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The Combustion of Polymers and the Mechanism of Action of Fire-proofing Agents

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The sequence of stages involved in the combustion of polymers—ignition, flame propagation, and burn-out—has been examined. The limits of existence of the flame and the role of radiation in combustion processes have been discussed. The influence of halogen- and phosphorus-containing fire-proofing agents on the combustion processes has been analysed. The promising possibilities provided by micro-encapsulated fire-proofing agents have been demonstrated.
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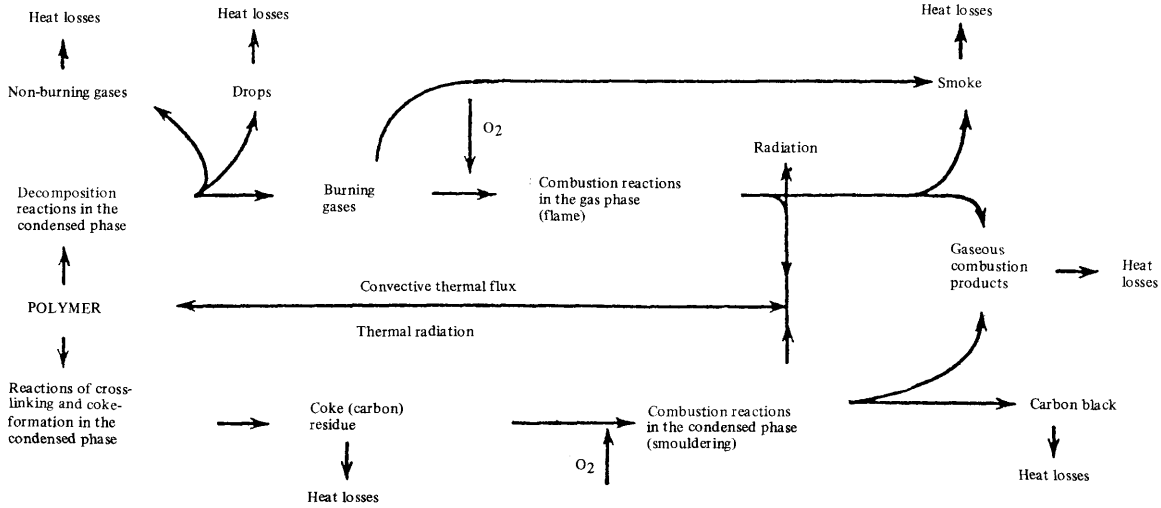
I. INTRODUCTION

Polymers are finding increasing application in various branches of the national economy, but in a number of fields the increase in their use is being held back because of the increased fire hazard associated with materials based on them. This applies particularly to polymers in building, transport, the electrotechnical industry, and other fields. Thus the problem of decreasing the combustibility of polymers and the development of non-combustible materials based on them is one of the most important tasks in polymer chemistry.

Most work aimed at lowering the combustibility of polymeric materials has been and is being carried out on the basis of an empirical search for fire-proofing additives. In recent years, under the direction and with the active participation of Academician N.S.Enikolopov, fundamental studies have begun and are being successfully continued in the Soviet Union in the field of the combustion of polymers and the mechanism of the action of inhibitors. The results of these studies make it possible to formulate the principal ways to reduce the combustibility of polymers and to create non-combustible materials based on them.

The sequence of phenomena in the combustion of polymers can be represented by a scheme which shows that the combustion of polymers is a complex multi-stage process which maintains itself and is controlled by mass and heat transfer[1-4]. The products of the transformation and gasification of polymers are various hydrocarbons[1], so that the diffusion combustion of polymers is largely analogous to the combustion of gaseous and liquid hydrocarbons.

The combustion of polymers is a process that develops with time. Five basic stages in the development of this process can be distinguished: ignition, flame propagation, combustion itself, smoke formation, and collapse of the flame[5]. It is possible to distinguish provisionally five spatial zones in the combustion of polymers: a polymer heating zone, a zone



of chemical transformations in the condensed phase, a zone under the flame, the flame itself, and a zone of reaction products and oxidant[1].

From the above qualitative scheme for the combustion of polymers, it is possible to reach preliminary conclusions about the paths leading to a lowering of the combustibility of polymeric materials. These are primarily an increase in the heat of gasification L, a decrease in the supply of heat to the polymer by increasing the heat losses or by decreasing the heat of combustion Q or by lowering the temperature of the flame by diluting it with non-combustible thermal degradation products[1,3]. It is usually assumed that the formation of a carbonised residue insulates the polymer from heating by the flame[4]. Smoke formation indicates incomplete combustion of the fuel and a decrease in the heat of combustion, and also makes it possible to reach qualitative conclusions about the degree of combustibility of polymers[6,7]. The chemistry of the processes taking place in a polymer gas flame is extremely complex, and has still been insufficiently studied. This question has been dealt with in a number of recent publications[1,8].

The mechanism of the influence of inhibitors on the various stages of the combustion of polymers has not yet been finally resolved. Generally speaking, only qualitative schemes for the action of fire-proofing agents have been published. In this connection, the study of the regular features of the combustion process, and the influence of fire-proofing agents and gas-phase inhibitors on this process and on reactions in diffusion flames in general, is of considerable scientific and practical interest. The aim of the present review is to examine work published up to the present on this problem, and to summarise the results obtained.

II. PROCESSES INVOLVED IN THE IGNITION OF POLYMERIC MATERIALS

The development of theories of flame production and ignition began with the thermal theory of explosion developed by Frank-Kamenetskii[9]. Because of the variety of polymeric materials and the conditions of their application, it is possible in practice to have ignition processes of different types, which do not fit into the framework of a single sufficiently simple theory. The ignition process is often determined by an induction period, during which the surface layer of a substance is heated to a temperature determined by the conditions of stationary combustion, with simultaneous initiation of the combustion of the gaseous products of the thermal decomposition of the polymers.

Since up to 80% of fires arise from low-calorie sources[1], it is appropriate to pay particular attention to the ignition of polymers by these sources. At the present time there are many theories of ignition to describe systems reacting in the condensed phase[10], but these theories cannot explain the observed practical dependence of the ignition process on the conditions of the surrounding gaseous medium and do not take account of the probability of endothermic reactions involving degradation of the polymer in the condensed phase. The models of ignition in the gas phase published up to the present are one-dimensional models in which the source of the oxidant is the surrounding gaseous medium, and the source of the fuel is the products of the gasification of the solid polymer.

The ignition process is initiated by the transfer to the polymer of the heat from the source, which may be an electric discharge, a heated body, a burner flame, etc. In contrast to theories of the ignition of a condensed fuel, in the case of the ignition of polymers it is necessary to bear in mind that: 1) when a thermal flux acts on a polymer, its gasification begins at a rate which depends on the thermal flux power[14]; 2) the temperature at the polymer surface (T_s) is determined by the thermal decomposition conditions[11]; 3) the products of the thermal decomposition of the polymer mix with the oxidant, forming a "previously mixed" mixture; 4) when the gaseous phase reaches critical conditions, ignition of the mixture takes place[12], that is exothermic oxidation reactions are initiated; 5) the relaxation time of the processes taking place in the gas phase τ'' is extremely short compared with τ', that is the relaxation time (the time of the change in the heat distribution in the condensed phase): $\tau'/\tau'' \cong 10^4$;[13] 6) the time of ignition delay, that is the attainment of conditions in which ignition has taken place in the gas phase and the polymer specimen is able to burn in the absence of the source, is determined by the time taken to create the necessary heated layer in the condensed phase[14].

When an ignition source acts on a polymer and the resulting mixture of oxidant and thermal decomposition products, the initiation of the wave of the chemical reaction in the gas phase takes place in accordance with the theory of the ignition of a hot mixture by heated surfaces[12] in the case where the removal of heat from the heated surface (q_*) reaches a critical value, defined by the relationship

$$q_*^2 = 2\lambda'' \frac{RT_s^2}{E} Qk_s e^{-E/RT_s}$$

where λ'' is the thermal conductivity of the gas phase, T_s the temperature of the heated surface, E the effective activation energy of the reactions, Q the heat of the reaction in the gas phase, and k_s the pre-exponential factor in the expression for the rate constant of the chemical reaction. The right-hand part of the expression for the thermal flux contains the kinetic characteristics of the chemical reaction taking place in the gas phase; the quantity q_* is determined by the conditions of heat exchange between the hot wall and the surrounding gas. As a rule, when polymers are ignited by heated solids, there is produced (as a result of natural convection) a stream of gas which flows over the heated surface. The field of flow of the gas stream is determined by the rate of flow and the shape and characteristic dimensions of the solid.

Table 1. Values of the parameters of the ignition process for a number of polymers*.

Polymer	T_i, °C	OI	T_{fp}, °C	T_{sfp}, °C
Polyformaldehyde	975	15.1	—	—
Polystyrene	1002	18.1	296	491
Polymethyl methacrylate	1050	17.5	280—300	450—462
Polyethylene	1055	17.4	341	349
Polyamide	1075	25	421	424
Polycarbonate	1176	28	—	—
Polyvinyl chloride	1260	45	391	454

*T_i values from Ref. 13; OI, T_{fp}, and T_{sfp} from Ref. 16.

Table 1 gives experimental data on the temperature of the surface of a heated solid $T_s = T_i$, where T_i is the temperature at which ignition of the degradation products of the

polymers takes place under conditions of identical heat exchange. For comparison, Table 1 gives the values of the oxygen index (OI), the temperature of flame production T_{fp}, and the temperature of spontaneous flame production T_{sfp}. The limiting characteristics, that is the OI values characterising the combustion process, change in the same sense as T_i, which determines the kinetics of the chemical reactions in the gas phase. The values of T_{fp} and T_{sfp} are apparently integral characteristics which include the thermophysical characteristics of the material, the geometric dimensions of the specimen and the compartment, the flow rate, etc., so that there is no direct correlation between these values and T_i.

Since in some branches of industry polymeric materials are used at increased concentrations of oxygen in the atmosphere, it is important to discuss the dependence of the ignition temperature on the oxygen concentration. The data in Fig. 1 [13,14] show that in mixtures enriched in fuel, the ignition temperature decreases with increase in the oxygen concentration; at an oxygen concentration in the mixture greater than the stoichiometric concentration, T_i is independent of the oxygen concentration ($[O_2]$).

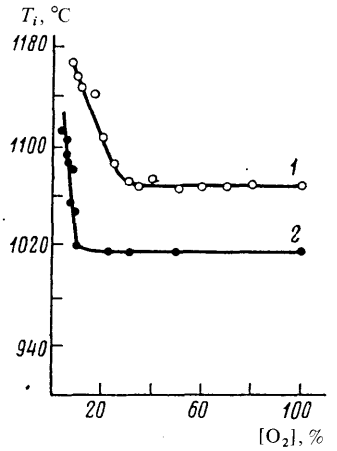


Figure 1. Dependence of the ignition temperature of the polymer on the oxygen concentration: *1*) polymethyl methacrylate[13,14]; *2*) polyoxymethylene[13].

Another characteristic determining the ignition of the material is τ_i, the time taken to create a heated layer, or the ignition delay time. With the assumption that the condensed phase is chemically inert[15], the necessary condition for ignition was found, namely that at the temperature of the polymer surface T_s the temperature gradient should not be greater than that given by the expression:

$$\frac{dT}{dx} = \frac{\rho' C_p''}{\lambda'} \frac{2RT_s^2}{E} \cdot \frac{u'}{e}$$

The ignition delay time[15] is given by

$$\tau_i = \frac{(T_s - T_0)\, EC_p'}{2RT_f^2 C_p''} \cdot \frac{\varkappa' e^2}{(u')^2}$$

where C_p'' and C_p' are the heat capacities of the gas and condensed phases respectively; ρ', λ', and $\varkappa'$ the density, thermal conductivity, and temperature conductivity of the condensed phase respectively; T_f the flame temperature, and T_0 the temperature of the polymer.

The heat required to create the heated layer is calculated using the equation

$$q_i = \frac{(T_s - T_0)^2 C_\rho'}{2RT_f^2 C_p''} \cdot \frac{\rho' e}{u'}$$

The regular features observed[15] cannot be transferred completely to the case of the combustion of a polymer, since, firstly, no account was taken of the endothermic reaction of thermal decomposition in the condensed phase and, secondly, during ignition the ignition source (for example a heated body) is present in the flame zone.

The conditions of existence of a stationary combustion front have been found[17] from an examination of the conditions of preservation of the mass fluxes of the oxidant and the fuel and the preservation of the thermal flux. The model examined includes a diffusion flame in the gas phase, the endothermic reactions of thermal decomposition in the condensed phase, and the production of the heated layer. Using these data[17], the present authors found that the ignition delay time is proportional to the temperature conductivity of the polymer $\tau_i \cong \text{const}\, \varkappa_1$, as in the expression obtained in Ref. 15. In addition, the data[17] were used to obtain the dependence of the ignition delay time on the oxygen concentration in the surrounding medium:

$$\ln \tau_i \simeq -2 \ln [O_2] + \text{const}$$

These conclusions are confirmed by experimental data on the dependence of the ignition delay time on the thermophysical characteristics of the polymers and the concentration of oxidant in the stream[13,18,19].

III. REGULAR FEATURES OF THE COMBUSTION OF POLYMERS

After stationary combustion conditions have been established close to the ignition source, depending on the conditions of the surrounding medium (the oxygen concentration, pressure, temperature, the velocity of the incoming flux), the thermophysical and thermochemical properties, the geometry of the specimen, etc., two cases may be realised. The flame either is localised or extends over the surface of the polymeric material, leading to an increase in the combustion region and the complete covering of the burning material by the flame. Since the consequences of a fire depend on the size of the combustion region, considerable attention has been paid in the literature to the separate topic of flame propagation[20-33].

Since an exact solution of the two-dimensional problem of flame propagation is not possible, a number of approximate models exist. The problem of the propagation of a flame over the surface of a polymeric material is usually divided into two cases. The first case corresponds to the propagation of the flame over the surface of a specimen of the polymeric material, the thickness of which is much greater than the thickness of the heated layer. These materials are usually classified as thermally thick fuels. The second case is when the thickness of the polymer specimen is comparable with the thickness of the heated layer; these are thermally thin materials. In addition, the exchange of heat between the flame and the polymer surface depends markedly on the direction on the rate of flow of oxidant relative to the rate of flame propagation[20,21].

Thus in De Ris' model[28], flame propagation over thermally thin and thermally thick fuels is examined with the assumption that for thermally thin fuels, heat transfer from the flame through the gas phase predominates, and that for thermally thick fuels, heat transfer takes place through the condensed and gas phases without allowance for the radiation from the flame. For thermally thin layers, the rate of propagation of the flame reaction is inversely proportional to the thickness of the layer of fuel

$$v = \frac{\sqrt{2\lambda'}}{\rho' C_p' \delta} \cdot \frac{T_f - T_s}{T_s - T_0}$$

where 2δ is the thickness of the layer of fuel. For thermally thick specimens, the following expression was obtained:

$$v = \frac{\rho'' C_p'' \lambda'' v_a}{\rho' C_p' \lambda'} \left(\frac{T_f - T_s}{T_s - T_0} \right)^2$$

where v_a is a parameter defining the rate of the incoming flow of oxidant.

Subsequently, models of flame propagation were proposed[29,32], in which the solutions of the equations of heat and mass cotransfer for the gas and condensed phases are examined, and subsequently combined; the dependence of the rate of flame propagation on the parameters of the medium and the characteristics of the polymer obtained in this way are given below. For thermally thin polymers:

$$v = \frac{\lambda' Q_c [O_2] f(p, [O_2])}{L \rho' C_p' (T_s - T_0)}$$

For thermally thick polymers:

$$v = \frac{[\lambda'' Q_c [O_2] f(p, [O_2])]^2}{\lambda' \rho' C_p' C_p''^2 (T_s - T_0)^2}$$

Here, Q_C is the heat of combustion of the polymer, p the pressure, and $[O_2]$ the oxygen concentration in the stream. These empirical relationships were confirmed experimentally[33]; the relationships obtained do not make it possible to obtain a physical picture of the process, however.

Solution of the equations of the thermal balance in the edge of a propagating flame (with the assumption that the transfer of heat from the flame to the polymer takes place as a result of convective heat exchange and radiation) [30,34] gave the following expressions for the rate of propagation of the flame over thermally thin fuels[34]:

$$v = \frac{1}{C_p' \rho'} \left(\frac{\lambda'}{\beta \delta} \right)^{1/2} \left[\frac{2(T_f - T_s) + Q_r}{T_s - T_0} \right]^{1/2}$$

and thermally thick fuels:

$$v = \frac{\alpha (T_f - T_s) + Q_r}{\beta \rho' [L + C_p' (T_s - T_0)]}$$

where α is the heat exchange coefficient, L the heat of gasification of the polymer, Q_r the thermal flux of radiation from the plane, and β a coefficient relating the rate of propagation of the flame to the rate of linear thermal decomposition in the nose of the flame. The expressions obtained contain in explicit form the dependence of the rate of propagation of the flame on the parameters of the external medium and the characteristics of the polymer. Although this model is approximate, it effectively describes the published experimental data.

To characterise the combustion of polymers under the conditions of the stationary (relative to the surface) diffusion edge of a flame (for example the combustion of polymers in a counter-current of gaseous oxidant, when a planar flame is created), Spalding introduced the parameter B (the Spalding number), which characterises the intensity of heat and mass exchange in the system and arises in the solution of the equations of heat and mass transfer at the phase boundary[1]. In the case of convective and molecular heat transfer, the parameter B is defined by the equation

$$B = \left\{ \frac{[O_2]}{r} \cdot Q_c - C_p'' (T_s - T_0) \right\} / L$$

where r is the stoichiometric coefficient of the oxidation reaction.

The rate of diffusion combustion ($\dot{m}$) in this case is given by the expression

$$\dot{m} \simeq \ln(1 + B)$$

The parameter B is an important characteristic for estimating the degree of combustibility of materials, and methods have been developed for calculating it for various materials by the treatment of experimental data on combustion for the configuration of a planar flame with sweeping by the oxidant from above downwards in a counter-current flame[35-38]. The values of the parameter B have been determined[37] for various polymers with sweeping of the flame by a stream of oxidant, and account has been taken of the contributions of various mechanisms of heat transfer to the quantity B for combustion in air and in oxygen (see Table 2).

Table 2. Values of the transfer parameter B for various polymers[37].

Polymer	Parameter B	
	in air	in oxygen
Polymethyl methacrylate	1.38	13.6
Nylon 6-6	1.2	14.0
Polyvinyl chloride	0.9	7.0
Polypropylene	0.67	11.6
Polystyrene	0.6	9.4
Low-density polyethylene	0.58	10.3
High-density polyethylene	0.55	9.7
Untrated cardboard	0.51	4.5
Cardboard containing 16% inhibitor	0.41	3.8
Cardboard containing 25% inhibitor	0.17	2.2
Maple	0.16	2.1

IV. LIMITS OF EXISTENCE OF A DIFFUSION FLAME FOR POLYMERS

A number of studies have shown that the products of the transformation of polymers and gaseous and liquid hydrocarbons in the zone under the flame are practically the same[1,40-44]. Collapse of the polymer flame takes place in the gas phase for the same reasons as in gaseous diffusion flames.

The foundation of the theory of diffusion combustion was laid by Burke and Schumann[12], who were the first to examine the problem of the combustion of coaxial parallel gaseous streams of fuel and oxidant. It is suggested that the chemical reaction in the flame takes place infinitely rapidly (much more rapidly than diffusion), and the form of the flame is determined by the rate of diffusion. In this model, the flame represents an infinitely thin surface with the oxidant on one side and the fuel on the other; the fluxes of oxidant and fuel reaching the flame are in the stoichiometric ratio. Hottel and Hawthorne[45] were the first to confirm experimentally the concept of the flame as a combustion surface with the fuel on one side and the oxidant on the

other. The calculated temperature of the flame in the reaction zone coincides with the adiabatic temperature of the previously mixed mixture of fuel and oxidant.

The conclusion that limits of a diffusion flame exist was first reached by Zel'dovich[46], who solved the one-dimensional problem of the combustion of complex streams of fuel and oxidant moving in opposite directions. With increase in the intensity of the fluxes of fuel and oxidant reaching the flame zone, the latter becomes broader (assuming a single-stage chemical reaction with a finite rate) and the temperature of the flame zone decreases to the minimum possible value (T_f^*):

$$T_f^* = T_f - 3RT_f/E$$

Collapse of the diffusion flame takes place because the chemical reaction, whose rate is exponentially dependent on temperature, is not fast enough to process the substance (fuel, oxidant) reaching the flame and cooling it, and this leads to further cooling and extinction of the flame. Collapse of a diffusion flame may take place similarly with a constant flux of oxidant and decrease in the concentration of oxygen in it. In practice, a diffusion flame is colder than predicted by theory[12], since an important role in the thermal balance is played by heat losses as a result of radiation into the surrounding medium, not usually taken into account in the theory.

In the analysis of the limiting conditions of a diffusion flame, it is convenient to use the parameter: $\mathrm{Dam} = \tau_d/\tau_c$, where Dam is the Damkohler number, τ_d the characteristic diffusion (convection) time, and τ_c the characteristic time of the chemical reaction[12].

A simplified form of the expression for the Damkohler number for a diffusion flame has been given[8]:

$$\mathrm{Dam} = \tau_d \cdot [\mathrm{F}] \cdot [\mathrm{O_2}] \cdot \frac{B}{[\mathrm{O_2}]} \cdot e^{-E/RT}$$

where τ_d has the same order of magnitude as the ratio l/w in the case of forced convection (l is the characteristic dimension, and w the rate of sweeping) or l^2/D in the case of diffusion; D the coefficient of mutual diffusion of the fuel and the oxidant; and [F] the concentration of the fuel. Collapse of the flame takes place at $\mathrm{Dam} = \mathrm{Dam}_{cr}$.

This expression, in particular, leads to a number of possible methods for inhibiting combustion by collapse of the flame[8]: 1) isolation of the fuel and a consequent decrease in its concentration in the flame; 2) decrease in the concentration of oxidant; 3) cooling of the condensed fuel and oxidant; 4) inhibition of homogeneous and heterogeneous reactions; and 5) increase in the rate of sweeping of the flame by the oxidant.

All these methods in the final analysis are directed towards a decrease in the flame temperature; instead of the condition for collapse of the flame $\mathrm{Dam} = \mathrm{Dam}_{cr}$, where Dam_{cr} is the value of the Damkohler number at the combustion limit, it is possible to consider the condition $T_f = (T_f)_{cr}$, where $(T_f)_{cr}$ is the flame temperature at the combustion limit[8]. On the basis of this equation, in the case where the value of $(T_f)_{cr}$ and the other necessary parameters of the system are known, it is possible to calculate the limiting conditions for the flame from the thermal balance equations[8].

The theory of the limits of a diffusion flame was subsequently developed[41-44] for polymers undergoing degradation and gasification without a residue, for the configuration of a planar diffusion flame. It was shown[47-51] that there is a relationship between the limiting conditions of combustion of polymeric materials and heat losses of different kinds. Equations were obtained, describing the influence on the critical conditions of convective and conductive heat losses and heat losses due to radiation, and the phenomenon of "break-through" of the fuel and oxidant through the flame zone as a result of incomplete combustion was calculated theoretically.

Another approach to the determination of the limiting conditions of the combustion of polymers, based on the thermal balance equation, is possible. Thus a model of the candle-like combustion of polymers has been examined[52] and made the basis of an experimental method for determining the limiting minimum oxygen concentration supporting candle-like combustion under conditions of natural convection.

V. HEAT TRANSFER BY RADIATION AND ITS INFLUENCE ON THE COMBUSTION OF POLYMERS

The role of radiation in diffusion combustion was first pointed out by Blinov and Khudyakov[53], who studied the dependence of the rate of combustion of the fuel under conditions of natural convection in air on the characteristic dimension of the combustion region. Beginning from a diameter of the combustion region of ~20 cm, the mechanism of the transfer of heat from the flame to the fuel changes from convective to radiative heat transfer[8]. Radiation from the flame on the one hand leads to increase in the supply of heat to the polymer and to an increase in the rate of combustion of the polymer and the rate of flame propagation, and on the other hand to a decrease in the flame temperature as a result of heat losses to the surrounding medium, a decrease in the width of the flame zone, and a decrease in the conductive and convective heat transfer.

Table 3. Various parameters* of the combustion of polymers in air under conditions of natural convection[55].

Polymer	T_f, K	$Q_{r.f}$, W cm^{-2}	Q_{con}, W cm^{-2}	$Q_{r.s}$, W cm^{-2}	$10^4 m$, g cm^{-2}s^{-1}	γ
Polyoxymethylene	1400	5	17.5	6.7	6.5	1.0
Polymethyl methacrylate	1400	20.1	7.62	10.7	10.5	0.85
Polyacrylonitrile	1350	28.7	6.84	18.2	8.5	0.87
Polystyrene	1190	37.2	2.9	14.6	14.5	0.57

Notation: $Q_{r.f}$ is the radiation heat flux to the polymer, Q_{con} is the convective heat flux from the flame to the polymer, $Q_{r.s}$ is the thermal radiation from the polymer surface, and γ is the degree of completeness of combustion.

There have been a number of studies of the influence of radiation on the combustion of polymers. Thus the influence of radiation on the combustion of polymethyl methacrylate in air has been analysed theoretically for the case of a one-dimensional flame of small dimensions[54]. An important role is played by radiation from the polymer surface, which is responsible for heat losses and heating of the flame. Completeness of combustion has practically no influence on the rate of burn-out of the polymer, since with decrease in the completeness of combustion there is a simultaneous decrease in the stoichiometric coefficient of the oxidation. The influence of the oxygen concentration in the stream on the intensity of the radiation from the flame has been analysed[56]. Table 3 shows that polystyrene, which is characterised by the lowest degree of completeness of combustion and the greatest radiation from the flame, burns

much more rapidly than other materials. For all polymers except polyoxymethylene, heat transfer to the polymer by radiation predominates; an important role in the combustion process is played by the re-emission of heat from the polymer surface. Because of the large heat losses due to radiation, the flame temperature for polystyrene has the lowest value.

Radiation from the surface also plays an important role in the case of polymers which burn with the formation of carbon. The temperatures in the condensed phase during the combustion of wood under the conditions of a planar counter-current flame have been measured[8]. A temperature of 1870 K is developed on the surface of hot wood with sweeping by an oxidant mixture containing 53% oxygen at a rate of 115 cm s^{-1}. Under these conditions, the chief mechanism of the losses, as in the combustion of coal, is thermal loss by radiation from the polymer surface, which leads to a decrease in the combustion rate. Usually, a temperature of 700–800 K is developed on the surface of wood under fire conditions, and the radiation power can reach 0.6 W cm^{-2}.

VI. MECHANISM OF THE INHIBITION OF DIFFUSION FLAMES BY HALOGEN-CONTAINING INHIBITORS

The diffusion flames of hydrocarbons are convenient model systems for the study of the mechanism of the inhibition of the combustion of polymers in the gas phase. Up to the present, however, there has been no unified view of the nature of the inhibition of diffusion flames of hydrocarbons by various chemical additives. It has been correctly pointed out[57] that the kinetics of a reaction in a flame of a mixture of gases and in a diffusion flame of the same gases are not necessarily identical. The basic difference in a diffusion flame is the existence of zones under the flame and after the flame. The zone under the flame is characterised by a relatively low concentration of oxygen (or its absence), a high concentration of fuel, a sufficiently high temperature, and a diffusion flux of free radicals from the flame. As a result, conditions are created in the region under the flame which are characteristic of gas mixtures rich in fuel, in which various processes are possible, leading to a change in the actual composition of the fuel and the inhibiting additive passing into the flame zone. When the oxidant contains additives, analogous processes of their transformation with the participation of radicals diffusing from the flame zone are possible. This may explain the difference, with respect to the reaction of inhibiting additives, in the behaviour of a diffusion flame and a previously mixed flame.

The action of halogen-containing additives can be considered in detail, since the amount of published data is greatest on this topic. There are two approaches to the explanation of the action of halogen-containing additives in flames—chemical and physical[58]. The chemical approach was first proposed by Fryburg[59]. A typical scheme for the chemical mechanism of inhibition[58] is given below for the addition of HBr to a previously mixed flame, where the radical H$^\cdot$ (O$^\cdot$, OH$^\cdot$) is replaced by the less active radical Br

$$\text{Fuel} + O_2 \rightarrow CO_2 + CO + H_2O + Q$$

Chain propagation and branching

$$OH^\cdot + CO \rightarrow CO_2 + H^\cdot$$
$$OH^\cdot + CH_4 \rightarrow H_2O + CH_3^\cdot$$
$$CH_3^\cdot + O_2 \rightarrow CH_2O + OH^\cdot$$
$$H^\cdot + O_2 \rightarrow OH^\cdot + O^\cdot$$

inhibition:

$$HBr + OH^\cdot \rightarrow H_2O + Br^\cdot$$
$$HBr + O^\cdot \rightarrow OH^\cdot + Br^\cdot$$
$$HBr + H^\cdot \rightarrow H_2^\cdot + Br^\cdot$$
$$HBr + CH_3^\cdot \rightarrow CH_4 + Br^\cdot$$

regeneration of inhibitor

$$Br^\cdot + CH_4 \rightarrow CH_3^\cdot + HBr$$

The efficiency of the action of halogen-containing inhibitors increases in the order F < Cl < Br < I.[58] This provides evidence in support of the chemical mechanism of inhibition. A large number of studies of mixed systems have shown that small quantities of added halogen-containing inhibitors (several mole %) decrease by a factor of ten or more the rate of propagation of the flame and have a marked influence on the limit of flame production[60].

The inhibiting action of halogen-containing compounds is generally related to the formation of the compounds HX (where X is a halogen atom) and their subsequent participation in inhibition according to the scheme given above. It has been pointed out[58], however, that the introduction of small quantities of a halogen-containing inhibitor into a polymer has little influence on the limiting conditions of combustion of the polymer (on the magnitude of the oxygen index OI). A decrease in the OI of the polymer by several units requires the introduction of up to 15–20 mass % of halogen-containing inhibitors[61].

Larsen and Ludwig[58] give data which support the so-called "physical" mechanism of inhibition, that is simple dilution of the hot system by the inhibitor and decrease in the temperature of the flame. Experiments to determine the minimum quantity of inhibitor which must be added to a previously mixed gaseous mixture of air and hydrocarbons to prevent flame propagation in this mixture showed that the concentration of halogen in the mixture is ~70 mass %, irrespective of the type of inhibitor and fuel. F, Cl, Br, and I were found to be equally effective in this comparison, in contrast to the usual method of comparison from the number of moles of inhibitor required for collapse of the flame. These results were confirmed for diffusion flames[62]. Petrella and Sellers[62] determined the concentration of inhibitor from the mass at the combustion limit; the measurements showed that, irrespective of the type of inhibitor (CF_2Cl_2, CF_2ClBr, CF_3Br) and fuel (C_3H_8, n-C_4H_{10}), the halogen concentration was 76.9 ± 2.2 mass %. This result indicates that in a comparison of the concentration of halogens in the flame from the mass, different halogens are almost equally effective, and that the mechanisms of the inhibition coincide to a large extent for mixed and diffusion flames.

The role of halogen-containing inhibitors introduced into a polymer reduces to increasing the mass of polymer which must be gasified to obtain the same fuel flux[58]. A number of studies have shown, however, that it is impossible to attribute the action of inhibitors entirely to an inert diluent, that is to a decrease in the adiabatic temperature of the flame. Thus the efficiency of many inhibitors depends on the total pressure in the system, although a number of exceptions to this rule have been found[63].

Studies of the action on the diffusion flames of halogen-containing inhibitors added to the gas phase are examined below. There are two familiar flame configurations in these experiments—with a parallel stream (Burke–Schumann burner) and with a counter-current of fuel and oxidant.

These configurations differ in the gas-dynamic parameters of the flame. Systems with a parallel stream are characterised by long residence times of the fuel in the zone below the flame, and lower convection in the direction of the flame; in these systems, however, the existence of partial mixing of the fuel with the oxidant at the point of origin of their boundary, that is at the cold wall, is not excluded. In counter-current systems, there is always convection in a direction perpendicular to the flame, which influences the concentration of the reagents and the distribution of temperature in the flame. When allowance is made for these possible differences, the conclusions from the experiments of the two types show fairly good agreement.

The inhibition of diffusion flames by halogen-containing compounds was first studied by Simmons and Wolfhard[64]. The critical concentration of CH_3Br added either with the fuel or with the oxidant, leading to collapse of the flame, was determined under conditions of a coaxial stream of fuel. The number of molecules of inhibitor at which collapse of the flame begins was ~20–30 times smaller when the inhibitor was added with the air than when it was added with the fuel. Studies of the influence of inhibitors on a flame with a coaxial configuration[65,66] confirmed the conclusion[64] that the efficiency of an inhibitor is greater when it is added with the air than when it is added with the fuel.

Friedman and Levy[67] give the dependence of the volume concentration of an inhibitor added with the fuel to a flame at the combustion limit on the rate of flow of the oxidant. In this comparison, the efficiency of the inhibitors decreased in the order $CF_3Br > CH_3Br > CCl_4 > CH_3Cl \gg N_2$. Comparison of the volume concentrations of combustion inhibitors should be supplemented by a comparison of the heat capacities of the fluxes of the gases introduced into the flame, as was done in Ref.58.

The influence of halogen-containing inhibitors on hydrocarbon and hydrogen flames has been studied spectrographically[68]. The introduction of the inhibitor decreases the luminescence of the OH and HCO radicals and increases the luminescence of the C_2 radical and carbon black, and the temperature of the flame decreases with increase in the concentration of the inhibitor.

A counter-current method has been used to compare the efficiency of different inhibitors[69] by determining the dependence of the concentration of inhibitor (mole %) in the air or the fuel required for collapse of the flame on the rate of sweeping of the flame. The fact that in this comparison CF_3Br is slightly more effective than CF_2ClBr, in spite of the higher heat capacity of the latter, indicates that the action of the inhibitors is chemical in character.

The influence of the inhibitor CF_3Br on the diffusion combustion of polymethyl methacrylate and its monomer under conditions of sweeping by a counter-current of the flame has been studied[44]. The inhibitor was introduced with the oxidant. The authors' suggestion that a better model of the diffusion flame of a polymer is obtained when the inhibitor is introduced with the oxidant appears doubtful, since in the combustion of a polymer, an inhibitor moving in the gas phase reacts with the gasified fuel in the zone under the flame. The introduction of CF_3Br into the flame with the oxidant led to the appearance of a luminous flame zone on the fuel side, and the colour of the flame changed from blue to bluish-green. This was due to the radiation of the carbon black and its precursor C_2 (emission in the green range, in accordance with Ref.64). An important result obtained by Seshadri and Williams[44] was the detection of the presence of oxygen at the boundary of a luminous flame. The introduction of an inhibitor into the flame increased the break-through of oxygen into the zone under the flame. The increase in carbon black formation, in the authors' opinion, is due either to the products of the transformation of the inhibitor or an increase in the concentration of oxygen under the flame. The increase in the break-through of oxygen through the flame may be due to a decrease in the temperature of the flame and the consequent decrease in the reaction rate in the flame zone. In the presence of CF_3Br, however, there is practically no decrease in temperature at the combustion limit.

The influence of C_2H_5Br, CCl_4, and $CHCl_3$ on a previously mixed and diffusion counter-current acetylene–air flame has been studied spectrographically[70]. The introduction of inhibitors into a diffusion flame increases in the spectrum the intensity of the emission bands of C_2 and decreases the intensity of the OH bands. The following mechanism has been proposed for the action of Cl-, Br-, and I-containing inhibitors[63]. The inhibitors introduced into the flame increase the formation of carbon black, on whose particles absorption of molecular oxygen can subsequently take place. In fact, this should decrease the concentration of oxygen in the flame and lead to a decrease in the reaction rate, and a decrease in the parameters of the limiting conditions. The authors cited[63] did not observe a change in the concentration of the OH radical in the flame in the presence of inhibitors, and this does not agree with published data. Moreover, their hypothesis that there is a decrease in the oxygen concentration in the flame is not confirmed experimentally and is contradicted directly by the data in Ref.44.

In a number of papers on the combustion of polymers (for example Refs.71–74) it is suggested that halogen-containing inhibitors "operate" in the gas phase in the same way as in gas flames. The action of halogens on combustion was attributed[73,75] to a decrease in the rate of the reactions and a decrease in the flame temperature. However, in Ref.76, which gives data on the combustion of mixtures of polymethyl methacrylate and chlorinated polyethylene, it was established that (in contrast to the gas phase, where Cl plays the role of inert diluent[58]) with the participation of Cl in the degradation processes in the condensed phase, carbon black, apparently formed by the removal of Cl in dehydrochlorination reactions, may accumulate on the polymer surface.

VII. PHOSPHORUS-CONTAINING COMBUSTION INHIBITORS

In addition to compounds of the halogens, compounds of P, B, N, and various metals of the type Sb and As are used as combustion inhibitors. Phosphorus compounds are more frequently used than the others; the possible mechanisms of their effect on the combustion of polymers, formulated in a review[77], are given below.

1. The effect on processes in the condensed phase, an increase in the non-burning residue, and a decrease in the quantity of fuel reaching the flame; the influence on the heterogeneous oxidation of coke.
2. The formation of a surface vitreous or viscous molten layer of high-boiling phosphoric acids, which prevent the processes of diffusion of the fuel and heat transfer.
3. Inhibition of gas-phase reactions.

The specific mechanism of the action of phosphorus-containing fire-proofing agents depends on the nature of the polymers. Thus when introduced into polyethylene, which does not form a residue on degradation, phosphorus compounds operate in the gas phase, but in epoxide compositions they operate by the first two of these mechanisms[78,79]. Some authors suggest that only phosphorus(V) compounds are active inhibitors[77], although other data[80] indicate that

amorphous red phosphorus is also a fire-proofing agent. The efficiency of inhibitors has been related to the way in which they are introduced into the polymer[81].

Analysis of published data shows that although the mechanism of the action of phosphorus-containing compounds in the condensed phase on the whole is not clear, its principal characteristics can be distinguished. Thus in cellulose materials in the presence of fire-proofing agents there is an increase in the yield of carbon as a result of dehydration[1]. Coke is formed according to the following hypothetical scheme:

$$(C_6H_{10}O_5)_x \rightarrow 6xC + 5xH_2O \quad .$$

A gas-phase mechanism of the action of phorphorus compounds in the combustion of polymers has been proposed[81,82]. Thus it has been suggested[82] that in the flame there is heterogeneous destruction of radicals on P_2O_5 particles formed during combustion; this lowers the reaction rate in the flame and leads to a decrease in its temperature.

On the whole, the question of the mechanisms of the action of phorphorus-containing inhibitors remains open. A number of effects have not yet been explained. For example, it has been shown[82] that in spite of the increase in the limiting characteristics of the combustion of polymethyl methacrylate inhibited by phorphorus compounds, the rate of burn-out of the material away from limiting conditions increases. None of the published mechanisms of the inhibition of the combustion of polymers can explain this fact. As noted in a number of publications, in the inhibition of the combustion of polymers by halogen- and phosphorus-containing compounds there is an increase in carbon black formation, smoke formation, or coke formation. Smoky sooty flames are highly luminous, and in them an important role is played by heat transfer by radiation[8]. In the combustion of carbon-forming polymers, a change from a gaseous diffusion flame to heterogeneous oxidation is possible; high temperatures are developed in the upper layer of the condensed phase of the burning polymer[37], and this may also lead to powerful radiation from the surface of the burning polymer.

VIII. CARBON BLACK FORMATION IN THE COMBUSTION OF POLYMERS

The mechanism of the formation of carbon black in diffusion flames is attracting the attention of many research workers[83-92]. A general scheme of the processes leading to the formation of carbon black in flames has been described[1]. Five stages in this process have been distinguished [90]: 1) the formation of nuclei of carbon black (the radicals $C_2^{\cdot}$ and $C_2H^{\cdot}$, polyaromatic radicals) as a result of thermal decomposition reactions in the zone under the flame with the participation of $H^{\cdot}$, $O^{\cdot}$, and $OH^{\cdot}$ radicals from the flame; 2) the formation of larger carbon black nuclei by a mechanism of the radical polymerisation and recombination type; 3) aggregation of the carbon black nuclei to form larger particles; 4) the development of surface growth of the carbon black particles; and 5) heterogeneous burn-out of the carbon black particles in the flame.

Stages 1 and 2 take place by a radical-chain mechanism. In stages 3 and 4, an important role is played by ionic processes[91]. There are other models of carbon black formation, but for these there is less experimental justification[93]. In the last stage, an important role is played by the degree of dispersion of the carbon black formed in the zone under the flame. The more finely dispersed the carbon black, the greater its surface area and the more actively it is oxidised in the flame.

The diffusion flames of methane and ethane at the combustion limit are blue, and carbon black is not formed; with increase in the oxygen concentration in the oxidant, there is an increase in the temperature of the flame, leading to an increase in the thermal decomposition of the fuel and carbon black formation[56]. This effect is also observed in the combustion of polymers, and the degree of completeness of the combustion of the fuel in the flame decreases with increase in the oxygen concentration[94]. The influence of various Br and Cl compounds on the formation of carbon black in diffusion flames of hydrocarbons has been studied[85,86]. Br compounds, when supplied to the diffusion flame with the fuel or with the oxidant, facilitate carbon black formation, but Cl compounds do not lead to any significant increase in carbon black formation. The apparent mechanism of this effect[85] is that the introduction of halogens into the flame lowers the concentration of $OH^{\cdot}$ radicals, and this in turn leads to an increase in the concentration of carbon black nuclei. The participation of the halogen-containing compounds in the stage involving the initiation of carbon black formation is not excluded. A similar effect is observed for various phosphorus compounds, for example $POCl_3$.[95]

IX. MICRO-ENCAPSULATED FIRE-PROOFING AGENTS

The most widely encountered fire-proofing agents, phosphorus- or halogen-containing compounds, are in most cases extremely toxic substances, which volatilise or seep from the material during its processing and use. It is for this reason that in recent years a new and promising method has been developed for introducing fire-proofing agents into polymeric materials in the form of micro-capsules. As a result of micro-encapsulation, the fine particles of liquid, solid, or gaseous fire-proofing agents introduced into a polymer covering are isolated from the surrounding medium, but retain the properties of combustion inhibitors.

By using an appropriate covering material, it is possible to stabilise and even improve the physicomechanical properties of a polymer composition, since the fire-proofing agent in this case simultaneously acts as a modifier. The use of micro-encapsulated fire-proofing agents (MFA) makes it possible to create materials with a working surface enriched in the fire-proofing agent, which increases its fire-resistance without a significant change in the physicomechanical properties. In addition, it becomes possible to use as fire-proofing agents substances which in non-encapsulated form are unsuitable for these purposes, for example water, and also substances with a low boiling point or a high toxicity. Moreover, it is possible to use in micro-encapsulated form fire-proofing agents which in the usual form are incompatible with the polymer matrix.

Micro-encapsulation methods are provisionally classified as chemical and physical. Phase separation methods are based on phase transformations in polymer solutions. The encapsulated substance is dispersed in the polymer solution, after which phase separation is initiated by changing the temperature, the pH of the medium, or the concentration of the components. As a result, the polymer separates from solution and is adsorbed on the particles of encapsulated substance, forming a micro-covering round them. Polymer encapsulation methods are based on the polymerisation or polycondensation of monomers or pre-polymers on the particles of the substance being encapsulated. Physical methods of micro-encapsulation use centrifuges, spray apparatus, etc. Phase separation and polymerisation methods are usually employed for the micro-encapsulation of fire-proofing agents.

The best known fire-proofing agent, containing phosphorus and halogen atoms, is tris(2,3-dibromopropyl) phosphate

$$(BrCH_2—\underset{\underset{Br}{|}}{CH}—CH_2—O—)_3—PO$$

which is a toxic liquid, obtained by brominating allyl alcohol and the subsequent reaction of the 2,3-dibromopropanol with $POCl_3$. This is one of the most widely encountered fire-proofing agents, used for polyalkenes, polyesters, polyurethanes, and polystyrene[96]; a number of methods for its micro-encapsulation have been patented[96–101]. The micro-capsules are obtained by aqueous-phase separation (covering material melamine–formaldehyde[97], urea–formaldehyde[97], polysiloxane[100], dextrin[96]) or by polymerisation, again in an aqueous medium (covering material polyurethane[98–100] or copolymers of ethylene with methacrylyl chloride[100] or of styrene with divinylbenzene[101]). Micro-capsules of tris-(2,3-dibromopropyl) phosphate have been used in fire-resistant carpets[97], paints, and polyurethane foam[102,103], and to impregnate fabrics to increase their fire resistance[100].

Methods for the micro-encapsulation of tris(2,3-dichloropropyl) phosphate[98,99], tris(1-chloro-3-bromoisopropyl) phosphate[101], and tris(1-bromo-3-chloroisopropyl) phosphate[101] have been patented. Methods have also been described for micro-encapsulating tricresyl phosphate, red phosphorus, ammonium phosphate, and other phosphorus-containing compounds. Tricresyl phosphate, an oily liquid, is micro-encapsulated in polyurethane[98,99,101], polymethyl methacrylate[101], and gelatin[104] coverings. Red phosphorus, which has found extensive application as a fire-retarding agent in many polymeric materials, has the disadvantage that at the temperatures of the processing of plastics in the presence of residual moisture it is capable of forming the toxic phosphine. The use of this fire-proofing agent in micro-encapsulated form prevents the formation of phosphine; a number of methods exist for the micro-encapsulation of red phosphorus[105–108].

When 10% of micro-encapsulated phosphorus is introduced into a polymer, the OI of the polyamide† increases by five units, and that of polyterephthalate, polypropylene, and polystyrene by approximately two units[106].

Of the halogen-containing fire-proofing agents, compounds containing chlorine and bromine have been most widely used. Bromine-containing compounds are generally more effective, although they are more toxic[96]. On the one hand, they bring about better initiation of the decomposition of the polymer chain, and on the other hand the hydrogen halides formed in the region before the flame are inert diluents and lower the flame temperature. Moreover, halogens can intensify carbon black formation in the flame. The following are now used in micro-encapsulated form: 1,1,2,2-tetrabromoethane[96,97,99] to obtain self-extinguishing polyurethane foam, 1,2-dibromoethane[96], and chloroalkanes containing 12–72% chlorine[102,110], which are used as fire-extinguishing additives to polyalkenes, polystyrene, natural rubbers, etc.

Micro-encapsulation makes it possible to use as fire-proofing agents substances which cannot be used at all in non-encapsulated form. These are primarily compounds with a low boiling point—Freons and low-boiling hydrocarbons. Methods have now been developed for micro-encapsulating tetrafluorodibromoethane, trichlorotrifluoroethane, and tetrachlorodifluoroethane, by aqueous-phase separation[103,111].

†The OI was determined by the published method[109].

The micro-encapsulation of water and aqueous solutions of fire-proofing agents is of particular interest. The method of phase separation in ternary water–oil–water emulsions and the method of interphase condensation and polymerisation are most frequently used for these purposes. Water is micro-encapsulated in the form of dilute solutions of salts such as sodium and potassium aluminates, borates, etc.[112–122] to obtain a stable double covering, or in the form of concentrated solutions of water-soluble fire-proofing agents (ammonium phosphates, chloride, and bromide). Micro-encapsulated water or its solutions are used as filler to decrease the combustibility of fibres, films, etc. The micro-capsules obtained, with diameter ~5 μm, contain 68 to 75 mass % water, and its concentration remains unchanged after treatment under normal conditions for one week or on heating to 100 °C for 1 h;[20] the external appearance of the micro-capsules also remains unchanged.

The conditions of the processing of polymeric compositions containing MFA (temperature, pressure) should be such that the covering of the micro-capsules does not break down in the process. The material of the covering should be inert with respect to the components of the polymer composition, or should react with the polymer or its components, leading to an increase in the strength of the coverings of the micro-capsules and in the strength of their attachment to the polymer.

The addition of polystyrene micro-capsules containing water or sodium metaphosphate has been recommended for the production of fire-resistant polyurethane[119]. Micro-encapsulated Freon-113 has been recommended for this purpose[123]. A method has been developed for obtaining fire-resistant cast polymer compositions containing an encapsulated inorganic filler and micro-capsules containing water[124]. These compositions are used to prepare plastics with a high mechanical strength, which can be used as constructional materials.

The migration of a fire-proofing agent from a polymer matrix has been studied in specimens containing dextrin micro-capsules with a 90% concentration of 1,1,2,2-tetrabromoethane[96]. When the specimens were kept at 100° for 20 h, the concentration of MFA decreased by 5%, and that of the non-encapsulated fire-proofing agent decreased by 99% (that is it volatilised practically completely).

The combustibility of an epoxide binding agent based on ED-20 epoxide resin, hardened by polyethylene polyamine and containing MFA, has been studied[125]. The fire-proofing agents used were tris(2,3-dibromopropyl) phosphate and Freon-$318B_2$ (polyvinyl alcohol covering). Micro-capsules with a diameter smaller than 200 μm were used; the mass fraction of the fire-proofing agent in the micro-capsules was 85–98%. Estimation of the fire-extinguishing action of the fire-proofing agents studied[125] showed that their efficiency decreases in the order: tris(2,3-dibromopropyl) phosphate > Freon-$318B_2$ > Freon-$114B_2$. The value OI = 40 is reached on the addition of 50, 60, or 70 mass % of these additives respectively, and the limiting oxygen concentration c_{lim} = 40% is reached for 65–74 mass % of the additive. The action of tris(2,3-dibromopropyl) phosphate as an MFA is shown in the condensed phase in the same way as in the case of the non-encapsulated fire-proofing agent[126].

To determine the mechanism of the action of MFA, the influence of the type of fire-proofing agent, the material of the covering, and the size of the micro-capsules on the temperature at which they open in pure form and in a polymer matrix was studied[127–129], and the efficiencies of the action of fire-proofing agents added to the polymer matrix in the free form and as micro-capsules were compared. The fire-proofing agents studied were carbon tetrachloride,

trichloroethyl phosphate, tris(2,3-dibromopropyl) phosphate, Freons 114-B_2 and 318-B_2, water, etc. Polyvinyl alcohol, gelatin, and polyurea were used as the covering of the micro-capsules, and an epoxide matrix was usually employed as the polymer matrix.

At a heating rate of 10 K s^{-1}, the temperature at which the micro-capsules open coincides with the temperature at which intensive decomposition of the material of the covering begins. Irrespective of the type of fire-proofing agent and the size of the micro-capsules, the temperatures at which they open for coverings of polyvinyl alcohol, polyurea, and gelatin are 210–240, 200, and 70–85° respectively[129], and the range of temperatures in which opening of 80% of the micro-capsules of fractions of the same size takes place does not exceed 10 K.

Fire-proofing agents can be divided into two classes, according to the type of opening of the micro-capsules. The first class consists of low-boiling liquids such as Freons, CCl_4, H_2O, etc., which are characterised by the fact that at the moment of opening, the liquid in the covering is greatly superheated, and when the opening temperature of the micro-capsules is reached they "explode", accompanied by a sharp decrease in the mass of the specimen; the second class consists of high-boiling liquids [fire-proofing agents such as tris(2,3-dibromopropyl) phosphate, trichloroethyl phosphate, etc.] or solid substances. A characteristic feature of MFA of the second class is that with increase in the temperature of the specimen, a smooth decrease in its mass takes place.

The mechanism of action of fire-proofing agents of the second class, added to a polymer matrix, will be considered first. When the material is heated, the micro-capsules open, and the fire-proofing agent is transferred to the polymer melt in the surface layer of the specimen. The presence of the fire-proofing agent in the thermal decomposition zone intensifies the process of carbon formation on the surface of the burning polymer, and this in turn leads to a change in the conditions of heat and mass exchange between the polymer surface and the flame. When the thermal balance is broken down, the combustion of the polymer stops. With increase in the concentration of the fire-proofing agent there is a smooth increase in the OI. The efficiency of MFA of this class is the same as that of the same fire-proofing agents in the free state. A significant increase in the OI values for these systems can be obtained only by adding large quantities of fire-proofing agent (up to 30–40 mass %) to the polymer composition. The addition of this quantity of fire-proofing agent in the free form is not possible, since it would seep from the polymer matrix; the use of MFA solves this problem.

For MFA of the first class, for which the opening of the covering of the micro-capsules is accompanied by critical phenomena ("micro-explosions"), the liquid at the moment of opening of the micro-capsules is highly superheated. The stable superheated state of the liquid inside the covering is apparently due to the absence of nuclei for vapour formation. When the decomposition temperature of the material of the covering is reached, defects are produced in it, leading to breakdown of the micro-capsule. The "micro-explosion" which accompanies the breakdown of the micro-capsule is stronger, the greater the superheating of the liquid. If the liquid in the capsule is not superheated and its boiling point is higher than the temperature at which the material of the covering begins to decompose, gradual decomposition of the latter takes place, with slow evaporation of the liquid.

Fig.2 shows that the addition of low concentrations of a low-boiling MFA to the polymer does not lead to a change in its decomposition temperature. A sharp decrease in the temperature at which decomposition starts takes place at a concentration of ~2 mass % MFA in the specimen. At this concentration, the so-called dispersion effect begins to appear. The size of the dispersed particles of the polymer and the rate of their removal depend on the strength of the "micro-explosion". In the "micro-explosion", the particles of the polymer are torn from the main mass and removed from the flame zone, without burning. For an increase in the MFA concentration by more than 3%, the temperature of the start of the decomposition remains constant and equal to the temperature at which the degradation of the covering of the micro-capsule begins, and is independent of the type of matrix[129].

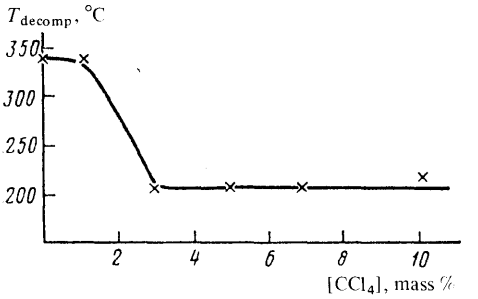


Figure 2. Influence of the concentration of micro-encapsulated fire-proofing agent (CCl_4) on the temperature of the start of the decomposition of the polymer matrix T_{decomp}.[129]

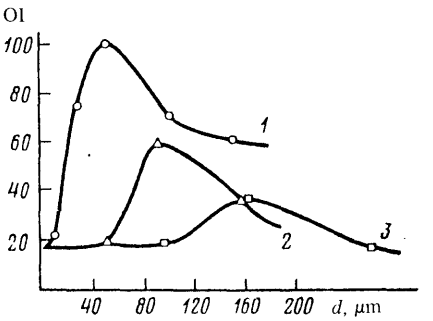


Figure 3. Influence of the size of the micro-capsules (d) and the type of MFA on the efficiency of the inhibition of the combustion of the epoxide composition ED-20 + polyethylenepolyamide: *1*) CCl_4, *2*) Freon-318B_2, *3*) Freon-114B_2, MFA concentration 7 mass %.[128]

A study of the combustibility of epoxide polymers in the presence of MFA using the published methods for determining the OI [109] and for estimating the minimum ignition

energy[130] showed that with increase in the percentage dispersion of the polymer there is an increase in its OI and ignition temperature, that is a decrease in the degree of combustibility. It was also established that the size of the micro-capsules has a significant influence on the efficiency of the decrease in the combustibility of the polymer in the presence of the MFA (Fig.3), and the maximum value of the OI is observed for different diameters of the micro-capsules, depending on the type of fire-proofing agent[127]. In spite of the complexity of the physical mechanism of their action, the use of fire-proofing agents in micro-encapsulated form provides an extremely effective method for reducing the combustibility of polymeric materials, and there is no doubt that the development of this field of the chemistry and technology of polmers is promising.

Thus an analysis of the data given in the present review indicates that in the development of methods for decreasing the combustibility of polymers it is necessary to pay particular attention to the structure of the polymer and the interaction of the inhibitor with the polymer and to take account of the reactions involved in the degradation in the condensed phase of the polymer and the inhibitor and the transformations in the gas phase.

Published data indicate the following principal ways of reducing the combustibility of polymers: 1) the addition of carbon-forming catalysts to the polymer. Depending on the type of polymer, these may be metal salts, phosphorus-containing compounds, halogen-containing compounds with antimony oxide, etc. When carbon is formed on the surface of a burning polymer, there is a deterioration in the heat and mass exchange between the flame and the polymer surface and a decrease in the flow of fuel into the flame zone, and the flame is extinguished; 2) the use of polymers combined with non-combustible materials with a high heat capacity and heat conductivity (filled, or in constructions); 3) the addition to the polymer of additives whose thermal decomposition adds inert diluents to the gas phase, decreasing the temperature of the flame and leading to its extinction; and 4) the addition to the polymer of additives whose decomposition leads to the appearance in the gas phase of active inhibitors of the gas-phase oxidation reactions (bromine-containing compounds are the most effective), again leading to collapse of the flame.

A new trend, namely the use of micro-encapsulated fire-proofing agents, is very interesting and promising. In this case, there are several simultaneous effects: dispersion of the polymer from the surface, leading to a decrease in the degree of combustion of the polymer (up to 50 mass % of the polymer is removed from the flame zone); physical dilution of the flame, leading to a decrease in its temperature; and chemical inhibition of the reactions in the flame in the case of the micro-encapsulation of effective gas-phase inhibitors.

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