ANALYSIS OF PROPELLANT QUENCHING CONDITIONS

S. S. Novikov and Yu. S. Ryazantsev

Zhurnal Prikladnoi Mekhaniki i Tekhnicheskoi Fiziki, Vol. 10, No. 2, pp. 93–97, 1969

In [1] the conditions of propellant quenching were subjected to experimental investigation. It was established that burning ceases when the combustion wave approaches to within a certain distance of the metal-propellant contact. The thickness of the unburnt propellant residue depends on the pressure at which the test is conducted. In [1, 2] experimental values of this quantity were compared with values calculated in accordance with the Zel'dovich theory [3, 4]. A more detailed analysis of the experimental results and the theory of propellant quenching reveals a series of new facts and shows convincingly that the existing theory is unable to give a consistent description of the experiments in question.

According to the Zel'dovich theory [3, 4], quenching takes place when the temperature gradient at the burning surface exceeds a certain critical value

$$\varphi^* = \frac{u^0(p, T_{0\,\min})}{\varkappa\,[T_s(p) - T_{0\,\min}]}.$$

Here $u^0(p, T_{0\,\min})$ is the minimum steady-state burning rate, p is pressure, $T_{0\,\min}$ is the minimum initial propellant temperature at which steady-state burning is possible, $\varkappa$ is thermal diffusivity, and $T_s(p)$ is the temperature of the burning surface. In this theory the quenching condition can also be written in one of the following equivalent forms:

$$\text{a) } u = u^0_{\min} = u^0(p, T_{0\,\min}),$$

$$\text{b) } T_0 = T_{0\,\min} = T_s - \frac{1}{\beta}$$

$$\beta = \left(\frac{\partial \ln u^0}{\partial T_0}\right)_p,$$

$$\text{c) } \varepsilon = \beta(T_s - T_0) = 1.$$

It is assumed that the temperature of the burning surface does not depend on the initial temperature and hence on the temperature gradient. It should be noted that in this model before quenching the burning rate can only decrease, the lower limit of the burning rate being nonzero and equal to $u_{\min}{}^0$.

The quenching conditions formulated are not applicable to the ballistite (N powder) used in the experiments described in [1]. This is associated with the following facts: 1) in [5, 7] it was established that N powder will burn stably in the steady state at values of the parameter ε considerably exceeding unity; 2) N powder has a so-called "anomalous" dependence of steady-state burning rate on initial temperature, β is a variable; 3) the dependence $u(\varphi)$ of the nonsteady burning rate of N powder on the temperature gradient φ at the burning surface differs sharply from the dependence

$$u(p, \varphi) = ap^\nu \exp[\beta, (T_s - \varkappa\varphi/u)],$$

valid for β = const and used in the theory [3, 4]. Curves 1, 2, 3, and 4 in Fig. 1, constructed in accordance with the data of [5–7], give the $\varphi(u)$ dependence for N powder at pressures p = 1, 10, 20, 50 at. Without dwelling on the assumptions used in constructing the $\varphi(u)$ dependence from the empirical steady-state dependence $u^0(T_0)$, we consider certain characteristic features of the function $\varphi(u)$ for substances with an anomalous temperature dependence of the steady-state burning rate. We first write out the following relations, which will be useful in what follows:

$$\frac{\partial\varphi}{\partial T_0} = \frac{u^0}{\varkappa}(\varepsilon + r - 1) \quad r = \frac{\partial T_s}{\partial T_0}, \quad \frac{\partial\varphi}{\partial u} = \frac{\partial\varphi}{\partial T_0}\left(\frac{\partial u^0}{\partial T_0}\right)^{-1}.$$

Clearly, the sign of the derivative $\partial\varphi/\partial u$ coincides with the sign of the quantity $\varepsilon + r - 1$.

The existence of a minimum on the $\varphi(u)$ curve for N powder may be assumed solidly established. The presence of a minimum is easily perceived merely from the fact that in the case of a condensed system with a sharply increasing temperature coefficient of the burning rate the parameter ε changes sharply from values substantially less than unity to values substantially greater than unity. Since in accordance with data of [7, 8] the quantity r is small (r = 0.0–0.5), there is a value of the initial temperature T_{02},* at which $\partial\varphi/\partial u = 0$. The values of the temperature gradient and burning

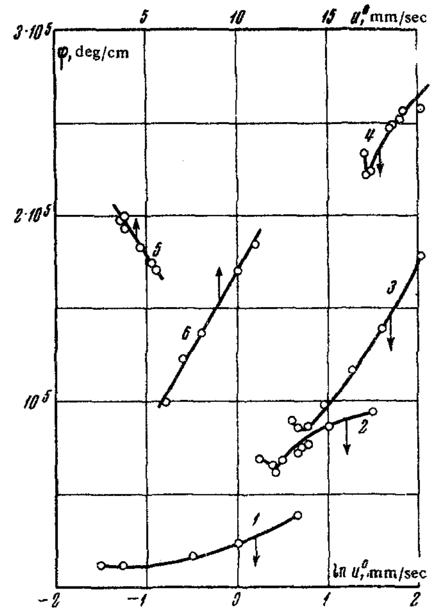

Fig. 1

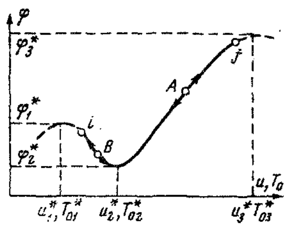

Fig. 2

rate at this point will be denoted by φ_2^*, u_2^*; in [9] it is assumed that in the region of values $u < u_2^*$ the $\varphi(u)$ dependence is interrupted at the "extreme" point $\varphi = \varphi_i$ corresponding to the onset of quenching. The qualitative characteristics of the $\varphi(u)$ curve are illustrated in Fig. 2.

However, this quenching criterion likewise does not account for the results of experiments on quenching near a metal-propellant contact. The experiments were conducted at room initial temperature, whereas $T_{02}^* < 20°$ C for pressures $p \gtrsim 1$ at. Therefore, as the combustion wave approaches the propellant–metal contact, when the temperature gradient at the burning surface can only increase, the representative point on the $\varphi(u)$ curve can move only to the right, in the direction of an increase in burning rate, moving away from the left-hand extreme point (u_i, φ_i). It is interesting to note that the known experimental data do not exclude the possibility of the existence of a maximum of the $\varphi(u)$ curve at $u < u_2^*$. Since, in accordance with [8], $r = 0$, at $T_0 = -183°$ C and $\beta = (1.9-2.2)10^{-3} \cdot \mathrm{deg}^{-1}$ $\varepsilon = 1.0-1.1$ and near this value of the initial temperature the derivative $d\varphi/du$ vanishes.

We assume that in the experiments on propellant burning near a metal contact at $T_0 < T_{02}^*$ quenching can take place both at $\varphi = \varphi_i$ (in accordance with [9]) and at $\varphi = \varphi_1^*$, i.e., at the "left-hand" maximum of the gradient. Clearly, an investigation of the transition of a combustion wave from one propellant to another across a plane interface will serve as a simple experimental method of investigating the $\varphi(u)$ dependence in the region $u < u_2^*$. By selecting an appropriate pair of propellants and a suitable pressure and initial temperature, it is possible to obtain values of the temperature gradient close to both φ_i and φ_1^*. The quenching conditions (T_0^*) in the region $T_0 > T_{02}^*$ can also be obtained, using Novozhilov's definition [10] of the combustion stability limit, in the form:

$$r(T_0^*) = \frac{[\varepsilon(T_0^*) - 1]^2}{\varepsilon(T_0^*) + 1}.$$

A comparison of the values of T_0^* and $\varphi(T_0^*)$ obtained from this equation with the values of the same quantities for the $\varphi(u)$ curve in the region $T_0 > T_{02}^*$ for N powder at $p = 1$ and $p = 20$ at [7] shows that on this basis a consistent explanation of the quenching experiments is impossible. This is associated both with the inaccuracy of the experimental determination of $T_S(T_0)$ and with certain limitations of the theory. At elevated values of the initial temperature and burning rate ($T_0 > T_{02}^*$) the idea of an inertia less reaction zone, on which the theory of [10] is based, loses its validity owing to the increase in the surface temperature T_S and the corresponding increase in zone width.

A consistent explanation of the experimental results described in [1] can evidently be obtained by assuming either that the $\varphi(u)$ dependence has a "right-hand extreme" point (T_{0j}, u_j), or that the $\varphi(u)$ dependence has a "right-hand" maximum (T_{03}^*, u_3^*) $T_{03}^* > T_{02}^*$; $(\partial\varphi/\partial u)_{u=u_3^*} = 0$. As the combustion wave approaches the metal-propellant contact, the representative point moves to the right from its starting position (point A in Fig. 2). Only this motion satisfies the requirements of an increase in the temperature gradient at the burning surface. When either of the points (T_{0j}, u_j) or (T_{03}^*, u_3^*) is reached, burning ceases, since the further motion of the representative point along the $\varphi(u)$

curve with increase in gradient becomes impossible. The relative position of the maximum point and the right-hand extreme point cannot be established a priori.

The physical nature of the right-hand extreme point may be associated with the instability of a sufficiently thick layer of strongly heated explosive, such as the reaction zone at high initial temperatures. It is interesting to note that a similar instability, caused by the difference between the propagation velocity of the exothermic reaction front in a condensed medium and the gasification rate, has been associated by Zel'dovich [3] with transition from combustion to detonation. It may be assumed that under certain conditions the reaction zone enters a critical state, a layer of material directly adjacent to the burning surface undergoes a form of thermal explosion, and the combustion wave is mechanically destroyed.

The assumption of the existence of a right-hand extreme point on the $\varphi(u)$ curve implies the physical corollary of nonsteady burning and quenching of the propellant in the presence of variable pressure. The $\varphi(u)$ dependence for a system with an anomalous $u^0(T_0)$ dependence is shown in Fig. 3 for two different pressures ($p_1 > p_2$); the starting position of the representative point is denoted by A, the final position for a steady slow fall in pressure by B; in the figure the line marked s is the trajectory of the representative point for a slow fall in pressure. In [9] it was shown that in the presence of a sharp small-amplitude pressure drop the representative point moves along the line T_S = const (line r). Clearly, in the presence of a right-hand extreme point j a situation is possible in which the r-line passes outside that point. A sharp pressure drop involves the possibility of quenching associated with the existence of a right-hand extreme point on the $\varphi(u)$ curve.

The assumption of the presence of a right-hand extreme point also leads to the possibility of an unusual physical effect — quenching associated with a sharp rise in pressure. The arrows in Fig. 4 indicate the trajectory of the representative point in the presence of a sharp pressure rise ($p_1 > p_2$). It is important that in the process of nonsteady variation of the burning rate the instantaneous burning rate $r \neq 0$ may exceed the equilibrium steady-state value u_B^0, corresponding to the pressure p_1. If the difference is sufficiently great, the burning rate may reach the value u_j and burning will cease.

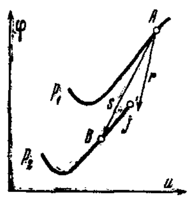

Fig. 3

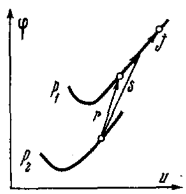

Fig. 4

At the point (u_2^*, φ_2^*) the derivative $\partial u/\partial\varphi = \infty$ and therefore in the neighborhood of this point the stability analysis performed in [10] is inapplicable. It may be assumed that in this case the inertia of the reaction zone is a stabilizing factor.

Let us now consider the possibilities of a theory of nonsteady propellant burning rates based on a linear-fractional approximation of the initial temperature dependence of the burning rate: $u^0(T_0) = ap^{\nu}(1 + \alpha T_0)/(1-\gamma T_0)$. In [11] for N powder at p = 1 at it was assumed that: $\alpha = 4 \cdot 10^{-4}$ deg^{-1}, $\gamma = 14 \cdot 10^{-4}$ deg^{-1}, r = 0, T_S = 600°K. For the quantity $\partial\varphi/\partial u$ we have

$$\frac{\partial\varphi}{\partial u} = \frac{ap^{\nu}}{\varkappa}\frac{1+\alpha T_0}{1-\gamma T_0}\left[\frac{(\alpha+\gamma)(T_s-T_0)}{(1+\alpha T_0)(1-\gamma T_0)} - 1\right].$$

Thus, the sign of the derivative $\partial\varphi/\partial u$ coincides with the sign of the quadratic trinomial $\alpha\gamma T_0^2 - 2\alpha T_0 + [(\alpha + \gamma)T_0 - 1]$, whose roots are $(T_0)_1$ = 1300° K; $(T_0)_2$ = 107° K. Therefore in the region of values of the initial temperatures $0 < T_0 < T_S$ we have the following relations:

$$\frac{\partial\varphi}{\partial T_0} > 0 \ \ (0 < T_0 < (T_0)_2), \quad \frac{\partial\varphi}{\partial T_0} = 0 \ \ (T_0 = (T_0)_2), \quad \frac{\partial\varphi}{\partial T_0} < 0 \ \ (T_0 > (T_0)_2)$$

and, consequently, the general character of the $\varphi(u)$ dependence for a linear-fractional approximation of $u^0(T_0)$ is similar to the case examined by Zel'dovich.

It is interesting to consider certain cases of propellant quenching caused by the existence of a minimum critical temperature gradient $\varphi_2^*(u_2^*)$ on the experimental $\varphi(u)$ curve. For example, when combustion waves propagate toward each other, as the burning surfaces approach, the temperature in the region between them increases and the temperature gradient at the burning surfaces will at a certain instant of time become less than φ_2^* and burning must cease. The problem of the burning of thin layers of propellant was solved theoretically in [11]. However, in order to obtain a nonsteady burning law the authors of that paper used a linear-fractional approximation and therefore were unable to detect quenching in "counterburning." Quenching may be expected at $\varphi = \varphi_2^*$ if the combustion wave propagates through a nonuniformly heated propellant specimen in the direction of rising temperature. In other words, a temperature wave moving toward the combustion wave may quench the propellant.

A simple experimental modification of counterburning is the combustion of a propellant close to its contact with a thermally insulating (adiabatic) substrate. In particular, the end of a propellant specimen in contact with a gas may be assumed thermally insulated. In this case under ordinary conditions there is no unburnt residue. This may be explained as follows: the progressive gasification of the material in the combustion wave may conventionally be called normal, if the relation between the temperature gradient φ at the surface and the gasification rate u satisfies the $\varphi(u)$ dependence obtained by calculation from $u^0(T_0)$. Obviously, apart from normal gasification, abnormal gasification not associated with combustion is also possible. If, for example, an external heat flux such that $\varphi > \varphi_3^*$, is supplied to the propellant surface (linear pryolysis), then the surface gasification will be abnormal. Volume abnormal gasification is also possible – internal thermal decomposition at a sufficiently high temperature. In counterburning after a minimum gradient φ_2^* is reached the unburnt residue may be heated to a temperature so high that volume thermal decomposition actually completes its gasification.

The state in which the propellant exists under conditions with $\varphi < \varphi_2^*$ is evidently realized in ordinary steady-state burning. The dispersed particles of condensed phase in the combustion zone have small dimensions on the order of $(0.1-0.01)\ \varkappa/u^0 = 10^{-4}-10^{-5}$ cm and a temperature close to T_S. For these particles the heating time is small $\tau \sim r^2/\varkappa = (10^{-5}-10^{-6})$ sec; therefore while a dispersed particle remains in the dark zone near the burning surface, the temperature gradient at the surface of the particle is small and normal surface gasification of the particle is impossible. The nature of the variation of the nonsteady burning rate before quenching is determined not only by the quenching conditions but also by the initial position of the representative point. It is clear from Fig. 2 that in the case of quenching on a thermally insulating substrate, depending on the choice of starting steady-state burning regime, determined by the initial temperature of the specimen, both an increase and a decrease in burning rate to $u(\varphi_2^*)$ are possible before quenching. If the starting regime is represented by the point A, i.e., $T_0 > T_{02}^*$, then as the temperature gradient at the burning surface falls, the burning rate must also fall. If at the same pressure the initial temperature is taken less than T_{02}^* (point B), then a fall in gradient before quenching must be accompanied by an increase in burning rate. In the experiments on the quenching of a propellant on an isothermal (metal) substrate, before quenching the burning rate must increase, if the representative point has a starting position in the region where $\partial\varphi/\partial T_0 > 0$ (point A). If the experiments take place at initial temperatures close to room temperature, the expected increase in burning rate should be not less than $u^0(160°\ C)-u^0(20°\ C) \sim 3$ mm/sec, i.e., a factor of 6. If the initial steady-state regime is located in the region $T_0 < T_{02}^*$ (point B) an increase in gradient must be accompanied by a fall in burning rate. The experimental verification of these laws requires a precision method of measuring the burning rate with high time resolution.

Condensed systems differing with respect to the steady-state burning mechanism also differ with respect to nonsteady burning laws. The $\varphi(u)$ dependences for tetryl and ammonium perchlorate are shown in Fig. 1. For tetryl the temperature of the burning surface is equal to the boiling point, and the parameter $\varepsilon < 1$ despite the fact that, in accordance with [12], the heat release in the condensed phase of the combustion zone is large.

For ammonium perchlorate the $T_S(T_0)$ dependence is not known. The nonsteady burning law $\varphi(u)$ shown in Fig. 1 has been constructed on the assumption that $T_S = 450°$ C, $r = 0$. In this case $\varepsilon > 1$, $\partial\varphi/\partial u > 0$. It should be noted that for ammonium perchlorate a left-hand extreme point on the $\varphi(u)$ curve undoubtedly exists. An example illustrating the correspondence of the theoretical and experimental $\varphi(u)$ relations is supplied by the data of [5] on nitroglycol, for which $T_S = T_b$, $r = 0$, $\varepsilon < 1$.

Thus, an examination of existing ideas concerning the combustion of condensed systems shows that the quenching criterion for condensed systems with an anomalous temperature dependence of the steady-state burning rate can be represented in three forms: 1) $\varphi = \varphi_i$ or φ_1^*), 2) $\varphi = \varphi_2^* = \varphi_{min}$, 3) $\varphi = \varphi_j$ or φ_2^*). The choice of a specific form of the quenching condition is determined by the experimental conditions. The results of experiments on the quenching of N powder near a metal contact can be explained by assuming, for example, the existence of a right-hand extreme point on the φ(u) curve. For condensed systems with an anomalous φ(u) dependence both an increase and a decrease in the burning rate before quenching are possible depending on the experimental conditions. The existence of a right-hand extreme point on the φ(u) curve implies the possibility of quenching in the presence of a sharp rise or fall in pressure. A physical consequence of the existence of a minimum temperature gradient is quenching in the presence of counterpropagation of a combustion wave and a temperature wave or two combustion waves.

REFERENCES

1. S. S. Novikov, P. F. Pokhil, Yu. S. Ryazantsev, and L. A. Sukhanov, "Investigation of propellant quenching conditions by the "frozen" combustion zone method," DAN SSSR, vol. 180, no. 6, 1968.

2. S. S. Novikov and Yu. S. Ryazantsev, "Theory of thermal interaction of the combustion zone with propellant-metal contact" PMTF [Journal of Applied Mechanics and Technical Physics], no. 4, 1968.

3. Ya. B. Zel'dovich, "Theory of combustion of propellants and explosives," ZhÉTF, vol. 12, nos. 11, 12, p. 498, 1942.

4. Ya. B. Zel'dovich, "Propellant burning rate at variable pressure," PMTF, no. 3, 1964.

5. A. I. Korotkov and O. I. Leipunskii, "Dependence of temperature coefficient of propellant burning rate at atmospheric pressure on propellant temperature," collection: Explosion Physics [in Russian], Izd. AN SSSR, no. 2, 1953.

6. P. F. Pokhil, O. I. Nefedova, and A. D. Margolin, "Anomalous dependence of propellant burning rate on initial temperature," DAN SSSR, vol. 145, no. 4, 1962.

7. A. A. Zenin, O. I. Leipunskii, A. D. Margolin, O. I. Nefedova, and P. F. Pokhil, "Temperature field at the surface of a burning powder and burning stability," DAN SSSR, vol. 169, no. 3, 1966.

8. V. V. Aleksandrov, E. V. Konev, V. F. Mikheev, and S. S. Khlevnoi, "Surface temperature of burning nitroglycerine powder," Fizika goreniya i vzryva [Combustion, Explosion and Shock Waves], no. 1, p. 68, 1966.

9. B. V. Novozhilov, "Nonsteady burning of propellants having variable surface temperature," PMTF [Journal of Applied Mechanics and Technical Physics], no. 1, p. 54, 1967.

10. B. V. Novozhilov, "Stability criterion for steady-state burning of powders," PMTF [Journal of Applied Mechanics and Technical Physics], no. 4, 1965.

11. Yu. A. Gostintsev and A. D. Margolin, "Nonstationary burning of thin propellant layers," PMTF, no. 5, 1964.

12. A. D. Margolin and A. E. Fogel'zang, "Combustion of tetryl," Fizika goreniya i vzryva [Combustion, Explosion, and Shock Waves], no. 2, p. 10, 1966.

13. E. I. Maksimov, Yu. M. Grigor'ev, and A. G. Merzhanov, "Burning mechanism of ammonium perchlorate," Izv. AN SSSR, Ser. khim., no. 3, p. 422, 1966.

3 December 1968

Moscow