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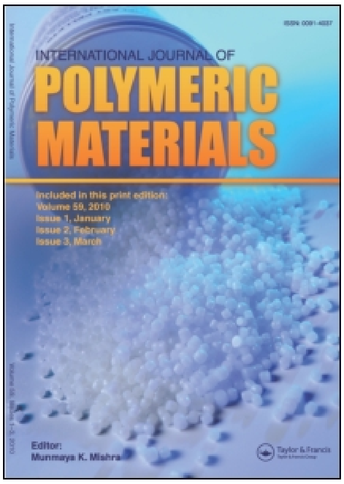

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Thermal Properties and Flammability of Chlorine-Containing Substances

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Thermal analysis of chlorine-containing substances obtained from C_{13}-C_{14} n-paraffins (chlorine content is 8–75 wt %) and olygoolefines with MM ≈ 10^4 (to 30 wt % Cl) is made. It is found that the kinetics and mechanism of the substances' gasification depend on their chlorine content and the nature of the original hydrocarbon. A method for the evaluation of flammability parameters of the substances used as flame retardants is developed. The increase of the limiting oxygen index of the substances with increasing chlorine content and hydrocarbon chain length may be described in accordance with the heat model as a result of the inert dilution of the gaseous fuel by the incombustible component. However, in addition to the change in the stoichiometric combustion coefficient, the additional heat losses related to the formation, evaporation and also the heating of HCl to flame temperature must be taken into account. It is found that the additional heat losses are equal to about 2.5 kJ per chlorine mass fraction.

KEY WORDS Flammability, chlorine.

INTRODUCTION

Chlorinated aliphatic hydrocarbons are often used as solvents, plastifiers, flame retardants, adhesive additives and other special components of polymeric materials. However, thermal properties and flammability of the substances have been insufficiently studied.[1,2]

The present work concerns the thermal analysis of chlorinated n-paraffins C_{13}-C_{24} and olygoolefins with MM ≈ 10^4, the consideration of the correlation between the thermal properties and flammability of the substances. A method for the evaluation of the limiting oxygen index (LOI) used as the main flammability parameter of chlorine-containing substances is developed. A heat model of the limits on the stable existance of a diffusion combustion of the fuel is used to analyze the experimental results.[3]

EXPERIMENTAL

Chlorine-containing substances used for the work are obtained by chlorination of individual C_{13}, C_{18}, C_{24} n-paraffins and also polyethylene or polypropylene waxes with molecular mass of ~10^4 in a melting state or CCL_4 solution according to well-known methods.[4] Chlorine gas is used as the chlorinating agent. The chlorine content is changed from 8 to 75 wt % into C_{13}-C_{24} chlorinated paraffins and to 30 wt % into chlorinated oligoolefins.

Thermal analysis of the substances is carried out under flowing nitrogen and by means of a derivatograph of the MOM system, Q-1500 D model (Hungary). TG, DTG and DTA curves are obtained at programmed heating at the rate of 5–6 degrees per min. The sample's weight is 100 mg. The kinetic parameters of the substance's gasification are calculated by the method proposed in reference 5.

LOI of chlorinated paraffins (CP) and oligoolefins are determined at standard conditions, using the following procedure. An asbestos paper strip (100 × 10 × 1 ÷ 2 mm) is saturated with the test substance in situ or in the form of the solution into ethyl ether. After the evaporation of the solvent or the removal of the surplus of CP viscous liquid the mass ratio of inert filler asbestos to the substance is found. The sample of asbestos strip saturated with substance is placed vertically on the special holder at the center of a glass chimney having a standard size (GOST 12.1.044–84). The test sample is ignited at the top by means of a burner. The ignition time is not more than 30 s.

The LOI value of chlorine-containing substances is obtained by means of the extrapolation of LOI dependence of a test sample on a saturation degree to zero content of asbestos filler or it is attributed to a limiting saturation of asbestos by the substance.

RESULTS AND DISCUSSIONS

Upon heating in air, the intensive weight losses of the initial $C_{13}H_{28}$ and $C_{24}H_{50}$ n-paraffins are revealed at temperature ranges of 112–165°C and 280–320°C, respectively. The effective activation energies of the gasification of n-paraffins equal 53 and 76 kJ/mole. These values correspond to evaporation enthalpy values for hydrocarbons in a liquid state (52.7 and 76.4 kJ/mole), which are calculated according to an empirical formula:

$$\Delta H_{\mathrm{evap.}} = 4.18\,(3.21\, n^{2/3} - 0.0193\, T + 2.92),\ \mathrm{kJ/mole}$$

where n is the number of carbon atoms in the molecule and T is the evaporation temperature in °K. The temperatures corresponding to maximum weight loss rates (143°C and 300°C) are used for the calculations of $\Delta H_{\mathrm{evap.}}$ values. In the case of initial olygoolefins it is found that the oxidation proceeds to their intensive volatilization. Upon heating of olygoolefins to the range of 205–330°C, the small weight losses (<10%) are accompanied by heat release. Endothermic degradation of polyethylene and polypropylene waxes takes place above 330°C with activation energies of 135 and 120 kJ/mole, respectively. The shape of the TG curves for chlorinated substances changes with increasing chlorine content and hydrocarbon chain length. The gasification of C_{13}CP with chlorine content to 30 wt % is a single-stage process. TG curves of C_{13}CP with chlorine content from 30 wt % to 70 wt % include a two-stage and a three-stage process for the substance with 75 wt % Cl. As an example, C_{13}CP with 16.4 wt % Cl is completely volatilized into the temperature range of 112–246°C. The kinetics of the sample weight losses are described by the equation of the zero-order reaction with an activation energy of 51 kJ/mole (the value is near to evaporation enthalpy of the initial paraffin). For C_{13}CP with 61.1% Cl it is found that dehydrochlorination and also the reactions of the molecule fragmentation may take place at the first stage of substance decomposition (140–360°C). $E^1_{\text{eff}} = 100$ kJ/mole. It is near to the E^1_{eff} value of poly(vinylchloride) dehydrochlorination for the random initiation case. The second stage of substance decomposition includes the reactions of cross-linking of molecular units and residue carbonization.

The two-stage decomposition process is revealed at lower chlorine content (~20% Cl) when the hydrocarbon chain length is increased from C_{13} to C_{24}.

The chlorinated olygoolefins are characterized by the three-stage decomposition process. The first and second stages of the decomposition involve dehydrochlorination reactions. Due to the presence of tertiary hydrogen atoms olygopropylene with 30% Cl eliminate HCl at a lower temperature (150°C) than the analogous olygoethylene (190°C).

Thus the thermal behavior of chlorinated substances depends on the chlorine content and the nature of the initial hydrocarbon.

Figure 1 shows the effect of these factors on the flammability of chlorine-containing substances. Figure 1 also shows the change of the substance's LOI relating to the LOI of the initial hydrocarbon (Δ LOI $= \text{LOI}_{\text{Cl}} - \text{LOI}_{\text{O}}$). A considerable change of LOI values of CP is only observed at sufficiently high chlorine content (more 40 wt %). The tendency of LOI to increase with increasing molecular chain length of hydrocarbon should be noted.

The regularities found in the change of LOI values of chlorinated substances are connected with the kinetics and the mechanism of their gasification at the condition of candlelike combustion. It may believed that flame combustion on the extinction limit is provided with volatile products of a low-temperature stage of the substance's gasification. The surface temperature under the leading flame edge is constant due to the high rate of formation of volatile decomposition products.

The heat model of diffusion flame limits based on the consideration of heat balance at the leading flame edge is used for the analysis of the experimental results obtained. It is shown that by using the simplified assumption, the LOI dependence for a filling composition on a filler content may be given in the following form (3):

$$\frac{100}{\text{LOI}} = \frac{\Delta H_c - L - C_T(T_f - T_s) - K\,q_f - 1,4r}{\text{C}\,(T_f - T_O)r}, \qquad (1)$$

where ΔH_c, L are the combustion heat and the gasification enthalpy of the composition, respectively; C, C_T are the heat capacities of the oxidant and gaseous fuel, respectively; T_f, T_s, T_O are the temperatures of flame, burning surface and surrounding, respectively; q_f is the heat absorbed by the filler; K is the mass ratio of filler to fuel; r is the mass stoichiometric coefficient of combustion.

The experimental results obtained for all test substances correspond with equa-

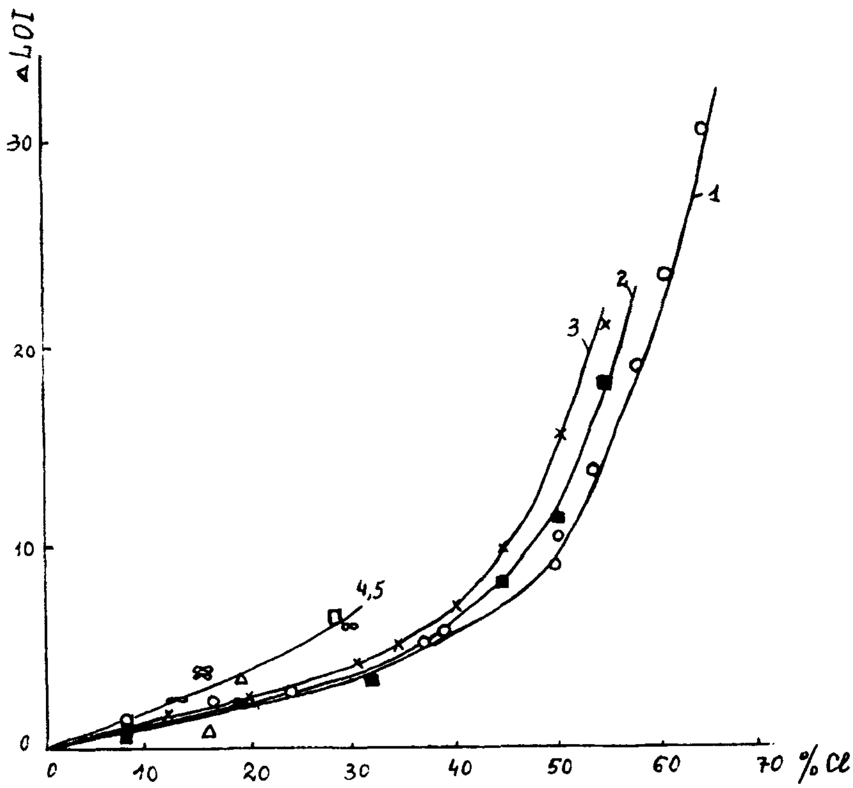

FIGURE 1 LOI dependence of chlorinated substances on chlorine content and the nature of the initial hydrocarbons: (○) 1-C_{13}, (■) 2-C_{18}, (×) 3-C_{24}, (△, □) 4-PE wax, (∞) 5-PP wax.

tion (1) into the coordinates of $1/Y - K$. Here Y is equal to LOI/100. The plot of $1/Y$ versus K yields a straight line from the slope of which r value is calculated:

$$tg\,\alpha = \frac{q_f}{C\,(T_f - T_O)r}. \tag{2}$$

The temperature into the leading flame edge at an extinction limit is taken to be the same for all substances: $T_f - T_O = 1000°C$. The heat absorbed by the filler depends on the surface temperature and a heat capacity of the filler: $q_f = C_f\,(T_s - T_O)$. At the calculation the next value is taken: $C_f = 0.84$ kJ/g, $C = 1.08$ kJ/g. T_s is taken as the temperature of the completion of the low temperature stage of the substance's gasification.

Table I gives experimental values of the stoichiometric combustion coefficient for chlorinated paraffins of the C_{24} series.

It should be noted that there exists the deflection of the experimental values of r from theoretical linear relationship: $r = r_O\,(1 - \gamma)$, where γ is the mass chlorine fraction and r_O is the stoichiometric combustion coefficient of the initial paraffin (Table I). This deflection may be related to the decrease in combustible volatile

TABLE I

Stoichiometric combustion coefficients of C_{24} chlorinated paraffins

Chlorine content, %	0	12	20	30	35	45	50
r_{exp}	2.6	2.1	1.9	1.7	1.5	1.2	1.0
γ	0	0.13	0.22	0.4	0.50	0.64	0.72
$r = r_O(1 - \gamma)$	—	2.3	2.0	1.6	1.3	0.9	0.7

yield with increasing chlorine content as the result of carbonization reactions taking place at the high temperature decomposition of the substances. A good coincidence of experimental and calculated data is observed when this effect is taken into account.

The results obtained in the work show that the LOI dependence on chlorine content into CP is related to the inert dilution effect of flame gases by nonflammable hydrogen chloride.

In this case the combustion of the chlorinated paraffin may be represented as one of the filling system in which a filler is HCl. Then the heat absorbed by this filler will consist of several components, i.e., of the heat losses on HCl formation, evaporation and heating to flame temperature.

According to equation (1) the dependence of $1/Y$ on K_{HCl} should be linear. Here K_{HCl} is the mass ratio of HCl to combustible volatile products. K_{HCl} values are calculated using TG data:

$K_{HCl} = 1/(\Delta m/m_{HCl} - 1)$, where Δm is weight loss at the first low-temperature stage of the substance decomposition and m_{Cl} is the chlorine content of the CP molecule.

From the slope of the plot of $1/Y$ versus K_{HCl} the additional heat losses are calculated. This value is 2.5 kJ per mass chlorine fraction.

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