# ON THE ROLE OF DISPERSION IN THE COMBUSTION OF PROPELLANTS

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## Abstract

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## PHYSICAL CHEMISTRY

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# ON THE ROLE OF DISPERSION IN THE COMBUSTION OF PROPELLANTS

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A. F. Belyaev ($^1$), studying the combustion of mercury fulminate in vacuum, discovered a new interesting phenomenon—the dispersion of a condensed substance during combustion. P. F. Pokhil ($^2$), as a result of fundamental systematic investigations, established that dispersion is an important factor in the mechanism of propellant combustion. Dispersion occurs as a consequence of the volumetric course of the reaction in the condensed phase. The expansion of the gaseous products formed in the decomposition zone inevitably leads to the spraying of the initial substance. According to Pokhil, during the combustion of pyroxylin propellant about 30% of the propellant decomposes in the condensed phase, while the remaining 70% is dispersed and carried away by the gas stream. However, after these works many questions connected with dispersion—namely, the role and laws of dispersion, the "fate" of the dispersed particles, etc.—remained unclear. The latter question received some treatment in works ($^3$,$^4$).

In the present work a relationship has been obtained between the burning rate, the surface temperature, and the depth of dispersion, and on the basis of an analysis of this relationship a conclusion is drawn concerning the role of dispersion.

We shall consider, in a first approximation, dispersion as a surface process proceeding without a thermal effect. Then the initial stationary system of equations, written in the approximations customary for combustion theory, will have the form

$$\lambda \frac{d^2T}{dx^2} + c\rho u \frac{dT}{dx} + Q\rho k_0 e^{-E/RT} = 0,$$

$$u = u_{\mathrm{p}} + u_{\mathrm{d}},$$

$$u_{\mathrm{p}} = \int_0^\infty k_0 \exp[-E/RT(x,u)]\, dx.$$

Boundary conditions:

$$x = 0, \qquad T = T_\text{p}; \qquad x = \infty, \qquad T = T_0.$$

Notation: $T$—temperature (°K); $T_\text{p}$—temperature at the surface of the burning propellant (°K); $T_0$—temperature of the propellant far from the combustion zone (°K); $x$—linear coordinate (cm); $u$—burning rate (cm/sec); $u_\text{d}$—linear rate of dispersion (cm/sec); $u_\text{p}$—linear rate of decomposition (cm/sec); $\lambda$—coefficient of thermal conductivity of the propellant (cal/cm • sec • deg); $c$—specific heat (cal/g • deg); $\rho$—density (g/cm$^3$); $a$—coefficient of thermal diffusivity (cm$^2$/sec); $Q$—heat of decomposition of the propellant (cal/g); $k_0$—pre-exponential factor (sec$^{-1}$); $E$—activation energy (cal/mol).

In the presence of dispersion, the linear burning rate is composed of the linear rate of decomposition and the linear rate of dispersion. Introducing into consideration the depth of dispersion $\eta_\text{d} = u_\text{d}/u$ and using

the results presented in work ($^4$), we obtain

$$u^2 = \frac{1}{1-\eta_\text{d}}\, ak_0 \exp[-E/RT_\text{p}]\, \frac{RT_\text{p}^2/E}{T_\text{p} - T_0 - \dfrac{Q(1-\eta_\text{d})}{2c}}. \tag{1}$$

This formula expresses the relation between the burning rate, the temperature at the surface, and the depth of dispersion. As is evident from (1), the effect of dispersion is equivalent, on the one hand, to a decrease in the heat of reaction in the condensed phase ($Q_\text{eff} = Q(1-\eta_\text{d})$), and, on the other hand, to an increase in the rate constant $\left(k_\text{eff} = \dfrac{k}{1-\eta_\text{d}}\right)$ or in the thermal diffusivity.

For flameless combustion, when the process is carried out only at the expense of the heat released in the condensed phase, we have

$$T_\text{p} = T_0 + \frac{Q(1-\eta_\text{d})}{c}, \tag{2}$$

$$u^2 = \frac{2}{(1-\eta_\text{d})^2}\, ak_0 \exp\left\{-E/R\left[T_0 + \frac{Q(1-\eta_\text{d})}{c}\right]\right\} \frac{c}{Q}\frac{R}{E}\left[T_0 + \frac{Q(1-\eta_\text{d})}{c}\right]^2. \tag{3}$$

Since the depth of dispersion enters into the exponent, the rate of flameless combustion depends strongly on $\eta_\text{d}$. As $\eta_\text{d}$ increases, $u$ falls sharply.* Thus, in the flameless regime the presence of dispersion retards the combustion process.

What would the burning rates be in the absence of dispersion? Let us consider this question using pyroxylin powder as an example. We shall calculate the burning rate from formula (3) at $\eta_\text{d} = 0$. The initial data for the calculation are: $T_0 = 20°\text{C}$; $a = 1 \cdot 10^{-3}$ cm$^2$/sec; $c = 0.35$ cal/g $\cdot$ deg; $Q = 270$ cal/g ($^1$); $k_0 = 10^{17.8}$ sec$^{-1}$ and $E = 44\,600$ cal/mole ($^5$). The calculation gives a very large value of the burning rate—about 250 cm/sec. This indicates that the heats of decomposition of nitrocellulose, in the presence of a comparatively large reaction-rate constant, are quite sufficient to ensure very high burning rates. The fact that such rates are not observed experimentally is explained solely by the presence of dispersion. The heat fluxes entering the condensed phase cannot in reality compensate for the potential heat carried away by the undecomposed powder particles. Thus dispersion is a brake on the powder-combustion process. If the decomposition of the powder proceeded endothermically, a different result would have to be expected.

The quantity $\eta_\text{d}$ enters expressions (1)–(3) as a parameter. In reality, the depth of dispersion is a complex function of temperature, pressure, and other factors. However, the question of the laws governing dispersion has at present not been studied at all. There are no data whatever on $\eta_\text{d}(T_\text{p}, p, \ldots)$. Since dispersion has a strong influence on the combustion process, the laws of dispersion can determine (especially at low pressures) the laws of combustion, i.e., the dependences of burning rate on pressure and temperature. The question of the laws of dispersion will apparently in the near future become one of the central questions in the theory of powder combustion.

Some information on the dependence $\eta_\text{d}(T_\text{p})$ can be obtained by using formula (3), which, when the kinetic constants are known, permits the depths of dispersion to be calculated from the measured rates of flameless combustion. For this purpose, a calculation was carried out for pyroxylin powder using the experimental data of P. F. Pokhil ($^1$). The results of the calculation, presented in Table 1, show, first, a fairly good coincid- agreement with experiment (Pokhil independently determined experimentally $\eta_d \simeq 0.7$ and $T_p = 280$–$300°\text{C}$), and, second, that the depth of dispersion increases with increasing temperature. Such a dependence $\eta_d(T_p)$ is easily understood if one proceeds from the notion of dispersion as the spraying of the substance in the liquid-viscous reaction layer.

The temperature dependence of the depth of dispersion can explain the low temperature coefficient of the flameless burning rate. From (2), (3)

$$\frac{1}{u}\frac{du}{dT_0} \simeq \frac{E_\text{eff}}{2RT_p^2},$$

where

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* It should be noted that in the region of unrealistically large values of $\eta_\text{d}$ (about 1) the function $u(\eta_\text{d})$ has a minimum.

$$E_{\text{eff}} = \frac{E}{1 + \dfrac{Q}{c}\dfrac{d\eta_d}{dT_p}}.$$

Since $d\eta_d/dT_p > 1$, it follows that $E_{\text{eff}} < E$.

**Table 1**

| Experimental data of Pokhil | Experimental data of Pokhil | Calculated values | Calculated values |
|---:|---:|---:|---:|
| $T_0$, °C | $u$, cm/sec | $\eta_d$ | $T_p$, °C |
| 90 | 0.08 | 0.716 | 298 |
| 120 | 0.11 | 0.746 | 316 |
| 140 | 0.14 | 0.767 | 319 |

The presence of an increasing dependence $\eta_d(T_p)$ prevents a strong change in the surface temperature and, consequently, in the burning rate. Indeed, if for some reason $T_p$ begins, for example, to rise, this will inevitably lead to an increase in $\eta_d$, which will hinder any further increase of $T_p$. Thus, owing to the increasing dependence $\eta_d(T_p)$, dispersion plays a regulating role in the burning mechanism.

The dependence $\eta_d(p)$, according to its physical meaning, must be decreasing. The greater the pressure, the greater the depth to which decomposition in the condensed phase must proceed for dispersed particles to form, and hence the smaller the depth of dispersion. It should be borne in mind that under burning conditions, with increasing $p$, $T_p$ always increases, and this prevents a strong decrease of $\eta_d$.

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*Note: Figure translations are in progress. See original paper for figures.*

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