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Progress in the Study of the Degradation and Stabilisation of Siloxane Polymers

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The most recent achievements in the study of the degradation and the stabilsation of polyorganosiloxanes, including those containing other atoms in the chain, are surveyed. The effect of polymer structure on their thermal stability is examined, and the part played by catalytic impurities in developing processes of thermal and thermo-oxidative degradation is shown. Known schemes for the decomposition of polyorganosiloxanes are discussed. Data are given on methods of stabilising siloxane polymers. The list of references contains 141 items.

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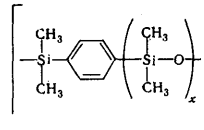
1. INTRODUCTION

The chemistry of monomeric and polymeric organosilicon compounds has made great advances during recent years. Polyorganosiloxanes possess several extremely important properties, in virtue of which they have found widespread and effective application in electrical engineering, radio engineering, and the coal, rubber, aircraft, and other industries. Such important properties of siloxane polymers as their resistance to the action of moisture, heat, cold, ultraviolet rays, oxygen, and ozone, their slight change in viscosity and modulus of elasticity with temperature, and their high dielectric properties are largely determined by the character of the siloxane chain and the organic radicals attached to the silicon atom. Polyorganosiloxanes can be regarded as occupying an intermediate position between organic and inorganic polymers. Several monographs[1-7] on the synthesis and investigation of the properties of siloxane polymers have been published during the thirty years since the appearance of the first papers in this field. However, problems of thermal and thermo-oxidative degradation and of stabilisation are inadequately dealt with in these works. The present review summarises available published data on the aging and stabilisation of polyorganosiloxanes published up to June 1967.

2. EFFECT OF THE STRUCTURE OF POLYORGANOSILOXANES ON THEIR THERMAL STABILITY

The spiral structure of the molecules of polyorganosiloxanes containing 3–6 silicon atoms in a loop of the spiral creates favourable conditions for the formation of rings. It is obviously for this reason that the decomposition of polydimethylsiloxane is accompanied by cleavage of the silicon–oxygen bond and separation of cyclic products of low molecular weight without appreciable disturbance of the silicon–carbon bond. It is therefore supposed[1,2] that the decisive factor in the thermal degradation of linear polysiloxanes is not the difference in energy between silicon–oxygen and silicon–carbon bonds but the spiral structure of the molecules.

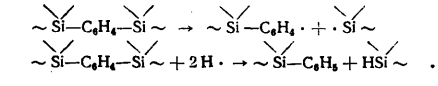
Enlarging the organic radicals attached to the silicon atoms diminishes the tendency of the polymer chain to coil into a spiral, so that depolymerisation of polydiethylsiloxane takes place with considerably greater difficulty and at a higher temperature than that of polydimethylsiloxane[2]. Polymers containing silaphenylene links possess fairly high thermal stability[8-14]. Those having the following structure



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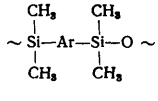
where $x = 1-4$, are considerably more thermostable than are ordinary polydimethylsiloxanes[14]. The maximum rate of loss of weight (1.4–1.9% min^{-1}) during the pyrolysis of such polymers is observed at 520–540°C, whereas with polydimethylsiloxane the maximum rate (2.1% min^{-1}) is already observed at 420°C. The polymer in which $x = 1$ proved to be the most stable.

It was assumed that cleavage of the silaphenylene link at temperatures above 450°C comprised the following reactions



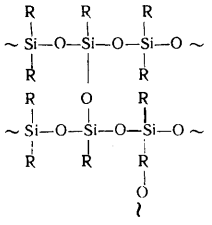
However, no evidence for this mechanism was given. The high thermal stability of these polymers was explained by the greater difficulty of breaking the silicon–carbon than the silicon–oxygen bond in polydimethylsiloxane.

Goldovskii, Kuz'minskii, and their coworkers[11] obtained comparative data on the thermal stability of the polymers



where Ar represents a *pp'*-phenyleneoxyphenylene or a *p*- or *m*-phenylene radical, and also data on the effect of small numbers of these units introduced into the chain of polydimethylsiloxanes. The polymer containing diphenyl oxide units proved to be the most stable, its decomposition temperature being 100 deg above that of polydimethylsiloxane, while the least stable polymer was one containing *m*-phenylene links. The introduction of up to 3 mole% of silarylene units into the chain of polydimethylsiloxanes has no significant effect on their thermal stability[11]. However, there are indications[13] that polymers containing biphenylylene and naphthylene bridges in the chain are stable even at 600°C, and will yield very strong thermostable films whose properties remain unchanged up to 400°C.

The thermal stability of polyorganosiloxanes is substantially influenced also by the structure of the polymer chains. Rupture of one silicon–oxygen bond is sufficient for the cleavage of linear macromolecules, but with polymers having a three-dimensional structure it is necessary to rupture siloxane bonds at two or even three points. Therefore the thermal stability of the latter is considerably higher than that of linear polymers. For example, polymers having the branched structure



undergo hardly any changes when heated in a vacuum at 550°C for 16 h.[15]

The thermal stability of polyorganosiloxanes is improved by vulcanisation with peroxides or γ-rays, the radiation products being the more thermostable[16-18]. The difference in thermal stability between these two types of vulcanised products is explained by a difference in the character of the cross-links[19]. In peroxide vulcanisates cross-linking is effected mainly by methylene bridges or silicon–silicon bonds. In radiation vulcanisates $Si-CH_2-CH_2-Si$ links are mainly formed, by the recombination of $Si-CH_2^{\cdot}$ free radicals. The thermal stability of radiation vulcanisates is higher because carbon–carbon bonds are more stable than silicon–carbon or silicon–silicon bonds, and also because at high temperatues a certain number of double bonds can be formed in the rubbers by the reaction

$$\equiv Si-CH_2-CH_2-Si\equiv \longrightarrow \equiv Si-CH=CH-Si\equiv .$$

The rupture of cross-linking double bonds is difficult, and prevents degradation.

It is characteristic of thermal oxidation that the oxygen acts directly only on the organic groups attached to the silicon atom. The structure of the groups framing the main chain exerts a strong influence, of course, on the thermal stability of the polyorganosiloxanes. As the alkyl side-chain becomes larger, the thermo-oxidative stability becomes lower. Thus polydimethylsiloxanes[15] begin to oxidise appreciably at 200°, polydiethylsiloxanes at 138°, and polydibutylsiloxanes at 120°C.[20] Replacing the methyl by vinyl groups also somewhat lowers thermal stability[21,22].

On the other hand, replacing the methyl by phenyl groups considerably improves the thermo-oxidative stability of polyorganosiloxanes[23-25]. Thus at 350°C the loss in weight of polyphenylsiloxane is insignificant, but after heating at 450°C for 24 h about 3.7% of carbon and 0.76% of hydrogen remain in it[3]. The enhanced stability of polyphenylsiloxanes is explained[26] by the screening effect of the phenyl groups on the siloxane bond. The introduction of one chlorine atom into the phenyl group has no substantial effect on the thermal stability of polyphenylmethylsiloxanes, but with two or more chlorine atoms the thermal stability falls[27]. Thus the temperature at which decomposition begins drops from 357° for the unchlorinated polymer to 312°C for a polymer containing four chlorine atoms in the phenyl ring[28].

In polydimethylphenylsiloxane containing methyl-3,3,3-trifluoropropylsiloxy-groups processes of rearrangement of the siloxane link occur at an appreciable rate, which increases with increase in the content of these groups[29]. Half-decomposition times have been calculated[24] for polyorganosiloxanes containing various framing groups. Depending on such groups, these polymers can be arranged in the sequence

$$C_6H_5>ClC_6H_4>Cl_3C_6H_2>Cl_2C_6H_3>CH_2=CH>CH_3>C_2H_5>C_3H_7>C_4H_9$$

according to their resistance to thermal oxidation.

Sobolevskii and Nazarova[30] investigated whether the thermal properties of organosiloxanes are determined by the arrangement of methyl and phenyl groups in the chain or by the overall CH_3/C_6H_5 ratio, and concluded that the principal thermal properties of these polymers are almost identical at similar values of the ratio, whether their structure is regular or irregular. The thermo-oxidative stability of polyorganosiloxanes is enhanced by the introduction of aromatic rings into the main chain[9-11]. The temperature at which a polydimethylsilarylene begins to be oxidised is 40–60 deg higher than with ordinary polydimethylsiloxanes, while the rate of elimination of methyl groups is smaller by factors of 5–8.[11] The introduction of *m*-phenylene links into the siloxane chain has an especially large effect on resistance to oxidation.

The thermal stability of polyorganosiloxanes containing arylene units in the main chain is slightly better than that of the corresponding polymers containing framing aryl groups when the ratio of these groups to the total number of siloxane units is the same[9].

A weak site in polymethylphenylsiloxanes is found at their terminal trimethylsiloxy-groups, which determine the thermo-oxidative stability[31]. Replacement of these groups by triphenylsiloxy-groups leads to an improvement in the thermal stability of the polymer of 50 deg.

The processes which occur during the thermo-oxidative degradation of polyorganosiloxanes depend in considerable measure on the structure of the polymer. These polymers can be either linear, branched, network, cyclolinear, or cyclo-network. The rate of elimination of organosilicon compounds is considerably lower when a three-dimensional polyorganosiloxane (R/Si = 1) is heated than in linear polymers, as is also the case in the absence of oxygen. Thus heating polydimethylsiloxane in air at 400°C for 3 h produces a loss of weight of 57%, whereas polymono-organosiloxanes under hardly any loss in weight up to 450°C.[2]

In the thermal oxidation of polyorganosiloxanes of three-dimensional cyclic structure $(RSiO_{1.5})_n$ having rings of different but definite size, it was found that polydimethylsiloxanes containing an even number of units in the ring are degraded more slowly than those with odd rings[32]. This is observed both at 350°C, when decomposition of the polymer is not yet complete, and also at 400°C. This effect of the parity factor was explained by the presence of polar forces, the strengthening of which was accompanied

by increased density of packing, so that the polymer became less subject to degradation. With polyethylsiloxane, however, the opposite phenomenon is observed: a polymer containing an odd number of units in the rings is the more heat-resistant.

The more frequent the cross-links in polyorganosiloxanes the greater their resistance to thermal oxidation, even if the total functionality of the polymer is lower[33]. Thus polymers of the type T–D–D–T are more thermostable than are T–D–D–D–T–T and T–T–D–D–D–D–T–T, where T and D represent tri- and di-functional units.

The considerably lower thermal stability of linear polyorganosiloxanes than of the three-dimensional polymers is explained by many authors on the one hand by the spiral form of the linear molecules, which creates favourable conditions for the cleavage of chains with the formation of cyclic products, and on the other hand by the fact that detachment of a chain segment in a linear molecule involves rupture of a smaller number of bonds[2–4].

The rate of oxidation of methyl groups also diminishes as the R/Si ratio falls[24,34].

From all the above discussion it follows that, to obtain the most thermostable polyorganosiloxanes, three-dimensional polymers must be synthesised containing arylgroups in the side-chains or in the main chain. Unfortunately, however, this is not always acceptable, since such polymers are less elastic.

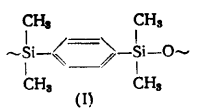
3. COMPOSITION OF DEGRADATION PRODUCTS OF POLYORGANOSILOXANES

The composition of the thermal degradation products of polydimethylsiloxanes was first studied by Patnode and Wilcock[35], who found that, in an atmosphere of nitrogen, polydimethylsiloxane decomposes at 350–400°C to form the following percentages of cyclic compounds of low molecular weight

$[(CH_3)_2SiO]_3$	44
$[(CH_3)_2SiO]_4$	24
$[(CH_3)_2SiO]_5$	9
$[(CH_3)_2SiO]_6$	10
above the hexamer	13

Compounds having a complicated cyclic structure were identified[36] among the products of the thermal degradation of three-dimensionally cross-linked polyorganosiloxanes.

When the silarylene polymer



(I)

was heated to 500°C (at a rate of 2.7 deg min^{-1}) and kept at that temperature for 3 h, hydrogen, methane, ethane, and ethylene were detected among the gaseous pyrolysis products, as well as dimethylsilane and tetramethyldisiloxane. The liquid products contained Si–H or Si–C_6H_4–Si groups. Elementary analysis, determination of the molecular weight, and spectroscopic data showed the solid reaction product to be a dimer. Thus the pyrolysis products indicate that degradation of the polymer chain takes place solely by rupture of silicon–phenylene bonds[14].

Thermo-oxidative degradation also yields solid and liquid products, among which a cyclic trimer—hexamethyltrisiloxane—predominates[19,24], but polymethylcyclosiloxanes of higher molecular weight are also present. Cyclic difunctional compounds mainly separate in the degradation of polymethylphenylsiloxane rubber[37].

Thus the thermo-oxidative degradation of polydiorganosiloxanes, like the thermal process, involves rupture of the silicon–oxygen bond to form cyclic products of low molecular weight. Substances indicating oxidation of organic side-chains are also found among the products of thermo-oxidative degradation. Thus in 1947 Atkins and Murphy[38] detected formaldehyde and formic acid among the thermal oxidation products of polydimethylsiloxanes. Subsequently carbon monoxide, carbon dioxide, methanol, water, and hydrogen have also been detected[21,24]. Furthermore, methane has been found in the oxidation of a siloxane rubber at 400°C.[39] These products are formed as a result of the oxidation and detachment of organic radicals.

As a consequence of the great resistance of phenyl groups to oxidation, only degradation of the main chain takes place in polyphenylsiloxanes up to 300–400°C.[21] From elementary analyses of polydi(and mono)methylsiloxanes which had been oxidised in air at 250–300°C Andrianov and Sokolov established[24] that the atomic ratio of hydrogen to carbon remained approximately 3 until a considerable degree of oxidation had occurred: i.e. methyl groups were split off during oxidation. Vinylated polymers form an exception among the polyorganosiloxanes. The vinyl groups do not split off from the main chain, since after oxidation at 200°C the carbon, hydrogen, and silicon contents of the residue do not differ appreciably from those of the original polymer. Infrared-spectroscopic data showed that the volatile products were siloxanes of low molecular weight, of the same composition as the initial material but containing carboxyl groups[21].

The oxidation of polyorganosiloxanes is accompanied by cross-linking: the viscosity of soluble polymers increases, and with further oxidation a gel is formed[39,21,23]; insoluble polymers show a rise in their glass point[40]. The fact that the rate of increase of the viscosity increases with increase in the oxygen content[38] suggests that the cross-linking is actually due to the action of oxygen. Electron-microscopic examination of the changes in a polydimethylsiloxane film when heated in air at 200°C show a coarsening of the macromolecular aggregates[41]. This is probably explained by cross-linking of the polymer chains under these conditions. Since the infrared spectra contained no bands corresponding to silicon–silicon bonds, it was assumed that the bridges between the chains were formed by siloxane bonds at the points of detachment of methyl groups[3]. The mechanism will be discussed below. Andrianov and Sokolov showed[24] that, as long as the molar ratio H/C = 3, approximately one oxygen atom replaces every two methyl groups eliminated. At the present time most scientists consider that the cross-links formed in the oxidation of polyorganosiloxanes are siloxane bonds[1,3,5,39], but inadequate grounds are given for this view.

4. THERMAL DEGRADATION OF POLYORGANOSILOXANES

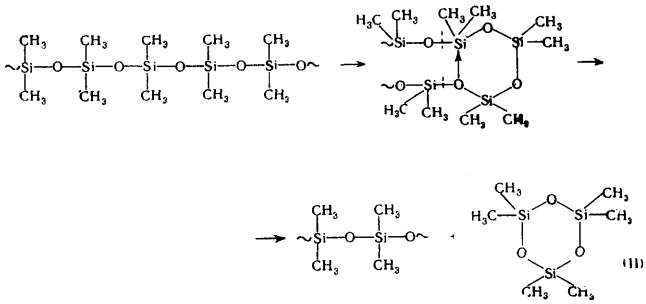
A limited amount of work has been done on the kinetics of the depolymerisation of polyorganosiloxanes in the absence of air. Andrianov et al.[42] investigated the kinetics of thermal degradation from the variation in the viscosity and the weight of the polymer. A striking fact is that the intrinsic viscosity begins to rise before loss of weight starts: with polydimethylsiloxane the latter is observed at 220°C, whereas the intrinsic viscosity has already begun to increase at 170°C. As the temperature

rises the viscosity increases, reaches a maximum value at 300°C, and then diminishes with further rise in temperature. The increase in viscosity was regarded as probably due to increase in the molecular weight of the polymer as a result of polycondensation involving the terminal hydroxyls. Above 220°C the structural changes begin to be accompanied by thermal breakdown of the polymer with the separation of products of low molecular weight which is responsible for the loss in weight; above 300°C depolymerisation becomes the dominant process.

In the initial stage the thermal degradation conforms to a first-order kinetic equation, but as the extent of conversion increases to 30–35% the order of the reaction increases slightly. The explanation given for this increase is that, together with the formation of cyclic compounds resulting from depolymerisation, other processes occur, leading to structural changes in the polymer.

Until recently, only fragmentary data of tentative character were available on the mechanism of the thermal decomposition of siloxane polymers. It was found in particular that linear organosiloxanes break down in the ionisation chamber of a mass spectrometer at 150–200°C to form dialkylsiloxanes[43,44]. From this it was suggested that the depolymerisation of linear organosiloxanes involves an intermediate stage in which dialkylsilanes are formed, these polymerising to cyclic products. However, in this case rupture of the siloxane bonds occur under the ionising action of the chamber of the mass spectrometer, not by the action of heat on the polymer under conditions of thermal degradation.

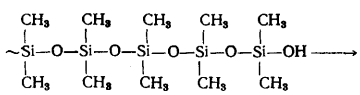
A mechanism has also been suggested for the formation of cyclic products in which depolymerisation of polydimethylsiloxane produces an intermediate compound which lowers the energy barrier to the rupture of silicon–oxygen bonds:

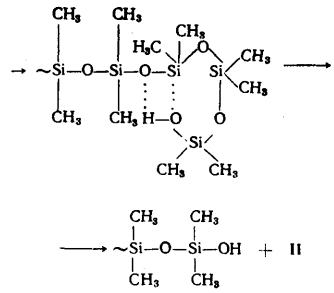


(III)

Unfortunately, no experimental data were given to support this mechanism.

The dependence of the depolymerisation rate constant on the degree of polymerisation of polydimethylsiloxanes was found to correspond to initiation of this reaction by terminal groups[45,46]. Examination of the thermal degradation of polydimethylsiloxane containing various kinds of end-groups showed that the rate of depolymerisation is diminished considerably when the terminal hydroxyls are replaced by methyl groups or by groups containing copper, iron, or titanium atoms. The following scheme was therefore proposed for the depolymerisation of polydimethylsiloxane:





Formation of an activated transition complex is favoured by the presence of hydroxy-groups and a spiral structure of the siloxane chains. The proposed mechanism is supported by the fact that, with decrease in the degree of polymerisation of the polydimethylsiloxane, the experimental values of the effective activation energy of depolymerisation (14–16 kcal mole^{-1}) approach the calculated energy of formation of the activated complex.

With increase in molecular weight, random cleavage of the chain plays an increasingly important part, so that the activation energy increases (to 32 kcal mole^{-1}).[40]

On the basis of thermogravimetric results Andrianov et al.[72] put forward a two-step mechanism of the degradation of polyorganosiloxanes. The first stage of decomposition (loss in weight 15–20%) has an activation energy of around 40 kcal mole^{-1}, and was regarded as involving the degradation of polydimethylsiloxane chains having terminal hydroxyls, with the formation of a network structure. In the second stage the polymeric networks undergo thermal cleavage, as indicated by the high activation energies of this process (60–80 kcal mole^{-1}).

5. THERMO-OXIDATIVE DEGRADATION OF POLYORGANOSILOXANES

Much work has been done on the kinetics of the thermal oxidation of polyorganosiloxanes. A kinetic investigation has been made of the separation of formaldehyde, the separation of formic acid, and the change in viscosity at low degrees of oxidation of a polydimethylsiloxane rubber[38], and also of the loss in weight of the polymers[21]. The time variation in the quantity of formaldehyde and formic acid which separated in a stream of oxygen at 200°C was approximately linear. However, the process cannot be assessed from these kinetic results, since formaldehyde and formic acid are not the only products of the oxidation of methyl groups. Furthermore, these results related only to the initial period, and differed markedly for different specimens, the difference in whose compositions was not indicated. Results for the variation in viscosity also cannot be applied as a quantitative measure, since they were not converted to the number of cross-links formed. It is impossible to assess the course of oxidation by means of curves for the loss in weight, since the latter is caused not only by the oxidation of methyl groups but also by breakdown of the main chain.

A characteristic feature of the kinetics of the decrease in weight of polymonomethylsiloxanes and other polymonoorganosiloxanes[24,37,39] is the sharp decrease in rate of loss of weight after the initial period. Approximately half the loss takes place in the first hour. Since the weight losses in such polymers are due merely to oxidation of lateral groups (when these polymers are heated, no separation of

products of low molecular weight is observed up to 400–500°C), these results enable the course of oxidation of the polymer to be assessed. A rapid decrease in the rate of the process after the initial period was observed by Scala et al.[21] also in a kinetic study of the absorption of oxygen by a polydimethylsiloxane resin at 250°C. Heating a phenylsiloxane rubber[37] in air established that the rate of decrease in weight obeys the empirical equation

$$\frac{df}{dt} = ke^{-k_1 t}$$

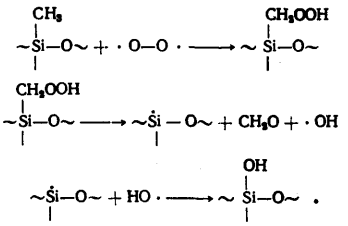
where f is the loss in weight of the specimen, and k and k_1 are constants. It was found that removal of the strongly oxidised upper layer of the specimen led to an increase in the rate of loss of weight. The explanation given was that, owing to cross-linking during oxidation, the diffusion of volatile products was impeded, and their concentration in the specimen increased. The activation energy of the thermo-oxidative degradation of a phenylsiloxane rubber was 22.2 kcal mole^{-1}.

Scala et al.[39] investigated the effect of the air pressure on the thermal oxidation of polymethylphenylsiloxanes (at 700, 600, 500, 300, 100, and 50 mmHg). Comparison of the final losses in weight in air and in argon showed that the purely thermal effect was responsible for 70% of the losses over the pressure range 700–300 mmHg, and for 92% at 50 mmHg of air. From the variation in the ratio of the quantity of gaseous compounds formed to the amount of oxygen absorbed it was suggested that oxidation takes place by different mechanisms at air pressures of 700–300 and below 300 mmHg.

While studying the relaxation of stress in preoxidised specimens of a polydimethylsiloxane rubber, Kuz'minskii and Goldovskii established[47] that the rate of relaxation diminishes with increase in density of the three-dimensional network. Such a relation is observed if cleavage takes place predominantly in the main chain, not at cross-links. The results given in this paper suggest that some kind of active groups accumulate in the polymer during oxidation. The kinetic curves representing the separation of organosilicon compounds of low molecular weight are S-shaped, which indicates the presence of a period of autocatalysis[48], also associated with accumulation in the polymer of active centres capable of breaking down the main chain. The rate of separation of these compounds increases for a certain time, after which it begins to fall, probably owing to the formation of cyclic segments, which impede further cleavage of the siloxane chain.

Thus oxygen does not act directly on the siloxane bond, but is responsible for the formation of active groups which accelerate depolymerisation. However, the mechanism of such acceleration has not been elucidated. It has merely been suggested that the process is hydrolytic in character, and that the active groups influencing cleavage of the main siloxane chain are Si–OH groups[49–51].

In view of the structure of polydimethylsiloxane, the mechanism of the oxidation of the lateral radicals should have much in common with the mechanism of the oxidation of organic polymers such as polypropylene. It has been suggested that oxidation of the side-chains involves formation of hydroperoxides[24] by a mechanism similar to the oxidation of polypropylene[52–55]. Andrianov and Sokolov[24] consider that oxygen attacks a carbon atom attached to silicon in the polymer molecule; a hydroperoxide is first formed, and rapidly decomposes with the separation of formaldehyde and the HO· radical, the latter adding to the silicon atom:



Condensation of the polymer molecules then takes place by means of the hydroxysilyl groups. The thermal decomposition of formaldehyde yields carbon monoxide and hydrogen, and its oxidation produces carbon dioxide and formic acid.

An analogous mechanism was suggested by Scala[39], who regards the process as a chain reaction;

chain initiation: $RCH_3 + O_2 \rightarrow RCH_2^{\cdot} + HO_2^{\cdot}$

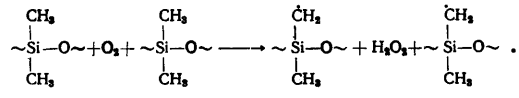
chain growth:
$RCH_2^{\cdot} + O_2 \rightarrow RCH_2O_2^{\cdot}$
$RCH_2O_2^{\cdot} + RCH_3 \rightarrow RCH_2O_2H + RCH_2^{\cdot}$
$RCH_2O_2H \rightarrow RCH_2O\cdot + HO\cdot$
$RCH_2O\cdot \rightarrow R\cdot + CH_2O$

where R is a polymer radical having its free valency on a silicon atom.

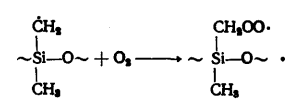
It has been established[56] that the rate at which methyl groups are split off increases with increase in the thickness of a film. The rate of oxidation increases up to a certain thickness, after which it decreases. Thus an "optimum" thickness corresponds to each temperature: 0.3, 0.75, 2.5, and 4 mm at 300°, 270°, 250°, and 230°C respectively.

The increase in the rate of oxidation is explained by the catalytic action of the oxidation products (perhaps formaldehyde), but when the optimum thickness is reached, delays involved in the diffusion of oxygen overlap the first factor. From these conclusions it can be assumed that the oxidation of methyl groups has a chain mechanism. Formaldehyde causes branching of the catalytic chain in the thermal oxidation of the side-groups in polydimethylsiloxane[57]. A chain mechanism is supported also by the sharp decrease in rate of oxidation produced by introducing antioxidants, e.g. 0.5–1.0 wt.% of di-2-naphthyl-*p*-phenylenediamine, into the polymer[56]. An analogous phenomenon is observed when such compounds as titanium dioxide and powdered silica gel are added to the polymer[49].

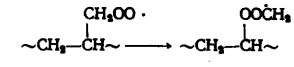
Oxidation is said[57] to be initiated by the abstraction of a hydrogen atom from a methyl group by an oxygen molecule:



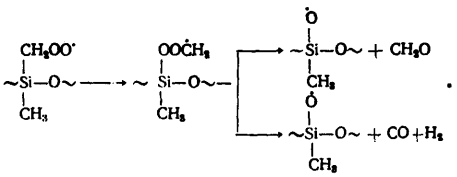
As in the oxidation of hydrocarbons, radicals with a free valency on a silicon atom should react preferentially with oxygen:



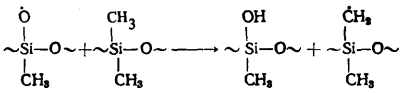
The most probable reaction of the peroxy-radical is its rearrangement by analogy with that of a peroxy-radical of polypropylene[53–55]:



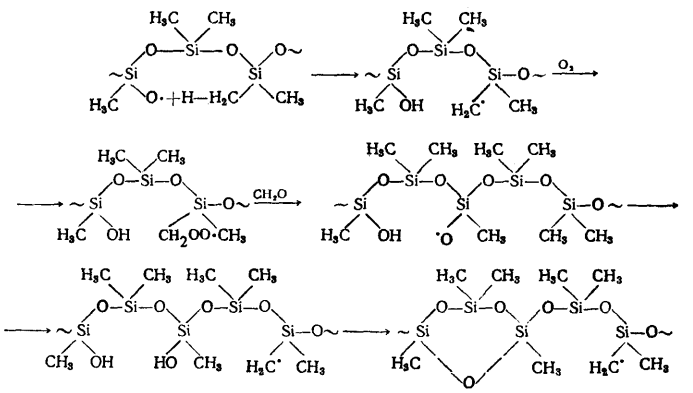
This reaction would be still more probable in polydimethylsiloxane, since its methylene C–H bonds are more stable than those in polypropylene: i.e. the $\geqslant SiCH_2OO^{\cdot}$ radical is more active than $\geqslant C-CH_2OO^{\cdot}$. In the authors' opinion the peroxy-radical undergoes the following reactions[48]



The resulting radical reacts with a methyl group of the same or a neighbouring molecule to form a hydroxy-group:



Since the number of methyl groups split off during the initial period of oxidation considerably exceeds the number of intermolecular siloxane bonds formed, the authors suppose that the start of oxidation involves predominantly the formation of intramolecular siloxane bonds:



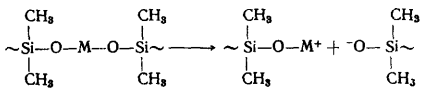
6. EFFECT OF CATALYTIC IMPURITIES ON THE THERMAL STABILITY OF POLYORGANOSILOXANES

Polydimethylsiloxane, when free from acidic or basic impurities, is extraordinarily stable at relatively high temperatures. In most cases polydimethylsiloxanes are obtained by the anionic polymerisation of cyclic compounds, and the presence of catalysts in them is inevitable. Several papers have shown that the presence of polymerisation catalysts lowers the thermal stability considerably.

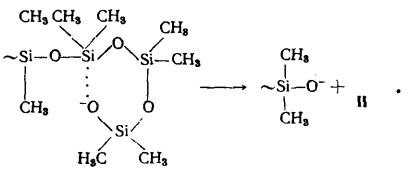
The thermal stability of polymers is greatly dependent on the type of catalyst used for their preparation. Thus the losses in weight of the SKTV brand of siloxane rubber, produced with an acid catalyst, are 25% on heating in a vacuum at 350°C for 2 h, but when an alkaline catalyst is used the same loss in weight is already observed at 265°C.[58] Under conditions of thermal oxidation, polymers prepared with acid catalysts possess diminished thermal stability, since acids accelerate the oxidation of the side-groups. Kučera et al.[59] studied the depolymerisation and oxidation of the lateral groups in polydimethylsiloxanes prepared by anionic polymerisation and neutralised with several acidic agents. The smallest losses in weight were observed in a polymer stabilised with benzoic acid, whereas carbon dioxide had hardly any stabilising effect. The greatest resistance to depolymerisation is exhibited by a mixture of polymers obtained with caustic potash and sulphuric acid as catalysts: depolymerisation of this mixture is completely suppressed at 350°C and 10 mmHg. However, the additives do not protect the polymer from thermo-oxidative degradation: the mixture of polymers obtained with the two catalysts undergoes change in structure especially rapidly.

The two polymers obtained with potassium hydroxide and tetrabutylphosphonium hydroxide as catalysts undergo similar thermal degradation, but the latter polymer undergoes great changes in the course of thermo-oxidative degradation. This is due to breakdown of the catalyst with the formation of acidic products, which accelerate the oxidation[60]. It has been established[59] that the rate of oxidation is a function of the dissociation constant of the acid used as catalyst.

Lewis[61] observed a sharp increase in the rate of decomposition of the polymer after the loss in weight had reached 20%, and assumed this acceleration to be caused by certain components, present in the polymer, which catalysed the process of thermal decomposition. Spectral analysis established the presence of metallic impurities in the polymer (0.05% of barium, 0.01% of lead, 0.0005% of silver, 0.005% of aluminium, and 0.001% of magnesium). Since the concentration of these impurities was too small to catalyse the fission of a silicon–oxygen bond, they were assumed to react with the ends of the chain or to split "abnormal bonds" (silicon–silicon or oxygen–oxygen). This involved formation of so called "live" active centres, which accelerated depolymerisation[61,62]. The polymer molecules underwent dissociation at the point of incorporation of the impurity atom:

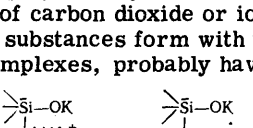


the resulting ions causing depolymerisation with the formation of volatile cyclic products of low molecular weight:



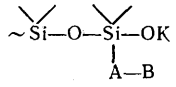
The rate of depolymerisation has been shown to be directly proportional to the square root of the concentration of active centres[63] and to increase with rise in temperature[59].

Several methods have been described for deactivating the active centres, such as the use of thermolabile catalysts, rinsing catalytic impurities out of the polymer, or else neutralising them. Kučera et al.[60] noted that the thermal stability of polydimethylsiloxanes was improved by the introduction of carbon dioxide or iodine. They assumed that these substances form with the active centres relatively stable complexes, probably having the structure



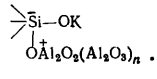
The carbon dioxide complex is stable only up to 150°C. The iodine complexes are considerably more stable, probably because of breakdown initially with the formation of potassium hypoiodite, which then disproportionates into the iodide and the iodate. Both the latter compounds are inert towards the siloxane bond, and neither catalyses the oxidation of methyl groups.

References have been made to the possible formation of stable complexes of the active centres with phenol, anisole, diphenylamine, and other compounds[64]. The stability of a complex, which can be represented by the general formula

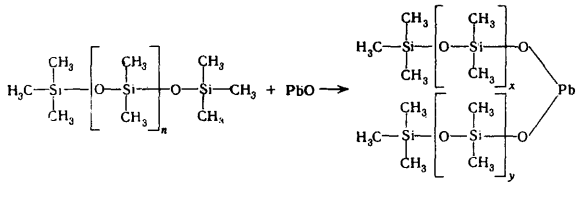


(where A is an electronegative group (oxygen, a halogen), while B is a hydrocarbon group or a metal atom), is determined by the nature of the donor and the type of atom or group combined with it.

Several papers[23,38,60] have dealt with the effect of metals and their oxides, employed for the polymerisation of siloxanes, on the thermal and thermo-oxidative stability of these polymers. Investigation of polymers contaminated with the oxides—ZnO, TiO_2, CdO, MgO, Fe_2O_3, Al_2O_3, BeO, SiO_2, etc.—showed the stabilising effect of these compounds to be very small. However, alumina and beryllium oxide are capable of completely suppressing depolymerisation for a very short time[60]. Only oxides with cations of small radius are able to form complexes with the active centres, which, perhaps, have the structure

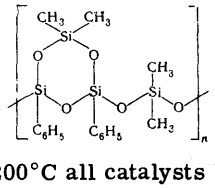


An investigation was made of the action of metals (tin, antimony, copper, lead, aluminium, nickel, selenium, silver, tellurium, zinc, and iron) on the thermal and thermo-oxidative stability of polydimethylsiloxane and polymethylphenylsiloxane. Lead and tellurium accelerated gel formation and the evolution of volatile products, but the other metals had no significant effect[23,38]. It was suggested[38] that lead oxide ruptures the chain under the influence of heat, and then reacts with the fragments to form larger fragments:

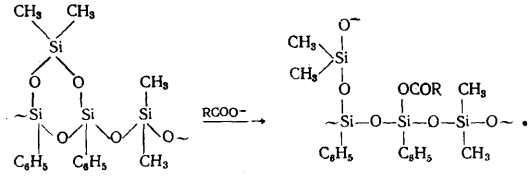


This compound is unstable, and decomposes into smaller fragments. This hypothesis is supported by the turbidity of solutions of the polymer in the presence of lead and tellurium.

Since siloxane polymers are often used as protective coatings and lacquers, it is interesting to examine the action of various pigments and hardening and drying catalysts on the thermal degradation. Andrianov and Fromberg[65] investigated the effect of drying accelerators for varnish films on the heat-resistance of a polymer having the cyclolinear structure



It was found that at 200°C all catalysts lower the heat-resistance of the coatings to roughly equal extents, although the naphthenates of zinc, cobalt, and magnesium have a rather stronger effect. The catalysts are supposed to promote rearrangement of the siloxane chains accompanied by opening of the rings and their recombination, which leads to the formation of cross-linked structures:



The mechanism of degradation varies with the chemical nature of the catalyst. Zinc naphthenate promotes only cleavage of the main chain, but does not affect oxidation of side-groups; whereas lead naphthenate catalyses both oxidation and the cleavage of the main chain. Among pigments (oxides of titanium, chromium, and lead) only chrome yellow catalyses the process of oxidation at 400°C. The remaining pigments do not lower the thermal stability of the films[65].

Investigation of the effect of fillers (titanium dioxide and powdered silica gel) on the thermal oxidation of polydimethylsiloxane showed that, when the degradation products are removed from the sphere of reaction, fillers enhance the thermal stability; if volatile products are not removed, the fillers lower the thermal stability[66]. The authors explain this by the occurrence of hydrolytic processes in the polymer, caused by water adsorbed on the filler (~ 6%).

With the aim of enhancing the thermal stability and improving the mechanical properties of polyorganosiloxanes containing active centres, Berlin et al.[67] proposed subjecting these polymers to a preliminary heat-treatment at 350°C for 1 h. In their view[67] this process occurs by a radical mechanism and comprises the following reactions—degradation of the chains at the weakest bonds and formation of macroradicals, chain transfer by the macroradicals, and cross-linking of the system by recombination of macroradicals with the formation of bonds which are quite stable under the conditions of heat-treatment.

Thus pigments, catalysts, and fillers have a substantial influence on the thermal stability of siloxane polymers. Although the action of these impurities on the silicon–oxygen bond can be quite easily diminished, it is considerably more difficult to inhibit their influence on the oxidation of the side-groups.

7. THERMAL AND THERMO-OXIDATIVE DEGRADATION OF POLYORGANOSILOXANES CONTAINING HETEROATOMS

In spite of the fairly high stability of polyorganosiloxanes, the limits of the fatigue life of these polymers no longer satisfy present-day demands of technology. In order to improve the thermal stability of polysiloxanes, polymers containing various heteroatoms in the chain have been prepared. Introduction into the siloxane chain of fragments the energy of whose bonds is considerably higher than that of the silicon–oxygen bond should increase the thermal stability of polyorganosiloxanes.

Polymers containing heteroatoms were first investigated by Andrianov. Great progress has now been made in the synthesis and investigation of several properties of polyorganosiloxanes containing titanium[68-74], tin[75,76], aluminium[77-80], boron[81-86], and other heteroatoms[87,88] in the chain. Chapters in monographs by foreign authors deal with these polymers[89-91].

The thermal stability of several such heterochain polyorganosiloxanes is far higher than that of polyorganosiloxanes themselves, and depends on the properties of the element introduced into the chain. Polymers containing titanium atoms in the chain exhibit the greatest thermal stability[92-96], and those containing boron and phosphorus atoms are hardly inferior to them. Thus the losses in weight in a vacuum at 450°C after 2 h were 12.7% and 19.3% in polyphosphaborasiloxanes and a polytitanasiloxane. A control specimen of polydimethylsiloxane containing no heteroatoms was completely degraded at 450–500°C.[92]

In an atmosphere of oxygen at 280°C the loss in weight of a phosphaborasiloxane polymer after 28 h was 12.2%, and that of a titanasiloxane polymer 2.47%. Polyborasiloxane retains its elasticity in air up to 390–400°C, polyphosphasiloxanes up to 400–420°C, and polyphosphaborasiloxanes up to 410–430°C; in a vacuum all these polymers remain elastic up to 540–570°C.[92]

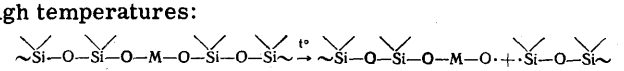
Thermogravimetric analyses indicate that the temperature at which polymethylstannasiloxane begins to decompose is 480°C, the corresponding temperatures for polyethylstannasiloxane and polyphenylstannasiloxane being 462° and 460°C.[97] Introduction of a germanium atom into the chain does not have a favourable effect on the thermal stability of a polyorganosiloxane[98].

The introduction of stannasiloxane copolymers into silicone rubber mixtures produces no improvement in the properties of the vulcanised products[99].

Adequate thermal stability is exhibited by polyphenylchromasiloxanes[100] (losses in weight at 300° and 450°C after 2 h were 12.23% and 43.2%), and also by polyorganoferrasiloxanes and polyorganoferra-alumasiloxanes[101]. Thus polyphenylferrasiloxane is highly stable and loses few volatiles at temperatures of 200–320°C.[101] A striking feature is the lack of correspondence between solubility and infusibility, which is associated with structural characteristics of these polymers.

On the basis of the elementary composition and the infrared spectra Andrianov and his coworkers[102-104] established that heterochain polyorganosiloxanes have a cyclolinear structure. The thermal stability of such rings is very great[103]. Differential thermal analysis indicates that ring-opening occurs at temperatures considerably higher than those at which the organic groups framing the inorganic part of the molecule are stable. The introduction of such groupings as B–O, P–O, P=O, Ti–O, Al–O, and Sn–O into the chain of polyorganosiloxane elastomers raises their thermal stability. It was suggested[95] that this was a consequence of the formation of supermolecular structures and the resultant orderliness of individual segments of the polymer chains.

Poddubnyi and Aver'yanov[105] explain the higher thermal stability of heterochain polyorganosiloxanes (420–430°C) compared with vulcanised SKT and SKTV silicone rubbers (370-380°C) by the inhibiting action of the metal heteroatom on chain radical processes of chain degradation at high temperatures:



where the more polar and stable M–O bond stabilises the Si–O bond and prevents chain cleavages at high temperatures from extending further than the heteroatomic unit. This hypothesis is consistent with the rupture of a silicon-oxygen bond in the immediate vicinity of a chain unit containing a heteroatom requiring the consumption not only of the energy evolved in its formation but also an additional quantity of energy equal to the difference between the internal energies of the radicals ≥Si· and ·O–M.[106]

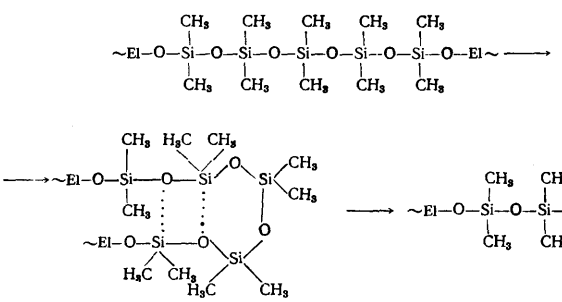
Andrianov[2] put forward the hypothesis that the enhancement of the thermal stability of the polymer by the introduction of heteroatoms into the chain was due to the possibility of forming coordinate bonds between the metal atoms and the oxygen of neighbouring chains.

It has also been established[41] that increasing the functionality and the coordinating power of the heteroatom leads to an improvement in thermal stability, while strengthening the basic power and diminishing the energy of the heteroatom–oxygen bond impair the thermal stability of heterochain polydimethylsiloxanes. Heteroatoms form the sequence—Al < B < Fe < Ti—according to their effect in improving the thermal stability of polymers.

Investigation of the thermal degradation of heterochain polyorganosiloxanes of regular structure containing aluminium, titanium, and boron atoms has shown that, as with polyorganosiloxanes themselves, the major part of the volatile products responsible for the losses in weight consists of hexamethylcyclotrisiloxane formed by cleavage of the silicon–oxygen bond. At high temperatures homolytic cleavage of silicon–hydrogen and carbon–hydrogen bonds also takes place, with the evolution of small amounts of hydrogen, methane, and ethane[41,107,108].

It has also been found[41] that the introduction of heteroatoms leads to a change in the mechanism of degradation. As a consequence of the presence of heteroatoms in the siloxane chain, the formation of an activated complex takes place according to the law of chance, not at the end-groups, as in linear polydimethylsiloxane. It is possible that depolymerisation at terminal groups ceases at the nearest heteroatom, and plays no part in the overall process.

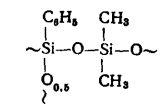
In view of the spiral structure of the siloxane chains, with three silicon atoms in a loop, formation of an activated complex followed by the elimination of cyclic products can be represented as



This hypothesis is supported by the good agreement between experimental and calculated values of the activation energy (29–33 and 32 kcal mole^{-1}) of formation of the transition complex shown. Formation of a transition complex involving a heteroatom is energetically unfavourable, since the activation energy will then considerably exceed 32 kcal mole^{-1}.

The thermo-oxidative stability of polyorganosiloxanes is strongly influenced by the introduction of a small quantity of polyorganoalumasiloxanes[109-111]. Thus the addition of polyphenylalumasiloxane to polydimethylpolyphenylsiloxane shifts the start of rapid decomposition under conditions of thermal oxidation from 400° to 450–500°C, while the loss in weight diminishes from 60% to 30%.[109]

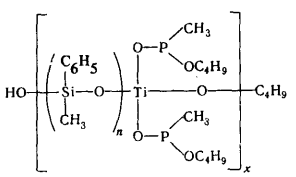
Andrianov and Petrashko[110] investigated the polyorganosiloxane having the structure



and its copolymers with polyphenylalumasiloxane containing 0.05%, 0.1%, 0.25%, and 0.5% of aluminium. Oxidation of the organic groups was found to be more vigorous in the copolymers than in the homopolymer. However, the losses in weight did not exceed the weight fraction of the organic portion, as in the case of polydimethylpolyphenylsiloxane. Hence no cleavage of the main chain takes place in the copolymers, and no organosilicon compounds of low molecular weight are evolved. The authors explain this by the formation in the copolymer of aluminium–oxygen coordinate bonds, which give rise to cross-linking and impede the formation of compounds of low molecular weight.

Thus the rate of thermo-oxidative degradation in the copolymers was found, on the one hand, to be increased in comparison with the homopolymer, owing to the more vigorous oxidation of the phenyl groups, and on the other to be decreased by cross-linking of the polymer. One or other process prevails depending on the aluminium content.

No published data are available on the effect of elements, introduced into the siloxane chain, on the mechanism of thermo-oxidative degradation, or on the composition and quantity of degradation products. Only in one paper is it noted that the thermal oxidation at 400°C for 4 h of poly-bis(organophosphinoxy)titana-methylphenylsiloxanes[112]



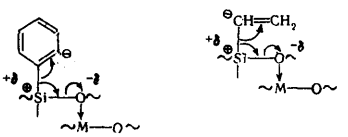
where n = 30, 50, 90, 120, 200, yields carbon dioxide together with liquid and solid organosilicon compounds of low molecular weight. With increase in the distance between the bisorganophosphinoxytitanoxane groups the quantity of cyclic products evolved diminishes, while the amount of carbon dioxide somewhat increases.

Very interesting work was done by Petrashko and Andrianov[96] on the effect of metal atoms in the siloxane chain on the rate of detachment of various organic groups during thermal oxidation. A polymer containing organosilasesquioxane units was investigated, whose thermal oxidation did not involve cleavage of silicon–oxygen bonds, so that the losses in weight could serve as a criterion of the stability of the organic radicals in this process. The rates of elimination of the radicals were compared by means of the dependence of the R/Si ratio on the time of heating. It was found that phenyl groups were eliminated considerably more vigorously than vinyl groups from the heterochain polymers, whereas the opposite relation was observed in the polyorganosiloxanes themselves. The intensity of detachment of a phenyl radical depends on the metal in the siloxane chain, increasing in the sequence Ti < Sn < Al. When the same metals are introduced into polydimethyl- and polydiethyl-siloxanes the stability of such polymers increases in the sequence Ti < Al < Sn.

The reason for the different effects of the organic radicals on thermal stability in polyorganosiloxanes and in the heterochain polymers is that phenyl and vinyl radicals exert a negative induction effect on the silicon atom. These radicals will therefore tend to attract a pair of electrons away from the silicon atom:



A bond of this type produces enhanced resistance to oxidation. When an Si–O–M bond is present in the molecule, the metal atom coordinates with the oxygen in the chain. The coordinate bond causes deformation of the electron sheath of the siloxane bond towards the oxygen atom, and the silicon atom acquires an induced positive charge +δ. The electron pair of the silicon–carbon bond shifts in the opposite direction to that caused by interaction of this electron pair with the π-bonds of the radical. This bond is thereby weakened:



Allyl radicals exert a positive induction effect on the silicon atom. The positive charge on the silicon atom induced by the metal–oxygen coordinate bond produces a displacement of the electron pair in the same direction as the induced effect of the radical. The stability of the radical is thereby raised.

8. STABILISATION OF POLYORGANOSILOXANES

The literature contains references to the possibility of stabilising polyorganosiloxanes, but there is no common approach to this problem. Since thermo-oxidative degradation comprises two independent processes—oxidation of side-groups and cleavage of the main chain with the evolution of volatile products of low molecular weight—all stabilisers which have been recommended can be provisionally divided into two groups—those which inhibit the oxidation of side-groups, and stabilisers which prevent rupture of the main chain in siloxane polymers.

Since the oxidation of side-groups in siloxane polymers has much in common with the oxidation of aliphatic groups in organic polymers (e.g. polypropylene), many authors suggest the use of antioxidants, which have proved to be very satisfactory for the stabilisation of polypropylene. The use of amines as stabilisers in the oxidation of a liquid polyethylsiloxane at 175–200°C increased the induction period of the increase in viscosity, the most effective at 200°C being phenyl-1-naphthylamine[113,114], aldol-1-naphthylamine[114], diphenylamine[115], Neozone D[113,115], and dinaphthylamine[115].

With liquid polydimethylsiloxane an increase in the duration of oxidation before a gel is formed at 200–400°C is observed[116] in the presence of antioxidants like aromatic amines and phenols. Since the latter may themselves decompose at high temperatures, the use of phenoxazine is recommended. The stability of polyorganosiloxanes can be improved[117] by means of amides (e.g. adipamide and urea). The use of antioxidants containing phosphorus is also advised, in particular phosphites of the type $P(OR)_3$ where R is an alkyl or an aryl group[118].

A solution of a polyorganosiloxane resin to which hardening catalysts have been added is stabilised against change in viscosity during storage by the addition of 0.5 wt.% of a

monohydric aliphatic alcohol containing four or more carbon atoms (e.g. 2-ethylhexanol).[119]

The thermal stability of polyphenylethyl- and polyphenylmethyl-siloxanes enamels at 250°C can be enhanced by the use of ethylated and butylated amine–formaldehyde resins[120].

To raise the stability of liquid polydimethylsiloxanes to gelatinisation under the influence of high temperatures it is recommended that 0.5–5 wt.% of bromine should be introduced[121]. The time of gelatinisation is then increased from 24 h for an unstabilised specimen to 1900 h for a specimen containing 0.9 wt.% of bromine (after degradation at 250°C).

Bass, Berlin, et al.[122] proposed stabilising siloxane polymers against thermo-oxidative aging by means of fused aromatic compounds, e.g. anthracene, previously in a vacuum at 300–450°C.

Substances capable of forming stable complexes with the active centres have been proposed as stabilisers to prevent cleavage of the main chain. Thus 0.06 wt.% of iodine[51] or 0.01–0.5 wt.% of partly dehydrated hydroxides of aluminium and iron[123] have been suggested; oxides of various metals—Fe, Al, Be, Si, Ti,[59] Co and Cu,[124] Ni, Mn, Cr[125]—are employed for the same purpose.

It has been observed that, when various compounds of metals are introduced into polyorganosiloxanes, the rate of depolymerisation falls considerably. Therefore most authors propose the addition of a great variety of metal compounds. Especially good results are given by compounds of transition metals, among which such salts have been suggested as the acetates and octanoates of iron[126], the naphthenates of lead[127], zinc, cobalt, iron, and manganese[65], the naphthenates and octanoates of indium and cerium[128]. The use has been proposed of the chlorides, acetates, fluorides, sulphates, nitrates, naphthenates, and oxides of such rare-earth metals as lanthanum, neodymium, praseodymium, samarium, gadolinium, and ytterbium[129].

More complicated compounds have also been recommended, such as cerium complexes[130], and Schiff bases with copper, cobalt, nickel, lead, cadmium, and tin ions[131]. The most effective is a stabiliser formed from the Schiff base *NN'*-bis-2-hydroxy-1-naphthylidene-ethylenediamine with copper ions, which increases the stability to thermal oxidation ninefold.

Compounds of ferrocene—acetylferrocene, 1,1'-diacetylferrocene[132], 1,1'-bisdimethylethoxysilylferrocene, and 1,3-bis-(1,1'-ferrocenylene)tetradimethylsiloxane—have been suggested as stabilisers[133].

Good results are obtained by using as stabilising additives dialkyl sebacates[134] and also dialkyltin oxide[135,136]. A stabilising effect has been noted with the acetylacetonates of chromium, zinc, magnesium, nickel, and cobalt[137], and also with trihexyloxyiron and tributoxyzirconium[138]. The authors showed that the improvement in stability of polydimethylsiloxanes produced by adding the above compounds was due to the formation, in the process of thermal degradation, of a new polymer having heteroatoms in the chain[139].

There are also references to the stabilisation of siloxane oils by treating them at 100–200°C with compounds capable of forming monofunctional trialkylsilyl groups in the presence of cation-exchange polymers of natural type[140].

Gruber, Klebanskii, et al.[141] recommend improving thermal stability by introducing compounds capable of acting as centres of orientation and thereby creating an ordered secondary structure. Among such recommended additives are oxides, both similar in nature to and different from the siloxane chain, as well as certain finely divided metals and oxides.

Although quite a wide range of stabilisers have already been proposed for polyorganosiloxanes, the problem of their stabilisation still remains a complicated task. The most effective would obviously be stabilisers combining the properties of an antioxidant with the ability to increase the stability of the main siloxane chain. Since polyorganosiloxanes are thermostable polymers, their thermal stability can probably be improved also by using thermally stable, non-volatile compounds which develop a stabilising action at high temperatures.

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