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Study of Solid Propellant Combustion under External Radiation

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ABSTRACT

The influence of constant and transient radiant flux on the burning rate of solid propellants is considered. The validity of the equivalence principle for the radiant flux and increase in initial temperature and also the problem of possible photochemical effect of thermal radiation are discussed. Experimental data on burning rate response to periodical perturbations of radiant flux for different types of solid propellants are reported. The problem of correlation between burning rate response to perturbations of pressure and external radiation is considered. Formulation of the problem on transient combustion in terms of the Zeldovich-Novozhilov phenomenological approach is described and the results of numerical integration are presented.

1. INTRODUCTION

The contribution of intrinsic radiation of the flame-to-thermal balance at the burning surface of solid propellants is known to be below 10-15 per cent[1]. Therefore, in the studies on the steady-state self-sustaining combustion, the radiation effect is neglected as a rule. However, in transient combustion, particularly under conditions of temporary extinction, the effect of external radiation may be a decisive factor in combustion stability. Moreover, investigation of combustion under external radiation provides a unique opportunity for deep understanding, giving an insight into the combustion mechanism of solid propellants due to relatively simple and reliable measurements of radiation energy, possible time variations of radiant flux, and variations of radiation absorption depth in the condensed phase.

While using external radiation as an energy stimulus, one has to solve a number of problems. One of them concerns the possibilities of the photochemical effect of radiation. Another problem relates to the equivalence principle for the increase in burning rate due to either external irradiation or increased ambient temperature. One more question refers to the possibility of comparing data on transient combustion of solid propellants under varying radiant flux and pressure. The above and other similar questions should be solved on the basis of a detailed analysis of interaction between radiation and substance as well as systematic experiments to find out the effect of external radiation on the characteristics of solid propellant combustion.

2. EXPERIMENTAL RESULTS

2.1 Optical Characteristics of Solid Propellants

To calculate the radiation absorption in a solid propellant, one should know the reflection and extinction coefficients. However, these values can be readily measured only for initial and extinguished samples. Data on optical characteristics of burning solid propellants, especially under transient conditions, are at present not available.

According to published data[2,3], the extinction coefficients for virgin and extinguished samples are almost the same and account for 3-8 per cent of different types of solid propellants. As an approximation, radiation absorption in the depth of the condensed phase obeys the Beer Law (exponential distribution),

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the extinction coefficient being essentially dependent on the substance nature and radiation wavelength.

In the experiments on thin slides of a solid propellant, it was established that a_{ef} for double-base propellants within the wavelength ranges 0.1–0.3 μm and 10–14 μm is approximately 1000 cm^{-1}; however, in the near infrared region such propellants are rather transparent. For instance, the propellant N (55 per cent nitrocellulose, 28 per cent nitroglycerin, 11 per cent dinitrotoluene, and 6 per cent technical additives) has $a_{ef} \approx 7$ cm^{-1} while for the catalysed propellant N+cat (1 per cent PbO) $a_{ef} \approx 35$ cm^{-1} within 1–1.5 μm. Close values for typical double-base propellants, averaged over a wide spectral range, are reported[4]. These are $a_{ef} \approx 10$ cm^{-1} for the propellants without carbon black and $a_{ef} \approx 150$ cm^{-1} for the propellants doped with 1 per cent carbon black.

Specific problems arise in measuring transmissivity of heterogeneous solid propellants containing components of different transparencies. A typical composite propellant contains 50–80 vol per cent of relatively transparent ammonium perchlorate crystals and 5–10 vol per cent of polymer binder. The effective value $a_{ef} = 64$ cm^{-1} is reported[3] for nonmetallised composite propellant A-13 (76 wt per cent of ammonium perchlorate) at a wavelength of 10.6 μm, while for the standard polybutadiene binder HTPB $a_{ef} \approx 500$ cm^{-1}.

2.2 Radiation-assisted Steady-State Combustion

It should be noted that radiation can have both thermal and photochemical effects on solid propellant combustion. However, no direct evidence of photochemical effects of radiation of 0.4–10 μm wavelengths has been observed. Therefore, it is customary to regard the radiation effect on solid propellant combustion as purely thermal[2,4] (perhaps more detailed studies using powerful sources of UV radiation will allow one to detect the photochemical effects) In terms of this assumption, the equivalence principle has been formulated[5] according to which the steady-state burning rate r_b^o under the radiant flux q_r is equal to the burning rate at the effective initial temperature T_{in}^* :

$$r_b^o(T_{in}, q_r) = r_b^o(T_{in}^*)$$
$$T_{in}^* = T_{in} + q_r / c\rho r_b^o \qquad (1)$$

The theoretical grounds of the principle have been presented elsewhere[2,4]. It has also been shown that Eqn (1) holds only under rigid limitations, for example, on the assumption that the burning surface temperature T_s is constant and, at the same time, the heat feedback from the gas phase q_f is absent. Analysing the general expression for thermal balance at the burning surface in the form

$$c\rho r_b (T_S^o - T_{in}) = Q \rho r_b + q_f + q_r$$

where c and ρ are the specific heat and density of solid propellant respectively, Q is the heat released in the condensed phase[6]. One can readily find that for real propellants the equivalence principle should be satisfied only as an approximation in a limited range of parameters.

For quantitative determination of the experimental dependence of solid propellant burning rate on radiant flux, one should know not only the reflection from the propellant surface, but also the portion of gas-phase absorbed and the scattered radiant flux, which is dependent on the gas and dispersed parameters as well as on radiation wavelength. The attenuation of radiation after passing through flame has been estimated[2,3] to be from 5–50 per cent and hence it is necessary to take this factor into account. Figure 1 presents plots for

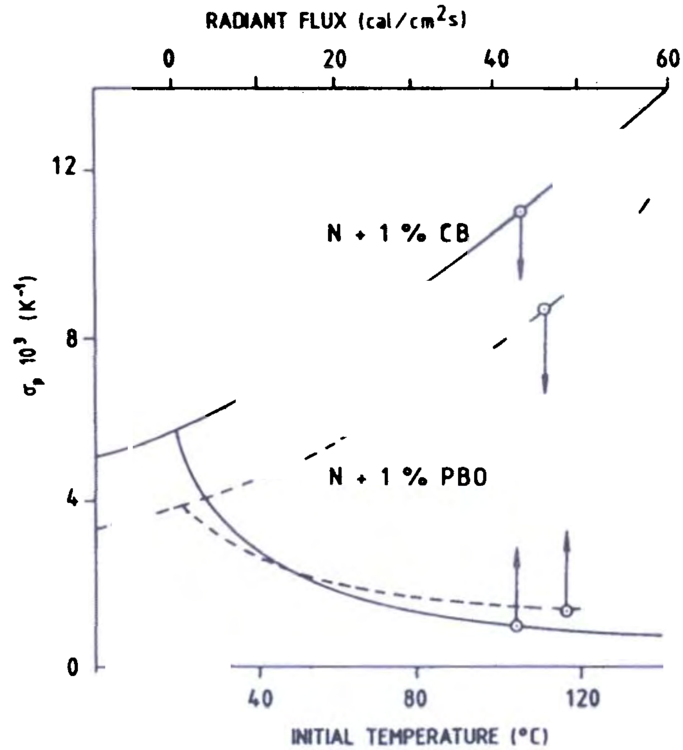

Figure 1. Burn rate temperature sensitivity vs initial temperature and radiant flux.

temperature sensitivity of burning rate for two types of double-base propellants. Radiation of a xenon lamp was used for this purpose.

Using the experimental dependence $r_b^o\ (T_{in})$ and $r_b^o\ (q_r)$ and setting

$$T^*_{in} - T_{in} = \psi\ q_r\ /\ cp\ r_b^o\ (T_{in}, q_r),$$

where $\psi = \psi(q_r)$, one can obtain a modified correlation similar to Eqn (1). For $N + 1$ per cent carbon black (a_{ef} = 400 cm^{-1}) ψ changes from 0.8 to 0.5 with radiant flux changing from 5 to 15 cal/cm^2 s. For $N + 1$ per cent *PbO*, ψ at the same radiant flux values is equal to 0.47 ± 0.03. Note an important feature of $r_b^o\ (T_{in})$ dependences for real propellants. $\sigma_p = (\partial \ln r_b^o / \partial T_{in})_p$ depends essentially upon T_{in}, that makes it impossible to use the simplified formula in the form r_b^o = const. exp $(\sigma_p . T_{in})$ for burning rate calculation. One more characteristic feature is that from the dependence $r_b^o\ (T_{in},\ q_r)$ follows the decreasing dependence $\sigma_{p,q} = [\partial \ln\ r_b^o\ (T_{in},\ q_r)\ /\ \partial T_{in}]_{p,q}$. Calculation of $\sigma_{p,q} = 1/r_b^o\ (\partial r_b^o / \partial T_{in}{}^*)\ (\partial T_{in}{}^* / \partial T_{in})$ with the indicated ψ yields approximately two times higher $\sigma_{p,q}$ values, that probably is indicative of the insufficiently adequate description of radiation-assisted solid propellant combustion.

2.3 Transient Radiation Driven Combustion

Among the varieties of transient combustion regimes, consider combustion transients during ignition and combustion affected by the stepwise action of a constant radiant flux as well as vibrational combustion under a sinusoidal radiant flux. This choice is decided by the possibility of correct formulation of problem in experiment and theory and practical importance of such processes. Note that technical difficulties appear in measuring transient burning rate when one needs the sensitivity of detection techniques not less than 10^{-4} g in mass (samples 1 cm dia) or 10^{-5}– 10^{-6} m in length at a detection frequency of atleast 1 kHz. In the experiments, the parameters of transient burning rate were determined using capacity-type microforce transducer, which allowed measurement of the combustion product recoil proportional to the square of mass burning rate, or measurement of transient sample weight at a frequency up to 500 Hz and a sensitivity of 10^{-3} g.

Figure 2 shows a generalised diagram of the recoil signal R of a burning double-base propellant under the

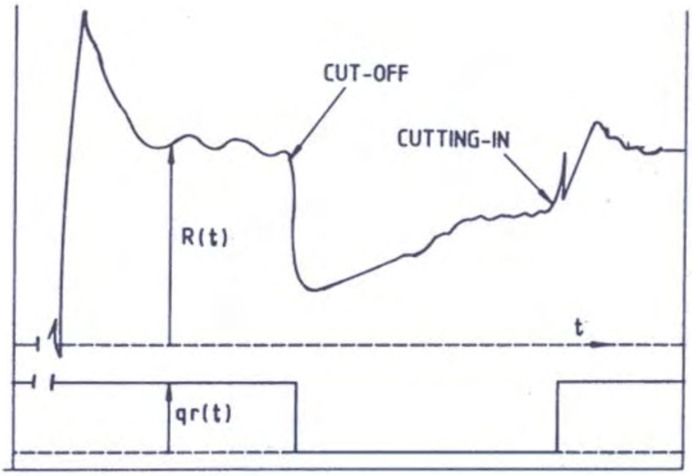

Figure 2. Generalised diagram of double-base propellant recoil response to stepwise radiant flux.

stepwise action of a radiant flux. The duration of recoil signal increase in ignition of samples with blackened surface turned out to be an order of magnitude less than it was in ignition of virgin propellant. The initial stage has a peak of recoil signal, followed by establishing the steady-state level under a constant radiant flux. A qualitatively similar behaviour is observed in ignition of mixtures of fine grained ammonium perchlorate with binder. In ignition of pressed crystalline ammonium perchlorate or mixtures of coarse oxidiser with binder, the recoil signal curve is saturated monotonously (from below).

Abrupt drop of the radiant flux leads to a deep decrease in burning rate, right down to extinction. Stability of transient burning essentially depends on the presence of oxidiser in ambient gas, propellant transparence, and burning rate temperature sensitivity. Thus, for example, at atmospheric pressure, in nitrogen, samples of pressed nitrocellulose are extinguished by a radiant flux drop of 1.5 cal/cm^2 s, while $N + 1$ per cent carbon black samples by a radiant flux drop of 3 cal cm^2 s. At the same time, in air these propellants continue burning after abrupt cut-off of a 10 times greater radiant flux. It has been observed by means of high speed movie that immediately after cutting off irradiation, a net of small bubbles is formed on the burning surface of double-base propellant and local spot type reacting is established, then burning propagates over the surface of the sample. Note that the character of the transient combustion processes described depends on the relationship of characteristic times for thermal relaxation in the propellant condensed phase, t_c, and for radiant flux cut off, t_r. Obviously, highly nonstationary combustion takes place only at $t_c >> t_r$; however, an increase in burning rate with initial temperature or pressure can lead to change of the inequality sign since $t_c \simeq r_b^{-2}$.

The investigation of the burning rate response on sinusoidal perturbations of radiant flux yields valuable information for prediction of combustion stability in rocket motors. Indeed, theory[6,7] predicts for the propellants with certain ballistic parameters, the resonance response at certain perturbation frequency, the resonance frequency being close to the frequency of nonacoustic instability (L-instability) of propellant combustion in a rocket chamber. Figure 3 presents

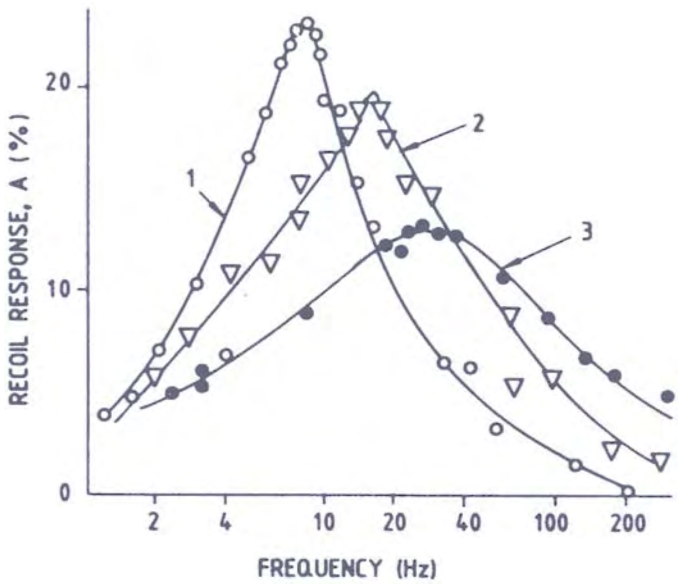

Figure 3. **Amplitude of N+cat recoil response vs radiant flux frequency (xenon lamp); (1) AP/Polyformaldehyde—67:33; (2) AP/Polymethylmethacrylate—77:23; (3) AP/Polymethylmethacrylate—85:15.**

burning rate response curves for a catalysed double-base propellant at different pressures and initial temperatures. It is seen that pressure-increased burning rate leads to decreased resonance response amplitude and increased resonance frequency. Under laser radiation, one can detect two resonance peaks of burning rate response. Burning rate response curves for mixtures of different stoichiometries of ammonium perchlorate and a polymer fuel are depicted in Fig. 4 and indicate that the resonance character of the response is particularly pronounced in fuel-rich formulations. It has been shown in special experiments on model heterogeneous mixtures[8] that the addition of

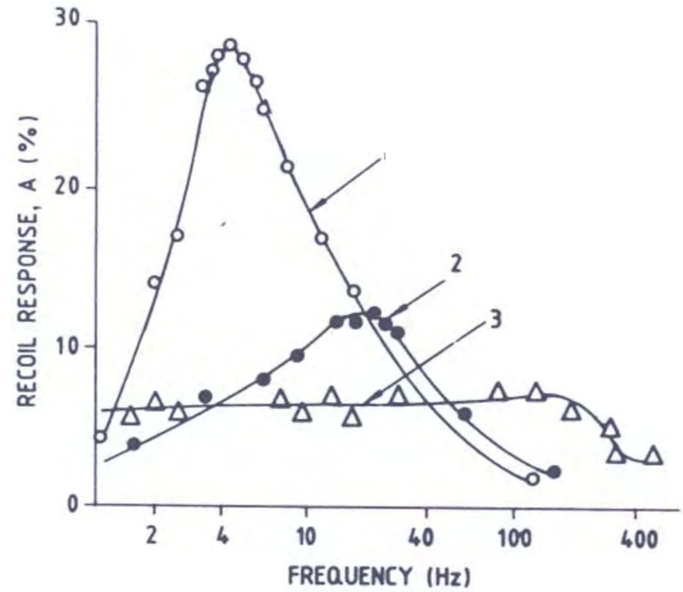

Figure 4. **Amplitude of heterogeneous mixture recoil response vs radiant flux frequency (xenon lamp); (1) AP/Polyformaldehyde—67:33; (2) AP/Polymethylmethacrylate—77:23; (3) AP/Polymethylmethacrylate—85:15.**

coarse grains of ammonium perchlorate has a weak effect on burning rate response curves, while the addition of octogen leads to increased resonance frequency.

Besides the absolute value of response amplitude, of importance is the phase shift of burning rate response relative to perturbations of the external radiant flux. The phase shift value is considerably in error due to noise of recoil (burning rate) signal. Figure 5 shows phase shift curves for two types of double-base

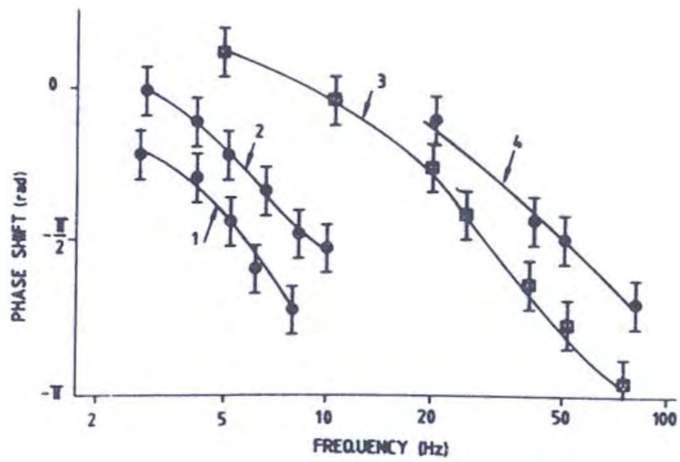

Figure 5. **Phase shift of recoil response vs radiant flux frequency (Nd:YAG laser) : (1) R_{min} (N + cat); (2) R_{max} (N + cat); (3) R_{max}, R_{min} (N + 1% CB); and (4) R_{max}, R_{min} (N + cat).**

propellants under radiation of a *Nd/YAG* laser. It is seen from the figure that for a less transparent propellant doped with 1 per cent carbon black ($a_\lambda \approx 400\ cm^{-1}$) at low frequencies, phase lead for the burning rate response is observed. For a transparent catalysed propellant in the vicinity of the first resonance frequency, the phase shift for the minimum and maximum of recoil signal exhibits significant difference which disappears in the region of the second resonance frequency. In the frequency region between the two resonances (catalysed propellant) phase shift measurements are not reliable because of the randomness of response signal. It is noteworthy that in all cases the phase shift of burning rate response at the resonance frequency is positive, i.e., the finite value lag of response signal is detected, but not zero shift, as it is predicted by the simplest theory for the case of sinusoidal perturbations of pressure[7].

3. THEORETICAL APPROACHES

For description of combustion under irradiation one should know the mechanism of interaction between radiation and solids under study as well as optical characteristics of the propellants, which depend on temperature, phase transitions, degree of substance completion, etc. In studies on combustion, it is initially assumed that the radiation is observed exponentially in the bulk of the solid propellant. Proceeding from this hypothesis (Beer's Law), formulae for burning rate under irradiation have been derived[2,4].

For the sharp flame gas-phase controlled model, the approximate expression for the burning rate augmentation under the action of a radiant flux q_r is as follows[4]:

$$r_{bq}/r_b^{\circ} = \exp\left[(E/2RT_{fo})(1-T_{fo}/T_f)\right] \qquad (2)$$

where $r_b^{\circ} = r_b^{\circ}(P, T_{fo})$ and $r_{bq} = r_b^{\circ}(P, T_f, q_r)$, E is the activation energy of the gas-phase reaction and

$$T_f = T_{fo} + q_r/C_p.\rho.r_{bq}$$

Equation (2) suggests[4] the limiting cases for $r_b^{\circ}(q_r)$ dependence:

$$r_{bq}/r_b^{\circ} = 1 + \zeta + \ldots\ldots\ldots ;\ \text{at}\ \zeta <<$$
$$\text{and}\quad r_{bq}/r_b^{\circ} = \zeta/\ln \zeta + \ldots\ldots ;\ \text{at}\ \zeta >> \qquad (3)$$
where $\zeta = E.q_r/(2\rho r_{bq}\, C_p\, RT_{fo}^2)$

When the burning rate is controlled by solid-phase reactions and the radiation is completely absorbed in the bulk of the solid, Eqns (2) and (3) are the same, but E is substituted by E_s (activation energy for solid phase reaction) and T_f is substituted by T_s (burning surface temperature). It follows from Eqns (2) and (3) that burning rate augmentation is larger when the radiation is absorbed in propellant layers below the zone controlling the burning rate.

Possibilities of analytical description of transient combustion are extremely limited. As such, numerical integration methods are applied. Assuming that relaxation time in the gas phase is negligible with respect to thermal relaxation time of the solid propellant, the problem is formulated in terms of the Zeldovich-Novozhilov (Z-N) phenomenological approach[7].

$$c\rho\, \partial T/\partial t + c\rho r_b\, \partial T/\partial x = \partial(K\partial T/\partial x)/\partial x + a_\lambda q_r \exp(-a_\lambda x) \qquad (4)$$

$$T(x, 0) = \tau(x);\ \tau(x \to -\infty, t) = \tau_a$$

To close the problem, the Z-N approach uses the Pyrolysis Law $r_b = r_b(T_s, P)$ and the relationship following from the first integral of the stationary equation of heat conduction at

$$q_r = 0 : kf^{o} = c\rho\, r_b^{\circ}(T_s^{\circ} - T_a),$$
where $f = (\partial T/\partial x)_{x=0}$

and the index 0 corresponds to steady-state conditions. According to the Z-N approach, this equation is also valid in the nonstationary case if r_b°, f^{o} and T_s° values are substituted by corresponding nonstationary parameters and the real value of T_a is substituted by its effective value $T_a(r_b, P)$ corresponding to the instantaneous burning rate r_b and derived from the empirical dependence $r_b^{\circ} = r_b^{\circ}(T_a, P)$. Thus. in addition to Eqn (4) we have

$$kf = c\rho r_b\left[\tau_s - \tau_a(r_b, P)\right];\ r_b = r_b(\tau_s, P)$$

Problems of combustion under stepwise and sinusoidal radiant flux have been resolved in terms of the described approach. Figure 6 demonstrates solid propellant burning rate evolution after sharp drop of a radiant flux. It has been found that the lower the flux drop amplitude and the higher the solid propellant transparence, the higher is the stability of transient

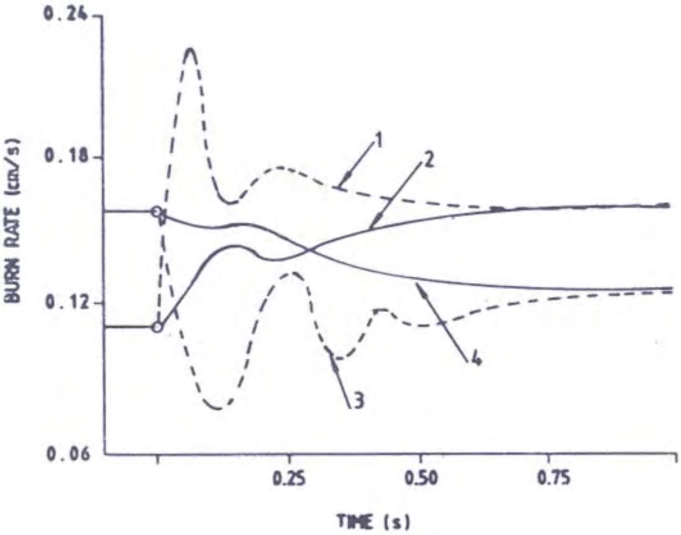

Figure 6. Time-dependent burn rate behaviour after sharp radiant flux rise, (1,2) or drop (3,4); 1,3: a_{ef} = 115 cm^{-1}; 2,4: a_{ef} = 15 cm^{-1}.

combustion. This is in good qualitative agreement with the experiment.

In modelling the burning rate response to sinusoidal radiant flux, it has been established that the more transparent the solid propellant the lower the response amplitude and the larger the phase shift; the finite lag of the response is observed at the resonance frequency. At frequencies lower than the resonance one, relatively low transparent propellants show response phase lead while transparent propellants exhibit only the phase lag. At finite flux perturbation amplitude the response becomes nonlinear, phase shifts for the response signal maximum and minimum are different, the nonlinear effects are more pronounced in low-transparent propellants.

Special attention should be paid to the question on the relationship between the pressure coupled response

$$R_p = (\Delta r/r_b^{\circ})\,(\Delta P/P^{\circ})^{-1}$$

and the radiant flux response

$$R_q = (\Delta r//r_b^{\circ})\,(\Delta q_r/q_r)^{-1}$$

In terms of the Z-N approach, it can be shown that on the assumption that ΔP and Δq_r are infinitecimal, the radiant flux is completely absorbed at the burning surface and $r_b = r_b^{\circ}\,(T_s)$, then $R_p\,(\omega)/R_q\,(\omega) = v_p/v_q$, where ω is the perturbation frequency and

$$v_p = (\partial \ln r_b^{\circ}/\partial P)\ _{\tau_s}$$

$$v_{q_1} = (\partial \ln r_b^{\circ}/\partial q_r)\ _{\tau_s}$$

In the case when the above mentioned assumptions are not met, R_p and R_q should be calculated separately, using corresponding combustion models. The same conclusion has recently been stated[3].

4. CONCLUSION

The use of thermal radiation offers ample scope for studying solid propellant combustion mechanism. However, reliability and interpretation of data are essentially dependent on radiation absorption mechanism as well as on the influence of propellant conversion degree and environmental conditions on the optical parameters.

For obtaining new experimental information it is necessary to develop apparatus for simultaneous measurement of a number of combustion characteristics including the nonstationary burning rate. Special attention should be paid to the use of laser sources, in particular, powerful sources operating in the UV spectral region.

The theoretical approaches available lower the good qualitative description of experimental results. However, a good deal of effort should be undertaken in substantiating and working out details of combustion models as well as determining reliable thermophysical, optical and kinetic parameters of solid propellants.

Of principal importance is developing combustion models, including transient combustion ones, for heterogeneous solid propellants containing coarse components with different thermal, optical and ballistic characteristics.

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