Def Sci J, Vol 41, No 3, July 1991, pp 251-262

Stability of Ignition Transients*

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ABSTRACT

The problem of ignition stability arises in the case of the action of intense external heat stimuli when, resulting from the cut-off of solid substance heating, momentary ignition is followed by extinction. Physical pattern of solid propellant ignition is considered and ignition criteria available in the literature are discussed. It is shown that the above mentioned problem amounts to transient burning at a given arbitrary temperature distribution in the condensed phase. A brief survey of published data on experimental and theoretical studies on ignition stability is offered. The comparison between theory and experiment is shown to prove qualitatively the efficiency of the phenomenological approach in the theory. However, the methods of mathematical simulation as well as those of experimental studying of ignition phenomenon, especially at high heat fluxes, need to be improved.

1. INTRODUCTION

The analysis and mathematical description of ignition involve terminological and methodological difficulties caused by the fact that in general the term 'ignition' implies not only the initiation of fast chemical reaction, but also the beginning phase of combustion. The latter, in turn, yields the concept of ignition stability which characterises the possibility for ignited substance to burn under self-sustaining conditions after cutting off an external energy stimulus. Studying ignition stability not only presents great practical interest, but also is a problem of considerable scientific

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Received 28 May 1990, revised 2 January 1991

*Paper presented at the Fifth National Seminar on High Energy Materials, 22–24 February 1989, Pune, India.

importance since such investigations aim at obtaining fundamental information on unstable burning. As the results obtained until lately are not complete enough, this paper aims to make a critical review of available information and outline the ways for solving the problem.

2. DEFINITION AND PHYSICAL PICTURE OF IGNITION

Before discussing ignition stability, it seems to be reasonable to consider the available definitions of ignition and give some details of the physical picture of the phenomenon under study. The definitions are given in a number of papers including some reviews published in the last 25 years[1-4]. An essential feature of these definitions is that only stable ignition is considered as complete and true. At the same time, the limitation of such an approach is evident since both experiment and common sense show that unstable ignition in many cases can be transformed into the stable one provided that the intensity of external energy source is varied appropriately in time. Besides, the cases of igniting substances able to burn only under external heat supply are then out of consideration. Burning of pure ammonium perchlorate at pressures below 20 atm, which takes place only if there are external heat fluxes of about 10 cal/cm^2 s, is a classical example of such a case. So, it is clear that the term 'ignition' is to be defined more correctly. It is of major importance to determine reliably the ignition instant, which is difficult to realise under the intricate conditions of heat exchange inherent in real ignition processes Determining the ignition instant under the action of powerful energy sources offers the most difficulties.

Experimental data obtained by Kuo and co-authors[5] may serve as an illustration of the difficulties connected with the interpretation of this phenomenon (Fig. 1). Ignition of solid propellants was investigated under rapid pressure loading (up to 10^6 atm/s). The heating of propellant samples was recorded by high-speed movie and monitored by the signals of thermocouples and photodiodes. It is seen that the instant

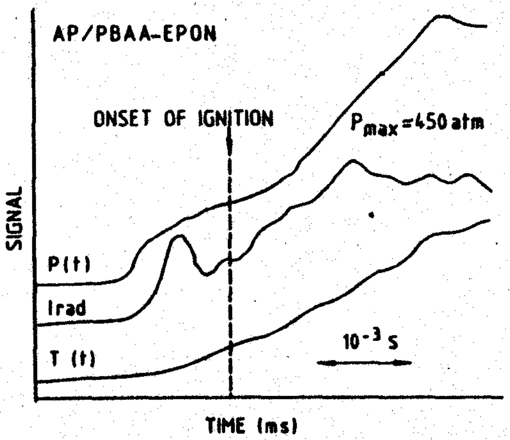

Figure 1. Time-correlated pressure, light intensity, and thermocouple signals[5].

of flame appearance, which was taken as ignition instant, is detected with great difficulties. It is interesting to note that this instant is classified as the onset of ignition in experiments with ammonium perchlorate-based solid propellants and as evaporation set on in those with nitramine-based solid propellants. This classification is proposed because of stable burning in the former case and extinction in the latter one.

It seems to be obvious that for a more detailed study it is reasonable to deal with comparatively low levels of heat fluxes and the most simple conditions of heat and mass transfer. It should be noted however that the real physical picture of ignition is highly complex in all cases and one can see it clearly if recording devices fit the phnomenon adequately. Let us consider the qualitative picture of solid propellant ignition by constant radiant flux. Figure 2 shows signals of a surface thermocouple, photodiode, and propellant recoil (reactive force) transducer. The behaviour of the curves is seen to be dependent on propellant transparency. For catalysed double-base propellant, flame appearance precedes the peak of recoil signal. The ignition of composite propellants with crystalline oxidiser shows no initial peak of the recoil signal and the rate of the signal growth depends on the size of the oxidiser crystals. The propellant recoil growth rate increases with increasing heat flux, sample extinction taking place at a fairly high heating intensity after deradiation. It is quite difficult to determine the ignition instant by signal records because of the absence of points with the break of the first derivative (corner points), a picture with abrupt increase of the signal is detected only in the case of low-sensitive primary transducers.

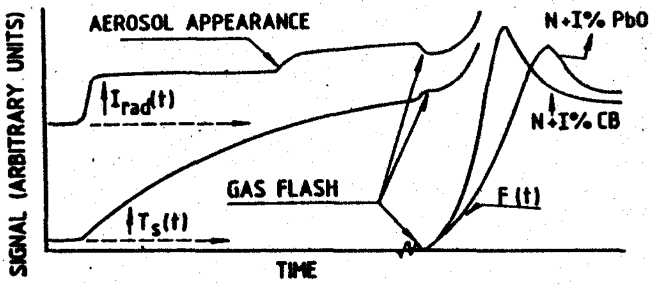

Figure 2. Temporal behaviour of double-base propellant radiative ignition in air.

Here the question of the adequacy of ignition criteria in theory and experiment arises. It is well-known that at present there are many experimental and theoretical criteria of ignition[3-6]. In particular, besides the detection of flame appearance by means of a photodiode or high-speed movie, experimentalists can determine the instants of sharp changes in mass loss or in reactive force, in thermocouple or ionising probe signals, or find the boundary of 50 per cent probability of propellant extinction after removing external thermal stimulus. On the other hand, attaining critical values by a series of parameters, such as gas temperature, radiation intensity, the first or second derivative of surface or gas temperature, rate of heat release due to internal chemical sources, are taken by theorists as an ignition criterion.

It has been mentioned[6,7] that using arbitrary couples of the criteria can lead to a considerable discrepancy between experimental and theoretical results. It is also clear that kinetic parameters determined by experimental ignition delays can be reliable only when theoretical criteria correspond directly to experimental ones, the method of recording the parameters of the process being indicated.

Let us now determine ignition as a transient process involving local initiation of exothermic reactions in the condensed or gas phase of a gasified solid propellant under the action of a pulse or continuous external energy stimulus. Ignition stability is hence the stability of transient burning at an arbitrary initial distribution of temperature in the condensed phase of the solid propellant.

It should seemingly be underlined that searching for a universal criterion of ignition is unreasonable since characteristics of the process differ substantially for different condensed substances and heating conditions. At the same time, the essence of an ignition criterion depends on the problems to be solved among which one can distinguish determination of global kinetic parameters of an exothermic reaction from data on ignition delays and simulation of the transition of an ignited system to developed combustion. In terms of the latter problem, when one simulates a transient process from initial non-reacting state of a solid propellant to combustion using a complete mathematical formulation of the problem, it is unnecessary to determine specifically the ignition instant and criterion. This correponds to the detailed physical pattern of the phenomenon, according to which the process characteristics change continuously with time. The necessity to indicate the instant of 'switching on' a global exothermic reaction, which ensures self-accelerating heating of a substance, arises only in the case of approximate formulation of the problem.

Consider finally the question of limiting 'overexposures' of the heat flux in ignition. It should be noted that such a question may be solved logically and rigorously only for a constant heat flux, with the time dependence of heat flux cut-off being indicated. For time-variable heat flux, the question about ignition stability should be formulated for each particular mode of flux change in time.

It is clear from general considerations that at overexposures long enough for external heating-supported steady state combustion to establish after cutting off the external stimulus, the normal transient processes from one stationary regime to another, namely to self-sustaining burning, must take place. The result is dependent on the steepness of the back side of the heat pulse. It is evident that ignition stability may be considered only for overexposures no longer than the consumption time for the pre-heated subsurface layer and for characteristic external stimulus removal times much shorter than thermal relaxation time for the condensed phase of a propellant.

3. EXPERIMENTAL RESULTS

In practice, ignition of solid propellants is known to be realised due to simultaneous convective, radiative and conductive heating. Conventionally, for better understanding of the physics of the phenomenon, ignition is explored under the action of a certain heat transfer mode. Here it seems to be of importance to control carefully the correctness of the physical formulation of the problem and to estimate probable extension of known mechanisms to the case of the combined heat transfer.

The effect of propellant roughness on ignition delay should be mentioned specially. It has been found in early works on ignition of double-base propellants heated by reflected shock waves that the calculated surface temperature corresponding to ignition instant, as a rule, will be in the range of 60–100 °C, i.e., abnormally low. One of the first explanations of this fact was given by Kiselev, *et al*[8]. They pointed out the possibility of overheating some local areas of heated surface and verified this assumption by experiments with ideally smooth and artificially roughened propellant surfaces. A more detailed interpretation has been given recently by Vorsteveld and Hermance[9] who presented a rigorous mathematical consideration of the problem on heating a wedge by a high heat flux. The effect of asperities has been found to manifest itself when their dimensions are less or comparable with the thickness of pre-heated ignition surface layer.

One of the first systematic experimental studies of the ignition stability under thermal irradiation has been carried out by Mikheev[10]. Using a graphite radiator, he has obtained a map for ignition stability of double-base propellants under atmospheric pressure (Fig. 3) and radiant fluxes below 9 cal/cm^2 s. It has been found that when the time of radiant flux cut-off is 0.03 s, the double-base propellant *N*, doped with 1 per cent carbon black ignites steadily at arbitrary overexposures of radiant flux if the latter is less than 1 cal/cm^2 s and extinction takes place after deradiation if radiant fluxes are above 3 cal/cm^3 s.

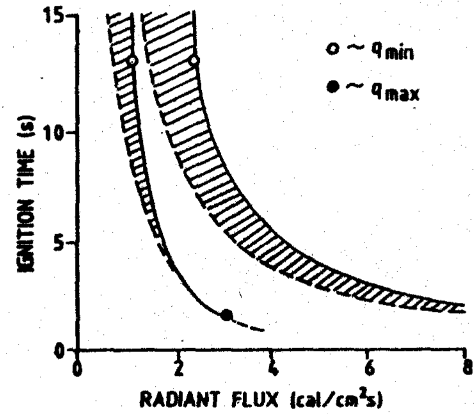

Figure 3. **Stability map for radiative ignition of double-base propellants (dashed line—the minimum ignition time, solid line—the upper limit for self-sustained ignition[10]).**

Similarly for the more transparent virgin propellant *N*, the lowest limiting value of radiant flux, q_{min}, is 2–2.5 cal/cm^2 s and its upper limiting value, q_{max}, exceeds 9 cal/cm^2 s. It has been refined by latter experiments that the upper limiting value is approximately 20 cal/cm^2 s.

More detailed physics of the phenomenon under study has been revealed in further experiments carried out with the participation of the author. The continuous measurements of recoil signal have shown that a drastic cut-off of the radiant flux from a xenon lamp causes a two-step decrease in gas release intensity (or mass burning rate), first sharp and then more smooth. With radiant fluxes above 4 cal/cm^2 s and the deradiation time 0.01 s, if external stimulus is removed immediately after ignition (gas flash above propellant surface), the recoil signal is observed to decrease practically to zero which corresponds to complete extinction on ignition in nitrogen. If the experiment is performed in the air, temporary extinction is followed by gradual repeat ignition with a time of transition to combustion of the order of 10 characteristic thermal relaxation times in the condensed phase under steady state combustion. High-speed movie and momentary photography of the transient process have shown that after sharp deradiation the double-base propellant surface gets covered with a dense net of gas bubbles and the initial phase of subsequent combustion is of local character. The pattern is confirmed also by local thermocouple measurements of temperature in gas or on propellant surface. At the same time experimental data show the critical values of heat fluxes to be dependent on the optical characteristics of solid propellant (or spectral composition of radiation) and the mode of flux variations with time.

Similar physical data have been obtained by De Luca, *et al*[11,12]. The upper limit of ignition stability has been found to depend on the steepness of the back front of the heat pulse and ambient pressure level (Fig. 4). It should be emphasised that the position of the upper limit of ignition stability is determined within a considerable error since the absorption and reflection coefficients of radiant flux considerably differ for virgin and burning sample surfaces.

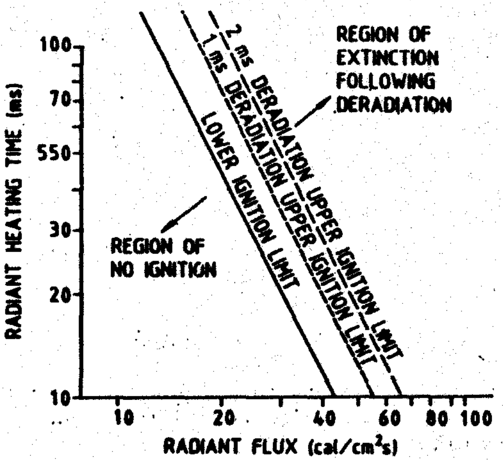

Figure 4. **Effect of deradiation interval on measured upper and lower limits of double-base propellant, $P = 1$ atm (57.8% nitrocellulose, 40% nitroglycerin, 2.2% additives)[11].**

Interesting results on ignition of composite solid propellants have been obtained by Harayama and co-authors[13]. They have detected pulsing ignition at low (sub-atmospheric) pressures and plotted an original map for ignition stability at $P = 100$ torr (Fig. 5). According to these data, there is one critical value of heat flux above which extinction takes place at every short overexposure of thermal radiation and below which the propellant burns steadily at every radiation overexposure.

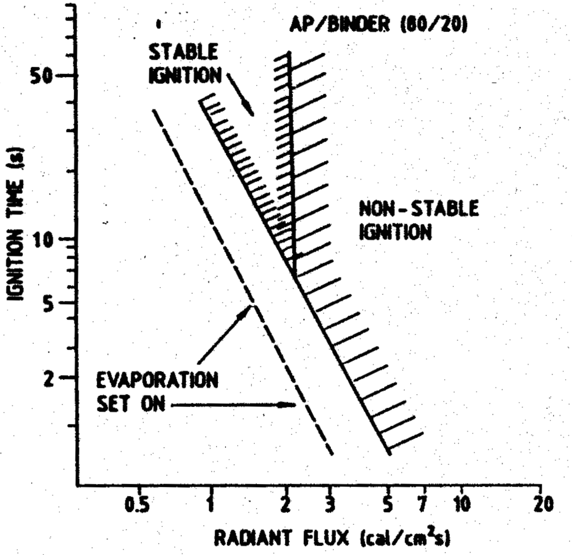

Figure 5. **Stability map for radiative ignition of CTPB propellant at sub-atmospheric pressure[13] (*Ar*, 100 torr).**

Similar data on pulsing ignition in the air have been obtained by the author in experiments with a non-catalysed double-base propellant *N*. Pulsing regression with characteristic frequencies of 4–8 Hz was observed when propellant samples were heated by frontal blowing of the surface by a hot gas stream (air, nitrogen) with a velocity not less than 10 m/s and a temperature not higher than 500 °C at atmospheric pressure. The propellant extinction took place after the blowing was stopped.

Thus, the experiment shows that stability of transient process in ignition depends on accumulated heat, external energy stimulus cut-off rate, pressure level, and physico-chemical properties of the propellant including its transparency and kinetic parameters.

4. THEORETICAL APPROACHES

The question arises of how adequate is the theory explaining the facts observed experimentally.

One of the first attempts to describe the phenomenon analytically was made in 1963 by Librovich[14]. To consider the problem on solid propellant ignition by intense convective fluxes, he used the hypothesis[15] that stable transition to combustion is ensured if the surface temperature equals a given value of the steady state burning surface temperature T_s^0 and the temperature gradient on the surface is below a critical value. At the same time the assumptions were made that the surface temperature of a stationarily burning propellant under a given pressure was constant and there was endothermal gasification of the propellant. Solution of the problem of propellant heating followed by substance gasification yields the dependence of ignition time on convective heat flux value. Such an approach is however insufficient for describing the transient dynamics. Neglecting the heat supply and temperature distribution in the condensed phase, as well as the burning-rate temperature sensitivity, it is impossible to predict *a priori* neither the transient duration nor its stability.

Possibilities of analytical description of non-steady state combustion are limited since this problem is substantially nonlinear. Hence, one should employ the methods of numerical simulation with subsequent generalisation of results. The first attempt of such a simulation was probably made by Vilyunov and Sidonskii[16] who considered in succession propellant heating by an external source and the transient after cutting off the external energy stimulus. They made a global assumption on the adiabacity of the process in the propellant condensed phase (heat feedback from the gas phase was neglected) and took into account the first-order exothermic reaction in the solid propellant.

In the beginning of 70s, Summerfield, *et al*[11] performed calculations on ignition by thermal radiation pulse in terms of the Zeldovich-Novozhilov phenomenological theory. Fairly good qualitative agreement with experiment has been obtained for the effect of the back front steepness of radiation pulse. It followed from the calculation that ignition stability decreases with increasing rate of radiant flux cut-off. The qualitative behaviour of burning rate in transient process after switching-off the radiant flux may be shown to be predicted by comparing the values of accumulated heat (available in the propellant at a given instant of time and corresponding to steady state combustion wave).

Integrating energy equation and using phenomenological correlation between the instantaneous burning rate, gradient and burning surface temperature, one obtains that the heat accumulation can be enlarged only if non-stationary burnig rate is lower than that of stationary combustion. On the contrary, to lessen the accumulated heat in a propellant, the latter should burn at a rate higher as compared to the stationary rate (see Appendix).

Since in this case a relatively deep decrease in burning rate may occur, the questions arise of what are the lowest values of burning rates. An attempt of analytical solution of the problem for particular cases of boundary conditions has been made by De Luca[17]. In a general case, however, one should use numerical calculations. Using these calculations, one may try, in particular, to elucidate the questions on the specificity of the substantial increase in ignition stability at rising ambient pressure and also the influence of the burning rate temperature sensitivity on the ignition stability.

These problems are partially solved in the paper by Assovskii and Zakirov[18]. Thus, decrease in the burning rate temperature sensitivity, as expected from general physical considerations, leads to increase in ignition stability (Fig. 6). Results concerning pressure level effects, unfortunately, appeared to yield insufficient information. All calculations were performed for identical steepnesses of the back-front of radiant flux ignition pulse. That is why at high pressure the time of radiant flux cut-off appeared to be approximately equal to the time of thermal relaxation of burning propellant and, consequently, the ignition was anomalously stable. It is of interest that a similar result has been obtained by De Luca.

N	$\sigma_p (10^3 . K^{-1})$	r,(cm/s)	P,(atm)	t_h,(s)
1	8.0	0.13	1	0.05
2	7.0	0.07	1	0.16
3	6.4	0.13	1	0.05
4	7.0	0.20	15	0.02

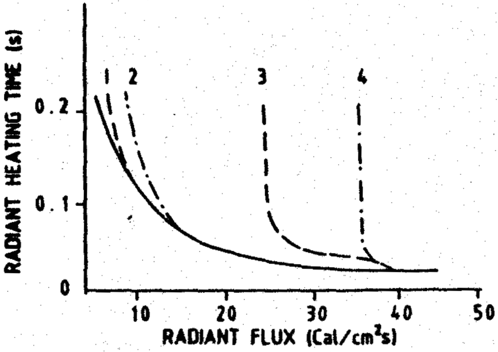

Figure 6. **Effect of burning rate and $\sigma_p = \partial_{\ln} r / \partial T_{\ln}$ values on the upper boundary of self-sustained ignition; solid line—lower ignition boundary for single-base propellant[18]. $t_d = 0.02$ s.**

5. CONCLUSION

It is to be noted that studies on ignition stability are far from being complete and should be continued. As for experiments, the informativity of the records of the process characteristics is to be improved by providing continuous measurement of passed radiant flux (to measure continuously the coefficients of attenuation in gas and reflection from surface) and continuous measurement of instantaneous burning rate of propellant recoil.

From theoretical point of view, mathematical description of the phenomenon is to be deepened by detailed consideration of the reaction kinetics in gas and condensed phases. Special attention should be paid to describe ignition of heterogeneous systems, for which the aspects of particular importance are mass-transfer processes, and also to substantiate the applicability of available theories of non-stationary burning to the description of ignition.

APPENDIX

NOMENCLATURE

c	specific heat, cal/g K
E	activation energy in pyrolysis law, cal/g mol
Q	specific enthalpy, cal/cm^2
q	radiant flux, cal/cm^2 s
r	burning rate, cm/s
R	universal gas constant, cal/g mol K
t_d	characteristic time for heat flux cut off, s
t_h	characteristic time for condensed-phase thermal relaxation, s
T	temperature, K
a	thermal diffusivity, cm^2/s
λ	thermal conductivity, cal/cm s K
ρ	density, g/cm^3
σ_p	burning-rate temperature sensitivity at constant pressure, K^{-1}
b	constant, cm/s
D	constant, cm/s

Subscripts

S	surface
in	initial

In terms of the Zeldovich-Novozhilov phenomenological theory[19] the problem on non-stationary burning of solid propellant is formulated as follows (ρ = const) :

$$c\rho \frac{\partial T}{\partial t} + c\rho r(t) \frac{\partial T}{\partial x} = \lambda \frac{\partial^2 T}{\partial x^2} \quad -\infty < x < 0 \tag{1}$$

$$x = -\infty, \quad T = T_{in}; \quad t = 0, \quad T = T(x) \tag{2}$$

$$x = 0 \quad T(0, t) = T_s(r) = \frac{E/2R}{\ln(D/r)} \tag{3}$$

$$r(t) = r(\varphi_s, T_s); \quad \varphi_s = \left.\frac{\partial T}{\partial x}\right|_{x=0} \tag{4}$$

To determine the function $r\ (\varphi_S,\ T_S)$, consider the first integral of stationary equation of energy (Eqn 1) :

$$c\rho r^0(T_S^0 - T_{in}) = \lambda\varphi_S^0 \tag{5}$$

Here the upper index ° corresponds to stationary values. In accordance with the main assumption of the phenomenological theory let us suppose that under conditions of quasistationarity of the process in the gas phase (thermal relaxation in the gas phase is much faster than in the condensed phase) ratio Eqn (5) holds for non-stationary burning, but in this case the effective value $T_{in}\ (r)$ corresponding to instantaneous rate $r\ (t)$ should be substituted in Eqn (5) for real value T_{in}. $T_{in}(r)$ value can be easily determined from the empirical stationary correlation $r^\circ = r^\circ\ (T_{in})$. For example, if $r^\circ = b \exp\ (\sigma_p\ T_{in})$,

then $$T_{in}\ (r) = \frac{\ln\ (r/b)}{\sigma_p}$$

Thus, the following expression is assumed to be true in non-stationary processes :

$$c\rho r(t)\ [T_S(t) - T_{in}(r)] = \lambda\varphi_S(t) \tag{6}$$

Now, refer to the initial formulation of the problem Eqns (1) to (4). Including Eqn (6), let us take an integral of Eqn (1) over coordinate.

$$c\rho \int_{-\infty}^{0} \frac{\partial T}{\partial t}\, dx = \lambda\varphi_S - c\rho r(T_S - T_{in}) = c\rho r(t)\ [T_{in} - T_{in}(r)] = \frac{\partial Q}{\partial t} \tag{7}$$

From Eqn (6) it follows that $\partial Q/\partial t > 0$ at $T_{in} > T_{in}(r)$ or at $r(t) < r^\circ$ and vice versa.

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