ,$$

where k is a constant.

Dithionites (for example sodium hyposulphite $Na_2S_2O_4$) can be used as oxygen absorbers. In the presence of alkalies, they readily interact with O_2 in the following way[132]:

$$S_2O_4^{2-} + 2OH^- + O_2 \xrightarrow{MOH} SO_4^{2-} + H_2O.$$

However, dithionites are as a rule unstable and decompose on heating:

$$2\,M_2^I\,S_2O_4 \xrightarrow{t°>100°} M_2^IS_2O_3 + M_2SO_3 + SO_2.$$

The double salts of alkali metals and zinc dithionite ZnS_2O_4 are more stable.

Sulphites[139-141], pyrogallol mixed with alkalies[142-145], and other compounds[135,146,147] can sometimes serve as oxygen acceptors in model reactions.

Highly dispersed metals generated in polymers at high temperatures are active oxygen acceptors. Thus, copper with a high surface area absorbs oxygen even at low temperatures[148]. In the temperature range 400–500°C, the rate of the process is extremely high, but owing to the high dissociation pressure of CuO, oxygen cannot be removed completely from the system at these temperatures[135]. Metallic silver and silver on carriers (Al_2O_3, etc.) absorb O_2 at temperatures of 200–300°C; palladium catalyses the reaction of H_2 with O_2 at low temperatures, which proceeds rapidly and completely[149-151]. Finely dispersed iron reacts vigorously with oxygen even at low temperatures, forming oxides[117,149-152]. The thermodynamics of the oxidation of metals and various substances in the solid phase has been thoroughly studied[149-151]. Studies devoted to the thermodynamic aspects of the protection of highly thermostable materials against oxidation by the introduction of metals have also been made[153].

The kinetics of the oxidation of solids are frequently complex and, depending on their nature, the nature of the surface, and the thickness of the oxide film, are described by equations of different types[117,118,135,149-151,154,155]. For a constant concentration gradient of the component diffusing during oxidation, a parabolic law holds:

$$(\Delta l')^2 = 2k't \quad \text{or} \quad \left(\frac{\Delta m}{s}\right)^2 = k''t, \qquad (13)$$

where l' is the thickness of the oxide layer (cm), k' a constant ($cm^3\ s^{-1}$), $\Delta m/s$ the increase in the weight of the oxide per unit area ($g\ cm^{-2}$), and k'' another constant ($g^2\ cm^{-4}\ s^{-1}$).

If the rate of oxidation is determined at interfaces, the following linear law holds:

$$\frac{\Delta m}{s} = k'''t, \qquad (14)$$

where k''' is a constant ($g\ cm^{-2}\ s^{-1}$).

In a more complex case, where account must be taken of both laws, the following equation is frequently valid:

$$\frac{\Delta m}{s}\cdot\frac{1}{k'''} + \left(\frac{\Delta m}{s}\right)^2\frac{1}{k''} = t. \qquad (15)$$

A cubic relation between $\Delta m/s$ and time is observed in the oxidation of very thin films or superdisperse metals:

$$\left(\frac{\Delta m}{s}\right)^3 = k_c''t \quad , \qquad (16)$$

where k_c'' is a constant ($g^3\ cm^{-6}\ s^{-1}$); sometimes logarithmic or inverse logarithmic relations are valid:

$$\Delta l' = k_1 - \text{const}\cdot\ln t,$$
$$\frac{1}{\Delta l'} = k_1 - \text{const}\cdot\ln t. \qquad (17)$$

The use of Eqns. (13)–(17) makes it possible to calculate the rates of reactions Z + O_2 → inert product as a function of the degree of dispersion of the substance (metal, sulphide, etc.) and one can find the optimum conditions for the employment of the polymer stabilised by one or other active stabiliser.

If a highly active stabiliser Z exists in the polymer in an atomic, molecularly disperse, or finely disperse state, the rate of its oxidation is determined, as already stated, by the diffusion of oxygen into the specimen and the movement of the reaction front (in the absence of counter-current diffusion of Z) obeys a parabolic law rigorously.

IV. THE GENERATION OF HIGHLY ACTIVE STABILISERS IN POLYMERIC COMPOSITIONS

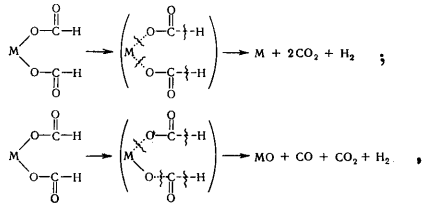
Many chemical processes yielding highly active compounds which are effective acceptors (absorbers) of oxygen or free radicals are known. Many of these reactions can be used for the high-temperature stabilisation of polymers or can serve as models for a detailed study of the mechanism of the inhibited ageing of thermostable polymeric materials. Naturally, in view of the wide variety of mechanisms of such processes, the conditions governing their occurrence, and the subsequent reactions of their products, in choosing the stabilising systems account must be taken of the characteristics of the particular polymeric system.

We shall consider a number of processes involving the generation of highly active stabilisers, which can serve as models. The formation of finely dispersed metals and lower-valence metal oxides from organic salts of the metals is of greatest interest[75,132,137].

Table 2. Temperature ranges corresponding to the decomposition of formates[156].

Formate	Temp. range of decompn., °C	Gaseous decomposition products
Na (HCOO)	320—420	H_2, CO, CO_2, CH_4 etc.
K (HCOO)	360—480	ditto
Ca $(HCOO)_2$	400—495	»
Sr $(HCOO)_2$	340—500	»
Ba $(HCOO)_2$	400—460	»
Mg $(HCOO)_2$	330—460	»
Mn $(HCOO)_2$	260—410	»
Zn $(HCOO)_2$	210—360	»
Cd $(HCOO)_2$	230—305	»
Cu $(HCOO)_2$	170—225	only H_2, CO, CO_2, and CH_4
Co $(HCOO)_2$	245—300	ditto
Ni $(HCOO)_2$	260—290	»
Pb $(HCOO)_2$	260—340	»

The decomposition of various formates, which can result in the formation of pyrophoric metals or their oxides is well known. Cobalt, nickel, copper, and lead formates decompose via the following mechanisms[156]:



while alkali metal formates decompose with formation of oxalates and carbonates:

$$2\,HCOOM \rightarrow \begin{cases} M_2C_2O_4 + H_2 \\ M_2CO_3 + H_2 + CO \end{cases} .$$

Side reactions of the type

$$3H_2 + CO \rightarrow CH_4 + H_2O \ ;$$
$$2H_2 + CO \rightarrow CH_3COH \ ;$$
$$H_2 + CO \rightarrow HCHO \ ;$$
$$2\,HCHO \rightarrow HCOOCH_3 \ ,$$

occurring in the decomposition of these substances, lead to the formation of other products. However, the role of side reactions in the decomposition of cobalt, nickel, copper, and lead formates is small and the main products are M, MO, CO, CO_2, and H_2.

Tables 2 and 3 present data for the decomposition reactions of various formates[156].

Table 3. The ratios of the amounts of reaction products in the decomposition of certain formates[156].

Formate	$[M^{2+}]/[M^{2+}+M]$, %	$[CO]/[CO+CO_2]$, %	Formate	$[M^{2+}]/[M^{2+}+M]$, %	$[CO]/[CO+CO_2]$, %
Co $(HCOO)_2$	49.1	24.5	Cu $(HCOO)_2$	9.6	4.0
Ni $(HCOO)_2$	19.7	10.3	Pb $(HCOO)_2$	16.3	7.5

The metals and their oxides can be readily generated by the decomposition of the oxalates (Table 4). The process can be described by the general mechanism

$$M(COO)_x \rightarrow M + CO + CO_2 + M_nO_m \ .$$

It presupposes the occurrence of various reactions of the following type[157-160]:

$$M(COO)_2 \rightarrow M + 2CO_2 \ ;$$
$$M + CO_2 \rightarrow MO + CO \ ;$$
$$M(COO)_2 \rightarrow MO + CO + CO_2 \ ;$$
$$MO + CO \rightarrow M + CO_2 \ , \text{ etc.}$$

The oxalates of transition metals, for example iron and nickel, decompose with formation by pyrophoric products:

$$FeC_2O_4 \rightarrow Fe + 2\,CO_2\,(FeO + CO + CO_2) \ ;$$
$$NiC_2O_4 \rightarrow Ni + 2\,CO_2 ,$$

while alkali and alkaline earth metal oxalates are converted into stable oxides on decomposition, for example:

$$MgC_2O_4 \rightarrow MgO + CO + CO_2 \ .$$

Table 4. Temperature ranges corresponding to the decomposition of oxalates[159,160,162,163].

Oxalate	Temp. range of decompn., °C	Oxalate	Temp. range of decompn., °C
Mg $(COO)_2$	390—430	Ni $(COO)_2$	200—290
Mn $(COO)_2$	340—370	Cu $(COO)_2$	270—330
Fe $(COO)_2$	320—340	Ag $(COO)_2$	100—160
Co $(COO)_2$	310—330	Zn $(COO)_2$	310—350
Ni $(COO)_2$	260—320	Pb $(COO)_2$	310—370

The kinetics of the decomposition of oxides are frequently described satisfactorily by Erofeev's equation[157,159-161]:

$$\alpha = 1 - \exp(-kt^n).$$

Metals and their oxides can also be generated by the decomposition of other metal compounds[75]. Under these conditions, various gaseous products are formed together with the metals, for example H_2 and CO in the decomposition of formates; these can participate in chain termination or thermal degradation reactions at high temperatures. Furthermore, hydrogen can regenerate the metal and can also hydrogenate "weak sites" of the type of an impurity. All these factors are responsible for the improvement of the initial properties of the polymer and enhance its thermal stability[186,187].

The decomposition of carbonates is accompanied by the formation of oxides, which can serve as active fillers. If the lowest-valence metal oxide is formed, it serves as an oxygen acceptor. A classical example is the decomposition of cobalt(II) carbonate with formation of cobalt(II) oxide[137,164]:

$$CoCO_3 \xrightarrow{330-340^\circ C} CoO + CO_2 \quad .$$

The thermochemical decomposition of carbonyl, cyclopentadienyl, and arene derivatives leads to the formation of pure finely dispersed metals or readily oxidised products. For example, the decomposition of iron pentacarbonyl results in the formation of the so called carbonyl iron[165,166]:

$$Fe(CO)_5 \xrightarrow{200^\circ} Fe + 5\,CO \quad .$$

Dibenzenechromium, a representative of the arene derivatives, decomposes above 300°C with formation of pyrolytic chromium and benzene[167,168]:

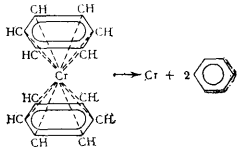


Table 5 presents the bond dissociation energies $\bar{D}$ for certain carbonyl, cyclopentadienyl, and arene derivatives of transition metals, which serve as a measure of their thermal stability[169,170].

Table 5. Dissociation energies ($\bar{D}$) of M–CO, M–C_6H_5, and M–ligand bonds.

Compound	Bond	$\bar{D}$, kcal mole^{-1}
$Ni(CO)_4$	M–CO	35.2
$Fe(CO)_5$	»	28.1
$Mn_2(CO)_{10}$	»	23
$Cr(CO)_6$	»	29.5
$Mo(CO)_6$	»	36.2
$W(CO)_6$	»	42.4
$Ni(C_6H_5)_2$	M–C_6H_5	60.8
$Fe(C_6H_5)_2$	»	74.1
$V(C_6H_5)_2$	»	88.
$Ti(C_6H_5)_2$	»	108
$Cr(C_6H_6)_2$	M–ligand	40
$Mo(C_6H_6)_2$	»	51
$V(C_6H_6)_2$	»	68

The decomposition of certain compounds can also lead to the formation of oxygen acceptors. Thus basic cobalt silicates decompose with formation of cobalt(II) oxide or cobalt(II) silicates capable of rapid oxidation in air[171]:

$$Co_3(OH)_3OHSi_2O_5 \xrightarrow{400-500^\circ} 3\,CoO + 2\,SiO_2 + 2H_2O \quad ;$$

$$Co_3(OHSi_2O_5)_2 \xrightarrow{500-700^\circ} 3\,CoSiO_3 + SiO_2 + H_2O \quad .$$

Oxygen (free-radical) acceptors can be readily obtained in polymers by reducing various metal compounds to the pure metals or to the lowest-valence metal oxides. Methods have been described for the reduction of silver, copper, iron, nickel, cobalt, etc. compounds by reducing agents such as H_2, CO, CH_4, etc.[172-178]. The latter are obtained in polymers on decomposition of metal carbonyls, formates, oxalates, and many other compounds. The decomposition of sodium formate

$$2\,HCOONa \xrightarrow{300-400^\circ} H_2 + Na_2C_2O_4$$

mentioned above may serve as an example of processes of this kind.

Solid-phase methods for the reduction of metal oxides by graphite are effective[175]. For example, the reaction

$$2Ag_2O + C \rightarrow 4Ag + CO_2$$

takes place at a temperature as low as 100–200°C when contact between the reactants is satisfactory[174].

The oxygen acceptors generated in polymers frequently prove to be active acceptors of the radicals initiating thermal degradation. It is sufficient to point out the well known reactions of lead, zinc, antimony, arsenic, and bismuth with alkyl radicals, leading to the formation of organometallic compounds[179], for example:

$$Pb + 4R^{\cdot} \rightarrow PbR_4 \quad .$$

As already stated, radical acceptors can be selected on the basis of data for the strengths of the corresponding bonds (for example C–M, Si–O–M, etc.) and the temperature range in which the polymer is used. Tables 6 and 7 list[180] the dissociation energies of certain M–CH_3 bonds and $(CH_3)_3E$–X bonds.

Table 6. Dissociation energies (ΔH°) of the M–R bonds.

Reaction	ΔH°_{298}, kcal mole^{-1}
$ZnCH_3=CH_3+Zn$	39
$Bi(CH_3)_3=CH_3+Bi(CH_3)_2$	44
$Cd(CH_3)_2=CH_3+CdCH_3$	44.2
$Zn(CH_3)_2=CH_3+ZnCH_3$	47.1
$Zn(CH_3)_3=CH_3+Zn(CH_3)_2$	47.2
$As(CH_3)_3=CH_3+As(CH_3)_2$	54.6
$Sb(CH_3)_3=CH_3+Sb(CH_3)_2$	57
$Hg(CH_3)_2=CH_3+HgCH_3$	57.2
$Ga(CH_3)_3=CH_3+Ga(CH_3)_2$	60
$Si(CH_3)_4=CH_3+Si(CH_3)_3$	71.8
$Sn(CH_3)_4=CH_3+Sn(CH_3)_3$	82

Table 7. Dissociation energies ($\bar{D}$) of Me_3E–X bonds (kcal mole^{-1})*.

X	Element (E)				
	C	Si	Ge	Sn	Pb
H	104	81	73	70	(49)
Me	88	76	68	61	40
MMe_3	80	67	62	53	(23)
OH	91	119	(85)	72	(58)
F	118	(143)	(113)	—	—
C	82	104	(81)	94	—
Br	69	87	(66)	83	—
I	56	78	(51)	69	—

* The numbers quoted in brackets were as a rule obtained from data for EX_4 molecules; the values of $\bar{D}(Me_3E-X)$ are usually greater than those obtained by the above procedure.

When metals are used as radical acceptors, one must also take into account their efficiency as chain-transfer agents and their capacity to abstract certain atoms from molecules[181]. These reactions may lead to initiation rather than inhibition of the decomposition of the polymer.

At relatively high temperatures, polymer chain decomposition processes may be retarded by radical acceptors such as CO, SO_2, etc.; these compounds enter into copolymerisation type reactions, which lead to the formation of the radicals R–CO·R–$SO_2^{\cdot}$ and others which are less reactive than the initial radicals R·.[179]

The use of clathrate compounds occupies a special place among methods for the generation of stabilisers[4,182]. This procedure has been called the "structural-chemical stabilisation of the filler or stabilisers". A very active stabilising substance in such compounds is structurally isolated and cannot interact with oxygen and other chemical agents when it is introduced into the polymer. On the other hand, during heat treatment or employment of the polymer the clathrate compound decomposes with liberation of the stabiliser.

A satisfactory model whereby one can investigate the generation of a stabiliser of this type is provided by vinyl polymerisation in the presence of the amylose–I_2 complex[182]. The processes occurring in such a system can be represented as follows:

1. Decomposition of the initiator: initiator $\rightarrow 2R^{\cdot}_{pri}$ (w_{decomp}).
2. Decomposition of the clathrate compound (generation of the inhibitor): clathrate compound $\rightarrow I_2$ (w'_{decomp}).
3. Initiation: $R^{\cdot}_{pri} + Mo \rightarrow R_1^{\cdot}$.
4. Chain propagation: $R_n^{\cdot} + Mo \xrightarrow{k_p} R_{n+1}^{\cdot}$.
5. Biradical chain termination: $R_n^{\cdot} + R_m^{\cdot} \xrightarrow{k_0}$ products.
6. Chain termination by the inhibitor:

$$R_n^{\cdot} + I_2 \xrightarrow{k_0'} RI + I^{\cdot}\ ; \qquad R_n^{\cdot} + I^{\cdot} \xrightarrow{k_0''} RI \quad . \tag{C}$$

Here $R^{\cdot}_{pri}$ is a primary radical, Mo the monomer, R· the growing radicals, and w_{decomp} and w'_{decomp} are the rates of decomposition of the initiator and the clathrate compound.

It follows from mechanism (C) that the rate of inhibited polymerisation w_{inh} is

$$w_{inh} = k_p [R^{\cdot}] [Mo] = \frac{k_p}{k_0^{1/2}} [Mo] (w_{in} - w_{i\,gen})^{1/2} \quad ,$$

where w_{in} and w_{gen} are the rates of initiation and generation of the inhibitor. Next it is easy to show that the following relation holds:

$$\lg (w_n^2 - w_{inh}^2) = \text{const} - \frac{2E_p - E_0 + E_{gen}}{2.3R} \cdot \frac{1}{T} ,$$

where w_n is the rate of the non-inhibited reaction and the quantities E with the appropriate subscripts are the activation energies for the corresponding processes.

Fig. 1 presents the variation of $\lg w$ with $1/T$ for the case under consideration; evidently, at a certain temperature the process begins to be sharply retarded owing to the generation of a powerful inhibitor on decomposition of the clathrate compound.

V. INTERPRETATION OF CERTAIN QUANTITATIVE RESULTS

It is seen from the above data that there is much evidence for the mechanisms of both chain and non-chain inhibition of the ageing processes of thermostable polymers. The chain inhibition mechanisms have already been investigated for a long time, but many of these are based on all possible hypotheses and analogies: hardly any constants for the elementary processes are available. This is probably because of the lack of a single general mechanism of inhibited degradation. On the other hand, although the mechanisms of non-chain inhibition have been discovered only recently in many important instances[4], their validity can be readily demonstrated because of their considerable generality.

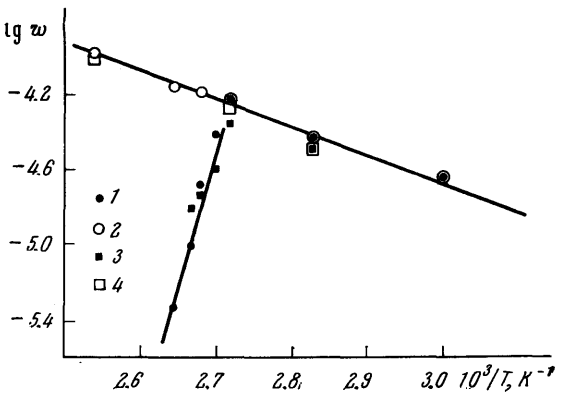


Figure 1. Variation of the logarithm of the rate of polymerisation of styrene at a constant rate of initiation with the reciprocal of temperature; $w_{in} = 3 \times 10^{-7}$ mole litre^{-1} s^{-1}; initiators: azobisisobutyronitrile ($T < 95$°C) and cumenyl peroxide ($T \geq 95$°C): 1) 18 g litre^{-1} of clathrate compound $\{[I_2] = 7 \times 10^{-4}$ M$\}$, dimethylformamide (DMF): styrene (ST) = 2.1; 2) clathrate compounds absent, DMF : ST = 2 : 1; 3) 18 g litre^{-1} of clathrate compound $\{[I_2] = 7 \times 10^{-4}$ M$\}$, DMF : ST = 5 : 1; 4) clathrate compounds absent, DMF : ST = 5 : 1.

Bearing in mind the possibility of non-chain inhibition in the presence of metal oxides, sulphides, and other compounds, it is possible to explain certain previously incomprehensible facts. Thus the stabilising activity of cobalt and other metal acetylacetonates[183] can be attributed not only to the termination of oxidation chains but also to the absorption of O_2 via a non-chain inhibition reaction. Similarly, other systems containing Co^{2+} [146,147,171] can convert oxygen into an ionic form and hence into a state which is inactive from the standpoint of the radical mechanism:

$$Co^{2+} + O_2 \rightarrow Co^{3+} + O_2^- . \tag{18}$$

It is noteworthy that reaction (18), which can be represented in the general case by Eqn. (3), is frequently one of the elementary stages in the chain mechanism and can also be classified as a non-chain inhibition process. However, the lack of quantitative data precludes the assessment of its importance in stabilisation.

The stabilising activity of certain sulphides[5], colloidal metals formed electrolytically in the polymer[75,184], and other compounds[53,67,72,185] can be attributed, as already pointed out, not only to a chain mechanism but also to a non-chain inhibition reaction between Z and O_2.

We have obtained a number of results which make it possible to demonstrate the possibility of the inhibition of the oxidative degradation of polymers by a non-chain procedure and to explain certain facts known previously. Thus the proposed stabilisation mechanism[4,37,113] operates when high-temperature oxidative ageing (300–500°C) of polyorganosiloxanes stabilised by active oxygen acceptors (Fe, Cu, Co, NiO, FeO, etc.), generated by the decomposition of the oxalates in the polymeric materials, is investigated. The non-chain mechanism of the stabilisation of polyorganosiloxanes in the presence of Fe, FeO, and Cu is proved by the following data:

1. The amount of oxygen acceptor generated in the polymer on decomposition of the oxalates corresponds to the amount calculated for the reactions

$$M(COO)_2 \rightarrow M + 2CO_2 \quad ;$$
$$M(COO)_2 \rightarrow MO + CO + CO_2 \quad .$$

2. As oxygen diffuses into the specimen, the entire metal (oxide) is converted into the corresponding stable oxide:

$$M + O_2 \rightarrow M_nO_m \quad ;$$
$$MO + O_2 \rightarrow M_nO_m \quad . \qquad (19)$$

3. The polymer, which is almost immediately decomposed in the absence of a stabiliser, in the presence of metals (acceptors) begins to decompose vigorously only after the entire metal has been consumed.

4. The theoretical equation (12) holds satisfactorily.

5. The calculated value of τ agrees well with the experimental value.

6. The rates of reaction of O_2 with RH and R$^{\cdot}$, calculated from the rate constants and concentrations of the components, are much lower under the experimental conditions than the rate of reaction (19).

7. The stabilisation effect is determined by the ability of the metal or the lowest-valence metal oxide to form a stable oxide and by the rate of absorption of oxygen under the experimental conditions.

Data for the stabilisation of thermostable polymers in the presence of metals or their mixture with the lowest-valence metal oxides, generated on the decomposition of the oxalates and other compounds in polymers, are presented below. Henceforth it is assumed that oxygen is accepted by the metal–oxide mixture, which will be referred to for brevity as the metal.

Fig. 2 illustrates the variation of the relative elongation and tensile strength of a siloxane rubber. Evidently the specimens stabilised by finely dispersed metals retain their properties over a period 3–4 times longer than the specimens stablised by one of the best stabilisers known previously for this system—redoxide.

Table 8 shows that specimens of the polymer based on methylphenylsiloxane, stabilised by finely dispersed Fe and CoO, retain their properties within permissible limits for a longer period than the specimens stabilised by one of the best stabilisers based on a cerium(III) salt.

Table 9 presents data for the absorption of oxygen by specimens[112] containing finely dispersed metals generated in the polymer. Evidently the amount of absorbed oxygen is close to the value calculated for the reaction Z + O_2 → oxide; certain deviations from the calculated values are associated with the additional absorption of oxygen by the surface layer of polymer, after the consumption in the latter of the stabiliser, and with certain other unspecified factors.

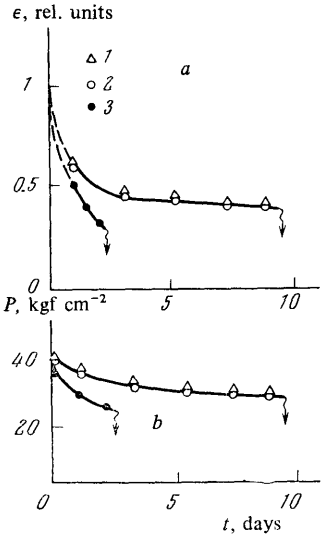


Figure 2. Variation of the relative elongation ϵ (*a*) and the tensile strength P (*b*) of methylphenylsiloxane rubber specimens during thermal ageing at 350°C: 1) stabilisation by finely dispersed Fe; 2) stabilisation by finely dispersed Cu; 3) stabilisation by Fe_2O_3 (redoxide); the arrows indicate the instant of decomposition of the specimens. The initial values of ϵ amount to 200–300%.

Table 8. The ageing of a polymer based on methylphenylsiloxane at 400°C in air [TiO_2 filler (30%); thickness of polymer specimen 1 mm (according to Shustova)].

Stabiliser (1%)	Time corresponding to retention of initial strength h(P_0 = 15 kgf cm^{-2})	Time elapsed at instant corresponding to 60% relative elongation ϵ on rupture*, h
Without stabiliser	5.0	5.0*
Cerium(III) salt	7.0	10.0*
CoO	12.0	19.5*
Fe	24.5	19.5**

* ϵ_{init} = 100%.
** ϵ_{init} = 160%.

Fig. 3 illustrates the variation of the lifetime of trimethylcyclopolysiloxane films of different thickness in air at 400°C in the presence of finely dispersed iron[37] and Fig. 4 presents the kinetic curve for the absorption of oxygen. The region where the rate of absorption of O_2 represented by the curve in Fig. 4 decreases is consistent with the lifetime of the specimen τ_{crack} and corresponds to the instant of the complete consumption of the stabiliser via the reaction $Fe \xrightarrow{O_2} Fe_2O_3 + Fe_3O_4$. It also follows from

Fig. 4 that the initial rate of absorption of oxygen by the specimen w'_{inh} is approximately four times greater than the rate of oxidation of the polymer w after the consumption of the stabiliser. Even if it is assumed that the oxidation of the stabiliser proceeds in the kinetic region, we have $4w = w'_{inh}$. The latter implies that the fundamental criterion of non-chain inhibition holds satisfactorily in the initial instant and the stabilisation under the given conditions is largely associated with the reaction of the finely dispersed iron with oxygen. Figs. 3 and 4 show that Eqn. (12) holds satisfactorily for the system investigated.

Table 9. The absorption of oxygen in the polymer by the stabiliser generated in a trimethylcyclopolysiloxane specimen (400°C).

Stabiliser	Reaction	Amount of O_2 absorbed by specimen, cm^3	
		calc.	expt.
Fe	$Fe+O_2 \rightarrow Fe_2O_3$ (Fe_3O_4)	1.00 1.28	1.02 1.33
Cu	$Cu+O_2 \rightarrow Cu_2O \rightarrow CuO$	1.00 1.30	1.05 1.32

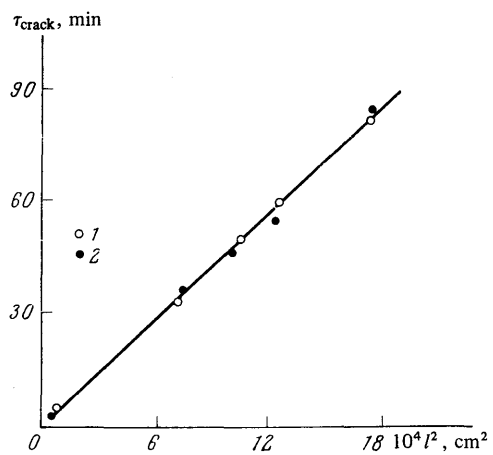


Figure 3. Variation of the lifetime τ_{crack} of hardened trimethylcyclopolysiloxane films stabilised by finely dispersed Fe {[Fe] = 0.3 mole kg^{-1}} with the square of the thickness of the specimen l^2 at 400°C; the lifetime of the specimens was determined from the cracking of the films (1) and from the absorption of oxygen (2).

Figs. 5 and 6 present the results[186,187] of the determination of the time required for the consumption of the stabiliser and the lifetime of polymer compositions based on trimethylcyclopolysiloxane stabilised by finely dispersed iron at 500°C. As the iron is converted into the iron(III) oxide, the intensity of the signal with $g = 2.0$ increases, the increase terminating at the instant τ_{ESR}.

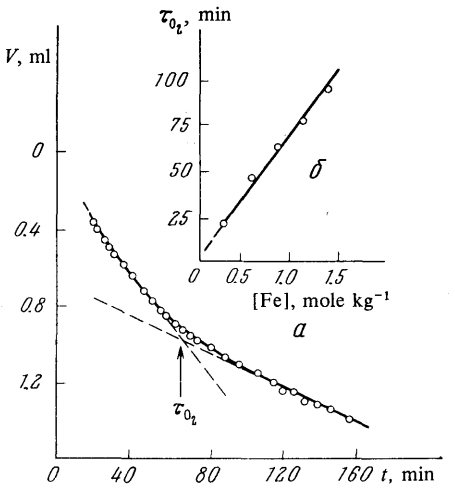


Figure 4. Kinetics of the absorption of oxygen by trimethylcyclopolysiloxane film {l = 140–150 μm, [Fe] = 0.3 mole kg^{-1}} stabilised by pyrophoric iron (a) and the variation of the lifetime of the specimen τ_{O_2} with the concentration of pyrophoric iron (b).

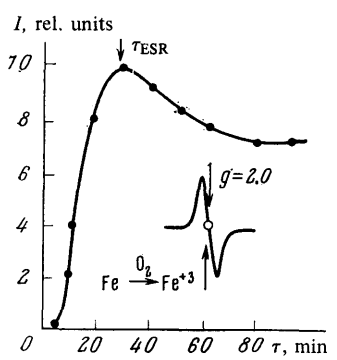


Figure 5. Determination of the time required for the consumption of the stabiliser τ_{ESR} in trimethylcyclopolysiloxane films {l = 160 μm, [Fe] = 0.3 mole kg^{-1}} by ESR from the variation of the signal intensity I (rel. units) at 500°C.

Thus the values of τ determined by the "cracking" method (τ_{crack}), by measuring the rate of absorption of oxygen (τ_{O_2}), and by ESR (τ_{ESR}) agree satisfactorily with one another[186,187].

It is noteworthy that, in the study of the degradation of thick films, deviations are observed from the parabolic law [Eqn. (12)], owing to the considerable absorption of oxygen by the polymer after the consumption of the stabiliser[39,110].

Table 10 lists the rates of the non-chain inhibition reaction Z + O_2 → oxide (recalculated in terms of the rate of the homogeneous process) evaluated to within a factor

of 3 using the experimental data and the parabolic equation (13). It follows from Table 10 that the general phenomenological criterion (see Section III) $w_{Z+O_2} \gg w_{R+O_2}$, w_{RH+O_2}, $w_{^2RH+O_2}$ holds satisfactorily.

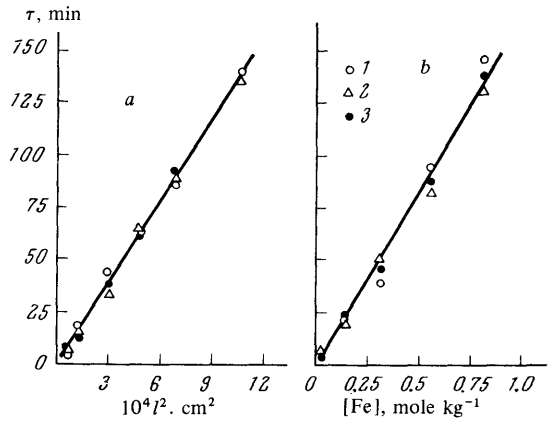


Figure 6. Dependence of the lifetime of trimethylcyclopolysiloxane polymeric films, stabilised by finely dispersed iron in the presence of components decomposing with evolution of H_2, on the square of the thickness of the specimen (*a*) and on the stabiliser concentration (*b*); the lifetime of the film specimens was determined from their cracking (1), from the absorption of oxygen (2), and by the ESR study of the consumption of the stabiliser (3).

Table 10. The rates w of the reaction between Z and O_2 in oxidative degradation calculated from experimental data[117,149-151,188] (350°C).

Stabiliser generated in polymer (5%)	Specific surface, cm^2 g^{-1}	w, mole litre^{-1} s^{-1}
Fe	10	10^{-2}
	100	10^{-1}
Cu	10	10^{-1}
	100	1

The results presented suggest that, together with the chain inhibition methods, the procedures for the non-chain inhibition of oxidative degradation can be used successfully to stabilise many thermostable polymers.

Recently devised tests make it possible to estimate the reactivities of non-chain inhibition stabilisers[163]. Furthermore, a group of tests has been devised whereby one can estimate the reactivities of any inhibitors in radical chain reactions[40,189-191].

Apart from their practical importance, these studies are of theoretical interest. Thus it has been possible to show that the rate constants for many bimolecular radical reactions have a constant pre-exponential factor of $10^{7.2\pm0.2}$ (litre mole^{-1} s^{-1}) in the liquid phase and $10^{8.8\pm0.1}$ (litre mole^{-1} s^{-1}) in the gas phase[190,191]. Subsequently Tsepalov established that the pre-exponential factors for these reaction rate constants are different only in the case of radical substitution reactions. For many radical recombination reactions in both liquid and gaseous phases, the pre-exponential factors are $10^{8.8}$. It has also been established that the absolute values of the rate constants for these reactions in the gaseous and liquid phases are identical, which suggests that the rate constants are indeed elementary only for reactions with a constant pre-exponential factor of $10^{8.8}$ litre mole^{-1} s^{-1}. In reactions with a constant pre-exponential factor of $10^{7.2}$ litre mole^{-1} s^{-1}, the rate constants are apparently effective quantities produced by a combination of two or several elementary rate constants.

Studies have been published recently on the mechanism of the formation and degradation of metallopolymers[192-195]. It has been shown that these materials as well as certain polymeric and other heterogeneous compositions in which metals were generated[196,197] possess valuable properties. However, the increased resistance of these systems to thermo-oxidative degradation is not attributed by these workers[192-195], as in earlier studies[75,197], to the interaction of the active metals with oxygen, i.e. to non-chain inhibition processes[20,37,38]. As a rule, these studies[192-195,197] were carried out under conditions such that the rates of the thermal degradation reactions of the metallopolymers may be limited by the diffusion of oxygen and the degradation products. In many cases the high termo-oxidative stability of metallopolymers as well as polymers stabilised by metals[4,5,35,69,198] may be attributed not only to the nature of these materials but also to their stabilisation via a non-chain inhibition mechanism.

Interesting results have been obtained for the oxidation of polyethylene melts on metallic surfaces and in the presence of finely dispersed metals[199,200]; the characteristics of these processes can be explained in conjunction with known chain and non-chain inhibition mechanisms.

The non-chain inhibition of oxidative degradation at high temperatures is effective when pyrophoric lower-valence metal oxides, such as FeO and CoO,[37] sulphides, finely dispersed silicon,[201] and other oxygen acceptors[202,203] are used. The authors of this review have shown recently that the stabilisation of organosilicon coatings by FeO and by silicon makes it possible to increase by a factor of several tens their useful life at temperatures in the range 500–1000°C.

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