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PRESSURE DEPENDENCE OF THE BURNING RATE OF BLACK POWDER

- USSR -

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FOREWORD

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The problem of the burning rate of black powder is con-
sidered in this article.

A physical theory[1] has been given by Ya. B. Zel'dovich for
the case of the burning of smokeless powder, in which the basic
property in the burning of powder, the dependence of the burning
rate on pressure, was explained by the pressure dependence of the
mass velocity of flame propagation in the gaseous products from
the powder.

In this theory use is made of an idea proposed by A. F.
Belyayev[2] on the burning of volatile liquid explosive substances
in the gaseous phase. In the case of smokeless powder we consider
gasification rather than evaporation. Black powder is different
from smokeless in two respects: in the first place, it is a het-
erogeneous system and not homogeneous: the combustible (carbon)
and the oxidant (saltpeter) are compounds in the form of macro-
scopic particles; in the second place, the combustible, carbon,
has a low vapor pressure, and therefore the burning reaction can-
not proceed in the gas phase. It must necessarily proceed in the
condensed phase on the surface of the carbon particles.

These two differences, in particular the latter, do not
permit the routine use of the theory for smokeless powder in the
case of the burning of black powder. Explanations of the increased
rates of burning with an increase in pressure require further con-
sideration; however, as will be shown below, the situation is
basically the same as that developed by Ya. B. Zel'dovich for the
case of smokeless powder.

The reaction mechanism consists in the fact that oxygen re-
leased by the decomposition of saltpeter and diffusing in the gas
phase reaches a carbon particle and reacts on its surface, while
the reaction products also diffusing through the gas are removed
from the carbon particle. (It is possible that sulfur plays a
specific role in the oxygen transfer. We do not consider this,
since it is possible to make black powder without sulfur.)

Further, the pressure dependence of the rate of the elementary reaction step, the combustion of the carbon particle, is required. As is well known, in the kinetic region, i.e., where the reaction proceeds so slowly that diffusion does not limit the rate of the process, the burning rate of carbon is proportional to the oxygen pressure.

In the diffusion region, where the reaction of carbon with oxygen goes so fast that the diffusion rate limits the combustion rate, the burning time of a carbon particle depends on the conditions of diffusion.

Let us call q_o the amount of oxygen required for the combustion of a particle of the dimensions considered, D the coefficient of diffusion ($\sim 1/p$), c_o the oxygen concentration at infinity ($\sim p$), r_{eff} the effective diffusion path (the concentration gradient $= c_o/r_{eff}$); τ the burning time for the particle, and S the surface of the particle. Then

$$q_o \approx D \frac{c_o}{r_{eff}} \tau S; \quad \tau \approx q_o \frac{r_{eff}}{DSc_o} \qquad (1)$$

The denominator in the expression (1) does not depend on the pressure, and q_o also does not depend on the pressure. The time dependence of the burning of a particle on the pressure is determined by the pressure dependence of the effective diffusion path.

In the case of the burning of a small sphere of carbon in an atmosphere of oxygen the effective diffusion path is equal to the radius of the sphere; i.e., it does not depend on the pressure. Therefore, the burning time for a small sphere of carbon does not depend on the oxygen pressure (Nussel't /?/), and this can also be the case if the source of oxygen (the particle of saltpeter) and the carbon particle are located in the solid phase at a constant distance from each other. In the case of the burning of a flat lamina the diffusion path is equal to the thickness of a layer of oxygen necessary for the combustion of the lamina considered. The thickness of this layer is of the order $1/p$, and therefore according to (1) the combustion time is inversely proportional to the oxygen pressure.

Thus, the combustion time of a carbon particle can decrease or remain constant with an increase in pressure depending on the external conditions.

Saltpeter decomposes and the gases are released at a low temperature ($\sim 400^\circ$ C) where the combustion of carbon does not yet take place. Around this temperature sulfur also produces gaseous products -- sulfur vapor (sulfur boils at 444° C) and sulfur oxides. (On the other hand, sulfur is not an essential component of the heterogeneous carbon and oxidizer mixture, since the major part of the energy of combustion of the powder is produced from the reaction of carbon with oxygen.)

Therefore, it is necessary to assume, that the gases released on heating the surface of the powder, carry off unburned carbon particles, which are burned in a gas jet over the surface of the powder. By the same process the combustion of a sphere of carbon is accomplished; for this the time of combustion does not depend on the pressure.

The dispersion of powder during burning was first noted by P. F. Pokhil, who showed that the burning of smokeless powder is connected with the dispersion of particles of the powder mass. For black powder the amount of dispersion, the reaction mechanism is the gas mixture and the contribution of heterogeneous reactions would appear to be completely different from the case of smokeless powder. However, P. F. Pokhil and Romodanova have shown that in this case too the external picture is the same.

In order to evaluate the possibility of the combustion of carbon outside the surface of the powder, it is necessary to compare the burning rate of the powder with the velocity of flame propagation in the gas jet in order to determine whether the quantity of carbon carried off from the surface of the powder can be consumed in the jet. There are no data on the combustion of coal gas mixtures corresponding to the composition of the powder.

However, in the literature there are data on the rate of flame propagation in coal gas mixtures at atmospheric pressure. These refer to graphite-oxygen mixtures[3] and to anthracite-air.[4]

The graphite-oxygen mixture consisted of graphite dust (with a particle diameter $\leq 5\ \mu$) and 1 liter of oxygen per 0.2 g of graphite (from stoichiometry 1 liter of oxygen requires 0.5 g of graphite, i.e., the mixture was oxygen-poor). The flame propagation velocity was 12-18 cm/sec, i.e., 2.4-3.6 mg/sec-cm^2 of graphite was burned in the mixture. Per one centimeter length of powder there are about 250 mg of carbon per square centimeter. Thus, the observed velocity of flame propagation in the oxygen-graphite mixture would correspond to a velocity of flame propagation in the powder equal to 0.1 mm/sec. This quantity must be regarded as a lower limit to the burning velocity, since the graphite-oxygen mixture was oxygen-poor and it can be expected that in a stoichiometric mixture the burning would be faster.

The coal-air mixture consisted of 100 mesh coal dust (i.e., particle diameters $\leq 250\ \mu$) and 1 liter of air per 0.1-0.33 g of coal. The coal contained volatile components (up to 40% by weight). In this respect the coal-gas mixture is closer to black powder than is the gas-graphite, since in black powder there is also a volatile component -- sulfur.

The velocity of flame propagation varied from 10 to 50 cm/sec. The rate of carbon consumption in the flame was 3.3-11 mg/sec-cm^2, which corresponds to a burning velocity for the powder of 0.15-0.5 mm/sec.

The burning velocity of black powder depends strongly on the composition and density of the powder. Slightly pressed powder in a Bickford fuse burns with a velocity of about 10 mm/sec, gunpowder at 8 mm/sec, and tubular powder at 3 mm/sec.[5] For dense powder burning in parallel layers, one can take as a characteristic value, a burning velocity at atmospheric pressure of from one to several millimeters per second. This value is several times larger than the maximum of 0.5 mm/sec obtained in the references mentioned.[4] The discrepancy between the measured burning velocities of black powder and those determined from the velocity of flame propagation in gas-carbon jets lies within an order of magnitude, and it would seem to us to indicate the essential closeness of both processes. However, of course, for a complete solution of the problem of comparing the velocities it is necessary to measure the velocity of flame propagation in a gas-carbon mixture exactly equivalent in composition and dispersion to black powder. In the following we shall assume that black powder initially forms a gas-carbon mixture that burns above the surface of the powder.

According to this, the basic evolution of heat occurs in the gas phase above the surface of the powder, and the heat required for the decomposition of the saltpeter reaches the condensed phase from the reaction zone in the gas-carbon phase, i.e., the same situation holds as for the burning of smokeless powder.

According to the theory of Ya. B. Zel'dovich, the linear velocity of the gasified powder is proportional to the square root of the thermal powder released in the reaction zone. In a particular case with an increase in pressure, there is a proportional increase in the amount of carbon and oxygen in a unit volume, and therefore despite the lack of pressure dependence of the burning rate of the individual particles, the thermal power released in a unit volume increases proportional to the pressure. In the theory of Ya. B. Zel'dovich this case would correspond to a monomolecular reaction in the gas phase. Thus the type of burning considered for black powder is formally the same as the burning of smokeless powder, in which the combusting carbon particles are like large molecules reacting according to a monomolecular law, the entraining of carbon in the gas stream is like gasification, and the heat required for dispersing the powder and preparing the burning mixtures comes from the gas phase. Consequently, as with smokeless powder the burning velocity of black powder must increase proportional to the square root of the pressure according to the monomolecular reaction law. Not limiting ourselves to the analogy given above, we give an additional means of determining the pressure-dependence of the burning rate of black powder when the combustion rate of the individual particles is independent of pressure. The flow of heat to the surface, which determines the rate of gasification of the condensed phase, proceeds from the reaction zone

along the stream of the gas-carbon mixture coming out of the powder. Let us consider a layer of the burning coal-gas mixture, characterized by a definite burn-out depth, i.e., by a definite burning time. With an increase in pressure the linear velocity of the stream of gases decreases in inverse proportion to the pressure, and since the combustion time of the dust particles does not depend on the pressure, the distance from the surface at which are found the burning particles and the hot burning products of the layer considered decreases; and the temperature gradient, which determines the heat flow to the surface of the powder is correspondingly increased proportional to the pressure.

The increase of the temperature gradient in the layer of the hot gas-carbon mixture considered does not result in its cooling because as the pressure increases so does the concentration of the gas-carbon mixture; i.e., so does the bulk thermal power released. Therefore the temperature of the gas layer considered is constant, it merely approaches the surface. The increase of the temperature gradient leads to an increase in the heat stream to the surface of the powder, i.e., to an increase in the rate of gasification.

We shall write an equation for the quantities of heat produced in the reaction zone and used up during the gasification of the powder

$$v_c \, \rho_c (T_s - T_0) C_c = \eta \, \frac{T_{eff} - T_s}{X_{eff}} = \eta \, \frac{T_{eff} - T_s}{v_g \tau_{eff}} \qquad (2)$$

$$v_g \rho_g = v_c \rho_c$$

where v_c, ρ_c, c_c are the rate of gasification, the density and heat capacity of the condensed phase; T_0, T_s, T_{eff} are the initial temperature of the powder, the temperature of the surface of the powder, and the effective temperature of the reaction region adjoining the surface of the powder and determining the heat supplied to the surface. T_{eff} can be less than the burning temperature. Burning may be completed far from the surface and the later stages of the reaction may have no particular effect on the temperature gradient at the surface of the powder.

/Note: We do not consider the transfer of radiant heat. During the burning of gas-carbon mixtures at atmospheric pressure it is noted in Reference 3 that radiation amounts to a negligible fraction in the heated mixture. With an increase of pressure the absolute contribution from radiation will increase somewhat initially, thanks to the increased opacity of the flame, and it tends to a constant value independent of pressure, which is determined only by the temperature of the flame ($\sim T^4$). The relative

contribution will fall off with pressure. In the latter case the burning velocity will depend more weakly on the pressure, than according to formulas (3) and (4) (see below)./

x_{eff} is the distance from the surface to the region in the gas having a temperature T_{eff}; τ_{eff} is the combustion time of that quantity of carbon required to achieve the temperature T_{eff}; η is the coefficient of thermal conductivity

$$(v_c \rho_c)^2 = \frac{\eta}{c_p} \frac{T_{eff} - T_s}{T_s - T_o} \frac{\rho_g}{eff} \qquad (3)$$

It was shown above that, since with an increase in pressure there is a proportional increase not only in the temperature gradient but also in the bulk thermal power released, T_{eff} cannot change with an increase in pressure. Since T_s depends slightly on the pressure, and η and T_{eff} do not depend on the pressure, in accordance with (3)

$$v_c \rho_c \sim \frac{\sqrt{\rho_g}}{r} \sim \frac{\sqrt{p}}{r} \qquad (4)$$

i.e., the burning velocity of the powder is proportional to the square root of the pressure. /Note: For an exponential dependence of the rate of the dissociation reaction on T_s, a small change in T_s is sufficient to significantly increase the stream of gases from the surface./ In the case where the burning of the carbon particles proceeds in the kinetic region, the rate of reaction on the carbon surface $\sim p^n$, where $0 < n \leq 1$. Correspondingly the rate of combustion of a particle $\tau \sim r/p^n$. Then according to (3)

$$v_c \rho_c \sim \sqrt{\frac{\rho_g}{eff}} \sim \sqrt{\frac{p^{1+n}}{r}} \qquad (5)$$

i.e., the burning velocity is proportional to the pressure to the $(1 + n)/2$ power and inversely proportional to the square root of the radius of the particle.

Thus, for the combustion of carbon in the kinetic region the burning rate of the powder depends more strongly on the pressure than for combustion in the diffusion region, and it can be proportional to the pressure (for $n = 1$).

The dependence of the burning velocity on the dimension of the particles is less in the kinetic region than in the diffusion region.

(4) and (5) were obtained on the assumption that a carbon particle always moves with the velocity of the gas. N. N. Bakhman

noted the fact that this assumption is not fulfilled for not too small particles. B. V. Novozhilov studied the actual motion of particles resulting from the velocity of burning of black powder, and obtained the result that in the diffusion region

$$v_c \rho_c \sim \frac{\sqrt[3]{p}}{r} \tag{6}$$

The expressions (3)-(6) are not to be considered as a solution to the problem of heat conduction in the burning of black powder. They are merely qualitative illustrations of the physical considerations on the pressure increase of the temperature gradients and the bulk thermal power release in hot gas-carbon mixtures coming off the black powder. The solution of the heat conductivity problem has been replaced by the introduction of T_{eff} and τ_{eff} and a consideration of the independence or weak dependence of T_{eff} and τ_{eff} on pressure in the case considered.

The author thanks Ya. B. Zel'dovich for suggesting the problem and for making valuable comments.

Conclusions

The pressure dependence of the burning rate of black powder is considered. It is assumed that the dispersion noted by N. F. Pokhil occurs, that during the burning of the powder a gas-carbon mixture is formed, which is liberated from the decomposing saltpeter, and that there is combustion of carbon particles in the stream of the coal-gas mixture. The time of combustion of a carbon particle in the diffusion region does not depend on the pressure, and the pressure dependence of the burning rate is obtained similarly to the theory of burning of smokeless powder given by Ya. B. Zel'dovich, as a result of the increase of the bulk thermal power released in a jet of the gas-carbon mixture with an increase in the concentration of the components and an increase of the temperature gradients.

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