

Ignition of Energetic Materials Under Conditions of Complex Heat Exchange

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The ignition of energetic materials under conditions of complex heat exchange between energy source and ignited substance surface is studied. Expressions are obtained for the parameters of the ignition of energetic materials by transient heat fluxes. The results are generalized, and an approximate method for calculating the ignition parameters using a "universal curve" is suggested. It is shown theoretically and supported by experimental results that when heat-flux intensity increases dramatically in time, ignition delay depends weakly on kinetic and thermal parameters. A particularly interesting case, the ignition of energetic materials exposed to two-phase flows (gas + solid particles), is considered in detail. It is shown that in this case the penetration of solid particles into the surface layer of the reacting substance is essential. An approximate mathematical model of ignition that includes this effect is proposed.

Nomenclature

a	= thermal diffusivity
b	= series coefficient
c	= specific heat
D	= sample diameter
$D(\theta, x)$	= auxiliary function
d	= particle diameter
E	= activation energy
k	= power coefficient
k_0	= pre-exponential factor
m	= number of series members
n	= index in thermal conductivity equation, 0, slab; 1, cylinder; 2, sphere
Q	= heat of reaction
Q_{ign}	= heat storage in the preheated layer
q	= average heat flux
$q_s(t)$	= heat flux to the surface
R	= universal gas constant
Re	= Reynolds number
r	= substance–shell interface coordinate
T	= temperature
T^*	= softening temperature
t	= time
t^*	= instant of reaching softening temperature
U	= gas velocity
X	= auxiliary function, $X_{\text{ign}}^* = X(t_{\text{ign}})$
x	= space coordinate
Y	= auxiliary function, $Y_{\text{ign}}^* = Y(X_{\text{ign}}^*)$
α_d	= heat transfer coefficient at the cylinder face subjected to two-phase flow
α_k	= heat transfer coefficient at the cylinder face subjected to pure gas flow
β	= volume concentration of particles in two-phase flow
β_w	= weight concentration of particles in two-phase flow
$\Gamma(n)$	= gamma function
θ	= dimensionless temperature
λ	= thermal conductivity

ν	= kinematic viscosity
σ	= RT_{ign}/E

Subscripts

f	= flow
i	= initial
ign	= ignition
s	= surface
1	= film

Superscripts

d	= two-phase flow
n	= nitrocellulose
0	= gas

Introduction

As a rule, studies on the ignition of energetic materials (EM) deal with the investigation and quantitative description of the physicochemical processes occurring in the vicinity of the EM surface under rapid heating. As a result, condensed-phase, gas-phase, and heterogeneous ignition models have been developed.^{1–5} Actually, these models consider the internal problems that accentuate intrinsic ignition mechanisms. The processes of heat exchange between ignited EM and the energy source are described in the simplest form.

Heating by constant radiant fluxes or by hot gases with constant parameters (temperature, pressure, velocity), as well as by incandescent constant-temperature plates, are most commonly used in ignition experiments. These methods of heating are convenient since they allow one to perform the ignition under reproducible conditions suitable for mathematical simulation. It is evident that the above approaches do not encompass all types of heating that take place in reality, e.g., in the ignition of solid propellants in rocket motors. An essential characteristic feature of ignition under real conditions, which requires theoretical consideration, is heating with time-variable time not only due to variations in igniter intensity, but also because of physicochemical processes proceeding at the heated surface. Among these processes are EM gasification^{6–10} and heat losses by radiation¹¹ under radiative ignition, heating of a gas layer near the EM surface due to rapid pressurization,^{12–14} and change in effective heat feedback due to the reaction of decomposition products in the ignition by hot gases.^{15,16} Nonstationary heat transfer is one of the most important factors in the consideration of ignition stability and the simulation of transient combustion.^{17,18} The

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characteristic features of the ignition and transient combustion of heterogeneous systems involving condensed reaction products (thermites, initial mixtures for self-propagating high-temperature synthesis, etc.) have been discussed in the survey papers of Strunina, Merzhanov, and Barzykin.¹⁹⁻²¹

The present work deals with the external heat-exchange aspects of ignition theory. This article presents a general analysis of the ignition mechanism under complex heat exchange between the energy source and the ignited EM. Ignition by a two-phase flow is considered in detail as a particularly interesting case. The materials used were obtained in cooperation with Averson, Gol'dshleger, Ivleva, Rozenband, and Pribytkova.²²⁻³²

Theoretical Analysis of the External Problem of Ignition Theory

There are two approaches to this problem. The first one, based on detailed consideration of the heat transfer mechanism, enables one to relate heat transfer parameters to ignition characteristics. This approach can be used in particular cases, but does not allow generalization. The second approach implies that the heat flux to the surface is represented as an arbitrary function of time $q(t)$. The ignition is then considered for various forms of this function. This approach is formal since it is apart from particular heat-exchange mechanisms. It permits one to make general conclusions about the effect of variations in heat-exchange intensity during ignition, and can also be applied to the investigation of particular cases, with the form of $q(t)$ predetermined (experimentally or analytically) in inert models.

Bear in mind that real physical processes correspond to different forms of $q(t)$: the dependence can vary from decreasing (e.g., for gas flows with constant parameters) to increasing (e.g., for gases under pressurization).

Let us apply the second approach to the consideration of ignition by time-variable heat fluxes. In the analysis of the external problem, it is reasonable to disregard the details of the intrinsic ignition mechanism. It is advantageous to consider the simplest thermal ignition model:

energy equation

$$cp \frac{\partial T}{\partial t} = \lambda \frac{\partial^2 T}{\partial x^2} + Qk_0 \exp\left(-\frac{E}{RT}\right) \quad (1)$$

initial condition

$$t = 0, \quad T = T_i, \quad 0 < x < \infty \quad (2)$$

boundary condition

$$x = 0, \quad -\lambda \frac{\partial T}{\partial x} = q_s(t) \quad (3)$$

Let us define the time-variable heat flux from an energy source to the ignited surface in the form of the power series

$$q_s(t) = \sum_{k=0}^m \beta_k t^k \quad (4)$$

This representation appears to be rather general and is valid for a number of different functions $q(t)$.

Ignition delay time t_{ign} , ignition temperature T_{ign} , and heat storage in the bulk EM Q_{ign} are determined by an approximate method described by Averson et al.^{22,23} In this method, the ignition parameters are calculated using the solution obtained for an inert body in terms of thermal conductivity theory, and it is assumed that ignition occurs at the moment the heat feedback from chemical reaction is equal to that from the

external source. In this case, T_{ign} corresponds to $T_s(t_{\text{ign}})$ for inert heating, and $Q_{\text{ign}} = \int q_s dt$.

The critical condition for ignition is formulated as

$$q_s^2(t) = \lambda \frac{RT_s^2}{E} \cdot Qk_0 \exp\left[-\frac{E}{RT_s(t)}\right] \quad (5)$$

In Eq. (5), the value of $q_s(t)$ is substituted from Eq. (4), and $T_s(t)$ is the solution of the "inert" thermal conductivity problem [Eq. (1) with heat release term being neglected]. The form of this solution is

$$T_s = T_i + (\lambda cp)^{-1/2} \sum_{k=0}^m \frac{\Gamma(k+1)}{\Gamma(k+3/2)} \beta_k t^{k+1/2} \quad (6)$$

where

$$\Gamma(n) = \int_0^\infty u^{n-1} \exp(-u) du$$

is the gamma-function.

An analysis of Eqs. (1-4) has shown that for the arbitrary function $q_s(t)$, the solution can be approximately represented by a "universal" curve in the following form:

$$Y = \Gamma(X + 1/2)/\Gamma(X) \quad (7)$$

where

$$X = t \cdot q_s(t) / \int_0^t q_s(t) dt \quad (8)$$

$$Y = (t/\lambda cp)^{1/2} \cdot q_s(t) / [T_s(t) - T_i] \quad (9)$$

It should be noted that certain finite sections and points of the universal curve correspond to particular heat transfer mechanisms. For example, $q_s(t) = (\beta_1 + \beta_2 t)t^3$ corresponds to $0 \leq X \leq 5$ and $0 \leq Y \leq 1.23\sqrt{5}$; $q_s = \text{const}$ is represented by $X = 1$ and $Y = \sqrt{\pi/2}$; $T_s = \text{const}$ is represented by $X = 0.5$ and $Y = 1/\sqrt{5}$, etc. The universal curve is a generalization of the pure thermal problem of heating EM by various types of heat fluxes.

The existence of the universal curve essentially simplifies the calculation of ignition characteristics. To obtain the desired characteristics of ignition, one may use the value of $T_s(t)$ derived from Eq. (9) for substitution in Eq. (5):

$$T_s(t) = T_i + q_s(t) \sqrt{t/\lambda cp} Y[X(t)] \quad (10)$$

In the latter expression, $Y(X)$ should be used in the form of Eq. (7), and $X(t)$ in the form of Eq. (8). Finally, at given function $q_s(t)$, one derives the value of t_{ign} to form the expression for the ignition condition [Eq. (5)].

The equations for calculating the ignition parameters take the form:

$$q_s^2(t_{\text{ign}}) = \lambda Qk_0 \frac{R}{E} \left[T_i + \left(\frac{t_{\text{ign}}}{\lambda cp} \right)^{1/2} \frac{q_s(t_{\text{ign}})}{Y_{\text{ign}}} \right]^2 \times \exp \left[-\frac{E}{R} \frac{1}{T_i + \left(\frac{t_{\text{ign}}}{\lambda cp} \right)^{1/2} \frac{q_s(t_{\text{ign}})}{Y_{\text{ign}}}} \right] \quad (11)$$

$$T_{\text{ign}} = T_s(t_{\text{ign}}) \quad Q_{\text{ign}} = \frac{q_s(t_{\text{ign}}) \cdot t_{\text{ign}}}{X_{\text{ign}}}$$

Similar relationships can readily be obtained in the case in which the surface temperature is specified as a power series.²⁴ Lubchenko et al.^{33,34} have performed an asymptotic analysis

of the problem of the ignition of condensed systems by variable heat fluxes and have compared the results obtained with those reported by Averson et al.²⁴

The mere fact that there is a universal function that allows uniform representation of the ignition characteristics for different ways of heating is an important result of the approach under discussion. Using this function, one can analyze ignition dependencies.

Without loss in the generality of conclusions, let us use the simple heat-flux kinetics

$$q_s = \beta t^k \quad (12)$$

to consider the influence of heat-flux dynamics on the dependencies of the main ignition parameters (in particular, t_{ign}) on the thermal and kinetic parameters of the ignited substance. This problem merits detailed consideration since the accuracy of the determination of these parameters is not high.

The parameter that defines the heat transfer dynamics in Eq. (12) is the power k . At $k < 0$ the flux decreases with time, at $k = 0$ the flux is constant, at $k > 0$ it increases, and at $k \gg 1$ it increases dramatically.

Let us examine t_{ign} as a function of kinetic Qk_0 and E , and thermophysical λ parameters. Substituting Eq. (12) into Eqs. (5) and (6), we have the following system of equations for calculating t_{ign} and T_{ign} :

$$T_{\text{ign}} = T_i + (\lambda c \rho)^{-1/2} \cdot \frac{\Gamma(k+1)}{\Gamma(k+3/2)} \cdot \beta \cdot t_{\text{ign}}^{k+1/2} \quad (13)$$

$$\beta t_{\text{ign}}^k = \left[\lambda Q k_0 \exp \left(-\frac{E}{RT_{\text{ign}}} \right) \cdot \frac{RT_{\text{ign}}^2}{E} \right]^{1/2} \quad (14)$$

Having differentiated Eqs. (13) and (14) with respect to corresponding values, we obtain

$$\frac{Qk_0}{t_{\text{ign}}} \frac{\partial t_{\text{ign}}}{\partial (Qk_0)} = -\frac{1}{1 + (2k+1)D(\theta_i, \sigma)} \quad (15)$$

$$\frac{E}{t_{\text{ign}}} \frac{\partial t_{\text{ign}}}{\partial E} = \frac{1 + \sigma}{1 + (2k+1)D(\theta_i, \sigma)} \cdot \frac{1}{\sigma} \quad (16)$$

$$\frac{\lambda}{t_{\text{ign}}} \frac{\partial t_{\text{ign}}}{\partial \lambda} = \frac{D(\theta_i, \sigma)}{1 + (2k+1)D(\theta_i, \sigma)} \quad (17)$$

where

$$D(\theta_i, \sigma) = (1 + 2\sigma)(\theta_i/2) - 1$$

$$\theta_i = (E/RT_{\text{ign}}^2)(T_{\text{ign}} - T_i), \quad \sigma = RT_{\text{ign}}/E$$

Equations (15–17) suggest rather important conclusions.

1) The larger the k , the weaker the t_{ign} dependencies on Qk_0 , E , and λ . Thus, with rapidly increasing heat fluxes, the chemical nature of ignited EM manifests itself insignificantly and the value of t_{ign} depends totally on the flux dynamics, i.e., on heat transfer conditions. In this case, there is no need for precise formulation of t_{ign} . For example, as an ignition criterion, one can use a temperature rise up to a certain arbitrary value called ignition temperature. In this particular case, the calculations are weakly sensitive to the ignition model employed (condensed-phase, gas-phase, or heterogeneous).

2) The methods of determining kinetic constants from ignition experiments are used widely.^{35,36} Expressions (15) and (16) allow one to check the accuracy of the kinetic constants determined by these methods. For example, Eq. (16) suggests that for a given accuracy of activation energy E , the accuracy of experimental determination of t_{ign} should be high at large k and vice versa, if the accuracy of t_{ign} is constant, the accuracy of E decreases with increasing k . Therefore, the experimental conditions under which the heat-flux intensity decreases with

time, $k < 0$ (e.g., at a constant surface temperature), are most favorable for accurate determination of the kinetic parameters from ignition experiments. Kinetic parameters calculated using the t_{ign} values measured in experiments with heat fluxes dramatically increasing with time are less accurate; hence, it is unreasonable to determine parameters under such conditions.

Experimental Techniques and Subjects of Investigation

Two experimental setups were used. The first makes it possible to investigate the peculiarities of the ignition by a two-phase flow.^{27,28} Experiments are carried out under the simplest reproducible thermal and gasdynamic conditions. Gas passes through a furnace and enters a collector. Inert solid particles in a bin are preheated up to the gas temperature, and thereafter are carried to the collector where they mix with the gas. The two-phase flow from the collector is conveyed to the stabilization of the flow. Special measurements have shown that the average velocities of the particles differ insignificantly from the gas-flow velocity for all particle concentrations and sizes. The concentrations are uniform over the cross section of the test section. The characteristic parameters of the process are as follows: flow temperature $T_i = 250$ – 650°C , gas velocity $U = 13$ m/s, volume concentration of particles in the two-phase flow $\beta = (0.5$ – $6) \cdot 10^{-3}$, and ignition delay $t_{\text{ign}} = 0.5$ – 100 s. We used 60 – 380 μm spherical particles of aluminosilicate (melting point above 1000°C). Aluminosilicate is an inert material and does not catalyze the thermal decomposition of the substances studied. Cylindrical EM samples were inserted (insertion time less than 0.1 s) in the test section perpendicular to the flow direction. The ignition time was determined by the appearance of flame (visually for long delays, and by a photoelectric device for short delays) and by time-temperature records of a surface thermocouple. A simplified version of the setup was used for experiments with pure gas.

The second setup (ignition by the combustion products of the igniter in a model rocket chamber²⁵) was employed to study the effect of heat-flux intensity increasing with time on ignition delay. Pressed samples to be ignited were installed in the chamber so that the end face of the sample was flush with the inner surface of the chamber channel. An 8 - μm -thick thermocouple was pasted onto the sample surface. The combustion of the igniter produced a flow of hot gases that ignited the sample. Powdered or pressed igniters of different weights and compositions were used. The appropriate choice of out-flow diameter and area of the burning surface of the igniter provided the pressure rise in the chamber and, hence, the heat-flux increase with time. Pressure, gas temperature, and surface temperature of the ignited sample were detected by a light beam oscillograph. The ignition time was determined by an abrupt increase in surface temperature. To estimate the value of the heat-flux incident onto the sample, we measured the temperature of a symmetrically mounted inert sample with known thermophysical characteristics and then performed a calculation by means of a technique described by Kmonicek and Jaworski.^{37,38} The parameters observed were as follows: gas temperature 1500 – 3500°C , pressure 1 – 15 atm, heat-flux density up to 150 $\text{cal}/\text{cm}^2\text{s}$, ignition delay 0.03 – 1.5 s.

The well-known model for homogeneous and composite propellants (such as nitrocellulose, polyvinyl nitrate, and ammonium perchlorate mixtures with bitumen and polyethylene) were investigated. A similar technique was recently employed³⁹ in the investigation of the ignition of double-base propellants (gas velocity 150 – 400 m/s, pressure 20 – 100 atm, gas temperature 1000 – 1500°C , and ignition delay 0.6 – 40 ms).

Ignition by Convective Heat Fluxes of Variable Intensity

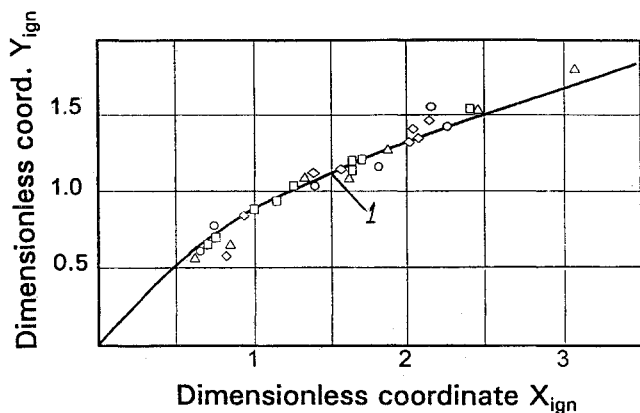
The experiments on ignition by convective fluxes concentrated on the following: 1) experimental verification of the

Table 1 Calculated and experimental data on the ignition of nitrocellulose by gas flow

[Moderate convective heating (first setup)]					
Flow parameters, $q_s = \alpha_r(T_s - T_f)$, cal/cm ² s		Ignition delay, t_{ign} , s		Ignition temperature, T_{ign} , K	
$\alpha_r \times 10^3$, cal/cm ² s deg	T_f , °C	Experimental	Calculated	Experimental	Calculated
1	400	51.2	57.9	494	505
2.5	400	15.8	16.5	507	521
3	400	11.8	12.4	510	515
4.5	400	7.6	7.4	525	519
2.5	500	7.1	7.0	512	532
6	400	4.7	4.4	530	538
2.5	600	4.2	4.7	515	539
6	450	3.5	3.8	540	545
7.2	400	3.5	3.8	532	523
6	520	2.2	2.4	548	552
6	640	1.6	1.5	578	562

[Intense convective heating (second setup)]

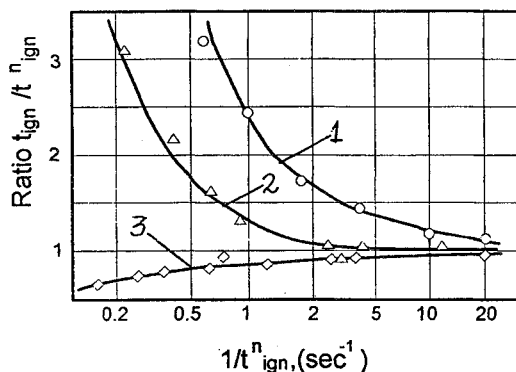
Flow parameters, $q_s = \sum_{k=1}^5 b_k t^{k-0.5}$					Ignition delay, t_{ign} , s		Ignition temperature, T_{ign} , K	
b_1	b_2	b_3	b_4	b_5	Experimental	Calculated	Experimental	Calculated
2.53	4.98	-9.05	3.71	0.39	1.35	1.35	599	570
1.39	50.8	-1.66×10^2	1.91×10^2	-73.1	0.89	0.95	569	579
7.63	-8.78	78.5	-2.57×10^2	1.23×10^3	0.61	0.68	567	586
20.3	-2.93×10^2	1.74×10^3	-3.89×10^3	2.94×10^4	0.52	0.53	609	594
23.9	-4.3×10^2	3.85×10^3	-1.3×10^4	1.5×10^4	0.30	0.34	577	602
65.4	1.03×10^4	5.96×10^5	1.08×10^7	6.68×10^7	0.058	0.063	635	640

Fig. 1 Universal curve. \circ , nitrocellulose; \diamond , polyvinyl nitrate; \triangle , ammonium perchlorate + bitumen; \square , ammonium perchlorate + polyethylene, 1, calculated curve.

validity of the universal curve, 2) verification of direct calculations in terms of thermal ignition theory at given kinetic and thermal parameters, and 3) verification of the conclusions about the weak dependence of the ignition delay time on the above parameters for intense fluxes increasing with time.

Experimental results concerning the universal curve for different propellants are shown in Fig. 1. The section of the curve at $X_{\text{ign}} < 1$ corresponds to the fluxes decreasing in time. The experimental points corresponding to this section were obtained on the first experimental setup.

The curve section at $X_{\text{ign}} > 1$ (increasing fluxes) was obtained on the second setup. The figure shows that the experimental point fit the calculated curve well. The direct calculations of the main ignition parameter t_{ign} were verified for pyroxylin (nitrocellulose with nitrogen content exceeding 11.5%) whose kinetic and thermal characteristics were known.³⁵ The results for various $q(t)$ as well as calculations for other ignition parameters are summarized in Table 1. It is seen from

Fig. 2 Dependence of $t_{\text{ign}}/t_{\text{ign}}^n$ vs $1/t_{\text{ign}}^n$. 1, ammonium perchlorate + polyethylene; 2, ammonium perchlorate + bitumen; 3, polyvinyl nitrate.

the table that the experimental ignition delays are in good agreement with those calculated. The discrepancy of no more than 10% testifies to the fact that the thermal theory is effective for these conditions.

Figure 2 shows that the effect of the kinetic and thermal parameters of the EM on ignition delay decreases when the EM is exposed to dramatically increasing heat fluxes. The time delays of the EM under study are compared (the t_{ign}^n of nitrocellulose is taken as a reference value). The value $1/t_{\text{ign}}^n$ is taken as a measure of flux intensity in order to compare the results for decreasing and increasing fluxes in this figure.

Figure 2 also shows that as flux intensity increases in time and flux changes from decreasing to increasing, the difference in time delays for different EMs lessens and practically vanishes at $1/t_{\text{ign}}^n \approx 10$, indicating that the experimental data support the analytical predictions.

Ignition by Two-Phase Flows

We come now to the problem of ignition by two-phase flows. This process is physically more complicated than that

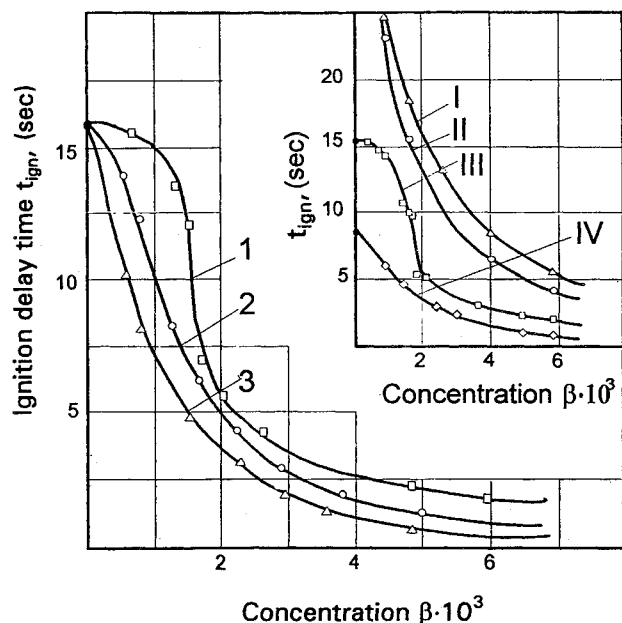


Fig. 3 Plots for t_{ign} vs β at various d . \bullet , ignition by pure gas flow ($\beta = 0$); 1, $d = 380 \mu\text{m}$, nitrocellulose, $T_f = 400^\circ\text{C}$, $T_i = 20^\circ\text{C}$; 2, $d = 130 \mu\text{m}$, nitrocellulose, $T_f = 400^\circ\text{C}$, $T_i = 20^\circ\text{C}$; 3, $d = 60 \mu\text{m}$, nitrocellulose, $T_f = 400^\circ\text{C}$, $T_i = 20^\circ\text{C}$; I ammonium perchlorate + bitumen, $T_f = 500^\circ\text{C}$, $T_i = 20^\circ\text{C}$, $d = 235 \mu\text{m}$; II, ammonium perchlorate + polyethylene, $T_f = 530^\circ\text{C}$, $T_i = 20^\circ\text{C}$, $d = 235 \mu\text{m}$; III nitrocellulose, $T_f = 400^\circ\text{C}$, $T_i = 20^\circ\text{C}$, $d = 235 \mu\text{m}$; IV polyvinyl nitrate, $T_f = 400^\circ\text{C}$, $T_i = 20^\circ\text{C}$, $d = 235 \mu\text{m}$.

considered previously. The ignition method in question is employed to intensify heat transfer processes. In most cases, pyrotechnical igniters with various compositions and duties are used. Heat transfer to ignited EM occurs due to the convective flows of gaseous combustion products of igniters, the immediate contact of solid particles with the EM surface, and radiation. Because the peculiarities of this process have not been studied sufficiently, it is therefore of interest to determine its mechanism and to study the quantitative relations between the ignition characteristics and two-phase flow parameters.²⁷⁻³²

Experiments carried out on the first setup have shown the essential influence of the main parameters of two-phase flow on ignition. Figure 3 depicts the dependencies of ignition delay $t_{\text{ign}}(\beta, d)$ on the concentration and diameter of particles at constant T_f , U , and T_i . It can be seen from the figure that the increasing concentration and decreasing diameter of particles considerably reduce the ignition delay t_{ign} (the maximum reduction factors for nitrocellulose and polyvinyl nitrate are 15 and 10, respectively, and for ammonium perchlorate/polyethylene and ammonium perchlorate/bitumen are 9 and 5, respectively). It has been established that in ignition by two-phase flows (unlike in ignition by pure gas flows) the state of the ignited surface is of importance.

It was found that the EMs under study are softened, giving liquid surface films (nitrocellulose at $165\text{--}175^\circ\text{C}$, polyvinyl nitrate at $48\text{--}60^\circ\text{C}$, ammonium perchlorate/polyethylene mixture at $185\text{--}200^\circ\text{C}$, ammonium perchlorate/bitumen mixture at $80\text{--}85^\circ\text{C}$). However, the sample geometry and size remain practically unchanged by the time of ignition. When a sample is heated up to its softening temperature, solid particles begin to penetrate into the surface layer. Particle penetration was established experimentally by means of microscopic examination of samples removed from the test section at different instants of the induction period.

In the analysis of t_{ign} dependence on the two-phase flow parameter, visual observation, cinematography, and examination of sample surfaces with a microscope allowed us to

formulate the following concept of the mechanism of igniting nonvolatile condensed substances by two-phase flows.

If the sample surface remains solid (i.e., the propellant is not softened at temperatures lower than the ignition temperature), the heat transfer is intensified due to boundary-layer turbulization, radiant flux from the particles, and impacts of the hot particles on the propellant surface. All of these factors can be accounted for in ordinary thermophysical measurements. Such measurements have been performed for inert samples and the results have been generalized²⁹ as the criterial dependence

$$(\alpha_d/\alpha_g) - 1 = 3.6\beta^{1.38}(D/d)^{0.8} \cdot (T_f/T_i)^{3.8} \quad (18)$$

where α_d and $\alpha_g = 1.14\lambda(U/D\nu)^{0.5}(\nu/a)^{0.37}$ are, respectively, the effective heat transfer coefficients at the cylinder face exposed to two-phase and pure gas flows. The dependence holds for $10^{-3} < \beta < 6 \cdot 10^{-3}$, $10 < D/d < 200$, $1.7 < T_f/T_i < 3.2$, and $80 < Re < 1200$.

Experimentally, the solid surface case was realized for pyroxylin and polyvinyl nitrate samples with the ignited surfaces protected by thin ($\approx 10 \mu\text{m}$) metal foil. In the $t_{\text{ign}}(\alpha)$ coordinates, the results of these experiments, as well as the experimental data on the ignition by pure gas flows, show good agreement with the thermal ignition calculations for the case of Newtonian heat exchange.

Thus, if the EM surface is not softened, the ignition is described in the familiar manner via the available heat transfer coefficient.

However, this simple heat transfer mechanism is unable to describe the ignition process in the case of a softening surface. Calculations through the heat transfer coefficient determined without regard for particle penetration reveal an essential (several-fold) discrepancy with experimental results.

In this case, one should take into account particle penetration into the propellant surface and the corresponding additional intensification of heat transfer. A comparison between the time dependencies of surface temperature at heat exchange coefficients equal for gas and two-phase flows shows that the curves coincide only at temperatures below the softening temperature. In the case of two-phase flow, the surface temperature rises abruptly, which is indicative of an additional amount of heat received by the sample.

Particle penetration depends essentially on the relation between softening temperature T^* and ignition temperature T_{ign} , as well as on heat-flux intensity. It can be shown that according to the relation between T^* and T_{ign} , there are three regimes of particle penetration into the surface:

1) $T^* > T_{\text{ign}}$. In this case the penetration is absent (see previous text).

2) $T^* \ll T_{\text{ign}}$. The mechanism changes early in the development of the process. The additional heat received by the sample has time to diffuse. Therefore, during most of the induction time, the sample is heated through a thin layer of particles that weakly affect the process.

3) $T^* \leq T_{\text{ign}}$. Particles start to penetrate the EM surface at the end of the induction period, where chemical reaction plays an important role. In this case the particle penetration effect is most important, and total ignition time t_{ign} depends mainly on the time of heating up to the softening temperature. Thereafter, the process runs rapidly and, perhaps, follows the hot-spot mechanism [see, e.g., the sharp rise of the $t_{\text{ign}}(\beta)$ curve for large particles in Fig. 3].

Special experiments were conducted in an effort to determine the effect of T^* on the penetration of particles into the surface. Since it is rather difficult to find EM with different T^* values and known kinetic and thermal parameters, we used nitrocellulose samples coated with a thin layer of a substance with a certain melting temperature. Compounds of aromatic hydrocarbons and paraffins were employed as coatings. Results of the experiments conducted (for correct com-

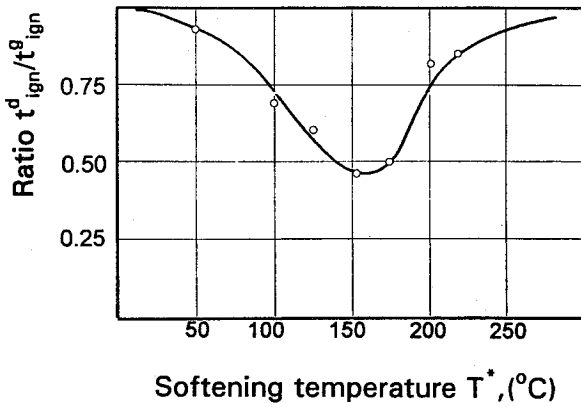


Fig. 4 Dependence of $t_{\text{ign}}^d/t_{\text{ign}}^g$ vs T^* , nitrocellulose with various coating, $T_f = 400^\circ\text{C}$, $d = 235 \mu\text{m}$.

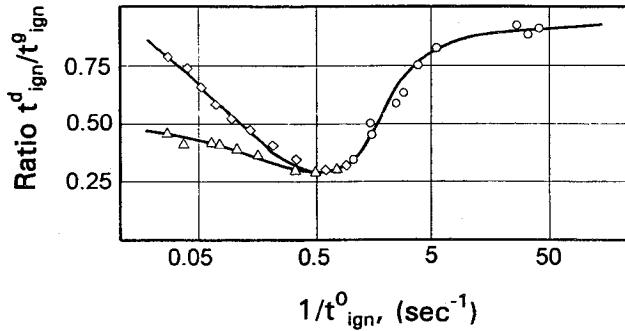


Fig. 5 Dependence of $t_{\text{ign}}^d/t_{\text{ign}}^g$ vs $1/t_{\text{ign}}^g$ for nitrocellulose. \diamond , first setup, $\beta_\omega = 3.5 \text{ kg/kg}$; \triangle , first setup, $\beta_\omega = 9 \text{ kg/kg}$; \circ , second setup, various concentrations.

parison) at the same heat transfer coefficient and gas-flow temperature are shown in Fig. 4. The ratio of t_{ign}^d for the two-phase flow to t_{ign}^g for the pure gas flow is taken to be the parameter characterizing the effect of softening temperature value, the value of t_{ign}^g being obtained both theoretically and experimentally. The figure shows that for the described experimental conditions, the largest penetration effect is observed at $T^* = 155^\circ\text{C}$, with T_{ign} being 237°C .

The heat-flux intensity also has an essential effect on the penetration process. This effect was studied experimentally on both the setups. To compare the results obtained on the different setups, the value $1/T_{\text{ign}}^g$, which incorporates the integral heat transfer disregarding the penetration, was used as the intensity characteristic. Figure 5 shows corresponding curves for different particle sizes and temperatures. At low heat-exchange intensities (ignition delay time 1–20 s, $q = 0.5\text{--}2 \text{ cal/cm}^2\text{s}$), the penetration effect increases with increasing intensity. At a certain value of $1/t_{\text{ign}}^g$, these values are different for different propellants, and the penetration effect reaches its maximum (the minimum on the curve).

With a further increase in intensity, the effect of penetration decreases, and at $q \sim 20 \text{ cal/cm}^2\text{s}$ ($t_{\text{ign}} \sim 0.03 \text{ s}$) the ratio $t_{\text{ign}}^d/t_{\text{ign}}^g$ is close to unity.

The penetration of particles can be taken into account in calculations using the following approximate model of the process.²⁸ The sample is heated up to the softening temperature due to the convective flux corresponding to the heat transfer coefficient determined disregarding the penetration. When the softening temperature is reached, the surface is immediately covered by a thin film of inert particles whose temperature is the same as the flow temperature and thickness is equal to the particle diameter.

The assumption that the film appears instantaneously can be supported by calculation of the time of covering the surface with particles. It is essentially less than t_{ign} . The assumption

that the film thickness is equal to d is confirmed by observations with a microscope, which show the particles to be arranged at the surface in one layer.

After the surface film forms, the external convective flux remains as before and affects the sample through the film. The mathematical description of this model is as follows.

Heating the sample up to softening temperature is described by the thermal conductivity equation with a chemical heat-release source and corresponding boundary and initial conditions:

$$c\rho \frac{\partial T}{\partial t} = \lambda \left(\frac{\partial^2 T}{\partial x^2} + \frac{n}{x} \frac{\partial T}{\partial x} \right) + Qk_0 \exp \left(-\frac{E}{RT} \right) \quad (19)$$

$$\lambda \frac{\partial T}{\partial x} \Big|_{r,t} = -\alpha_d [T(r, t) - T_f], \quad \frac{\partial T}{\partial x} \Big|_{0,t} = 0 \quad (20)$$

$$T(x, 0) = T_i \quad (21)$$

To describe the process for the moments when $t > t^*$ [which corresponds to $T(r, t^*) = T^*$], an accompanying problem is solved incorporating thermal conductivity equations with a source for the EM and without a source for the film, and with corresponding initial, boundary, and matching conditions:

$$c\rho \frac{\partial T}{\partial t} = \lambda \left(\frac{\partial^2 T}{\partial x^2} + \frac{n}{x} \frac{\partial T}{\partial x} \right) + Qk_0 \exp \left(-\frac{E}{RT} \right) \quad (22)$$

$$0 < x < r$$

$$c_1\rho_1 \frac{\partial T_1}{\partial x} = \lambda_1 \left(\frac{\partial^2 T_1}{\partial x^2} + \frac{n}{x} \frac{\partial T_1}{\partial x} \right), \quad r \leq x \leq r + d \quad (23)$$

$$T_1(x, t^*) = T_f, \quad \lambda \frac{\partial T}{\partial x} \Big|_{r,t} = \lambda_1 \frac{\partial T_1}{\partial x} \Big|_{r,t} \quad (24)$$

$$T(r, t) = T_1(r, t) \quad (25)$$

$$\lambda_1 \frac{\partial T_1}{\partial x} \Big|_{r+d,t} = -\alpha_d [T_1(r + d, t) - T_f]$$

In this case, the initial temperature distribution in the sample for the accompanying problem is the temperature distribution at t^* . Subscript 1 denotes the film.

This simplified model does not take into account the influence of particle concentration on the effect of penetration. However, special experiments with variable particle concentration at a constant heat-exchange coefficient have shown that there is a region ($\beta > 2 \cdot 10^{-3}$) wherein the ignition delay time is practically independent of the concentration.

The dependence of $t_{\text{ign}}^d/t_{\text{ign}}^g$ on the softening temperature T^* calculated in terms of the above model shows good agreement with the experimental data given in Fig. 4. The curve shape and the temperature (accurate to $\pm 15^\circ\text{C}$) of the minimum $t_{\text{ign}}^d/t_{\text{ign}}^g$ are the same in both the experiment and the calculations. The conclusion that the penetration effect decreases at $T^* < T_{\text{ign}}$ and $T^* \gg T_{\text{ign}}$ is confirmed.

The results of direct calculations of ignition delay for nitrocellulose (the $T^* \leq T_{\text{ign}}$ case) are in good agreement with the experiment. The discrepancy is less than 30% (see Table 2). The approximate model considered above is applicable to high particle concentrations in the blowing flow since it is assumed that at the softening temperature the EM surface is instantaneously coated with hot particles. The model fails to describe the process at low particle concentrations, when the particles penetrating the surface are sufficiently distant from one another. In this case the process follows the hot-spot mechanism, i.e., a particle penetrating the surface can cause local (hot-spot) ignition. The ignition of EM by single particles

Table 2 Comparison of calculated and experimental data on the ignition by two-phase flow

α , cal/cm ² s deg	β	d , μ	T_f , °C	t_{ign} , experimental, s	t_{ign} , calculated, s
6×10^{-3}	5.7×10^{-3}	380		1.4	1.15
		130	400	1.7	—
		60		2.0	2.25
			450	1.2	0.9
		235	520	0.8	0.6
3×10^{-3}	3×10^{-3}	640		0.45	0.33
		380		3.9	3.8
		130	400	5.1	—
		60		6.7	8.1

has been studied experimentally and theoretically.^{31,32} The hot-spot ignition model allowed interpretation of the experimental data on ignition by two-phase flows with small particle concentrations. The region of applicability of these two models has been distinguished³¹ according to the concentration value, with the heat-exchange coefficient, flow temperature, and softening temperature of the EM being constant. The hot-spot ignition of a metal powder in oxygen has been considered by Aristov et al.⁴⁰

Conclusions

The investigation of the external problems of the ignition theory, wherein the complex forms of heat exchange between the energy source and the EM surface are considered, is of unquestionable interest. In the present work, two approaches that yielded both general and particular results were applied to the solution of these problems.

It should be noted that the results presented here correspond to the simplest problem formulation when the depletion of the reactant in the condensed phase prior to ignition is neglected. Even so, it is known that depletion may play an important role in ignition, especially at high heating rates. In the last case, the effects of the reacting surface motion become significant prior to the instant of ignition and the decrease of heat release in the condensed phase due to the decrease of the reactant concentration in the subsurface layer.

Possible errors in the treatment of experimental data on ignition under intense heating might be estimated on the basis of numerical calculations within the framework of more sophisticated problem formulation. At the same time, the above considerations underline the importance of determining the global kinetic parameters, using the experimental data on ignition at constant or decreasing in time the heat flux of moderate intensity when the fast runaway of exothermic chemical transformations in the condensed phase is most apparent.

It is easy to see that the particular relationships derived in this article to calculate the ignition characteristics are based on the particular choice of the ignition criterion in the form of Eq. (5). Changing the ignition criterion will change the relationships for calculating the ignition characteristics. Nevertheless, the universal curve in Eq. (7) remains valid and can be successfully used in the calculation of ignition characteristics.

In the future it would be reasonable to determine if the peculiarities of ignition by time-dependent heat fluxes hold for systems with different physical chemistry ignition mechanisms. Also of interest are the ignition processes involving other complex forms of heat transfer (e.g., ignition by condensing vapor).

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