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# Determination of the Useful Lifetime of a Polymeric Material as a Physicochemical Problem

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The principal problems of the determination of the useful lifetime of a polymeric material under various operating conditions in a given article are formulated, the disadvantages of the traditional simplified empirical approaches to solutions of problems of this kind are analysed, and the principal trends in physicochemical research, which lead to success in solving the given problem, are discussed.
The bibliography includes 50 references.

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## I. INTRODUCTION

The quality of a material consists of the set of its properties which are important in practice. However, not only the properties of the material at a given instant, as it were, its instantaneous properties, but also the way in which the properties of the material vary under different operating conditions are of practical importance; this characteristic of the quality of the polymeric material (PM) in fact determines its useful lifetime.

The instantaneous properties of the material can be measured in different ways and the number of such methods is large and they have been thoroughly developed. At the present time one can characterise quantitatively virtually any instantaneous property of the material, it is possible to determine any of its mechanical or rheological characteristics, its spectrum of mechanical or dielectric losses or its absorption or luminescence spectra can be characterised, the composition of the material and that of its impurities can be determined, and it is even possible to determine the composition of the active species formed in the material under any conditions.

Unfortunately however, apparatus for measuring one extremely important property of the material, which determines the kinetics of the variation of its instantaneous properties under any conditions and hence its useful lifetime under these conditions, does not and apparently cannot exist. The solution of this problem, which requires investigation, is sometimes simple and sometimes fairly complex. The present review is devoted to problems of the methodology of such investigations. They are of urgent importance at the present time by virtue of two causes of different kinds.

On the one hand, the assortment of polymeric materials with different properties, materials which are either already produced industrially or whose industrial production can be achieved, has increased. In this connection the problem arises of the optimum application of the given material or the optimum material for a given article, and not simply the problem of the determination of the useful lifetime of the given material. Materials with enhanced stability are not always best for a given article, since an increase of stability usually entails also an increased cost of the material and excessive stability of the material creates the additional problem of the disposal of the residue after the given article has failed. Therefore if, as commonly occurs, the predicted useful lifetime of the material is too short, the result may be large unnecessary expenditure on excessive stabilisation of the material or reinforcement of the constructions produced from the material.

On the other hand, the present state of the theory of the ageing of polymeric materials makes it possible to pose the question of a more rigorous formulation of problems associated with the determination of their useful lifetime. More than ten years ago the principal problems of the fundamental research into the question of the ageing of polymeric materials were formulated[1,2] and a long series of studies on these lines was initiated. Considerable experience in work with polymeric materials has now accumulated, extensive experimental studies have been carried out, the foundations have been created for a theory of the ageing of polymeric materials, methods have been developed for the determination of the quantitative characteristics of this process, and the first successes have been achieved in the description of the kinetics of the variation of properties of polymeric materials of practical importance in the course of ageing on the basis of data on the mechanisms of the processes occurring in polymeric materials[3]. All these factors suggest that it is already possible to pose the question of the replacement of what is actually an empirical method of forecasting generally used at the present time by a scientific approach to the problem based on the understanding of the fundamental features of the mechanisms of the processes occurring in the ageing of polymeric materials.

## II. FORMULATION OF THE PROBLEM

### 1. The Necessary Initial Data

The instantaneous properties of the material can be characterised quantitatively by a point in the multidimensional space of properties or by a vector **Y** directed to this point. The components of vector **Y** are quantitative characteristics of the instantaneous properties of the material, its composition, strength ($\sigma$), dielectric losses tan $\delta$, optical density, etc.

The polymeric material should possess a set of properties in order to be suitable for use in a given article. This means that in the space of the instantaneous properties of the material there exists a region of operational suitability of the material $S_0$. If the vertex of the vector **Y** falls within this region, then such a material can fulfill its necessary functions in the given article at the given instant.

However, the condition that the vector **Y** falls within the region $S_0$ is itself insufficient for the material to be used in the given article. It is necessary that throughout the entire useful lifetime of the article the vertex of the vector **Y** does not leave the region of the operational suitability of the material. In the course of use and storage the properties of the material Y gradually change as a result of the ageing processes occurring in it. The vertex of the vector **Y** gradually shifts in the space of properties (Fig.1). The way in which it shifts depends not only on the properties of the material, but is also determined by the conditions under which the material is used. In the course of ageing the relative contributions of the properties change and the vertex of the vector **Y** shifts along different trajectories, which depend on the process conditions.

In the general case these conditions can be characterised by another vector **X** in the space of operating conditions. Its components will be, for example, temperature, stress, intensity and spectral composition of the incident radiation, humidity, oxygen pressure, etc. Thus the problem of the determination of the useful lifetime of the polymeric material is a special case of the more general problem of the determination of the kinetics of the variation of the properties of such a material under any conditions, i.e. the problem is to find the function

$$\mathbf{Y}=\mathrm{f}(\mathbf{X}, t). \qquad (1)$$

In this treatment the breakdown of the polymeric material in a given article is characterised by the time during which the vertex of the vector **Y** reaches the limit of the region of the operating suitability $S_0$ under conditions **X**.

Consequently the useful lifetime of the polymeric material is determined by (1) the properties of the material, (2) the operating conditions **X**, and (3) the requirements which the material must meet or the region of its operating suitability $S_0$.

Accordingly, the accuracy of the determination of the useful lifetime of the polymeric material depends not only on the extent to which the characteristics of the instantaneous properties of different specimens of a given material are uniform, but also on the accuracy of the determination of its operating conditions and of the characteristics of its operating suitability.

## 2. The Purpose of Prediction

When the question of the prediction of the useful lifetime of a material is considered, one usually examines two different problems: the problem of determining the useful lifetime of the given material under specified conditions of its use and storage and the problem of determining the guaranteed lifetime of the material in articles of a particular type.

The solution of the first problem is directed towards the determination of the most probable useful lifetime of the material under operating conditions which are known beforehand and have been determined accurately. This is in essence a physicochemical problem which must be solved on the basis of current ideas concerning the physicochemical ageing processes in the material and on the basis of the results of accelerated tests of the material carried out under rigorously controlled conditions.

The determination of the guaranteed lifetime of the material is a qualitatively different problem. In the course of the guaranteed lifetime the material can exist in a certain range of operating conditions and it is necessary that the probability of the loss of its operating suitability under these conditions should not exceed a certain quantity corresponding to a specified coefficient of reliability of the article made from this material[4,5]. In solving this problem, one must take into account the possible variability of the properties of different batches of the material or of the material in different articles, the possible differences in their operating conditions, and even the possible differences in the requirements which must be met by different articles of a given type.

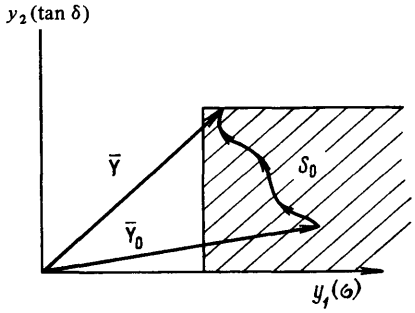



**Figure 1.** Trajectory of the variation of the properties of the polymeric material. For the significance of the notation, see text.

The basis of the problem is statistical and belongs to the theory of reliability. If the first problem has been solved, then the second can also be solved by statistical mathematical methods, provided that the distributions of the properties of the material, its operating conditions, and its operating suitability have been specified.

This review deals mainly with questions associated with the solution of the first problem. Problems of reliability are involved only in connection with the experimental error in the measurement of the rate of change of the properties of the material and in connection with the problem of averaging the time-variable operating conditions of the material.

## 3. Principal Ways of Determining the Useful Lifetime of a Polymeric Material

There exist two idealised ways of determining the useful lifetime of a polymeric material.

1. Modelling of the operating conditions of the polymeric material in the laboratory, i.e. laboratory tests on the material under conditions identical with its operating conditions in the given article.

2. The study of the detailed mechanisms of all the processes occurring in the material and calculation from these data of the useful lifetime of the material under any conditions.

Neither of these procedures can be recommended in the pure form as a realistic method for the solution of the problem of prediction.

Modelling cannot in essence be regarded as a method for the prediction of the useful lifetime of the material. With the aid of modelling, one can really only determine the useful lifetime of the material under the given conditions and one need know nothing about the processes which lead to an alteration of the properties of the material. It is sufficient to reproduce satisfactorily the operating conditions of the material in the laboratory, to place the material under these conditions, and to measure its useful lifetime. The accuracy of the determination of the useful lifetime depends in this case only on the accuracy with which the operating conditions are simulated.

However, not all operating conditions can be modelled in the laboratory and in choosing the material for a given article one can hardly seriously entertain the procedure involving the preparation of the article from all possible combinations of materials. Therefore modelling is usually employed in the last stages of the investigation when the material for the article has been chosen by some other methods and it only remains to refine its useful lifetime. In essence, the procedure involving the modelling of the operating conditions in the laboratory or the determination of the useful lifetime by interpolating the results of laboratory tests does not constitute prediction—with its aid one can only conclude what the result of the test is. This method in essence lacks any predictive power.

Nevertheless prediction is necessary, since one must know how all the properties of materials, which must be used for many years or under unique conditions, will vary. The question of the prediction of the stability of a polymeric material arises when one must decide whether a given material is or is not to be manufactured, or whether or not a given article is to be made from this material. A number of examples of problems the solution of which require the prediction of the useful lifetime of the polymeric material are listed below.

1. Determination of the useful lifetime of articles to be stored and used for a long time:
   (a) Constructional materials (medicine, building industry);
   (b) Specialised engineering applications (photographic materials, electronics);
   (c) Conservation of articles (spare parts, stock of spare articles).
2. Construction of articles:
   (a) Optimum materials for articles;
   (b) Optimum applications for the material.
3. New materials:
   (a) The search for applications of given materials;
   (b) Estimation of the scale of manufacture.
4. Mass applications of materials:
   (a) Estimation of the relative scales of industrial manufacture;
   (b) Elucidation of the time and extent of repairs;
   (c) Utilisation of waste.

In all these cases extrapolation of the results of preliminary tests to conditions under which the material has never been tested is required and not the interpolation of the results of tests on polymeric materials. In essence, the difference between the problem of the prediction of the useful lifetime of a polymeric material and the problem of the modelling of the operating conditions in the laboratory is the same as the difference between the problems of extrapolation and interpolation.

The second idealised method for the solution of the problem is also unrealistic. Evidently, a detailed study of the mechanism of ageing leads to the solution of the problem and ultimately makes it possible to determine the useful lifetime of the given material under any conditions, and usually with any degree of accuracy. However, this procedure is known to be laborious and long. Despite the fact that polymer chemistry has already existed for several decades, there are only a few materials whose useful lifetime can be predicted from the knowledge of the mechanism of their ageing and only under certain conditions. Nevertheless, this way of solving the problem is in fact used in the leading laboratories in the world in which fundamental research is being carried out, and this research actually determines the level of our knowledge about the mechanisms of the ageing processes in the polymeric material and makes it possible to cover the entire wide variety of materials, the methods for their synthesis, and the ways in which they can be modified and adapted to the solution of particular problems. The second method of solution therefore predominates in the initial stages of the study and in choosing the material.

Most of the work on the determination of the useful lifetime of polymeric materials is performed by methods which lie somewhere between these two idealised procedures. In real prediction both empirical methods involving the extrapolation of the results of laboratory tests on the material and the available information about the ageing mechanism are widely used. If the prediction is based largely on the results of tests on the given material, then one speaks of empirical and semiempirical methods of prediction; on the other hand, if information about the fundamental features of the mechanism of the ageing of the material predominates, then one speaks of describing the kinetics of the variation of the properties of the material on the basis of complete or incomplete knowledge of the process mechanism[6].

In both cases the prediction is based on the extrapolation of the results of laboratory tests on the material to its operating conditions, but extrapolation and laboratory tests are understood to have the same broad significance. The result of a test on the polymeric material includes not only the results of its study but also the set of all the accumulated experimental and theoretical information about the given material as well as any of its analogues, while extrapolation includes the development of methods of adjusting the results of tests for any operating conditions, which are as fully characterised as is possible.

## III. EXTRAPOLATION OF THE RESULTS OF TESTS ON THE POLYMERIC MATERIAL TO OPERATING CONDITIONS

### 1. Mathematical Difficulties

In predicting the useful lifetime of the polymeric material one must solve the following problem. There exists a region $Z_0$ in the conditions governing the tests on the material. In this region of conditions the tests are carried out. On their basis, one obtains in some way, for example, by interpolation, a mathematical description of the kinetics of the change in the properties of the material $\mathbf{Y}(\mathbf{X}, t)$. It is necessary to extrapolate this relation outside the limits of the region $Z_0$.

In this formulation of the tast, problems of a mathematical nature immediately arise. In mathematics the task formulated in this way is invalid[7]. In the general case any problem of extrapolation is invalid because one can always select a function which describes adequately all the available experimental data and which behaves arbitrarily outside the region of the tests.

On the other hand, common sense suggests that such absolute invalidity of the extrapolation problem is probably too extreme. In the vicinity of the region in which the tests are carried out there is bound to be a region in which extrapolation is possible. The problem formulated must not

concern the existence or non-existence of such a region and must deal with the information required to extend this region and to increase the accuracy of a well-founded extrapolation within this region.

The possibility of validating the problem which is invalid from the mathematical point of view by relatively straightforward methods can be seen from the following simplest example. Suppose that it is necessary to extrapolate over a long time interval the decreasing relation $Y(t)$ illustrated in Fig.2. The conditions are constant throughout the process and the extrapolation must be carried out on the basis of the results of tests indicated by points in Fig.2.

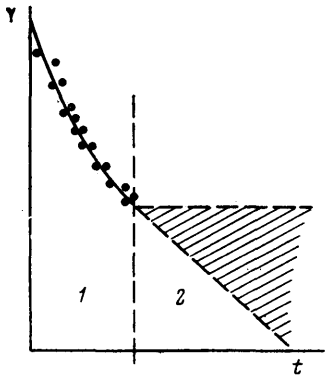



**Figure 2.** Example of the simplest extrapolation: 1) region of tests $Z_0$; 2) region of extrapolation. The shaded region represents the possible extrapolation in accordance with Eqn.(3).

If no limitations are imposed on the extrapolated relation, then, outside the range of measurements, it can vary arbitrarily. Indeed, the relation can be continued through any point outside the range of measurements, using, for example, a polynomial function containing more parameters than the number of experimental points. However, even a simple limitation, which is natural for many chemical processes, namely

$$Y<Y(0),\ \frac{dY}{dt}<0,\ \frac{d^2Y}{dt^2}>0, \tag{2}$$

and which postulates that the relation must decrease monotonically and must have no points of inflection, makes it possible to produce a well-founded prediction for virtually any time.

When $t>t_0$, any solution can be found between two straight lines:

$$f_1(t)=f(t_0);$$
$$f_2(t)=f(t_0)+(t-t_0)\left(\frac{df}{dt}\right)_{t=t_0}. \tag{3}$$

It appears that, when one specifies a narrower class of functions which can describe the given relation, then the accuracy of the extrapolation can be increased compared with Eqn.(3), and it is also possible to obtain data concerning the possible distribution of the error of the extrapolation for any $t$.

Thus the introduction of a series of such very simple constraints made the invalid extrapolation problem entirely valid and susceptible to solution by methods of modern mathematical statistics and computer techniques.

Unfortunately the region where such problems can be solved has so far been poorly worked out. Only problems in which the form of the $Y(X, t)$ relation is known exactly are solved. It is then possible to find not only the most probable extrapolation and the distribution of the expected error, but also to specify the optimum plan of tests whereby one can carry out the extrapolation with the minimum error[8].

When the mechanism of the ageing of the given material has not been established, it is usually impossible to predict exactly the form of the kinetic curve. However, the general understanding of the essential features of the processes occurring during ageing frequently makes it possible to specify the general characteristics of the expected relation. In some cases one may expect a monotonically decreasing relation analogous to that illustrated in Fig.2, while in others one can postulate a curve with a point of inflection or a relation with a characteristic induction period, etc. One can hardly assume that the $Y(X, t)$ relation will undergo a large number of oscillations for time-invariant external conditions $X$. All this qualitative information makes the problem of extrapolation valid from the mathematical point of view.

The greater the amount of the information available about the ageing mechanism, the more fully and more accurately can one describe the form of the kinetic curve and the greater the accuracy of the useful lifetime predicted by extrapolation.

This general consideration of the extrapolation problem shows that the problem of the characteristics of the form of the kinetic curves for the variation of the properties of the polymeric material under various conditions, i.e. the problem of the classification of the mechanisms of the ageing of polymeric materials and the characteristic features of each class of mechanisms, is particularly important for the prediction of the useful lifetime of polymeric materials. On the other hand, the mathematical problem reduces to ensuring that in the course of extrapolation there is the smallest possible loss of information accumulated both in the tests on the polymeric material and in the compilation of the *a priori* information about it.

## 2. Traditional Predictive Methods

For the majority of materials, the ageing mechanism has not yet been established. Therefore in predicting the useful lifetimes of such materials one frequently (see, for example Elizavetin[9]) uses methods based on the simplest hypothesis that the ageing of the polymeric material can be formally described as an elementary chemical reaction. The rate of this reaction is determined by a rate constant, which varies with temperature according to the Arrhenius law and which varies under the influence of mechanical stresses in accordance with Zhurkov's equation; in the presence of radiation, the constant increases in proportion to the intensity of the latter:

$$k=k_0 I e^{-(E-\gamma\sigma)/RT}, \tag{4}$$

where $E$ is the activation energy for the process, $\sigma$ the mechanical stress, $I$ the intensity of light, and $\gamma$ and $k_0$ are proportionality coefficients. The majority of methods for the useful lifetimes of polymeric materials used at present have been based on this hypothesis.

According to a USSR Government Standard (GOST),[10,11] it is recommended that the temperature dependence of the useful lifetime of the polymeric material be described in terms of the Arrhenius equation. The lifetime of the polymeric material under mechanical forces is described by the Zhurkov equation:

$$\tau = \tau_0 \exp\left(\frac{E - \gamma\sigma}{RT}\right). \quad (5)$$

The principle of the summation of the faults arising in the course of the ageing in the polymeric material, otherwise known as the principle of superposition, is widely used[12,13]. The mathematical expression of this principle is Bailey's equation[14], according to which, under the conditions of a time-variable influence on the polymer, its useful lifetime $\tau$ is defined by the equation

$$\int_0^{\tau} \frac{dt}{\tau_0(\mathbf{X}(t))} = 1, \quad (6)$$

where $\tau_0(\mathbf{X})$ is a function characterising the relation between the useful lifetime of the material and its operating conditions for constant $\mathbf{X}$ and $\tau_0\mathbf{X}(t)$ is the same function where the time-variable characteristic of the operating conditions $\mathbf{X}(t)$ has been substituted as the argument. On the other hand, the useful lifetime $\tau$ to be determined is involved in this equation as the integration limit.

Combination of the Arrhenius equation with Bailey's equation leads to the familiar principle of the temperature–time superposition, which establishes the equivalence of the influence of temperature and the duration of that influence. Thus in the field of mechanical stresses the useful lifetime of a polymeric material should be defined by the equation

$$\int_0^{\tau} k_0 e^{-[E-\gamma\sigma(t)]/RT(t)}\, dt = 1. \quad (7)$$

The superposition principle is valid when the change in the properties of the material is irreversible and when these properties vary in the space of properties along a single trajectory whatever the operating conditions. This also shows that the ageing of the material proceeds to the same extent whatever the sequence in which the operating conditions are altered.

A corollary of the superposition principle is that constant conditions, equivalent to variable operating conditions exist. Thus Eqns.(4) and (7) show that the time of accelerated tests ($\tau_{equiv}$), at the chosen temperature $T_0$ and under the conditions of a stress $\sigma_0$, which is equivalent to operation during a period $\tau$ at an arbitrary temperature $T(t)$ and stress $\sigma(t)$, is determined by the relation

$$\tau_{equiv} = \int_0^{\tau} e^{-\left(\frac{E-\gamma\sigma(t)}{RT(t)} - \frac{E-\gamma\sigma_0}{RT_0}\right)} dt. \quad (8)$$

By means of simple rearrangements, it is possible to obtain from Eqn.(8) the familiar equation for the equivalent temperature[15-17]

$$T_{equiv} = -\frac{E}{R \ln\left(\frac{1}{\tau}\int_0^{\tau} e^{-E/RT(t)}\, dt\right)}, \quad (9)$$

at which the properties of the material change would change by the same amount during the period $\tau$ as they do with a variable temperature $T(t)$.

All these principles and equations are valid for the determination of the useful lifetime of materials whose ageing can be described as a single elementary chemical reaction of any order. Even in the presence of two parallel stages one may expect the breakdown of the Arrhenius law and the failure of Bailey's equation. These questions will be examined in greater detail in the following Sections.

Nevertheless the principles discussed above have been used successfully to describe the kinetics of the variation of the strength and viscoelastic characteristic of polymeric materials under conditions such that the mechanical stress is the principal factor responsible for the change in the properties of the material. For example, Zhurkov's equation describes the lifetime of many polymeric materials acted upon by mechanical loads[18]. However, over a wide range of stresses, particularly under conditions such that, apart from the stress, the ageing process is influenced also by other factors (such as oxygen, light, ozone, etc.), Eqn.(6) does not hold. Even the "fatigue" characteristics of the material are very difficult to describe by these methods, let alone the "static fatigue" which causes the material to break down regardless of the applied stress. This is apparently due to the fact that the "fatigue" of the polymeric material, i.e. its breakdown when acted upon by small stresses, is determined mainly by the irreversible physicochemical transformations of the material, induced by other causes such as oxidation, photochemical transformation, interaction with a corrosive medium, etc., and not by stresses. The mechanism of these processes is usually fairly complex and cannot be described at the level of empirical functions of the susceptibility of the material to damage, which vary with time in the same way as in a pseudoelementary $n$th order reaction and it is therefore necessary to take into account the influence of the stress on each elementary step of the complex ageing process. A relatively wide range of studies has now been carried out[20,21] in which an attempt has been made to predict the useful lifetime of polymeric materials while retaining the principles of the above methods. For example, the breakdown of the linearity of the plot of the logarithm of the lifetime against the reciprocal of temperature is treated as the variation of the activation energy for a process, and the physical causes of this variation are sought. The so-called pole in Zhurkov's equation is displaced and the physical nature of this displacement is elucidated. The essence of these phenomena is probably associated with the non-elementary nature of the ageing of polymeric materials under these conditions. It is hardly possible to solve successfully the problems arising by assuming that the ageing process of the polymeric material and hence the kinetics of the variation of its properties can be formally regarded as a single chemical reaction.

A radical-chain mechanism of the mechanothermal degradation of a polymer, including a chain initiation stage involving the rupture of strained bonds in the macromolecules, depolymerisation, chain transfer with formation of a central radical, the decomposition of this radical under the influence of stresses, the migration of the free valence along the central radical, and chain termination, has been examined[22]:

$$\begin{aligned}
&\text{Polymer} \xrightarrow{k_1\sigma} 2\dot{R}_t \text{ (initiation)},\\
&\dot{R}_t \xrightarrow{k_2} \dot{R}_t + \text{monomer (depolymerisation)},\\
&\dot{R}_t + \text{polymer} \xrightarrow{k_3} \text{polymer} + \dot{R}_c \text{ (chain transfer)},\\
&\dot{R}_c \xrightarrow{k_4(\sigma)} \dot{R}_t + \text{polymer (radical decomposition)},\\
&\dot{R}_c \xrightarrow{k_5(\sigma)} \dot{R}_t \text{ (migration of free valence)},\\
&2\dot{R}_c \xrightarrow{k_6} \text{polymer (chain termination)}.
\end{aligned} \quad (10)$$

The stress has the most significant influence on the constants $k_1$, $k_4$, and $k_5$.

Analysis of the corresponding kinetic equations shows that, over relatively narrow ranges of variation of the stresses, the Zhurkov equation holds formally, but $\tau_0$, $E$, and $\gamma$ are effective quantities which do not characterise a single elementary reaction but refer to a complex combination of several rate constants for different elementary reactions. Consequently, for an arbitrary material, it is impossible to relate $\tau_0$ to the vibration period of any bonds in the molecule and $E$ cannot be related to the activation energy for any one elementary step of the chemical process. These quantities do not characterise the elementary step, but refer to decomposition of the material as a whole. Accordingly, these quantities are not constant and depend on the process conditions. When the mechanism of the ageing of the material is unknown, the terminology frequently employed[17,20] becomes only a jargon. There is no more point in speaking of the activation energy for the ageing process than there would be in speaking of the activation energy for thermal expansion.

Thus calculation shows that, for the example under consideration, over a wide range of stresses, the semilogarithmic form of the relation between the lifetime of polypropylene and the stress should be concave. Fig.3 shows that the results of the calculation using the rate constants for the mechanothermal degradation of polypropylene obtained independently agree satisfatorily with the experimental values[23]. These results have been examined in greater detail elsewhere[24].

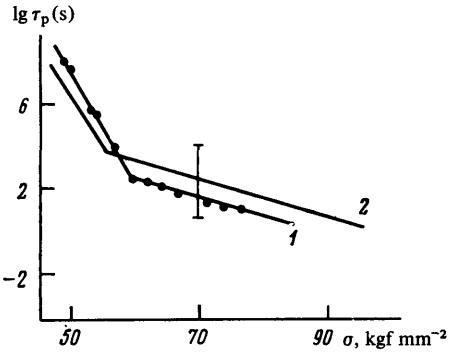



**Figure 3.** The influence of stresses on the useful lifetime of polypropylene: 1) experimental data[23]; 2) calculation[22] based on mechanism (10) with indication of the error of the calculation.

Analogous breaks in the semilogarithmic relations between the lifetime and the stress can be observed under the conditions of the joint action of oxygen and the stress, light and the stress, etc. In this case the relations become convex[25], since the polymer acted upon by small stresses breaks down almost independently of the kind of stress it is subjected to.

Over a wide range of temperatures, Eqn.(6) also does not hold. For example[26], $E$ for many polymers varies sharply in the vicinity of their brittle temperatures $T_{br}$, which is due to the fact that the relaxation processes at $T > T_{br}$ become capable of competing with the mechanical dissociation of the macromolecule.

## IV. THE "CHANGE IN THE MECHANISM" OF THE AGEING OF A POLYMERIC MATERIAL ON PASSING FROM TEST CONDITIONS TO OPERATING CONDITIONS

### 1. The Causes of the "Change in Mechanism"

In the determination of the useful lifetime of a polymeric material by extrapolation from the more severe conditions of accelerated tests to the milder operating conditions, the greatest difficulties do not arise from the extrapolation itself but from the fact that the ageing mechanism changes along the extrapolation path. Strictly speaking there is usually no actual "change in the mechanism" along the extrapolation path. Critical changes in the mechanism are extremely rare. They are normally observed probably only in the liquid–crystal phase transition, which is hardly ever observed in a pure form in polymeric materials. Even after crystallisation of polymers, the chemical changes usually involve the same mechanism as in the melt and in the remaining amorphous phase of the polymeric material.

There is usually a change not in the ageing mechanism but merely in the rate-limiting stage of the ageing process. For example, in a study[27] of the kinetics of the thermal oxidation of polyethylene at elevated temperatures the effective activation energy for the process was found, and on the basis of these data it was predicted that the insulation made of this polyethylene on pipes at 60 °C would be suitable for use over a period of approximately 15 years. However, in this prediction, no account was taken of the fact that at high temperatures the kinetics of the consumption of the thermal stabiliser are determined by its involvement in the oxidation process, while at a low temperature, where the oxidation process, which has a relatively high activation energy is sharply retarded, the thermal stabiliser begins to be consumed mainly by its diffusion from the specimen, which is a low activation energy process, and not due to the chemical transformation. As a result, it was found that the insulation of pipes breaks down after only $1\frac{1}{2}$ years, and not after 15 years.

An analogous effect was observed in a study of the lifetime of polymeric materials subjected to low stresses[25]. Under the conditions of high stresses, the rate of the process is limited by the step involving the dissociation of the macromolecules under the influence of the mechanical stress. Under these conditions, Zhurkov's equation holds satisfactorily and the logarithm of the lifetime of the material $\tau$ is linearly related to the stress $\sigma$ and the parameter $E/RT$ of the Arrhenius equation. For low stresses, the rate of this process becomes insignificant and other processes determine the variation of the properties of the material, for example, its chain oxidation. As a result, a sharp break is observed in the $\lg \tau - \sigma$ relation in the region of low stresses.

In neither case was there any change in the ageing mechanism either at low temperatures or under the conditions of low stresses. The thermal stabiliser diffused with an unchanged activation energy over the entire temperature range and also at higher temperatures, but under the latter conditions the rate of the process was negligible compared with the rate of oxidation and therefore could not be taken into account in the prediction. Similarly, for high stresses, the oxidation of the polymer proceeds in the same way as for low stresses, but in the former case the rate of the process can be neglected compared with the rate of dissociation of the strained molecules. Both effects described are associated with the usual phenomenon involving the competition of several elementary chemical or physical processes constituting the essential feature of the ageing mechanism,

the rate constants for these reactions varying monotonically along the extrapolation section in conformity with the Arrhenius or Zhurkov equations.

A somewhat more complex situation arises when there is a sharp change in the conditions for the elementary steps of either the chemical transformation of the substance or if there is a physical alteration in the structure of the material along the extrapolation section. This difficulty can be sometimes overcome when the features of the variation of quantitative characteristics of the elementary step are known for this change of conditions.

Thus it is known that the rate constants for bimolecular reactions are to a large extent determined by the nature of the molecular mobility in the medium. Molecular mobility influences both the transport of the reactants towards one another and the probability of the chemical interaction at the site where the reactants meet. It has been shown[28] that, on passing from liquid-phase systems to vitreous polymeric matrices, there is the so-called levelling of reactivity for series of molecules with different chemical structure participating in isotypical chemical reactions. Molecules whose reactivity in the liquid phase differs by 2–4 orders of magnitude have reactivities differing by only 1–2 orders of magnitude in the solid polymer. This phenomenon is associated with the sharp alteration of the molecular mobility in the medium and is independent of the chemical structure of the molecules of the latter.

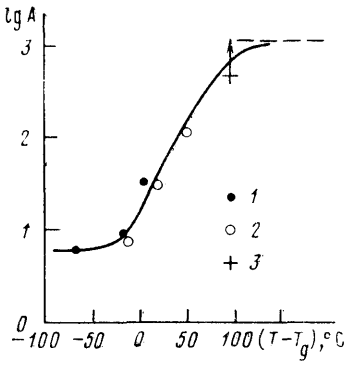



**Figure 4.** The influence of the molecular mobility of the medium on the relative rate constant ($A$) for the quenching of singlet oxygen. Polymeric matrices: 1) polystyrene; 2) butyl methacrylate–methacrylic acid copolymer (BMK-5, $T_g \approx 35$ °C); 3) polybutadiene. The dashed straight line corresponds to the liquid phase[29].

Fig.4 shows that the relative reactivity of the reactants in different polymeric matrices is determined by the difference between the experimental temperature and the glass point of the medium $T_g$, which is known[30] to be a measure of the molecular mobility of the medium over a wide temperature range. With the aid of a model taking into account the relative movement of the reactants in the cage where they meet, it has been shown[31] that the levelling phenomenon can be described quantitatively by the relation

$$\left(\frac{k_1}{k_2}\right)_S = \sqrt{\left(\frac{k_1}{k_2}\right)_L}, \qquad (11)$$

where $k_1$ and $k_2$ are the probabilities of the chemical transformation of two different substances in an isotypical chemical reaction when the transport of the reactants towards one another and the activation energy for the process can be neglected. The subscripts show that the process takes place in the solid polymer at $T < T_g$ or in the liquid phase.

Using Eqn.(11) and the data for the variation of the diffusion coefficients of the reactants and the molecular mobilities of the medium, it is possible to calculate the change in the reaction rate constant along the extrapolation path and to estimate the ratio of the rates of different processes under operating conditions. However, one should not forget here that Eqn.(11) refers to the elementary step of the chemical reaction and not to the ageing process as a whole and similar relations can therefore be applied in a real process when the kinetic mechanism of the ageing of polymeric material is known.

Not only chemical reactions in the polymeric material are responsible for its ageing. The change in its properties can be caused by physical processes which do not alter the chemical nature of the polymeric material. For example, a distinctive feature of the polymeric material is that it is frequently used in a thermodynamically non-equilibrium state. The great length of the polymer molecule sharply retards the occurrence of many physical processes, which makes it possible to use for a long time polymers in a state far from equilibrium from the physical point of view. Thus crystallising polymers are used in a partially amorphous state, the preliminary orientation of the polymer persisting for many years and the stresses arising in the polymer sometimes relaxing in the course of the entire useful lifetime of the material[27,32].

During the ageing of the polymeric material, chemical reactions are accompanied by its physical rearrangement and both processes can proceed at comparable rates. The change in the ratio of these rates can be one of the causes of the apparent "change in the mechanism" of the ageing of the polymeric material. Thus, when the polymer is used in the vitreous state, then owing to the non-uniformity of the chemical process in the bulk of the specimen local internal stresses arise which alter in their turn the rate constants for the elementary reactions. At higher temperatures the relaxation of stresses can be significantly faster than the chemical reaction of the substance, while in accelerated tests of the polymeric material this phenomenon could not be observed at all.

The solution of the problem of the possible occurrence of such phenomena along the extrapolation section is determined by the state of research into the problem of the influence of mechanical stresses on the kinetics of the ageing of polymeric materials, which is an important fundamental problem in chemical kinetics, as well as the question of the mechanism of the generation of internal stresses and the kinetics of their alteration in the course of the ageing of the polymeric material. Whereas relatively much attention has been devoted to the first problem at the present time[33], particularly in connection with the use of polymeric materials under load, only few studies have been undertaken on the second problem, despite its undoubted importance[34].

As a second example, complicating the influence of physical kinetics on the solution of the problem of the prediction of the useful lifetime of a polymeric material, one may examine the physical disorientation of the amorphous component of the half-crystallised polymer. Under operating conditions, the physical disorientation of the polymer filament proceeds at a negligibly low rate. Nevertheless it has been shown[35,36] that the chemical ageing process in such a highly oriented filament frequently differs qualitatively from the ageing of an isotropic non-oriented polymer. At the same time any

increase of temperature leads not only to the acceleration of the chemical process but also to the acceleration of the physical disorientation of the amorphous phase of the polymer and hence to a real qualitative change in the chemical mechanism of the ageing process. Thus, in accelerated tests processes whose role under operating conditions is negligible can begin to affect the ageing process.

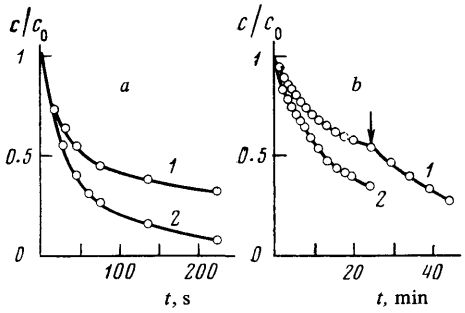



**Figure 5.** Kinetics of the photochemical oxidation of naphthacene (0.025%) (*a*) and anthracene (0.5%) (*b*) in polystyrene films in air under irradiation: 1) without intermediate heating; 2) with intermediate 15 min heating at 90 °C at instants indicated by circles. Intermediate heating was also applied at the instant designated by an arrow[37].

Fig.5 presents another example of a process in the polymer matrix in which the chemical transformation of the substance and the physical rearrangement of the local environment of the reactive species compete. The photochemical reaction of hydrocarbons with condensed nuclei within a vitreous polymer is inhibited sharply under conditions where the concentration of the reactants has altered relatively little—the so-called kinetic process arrest has occurred[37,38]. The reason for this phenomenon is that the photochemical process is significantly faster than the physical rearrangement of the local environment of the reacting species, the molecules existing under conditions favourable for the chemical reaction are rapidly consumed, and the photochemical process is retarded, since only molecules existing under conditions unfavourable for reaction remain in the specimen.

Under the real conditions of the employment of a polymeric material in which hydrocarbons with condensed nuclei have been introduced as special additives, for example, in photochromic materials or carriers of information, photochemically active light is less intense than in accelerated tests and does not operate all the time, while the physical rearrangement of the matrix proceeds continuously at the same rate and does not therefore limit the photochemical decomposition of the additive. As a result, no kinetic arrest is observed and the process is significantly faster than might have been expected on the basis of a formal inspection of the results of accelerated tests[39].

Thus at least three causes of the "change of the mechanism" of the ageing of polymeric materials when the ageing conditions are altered can be specified.

1. Competition between different elementary reactions constituting the ageing mechanism. A change in conditions can direct the ageing process via another pathway.

2. The influence of the physical structure of the polymer matrix on the elementary step of the chemical reaction. A change in this structure under different conditions can alter significantly the ratio of the rate constants for the elementary reactions.

3. Competition between the chemical transformation of the polymeric material and the physical change in its temperature.

In all the instances examined there is no actual change in the process mechanism and there is only change in its rate-limiting stage. Fundamental study of the ageing of the material might in fact render greatest assistance in the observation of such possible changes in the rate-limiting change of the process.

Even qualitative ideas about the process mechanism can sometimes help to solve the problem of a well-founded prediction. There is a possibility of a multistage extrapolation of different elementary processes proceeding independently in the polymer. For example, in the thermal oxidation of a stabilised polymer one must take into account not only the consumption of the thermal stabiliser in the oxidation reaction, but also its consumption as a result of its diffusion from the polymer. On the other hand, the rate of diffusion can be measured by independent methods. On comparing subsequently the results of the extrapolation of both rates to the operating conditions, it is possible to discover the process which determines the rate of consumption of the stabiliser. If there is a kinetic arrest in the photochemical process, the rates of rearrangement of the local environment of the species can also be obtained by an independent method[40] and hence one can estimate the role of this process under operating conditions.

Thus even a qualitative understanding of the principal stages of the ageing of a polymeric material significantly facilitates the solution of the problem of the prediction of the useful lifetime of the material.

## 2. Prediction of the Useful Lifetime of Polymeric Materials as a Kinetic Study

The possibility of "a change in the mechanism" of the ageing of a polymeric material makes the solution of the problem of the prediction of its useful lifetime extremely indefinite. One can actually claim that there should exist instances where a well-founded prediction is altogether impossible and in many cases the degree of risk cannot apparently be characterised quantitatively; nevertheless, since the problem of the determination of the useful lifetime exists, one must seek ways for its optimum solution.

The problem reduces in fact to the observation of a possible "change in the mechanism" of ageing already during tests on the polymeric material. A trivial procedure consists in carrying out tests under conditions as close as possible to the operating conditions. Naturally, all the possibilities of this procedure must be utilised but the method does not solve the problem of prediction, but merely reduces it to the modelling of the operating conditions in the laboratory, which is not always possible, as mentioned previously.

There remains a single method—the derivation of maximum possible information from the results of tests on the polymeric material.

A characteristic feature of the polymeric material is that in the latter there are virtually no abrupt changes in structure, characteristic of, for example, phase transitions in low-molecular-weight compounds. This gives rise to the hope that the "change in the mechanism" of the ageing of a polymeric material does not take place abruptly either. However, the "change in mechanism" can occur not only by virtue of a change in external conditions, but also as the ageing process proceeds and at different stages of the transformation of the material the process will be limited by different

steps. Therefore the study of the kinetics of the change in the properties of the polymeric material up to advanced stages of the transformation yields much more information than a simple determination of the useful lifetime of the material, since it can reveal signs of a "change in the ageing mechanism" under conditions where this change still does not determine the useful lifetime of the material.

We shall consider the advantages of the kinetic approach in relation to this formal example. Suppose that the kinetics of the change in the properties of the material can be described by the sum of two exponential functions:

$$U/U_0 = \gamma e^{-k_1 t} + (1-\gamma) e^{-k_2 t}, \qquad (12)$$

the constants $k_1$ and $k_2$ varying with temperature in accordance with the Arrhenius law with different activation energies, while the coefficient $\gamma$ is independent of temperature. For example, $\gamma$ can characterise the fraction of one of the components of a composite material when the quantitative characteristic of the property of the material $U$ is a result of the additive effect of the two components which exhibit different thermal stabilities.

If the useful lifetime of such a material is characterised in terms of the time taken for the decrease of $U$ to a certain limite $U^0$, then evidently the effect of activation energy for the useful lifetime measured in this way will depend on $U^0$ (Fig.6). Fig.6*a* shows how the effective activation energy $E_{eff}$ for the useful lifetime of such a material varies for different values of $U^0$. Evidently, depending on the ratio of the activation energies and the pre-exponential factors for the constants $k_1$ and $k_2$, the quantity $E_{eff}$ can both increase and decrease as $U^0$ varies.

Fig.6*b* shows how accurately the Arrhenius law holds under these conditions. The difference between the calculated activation energies $\delta E$ at 360 and 400 K was adopted as a measure of its validity. Evidently, appreciable deviations from the Arrhenius law, for example $\delta E = 1$ kcal, are observed over relatively narrow ranges of values of $U^0$, while for the remaining values of $U^0$ the Arrhenius law holds satisfactorily and it is virtually impossible to observe the complex variation of the useful lifetime of the material as a function of temperature.

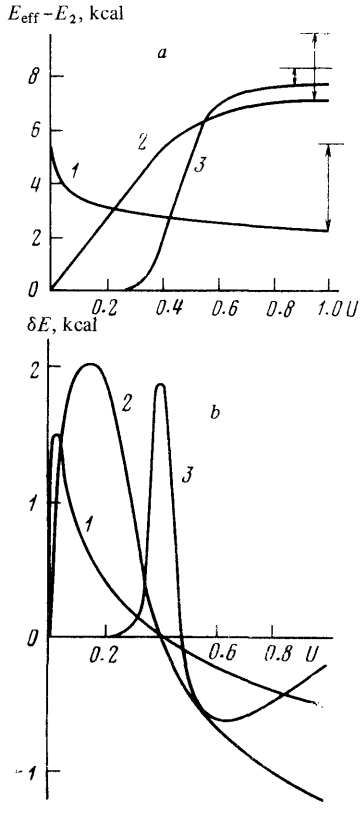



**Figure 6.** *a*) Variation of the effective activation energy for the attainment of a quantity $U^0$, the kinetics of the variation of which are described by Eqn.(13); temperature range 360–400 K; *b*) deviation from the Arrhenius law. The calculation was performed for $E_1 - E_2 = 5.5$ (curve *1*), 9.6 (curve *2*), and 8.3 kcal mol$^{-1}$ (curve *3*) and $\chi = (k_1/k_2)\exp(E_1 - E_2)/400R = 10^3$ (curve *1*) and $10^6$ (curves *2* and *3*). The values of the quantity $E_1 - E_2$ are indicated by arrows next to the corresponding curves.

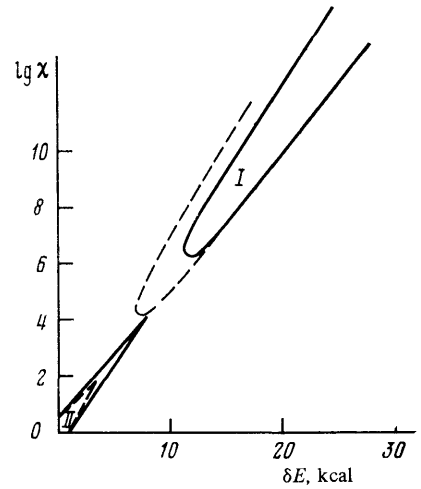



**Figure 7.** Conditions governing the observation of deviations from the Arrhenius law for process kinetics described by Eqn.(13); $\chi = (k_1/k_2)\exp(E_1 - E_2)/400R$; I is the region where $\delta E > 0.8$ kcal mol$^{-1}$ in the measurement of the initial rates; II is the region where deviations from the exponential law governing the variation of $U$ are not observed. The continuous lines correspond to the temperature range 360–400 K and the dashed lines correspond to 320–400 K; $\gamma = 0.5$.

If only the initial rates of change of $U$ are measured, then deviations from the Arrhenius law can be observed only when the rates of change of both terms in Eqn.(12) are comparable. Fig.7 presents the results of the numerical calculations, showing that, even over a fairly wide temperature range of the measurements in the coordinate plane $\chi - \delta E$, where $\chi = (k_1/k_2)e^{\delta E/RT}$ and $\delta E = E_1 - E_2$, there is only a small region in which it is possible to observe deviations from the Arrhenius law (the shaded region in Fig.7, where $\delta E > 1$ kcal mol$^{-1}$ in the temperature range 360–400 K). If the process kinetics are followed up to a degree of conversion of only 75%, then $\gamma = 0.5$ and, for a 5% accuracy of the

measurement, deviations from the exponential law governing the variation of $U$ (and hence the deviations from the Arrhenius law) can be observed for almost all ratios of the constants. An exception is a small region of low values of $\delta E$ and $\chi$.

The above example shows how much more information can be derived from kinetic measurements compared with "point" measurements of the useful lifetime of the material. Therefore prediction of the useful lifetime of materials should be based on extrapolation of the parameters which describe the kinetics of the variation of the properties of the material under different conditions and not on extrapolation of the dependence of the useful lifetime of the material on the conditions of the tests. It is desirable to have data not only for the small "permissible" changes in the properties of the material but also for the kinetics of the variation of these properties up to stages which are as advanced as possible.

It may be that such measurements of the rate of change of the properties of a polymer subject to mechanical forces would make it possible to observe the features of the influence of mechanical stresses on the ageing of the polymer for small loads and of the oxidation process for high loads and there would be no question of a change in the process mechanism. It may also be that a study of, for example, the kinetics of the consumption of the thermal stabiliser in the high-temperature oxidation of polyethylene would make it possible to observe the diffusional component of its consumption and to make a correct prediction of the thermal stability of polyethylene under operating conditions.

## V. ALLOWANCE FOR THE VARIABILITY OF OPERATING CONDITIONS

### 1. Formulation of the Problem

Extrapolation of the results of severe, forced, and accelerated tests on the polymeric material to mild conditions under which it is used, i.e. transition from high to low temperatures and from high irradiation intensities or high loads to low values of these parameters—all these constitute only one aspect of the problem of the prediction of the useful lifetime of the polymeric material. It is no less difficult to take into account the fact that during use the material usually exists under continuously varying conditions, and not simply the change in the operating conditions compared with accelerated tests. Day changes to night, a moist period is replaced by a dry one, intensive use is followed by a period of storage, etc.

Usually in accelerated tests the material is tested under conditions which remain constant throughout the test. By carrying out such tests under various conditions, it is possible to obtain a mathematical description of the process under any conditions. If the operating conditions are within the range of the conditions of the tests, then the problem of prediction is apparently solved, since, in contrast to extrapolation, interpolation can be carried out with any degree of accuracy and it is only necessary to have a sufficient amount of experimental data. However, this is true only if one predicts the variation of the properties of the material under constant conditions, as in the tests. On the other hand, the problem of the way in which the properties of the material should vary under variable conditions remains in essence open.

We shall assume that the kinetics of the variation of a property of the material $Y$ are described by the following equation under constant conditions:

$$Y = k_1(1 - e^{-k_2 t}), \tag{13}$$

where $k_1$ and $k_2$ are effective constants, which vary with temperature in accordance with the Arrhenius equation. We shall examine the problem of the description of this process under variable conditions—at a variable temperature. There is hardly any point in substituting the time-variable values of $k_1$ and $k_2$ in Eqn.(14), since a decrease of temperature, resulting in a decrease of $k_2$, usually does not lead to the same decrease in $Y$ and conversely the process kinetics at high temperatures are usually independent of the time during which the specimen remains at a low temperature, where $k_2$ is close to zero. It is not always possible to substitute an average temperature in Eqn.(13). For example, the question arises of an average temperature which must be invoked if it is necessary to discover how the properties of the polymeric material vary when the latter cools or conversely when it is heated at a constant rate.

The problem is complicated still further when the polymeric material is acted upon by several factors. For example[25], in the initial stage of the photochemical oxidation of polyolefins the kinetics of the variation of their mechanical properties are determined by the parameter

$$\Omega = kI^2 t^3, \tag{14}$$

where $k$ is a constant which varies with temperature in accordance with the Arrhenius law and $I$ is a quantity proportional to the intensity of the light incident on the specimen.

It is also not permissible to substitute the average temperature and light intensity in Eqn.(14), since one must take into account, on the one hand, the fact that the temperature and light intensity are usually strongly correlated and, on the other hand, it is evident that one can neglect the time intervals during which the light intensity and temperature are sufficiently small.

Some workers[6] suggest that Eqns.(13) and (14) be differentiated with respect to time and that time be subsequently eliminated from the resulting expression or that one seek from the very beginning a mathematical description of the process not in the form of a dependence of the rate of change of the properties on time but in the form of the dependence of the rate of the process on the current properties of the material, i.e. that one carry out transformations of the type

$$\begin{gathered}\mathbf{Y} = \mathrm{f}(\mathbf{X}, t),\ \mathbf{X} = \text{const},\ t = \varphi(\mathbf{X}, t);\\ \frac{\partial \mathbf{Y}}{\partial t} = \frac{\partial \mathrm{f}}{\partial t}(\mathbf{X}, \varphi(\mathbf{X}, \mathbf{Y})) = \psi(\mathbf{X}, \mathbf{Y}).\end{gathered} \tag{15}$$

We may replace the partial derivative by the total derivative, and obtain

$$\frac{\mathrm{d}\mathbf{Y}}{\mathrm{d}t} = \psi(\mathbf{X}(t), \mathbf{Y}). \tag{16}$$

Thus, instead of Eqns.(14) and (15), we obtain the expressions

$$\frac{\mathrm{d}Y}{\mathrm{d}t} = k_2(k_1 - Y), \tag{17}$$

$$\frac{\mathrm{d}\Omega}{\mathrm{d}t} = 3(kI^2\Omega^2)^{1/3}. \tag{18}$$

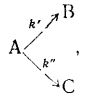
On solving similar equations under variable conditions, it is possible to find a mathematical description of the variation of the properties $Y$ and $\Omega$ with time:

$$Y = \mathrm{e}^{-\int_0^\tau k_2\,\mathrm{d}t} \int_0^\tau k_1 k_2\, \mathrm{e}^{\int_0^\tau k_2\,\mathrm{d}t}\,\mathrm{d}t, \tag{19}$$

$$\Omega = \left(\int_0^\tau (kI^2)^{1/3}\,\mathrm{d}t\right)^3. \tag{20}$$

In the general case, in the description of the kinetics of the variation of the properties of the polymeric material, one cannot arbitrarily apply any one of the procedures described. In essence, in this case one is faced with the same problem as the cybernetic problem of the prediction of the behaviour of a "black box", which cannot be solved when data for its behaviour are available only under constant conditions. Thus Eqn.(14) discussed above can describe the kinetics of the accumulation of the reaction product formed via two different kinetic mechanisms.

1. The accumulation of the reaction product of one of two parallel reactions:




(21)

$$[B] = \frac{k'}{k' + k''}[A]_0(1 - e^{-(k'+k'')t}). \quad (22)$$

The kinetic mechanism (22) can model the ageing process initiated by radicals formed in the decomposition of some initiator. In this case $C$ are the products of the interaction of active centres within the cage which do not alter the properties of the material.

2. The accumulation of an unstable product in a zero-order reaction:

$$\xrightarrow{w_i} B \xrightarrow{k_d}, \quad (23)$$

$$[B] = \frac{w_i}{k_d}(1 - e^{-k_d t}). \quad (24)$$

The kinetic mechanism (23) can also model the ageing process, B being an unstable reaction product capable of reverting to the initial state.

Thus two qualitatively different kinetic mechanisms lead to formally the same description of the process kinetics under constant conditions. However, under variable conditions, mechanisms (21) and (23) lead to different solutions. We obtain from Eqn.(21)

$$[B] = \int_0^\tau k'[A]_0 e^{-\int_0^t (k'+k'')dt} dt, \quad (25)$$

or, on converting to the notation defined by Eqn.(14), we have

$$[B] = \int_0^\tau k_1 k_2 e^{-\int_0^t k_2 dt} dt. \quad (26)$$

We obtain from Eqn.(23)

$$[B] = e^{-\int_0^\tau k_d dt} \int_0^\tau w_i e^{\int_0^t k_d dt} dt = e^{-\int_0^\tau k_2 dt} \int_0^\tau k_1 k_2 e^{\int_0^t k_2 dt} dt. \quad (27)$$

Evidently there is also a qualitative difference in the kinetics of the variation of the quantity [B] under variable conditions. According to mechanism (21), the concentration of B under any conditions can only increase irreversibly. On the other hand, the establishment of a steady-state concentration of B under constant conditions according to Eqn.(23) is a consequence of the equality of the rates of formation and consumption of this product, so that under variable conditions the concentration of B can both increase and decrease.

The above considerations can be illustrated by the following numerical calculations. Suppose that the specimen is heated instantaneously to a temperature $T_0$ and is then slowly cooled, so that the temperature varies in accordance with the equation

$$T = T_0/(1 + \gamma t). \quad (28)$$

If the variation of temperature is governed by this law, Eqn.(26) and (27) can be solved by the method of quadratures, provided that the rate constants $k_1$ and $k_2$ vary with temperature in accordance with the Arrhenius law.

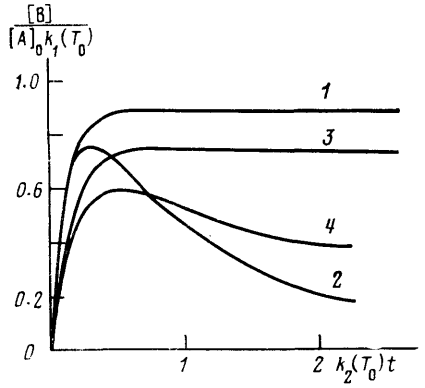



**Figure 8.** Kinetics of the variation of the concentration of B with temperature according to Eqn.(28) and subject to the kinetic mechanisms (21) (curves *1* and *3*) and (23) (curves *2* and *4*). Calculation performed for $k_2RT_0/E_2\gamma = 4$ (curves *1* and *2*) and 10 $s^{-1}$ (curves *3* and *4*) and for $E_1 = E_2$ ($E' = 2E''$, $E_w = 2E_d$).

In this case, when the specimen is cooled fairly slowly, i.e. when

$$\gamma < \frac{k_2(T_0)RT_0}{E_2},$$

the kinetic curve for the variation of [B], described by Eqn.(27), passes through a maximum, which can be in no way expected when the final product B accumulates in accordance with mechanism (21). Fig.8 presents a numerical example of the calculation of the kinetic curves from Eqn.(26) and (27). Thus, for the extrapolation of the results of laboratory tests to variable operating conditions, the results of tests under constant conditions are insufficient and one must develop special programs whereby the kinetics of the ageing of the material under variable conditions can be described.

## 2. The Superposition Principle or the Principle of the Summation Defects

In the practical determination of the useful lifetime of the polymeric material one can frequently employ the so-called superposition principle or the principle of the summation of defects arising in the course of ageing[12,14]. This principle is based on the hypothesis that the breakdown of the material under any conditions takes place irreversibly and independently of the previous history of the specimen. Depending on the conditions, only the efficiency of the decomposition of the material changes. In conformity with

this principle, it is assumed[8] that for each material there should exist a single-valued function, the damage to the material $\omega$, which increases monotonically in the course of ageing. Here the increment of $\omega$ is proportional to the efficiency of the ageing of the material under the given conditions and to the time during which the material has been exposed to these conditions:

$$\Delta\omega = \psi(\mathbf{X})\Delta t. \tag{29}$$

Accordingly, under variable conditions the quantity $\omega$ is obtained as a result of the summation of different influences $\mathbf{X}_i$:

$$\omega = \Sigma\psi(\mathbf{X}_i)\Delta t_i. \tag{30}$$

Since a change in the properties of the material represents the results of the independent action of different conditions, it is postulated that ageing proceeds with the same efficiency regardless of the sequences in which the material is acted upon by different influences.

Eqn.(30) can be formulated in a differential form for a continuous variation of operating conditions:

$$\frac{d\omega}{dt} = \psi(\mathbf{X}) \tag{31}$$

and can be extended to the case of multidimensional operating conditions for the materials:

$$\frac{d\mathbf{Y}}{dt} = \varphi(\mathbf{Y})\psi(\mathbf{X}). \tag{32}$$

The necessary feature for the applicability of the superposition principle follows from Eqn.(32), namely the presence of a single unambiguous trajectory along which the properties of the material vary under any operating conditions. Indeed it follows from Eqn.(32) that

$$\frac{\partial y_i}{\partial y_j} = \frac{\varphi_i(\mathbf{Y})}{\varphi_j(\mathbf{Y})}, \tag{33}$$

where subscripts $i$ and $j$ denote components of the vectors $\mathbf{Y}$ and $\phi(\mathbf{Y})$.

The material is finally damaged when the vector $\mathbf{Y}$ reaches a certain value $\mathbf{Y}_z$† i.e.

$$\int_{Y_0}^{Y_z} \frac{d\mathbf{Y}}{\varphi(\mathbf{Y})} = \int_0^{\tau} \psi(\mathbf{X})\,dt, \tag{34}$$

where the upper integration limit $\tau$ represents the useful lifetime of the material.

If the operating conditions are constant, then

$$\tau = \tau_0 = \frac{1}{\psi(\mathbf{X})} \int_{Y_0}^{Y_z} \frac{d\mathbf{Y}}{\varphi(\mathbf{Y})}; \tag{35}$$

We shall now express $\psi(\mathbf{X})$ in terms of $\tau_0$ and shall substitute the resulting expression in Eqn.(24) assuming that the argument $\mathbf{X}$ varies with time. After cancelling out, we arrive at the familiar Bailey equation:

$$\int_0^{\tau} \frac{dt}{\tau_0(\mathbf{X}(t))} = 1. \tag{36}$$

Thus Bailey's equation can be used only in processes whose mechanism can also be described in the form of Eqn.(32). In particular, it follows from Eqn.(32) that the superposition principle is applicable to all processes whose kinetics are determined by a single elementary step. However, it ceases to be applicable even for the description of the kinetics of the accumulation of reaction products in a process consisting of two parallel reactions (21), since the partial derivative is a function of temperature; for example, it follows from Eqn.(21) that

$$\frac{\partial[\mathrm{B}]}{\partial[\mathrm{A}]} = \frac{k'}{k'+k''}.$$

The superposition principle is frequently applicable when one considers the ageing of materials used under critical conditions where a small change in the properties of the material lead to the breakdown of the latter. In this case there is a sharp diminution of the requirement for a single-valued trajectory along which the properties of the material vary. In fact, the current properties of the material in the equation describing the variation of its properties can be replaced by the initial values. The superposition principle can then be always employed when the rate of ageing is determined by the initial properties of the material.

Thus it is applicable to a process consisting of two parallel reactions. Indeed the rate of accumulation is determined solely by the initial concentration of substance A:

$$\frac{d[\mathrm{B}]}{dt} = k'[\mathrm{A}]_0.$$

Nevertheless one cannot describe with its aid the accumulation of the product of a consecutive reaction or any reaction which takes place in accordance with the autocatalytic law.

In particular, it is generally accepted[3,41] that the ageing of any polymeric materials is a chain process with degenerate branching. The kinetics of this process are clearly autocatalytic. The ratio of the rates of accumulation of the branching product, usually formed in the chain propagation reaction, and the products formed in the chain initiation steps—the effective chain length—usually depends strongly on the process conditions, which leads to failure of Eqn.(33) and hence to a non-single-valued trajectory for the variation of the properties of the material. Bailey's equation is therefore usually inapplicable to branched-chain processes.

In connection with the relatively wide use of prediction methods based on the superposition principle, the problem of discovering the features of the process mechanism and the characteristics of variable operating conditions, for which the application of this principle can lead to significant errors, has now become particularly acute. It is especially important to be able to observe these features in the course of accelerated tests on materials, the mechanism of the ageing of which is virtually unknown.

### 3. Optimisation of the Superposition Principle

The superposition principle is a special case of a more general procedure examined above (Section V, 1), which consists in the measurement of the rate of change of the properties of the material under different conditions. Eqn.(32) is a special case of Eqn.(16). However, as shown above, the formal application of even the general Eqn.(16) could not always permit the prediction of the variation of the properties of the material under variable conditions.

Nevertheless, it is evident that, when the instantaneous rates of change of all the properties of the material have been measured for all possible combination of these properties,

$$w(\mathbf{Y}, \mathbf{X}) = \left(\frac{\partial Y}{\partial t}\right)_{\substack{\mathbf{Y}=\mathbf{Y}_0 \\ t=0}}, \tag{37}$$

†In the general case $\mathbf{Y}_z$ represents a characteristic of the limit of the region of the operational suitability of the material and not a point.

then the kinetics of the variation of the properties of this material under any conditions can be described by solving the differential equation

$$\frac{d\mathbf{Y}}{dt} = w[\mathbf{Y}, \mathbf{X}(t)]. \quad (38)$$

In essence, Eqns.(16) and (38) have the same significance; the only different feature of Eqn.(38) is that the vector **Y**, which it includes, must characterise all the properties of the material determining the kinetics of the ageing process and not only some of them (for example, those important for practical purposes). On the other hand, in the derivation of Eqn.(16) the partial derivative was replaced by the total derivative without any justification. A rigorous application of Eqn.(16) or (38) implies that Eqn.(16) represents a system of differential equations taking into account not only the kinetics of the accumulation of B and Ω in the examples discussed above, but also the kinetics of the consumption of the initial substance and the kinetics of the variation of the concentration of the chain branching product.

As a result we obtain a system of equations identical to a system of chemical kinetic equations. Instead of Eqn.(17), we obtain from the kinetic scheme (21)

$$\frac{d[B]}{dt} = k_1 k_2 \frac{[A]}{[A_0]}, \qquad \frac{d[A]}{dt} = -k_2[A], \quad (39)$$

and, instead of Eqn.(18), we have for the photochemical oxidation of polyolefins

$$\frac{d\Omega}{dt} = I[P], \qquad \frac{d[P]}{dt} = \sqrt{kI[P]}, \quad (40)$$

where [P] is the concentration of the branching product.

In the general case the systems of equations obtained can differ in form from systems of chemical kinetic equations, but their structure must reflect, as it were, the logic of the process occurring and must take into account the variation of all the properties of the material which actually determine the process kinetics.

Unfortunately data on the variation of all the necessary properties of the material cannot always be obtained. For example, in a chain process it is sometimes difficult to follow the kinetics of the variation of the concentration of the branching product, since its nature may be unknown and, when it is known, its concentration may be below the sensitivity of the analysis.

At the present time there is no rigorous method whereby one can discover the properties whose variation is the primary cause of the variation of the remaining properties of the material. Nor is it clear whether it is at all possible to devise such a general method or whether the solution of this problem will remain for a long time in the hands of highly qualified specialists greatly experienced in the study of polymeric materials of a given class. The methods for the estimation of the significance of various factors employing factorial analysis[42] are as yet hardly applicable in this field, since they do not make it possible to elucidate the causal relation between different external factors and the properties of the material. On the other hand, the derivation of equations analogous to Eqn.(38), which take into account the variation of all the properties of the material and all the factors associated with the external conditions, is too laborious.

Thus the generalised superposition principle shows that there exists a possibility, in principle, of solving the problem of extrapolating the results of laboratory tests to any variable operating conditions. However, this principle shows how difficult it is to solve this problem without using information about the mechanism of the ageing of the material.

From the experimental point of view, it follows from the superposition principle that the measurement of the rate of change of the properties of material aged in different ways is most significant for prediction, and not the kinetics of the change of these properties under some conditions even if they do model fairly satisfactorily the operating conditions of the material from some particular point of view.

## VI. INITIAL DATA FOR THE FORMULATION OF THE PROBLEM OF THE PREDICTION OF THE USEFUL LIFETIME

The accuracy of the determination of the useful lifetime of a material is usually not restricted solely by the difficulty of extrapolation of the results of tests to arbitrarily complex operating conditions. It is to a large extent determined by the accuracy with which the operating conditions of the material are known beforehand and how well the requirements which must be met by the material in a particular article have been formulated.

These at first sight simple tasks are in practice fairly complex, because one must understand which operating conditions in fact determine the kinetics of the ageing of the polymeric material and hence one can recognise how accurately these conditions are known beforehand only by having some idea about the factors which determine the variation of the properties of the material in the course of ageing. Only if it is known how the different properties of the material are inter-related can one formulate exactly the requirements which must be met by the stability of the article made of the given material.

Several examples illustrating this essential feature of the problem are discussed below.

### 1. Relation Between the Kinetics of the Variation of Practically Important Properties of a Polymeric Material and the Mechanism of the Ageing Process

Any polymeric material is characterised by a set of properties. From the practical point of view, the "external" properties of the material are important: its strength, lustre, permeability to moisture or gas, transparency, dielectric losses, combustibility, etc. These are not usually properties which determine the kinetics of the ageing of the material; their variation is a consequence of the physicochemical processes occurring in the material during its ageing. In order to record the kinetics of the ageing of the material and to elucidate the mechanism of this process, one usually measures quite different properties of the material: the variation of its composition, the formation and destruction of active species in it, the characteristics of the mobility of individual fragments of macromolecules, etc. Nevertheless, the useful lifetime of the material is determined by the kinetics of the variation of properties of practical importance. In this connection, the solution of the problem of the interrelation of different properties of the polymeric material is of primary importance in predicting its useful lifetime.

Relatively numerous studies have now been carried out in which the kinetics of the variation of properties of practical importance have been followed in the course of the ageing of many polymers[43]. The relation between certain properties of polymeric materials is known. For example, the dielectric losses are correlated with the number of polar groups in the polymer[44] and the elasticity of the polymer is related to the fraction and chemical structure of its amorphous phase[45].

However, unfortunately there have been virtually no studies on the quantitative relation between the kinetics of the variation of the properties of a polymeric material and the mechanism of its ageing. Such a relation has been established in a study[46] dealing with the kinetics of the variation of properties in the ageing of polyolefins. It has been shown that the variation of any physicomechanical characteristics of polyolefins is determined not only by the amount of light incident on the specimen but depends significantly also on the intensity of the photochemically active light. The higher the intensity of the light, the less effective (per quantum of light incident on the specimen) is the variation of the properties.

This result can be readily explained on the basis of data for the mechanism of the oxidation of the given polymer. The oxidation of polyolefins is a chain reaction with degenerate light-induced branching by the reaction products and with quadratic chain termination[45]. This process also proceeds more effectively at lower light intensities, since one of the principal branching products, the hydroperoxide, accumulates in the reaction which involves the propagation of a chain whose length, under conditions of quadratic chain termination, is known to be greater the lower the rate of initiation, i.e. the lower the intensity of the light.

An ambiguous quantitative relation has been established[46] between the kinetics of the variation of the mechanical properties of polypropylene and the total number of oxidation chain initiation steps occurring in the polymer throughout the process (the yield of radicals). This relation is purely empirical; neither its cause nor its characteristics are known exactly. Furthermore, it has actually been shown that the form of the relations between the mechanical characteristics and the yield of radicals is different for polymer specimens prepared in different ways. Nevertheless, the unambiguous nature of the relation already established made it possible to calculate the rate of change of mechanical properties under any conditions. The details of this study have been described by Slobodetskaya[36].

### 2. The Characteristics of Operating Conditions

The accuracy of the determination of the useful lifetime is governed to a large extent by the accuracy with which the operating conditions of a given material in the article have been specified. It is sometimes believed that the determination of the characteristics of the operating conditions is a simple task, attention being concentrated only on the difficulty of determination of internal stresses in the specimen or of the dynamics of the loads applied to it.

However, in practice there are too many factors acting on the polymer in the course of its use, so that even factorial design methods cannot always reveal which are the most significant. For example, only special studies revealed that the rate of atmospheric corrosion of metals is to a large extent determined by the concentration of sulphur compounds in the atmosphere[47].

Frequently only an understanding of the fundamental features of the mechanism of the ageing of the polymeric material makes it possible to discover the principal factors which determine its useful lifetime. It is then sometimes found that the determination of the characteristics of the operating conditions becomes an independent scientific task. For example, at the beginning of the 1970s the principal features of the mechanism of the ageing of polyolefins under atmospheric conditions became clear and all the necessary rate constants for the elementary reactions were found. However, even this could not lead to the solution of the problem of the determination of the useful lifetime of these polymers in different climatic zones. The point is that the ageing of polyolefins in open air takes place mainly as a result of the absorption of light by aliphatic hydroperoxides. On the other hand, aliphatic hydroperoxides absorb light only in the extreme ultraviolet region of the solar spectrum and the intensity of this component depends greatly on the angle of the sun above the horizon and on the latitude of the given site. Regular direct measurements of the ultraviolet component of the solar spectrum have not been made anywhere in the world except at the meteorological station of Moscow University. The problem of predicting the useful lifetime of polyolefins under real conditions therefore remained unsolved until a special study was carried out[48] showing how the average characteristics of the intensity and spectral composition of solar radiation in the ultraviolet can be calculated theoretically from data on the cloud cover and the geographical position of the given location. As a result, a special computer program was developed whereby it was possible to calculate the rate of change of the properties of olefins at any point on earth from data supplied by ordinary meteorological stations[49].

A completely different problem arose when prediction of the useful lifetime of polyolefins used to insulate pipes, already mentioned above, was considered[27]. The failure of the initial prediction is associated in this instance with the fact that no account was taken of the contact between the polymer and the environment.

An unusual characteristic of the operating conditions of a polymer may prove to be the size of the given article. Many polymeric materials are used in a plasticised state. The increase in the size of the articles made from such a material leads to two opposed phenomena. On the one hand, intense stresses arise in large articles which reduces the useful life of the latter. On the other hand, the plasticiser diffuses less from a large article and its initial properties are retained for a longer time.

The prediction of the useful lifetime of the material in such an article is a fairly difficult problem and the question arises of the extrapolation of the results of laboratory tests not only to the normal characteristics of the operating conditions (temperature, humidity, stress) but also to parameters of the size of the specimen.

The aim of this Section was not to consider comprehensively the problem of the formulation of initial data required for the determination of the useful lifetime of a polymeric material; this is an independent and fairly complex problem. The examples quoted merely illustrate the importance of this problem, to which inadequate attention is being devoted.

## VII. KINETIC CLASSIFICATION OF AGEING MECHANISMS

The analysis described in previous sections shows that simplified approaches to prediction, which are suitable when the ageing of the polymeric material is determined by one elementary step, are usually inapplicable to the prediction of the variation of the properties of real materials, the mechanism of the ageing of which involves a complex set of different elementary processes.

Well-founded prediction must therefore be based, on the one hand, on the determination of the fundamental features of the possible mechanism of the ageing of the material, and, on the other hand, on the development of a series of type-specific methods of prediction suitable for the most common ageing mechanisms. Thus the prediction must be based on the classification of the possible mechanisms of the ageing of polymeric materials in terms of features essential for such prediction.

Unfortunately, at present it is impossible to point to any one study in which a sufficiently complete classification of the mechanisms of the ageing of polymeric materials has been given. Nevertheless, such a classification is being set up, albeit somewhat sporadically. Ageing processes are divided into classes based on different features: the chemical structure of the polymer, the ageing conditions, the physical and chemical nature of the processes predominating in the course of ageing, and the properties of the polymer which are of greatest practical importance. Examples of different processes associated with different methods of classification are presented in the Table.

Methods of classification of ageing processes.

| Feature on which classification is based | Examples of processes |
|---|---|
| Chemical nature of material | Ageing of polyolefins<br>Ageing of poly(vinyl chloride)<br>Ageing of polyamides<br>Ageing of natural rubbers and elastomers<br>Ageing of polyurethanes<br>Ageing of epoxy-compounds |
| Influences acting on materials | Oxidative degradation<br>Photochemical oxidation<br>Thermal degradation<br>Photolysis<br>Mechanical degradation<br>Chemical degradation<br>Radiation-induced degradation |
| Nature of physicochemical process | Radical transformations in polymer<br>Photochemical transformations<br>Structure formation in polymers<br>Crystallisation<br>Relaxation processes |
| Properties essential for practical purposes | Variation of mechanical properties<br>Variation of dielectric properties<br>Gas evolution<br>Cracking |

However, these are not the features which must underlie the classification of ageing processes necessary for the determination of the useful lifetime of the polymeric material. A kinetic classification of the mechanisms of the ageing processes is essential. The beginnings of such a classification already exist.

It is known that the ageing of a polymeric material is frequently not a simple irreversible reaction. In many instances there is a chain process and the prediction of the rate of change of the properties of the material decomposing via a chain mechanism requires, as we have seen in the previous Sections, a qualitatively different approach from that for a simple irreversible reaction. Furthermore the kinetics of the chain process in different polymeric materials and under different conditions can be also qualitatively different. Thus pure polyolefins and apparently many natural rubbers are oxidised via the mechanism involving a chain reaction with degenerate branching and quadratic termination[36,41].

The introduction of a thermal stabiliser into the olefin leads to the appearance in the kinetic process mechanism of what is in fact only one additional elementary reaction—the interaction of the thermal stabiliser and the peroxy-radical. However, the process kinetics do not change qualitatively, since chain termination becomes linear. The relatively slow change in the rate of accumulation of the hydroperoxide along a quadratic parabola in pure polyolefins is replaced in the thermally stabilised polyolefin by a characteristic relation with a so-called induction period. At the beginning of the process, during a prolonged time interval, the branching product (the hydroperoxide) hardly accumulates and then its concentration increases almost exponentially[50]. Despite the chemical similarity of both processes, they are very different kinetically.

An unbranched chain process has altogether different kinetic features. Under constant conditions, its rate is almost unaltered, but its dependence on temperature and the rate of initiation may be complex. The photochemical decomposition of many polymers occurring as a result of the absorption of light by the polymer molecule itself may serve as an example of processes of this kind.

Different kinds of photochemical processes can be treated in the same way. Together with processes proceeding as ordinary single-quantum reactions, two-quantum processes, which take place with the consecutive absorption of two light quanta, and even multiquantum chain processes, in which each chain propagation step requires the absorption of a new light quantum, are known. From the kinetic point of view, all these are qualitatively different.

Together with chemical changes, physical processes also take place in the course of ageing: crystallisation and recrystallisation as well as diffusion of different components of the polymeric material and the reaction products. Different kinds of stresses arise in the polymer and relax, and the polymer undergoes orientation or disorientation. The role of all these processes must be taken into account in classifying the possible kinetic features of ageing processes.

The ain of current studies on the ageing processes of polymeric materials is usually to demonstrate the existence and to determine the quantitative characteristics of individual elementary steps of the process; one may say that they are designed to discover sufficient evidence that the elementary steps do occur. On the other hand, for the prediction of the useful lifetime, it is necessary to have the characteristics of the ageing process of the polymeric material as a whole. Naturally these essential process characteristics consist of the characteristics of individual elementary steps. When the characteristics of all the elementary steps are known, the prediction of the useful lifetime of the material does not involve fundamental difficulties, as already stated. However, usually, particularly at the beginning of the study, such characteristics are not available and even the ageing mechanism is largely obscure. In this case on must solve the "converse" problem: it is necessary to discover the type of the mechanism of ageing from a set of certain features and then to seek on this basis the quantitative characteristics of the process necessary for the determination of the useful lifetime of the material.

We are thus faced, for example, with the problem of the features of experiments with the aid of which one can decide whether Bailey's equation for the determination of the useful lifetime of the material under variable conditions is applicable to the given material. Evidently the applicability or inapplicability of this equation is determined both by the mechanism of the ageing of the material and by the nature of the changes in its operating conditions. Under conditions which change little, the equation is always applicable, while in the case of an extensive variation of conditions it is not easy to decide whether the equation is applicable or not.

Thus the kinetic classification of ageing processes must be based not only on data for the mechanism of the ageing of the polymeric material but also on the basis of information concerning the operating conditions of the material in the given article. Unfortunately the solution of problems of this kind is only just beginning and the necessity for their solution

becomes apparent only when the use of traditional simplified methods leads to emergencies.

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Summarising what has been said above, one can formulate the tasks for fundamental research on the performance of which depends the successful prediction of the useful lifetime of polymeric materials.

Firstly, it is necessary to discover, classify, and estimate the distribution of typical mechanisms for the variation of the properties of polymers under different conditions. The determination of the qualitative features of a particular mechanism is of greater importance than the detemrination of the rate constants for elementary processes. This makes it possible to discover on the basis of laboratory tests the type of the mechanism for the decomposition of the material and hence one can devise both a mathematical description of the ageing process of the material and a programme of accelerated tests directed to the determination of its useful lifetime.

Secondly, fundamental research should indicate the conditions governing the variation of the process mechanism. This will make it possible to establish the possible limits of the correct extrapolation of data obtained in accelerated tests or under conditions more severe than the operating conditions.

Thirdly, fundamental research should reveal the complete set of the properties of the polymeric material which determine the kinetics of the variation of its practically important characteristics in the course of its use. Only if the set of such properties and the way in which they can be characterised quantitatively are known will it be possible to compare two materials or to specify the variation of the properties of the material during its use.

Fourthly, fundamental research should indicate which factors in the operating conditions of the polymer induce changes in its properties and which can be characterised quantitatively.

Fifthly and finally, it is necessary to develop methods for the investigation of complex non-linear systems whereby one can predict their behaviour on the basis of preliminary studies and qualitative data on the relation between their properties.

On this basis, one must set up a method for the development of an optimum programme of preliminary studies on the material. The first four tasks refer to the field of chemical physics and that part of it where the kinetics and mechanisms of chemical processes are studied. The fifth task can be assigned to the field of applied mathematics, on the border between computational mathematics or mathematical statistics and experimental design.

A characteristic feature of the problem of prediction is the necessity for its daily solution. It is continually faced by various organisations occupied with problems of the application of polymeric materials. It arises when it is necessary to determine the guaranteed useful lifetime of articles produced by the new technology, when it is necessary to select the material for an article still only in the planning stage, and finally when one must devise a plan using a material already manufactured in various articles and in various branches of industry.

Errors in the solution of problems of this kind can cost the National Economy many millions of roubles and they can vitiate the efforts of many teams, directed towards the development of new articles and materials. Therefore the time available for the solution of the problem of prediction is usually dictated by practical considerations and the solution must be achieved regardless of the level, which, for example, studies on the mechanism for the variation of the properties of the given material have reached at the instant of the formulation of the given task.

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