# Observations on Burning and Flame-Spread of Black Powder

F.A. Williams*
*University of California, San Diego, La Jolla, Calif.*

**Results are reported concerning some experimental observations on the combustion of particles of black powder and some theoretical considerations on the process of flame spread through porous matrices of the material. The experimental work involved high-speed cinemicrography and scanning electron micrography of particles ignitied in air by a pulsed laser, by a spark, and by a hot wire. The theoretical work involved definition of two flame-spread models, a random walk of hot particles through the matrix producing ignition and multiplying in number at each stop, and a gas-like motion of the reacting region through the bed. The experiments demonstrate emission of hot high-velocity particles from a liquid layer on the surface of the burning propellant. They also identify extinctions subsequent to the short ignition stimuli and slow spread of flame along continuous surfaces. The theory produces formulas for the order of magnitude of the spread time and for its functional dependence on the void fraction of the matrix, the surface to volume ratio of the particles, and other design parameters. It is emphasized that many uncertainties remain, and that further experimental and theoretical work is needed.**

## I. Introduction

BLACK powder, the oldest propellant known to man, continues to be used today in certain specialized applications, notably in systems requiring rapid flame spread and production of multiple ignitions. Although the material has been subjected to scientific scrutiny continually since antiquity, its burning mechanisms remain poorly understood because of their complexity. Black powder is a mixture of salt peter, charcoal, and sulfur, in a ratio (weight percentages of about 75, 15, and 10) that corresponds almost exactly to stoichiometry for the reaction

$$2K\,NO_3 + 3C + S \rightarrow K_2S + N_2 + 3CO_2 \tag{1}$$

Thus, the powder itself is composed of three distinct solid phases, and in order to react, the materials from these three phases must find some way to intermingle molecularly. Intermingling is encouraged by blending finely divided particles of each phase into the final product, with consitituent particle sizes falling between 1 and 100 $\mu$ on the average. The blend is pressed into cakes, which are ground into sized pellets (mean diameter of roughly 300 to 3000 $\mu$) that are glazed with graphite. Measured products of combustion of pellets do not coincide with the right-hand side of Eq. (1), but instead include a variety of species, among which are NO, $NO_2$, and $K_2SO_4$.

Two important modern experimental studies on the combustion of black powder are those of Blackwood and Bowden[1] and of Campbell and Weingarten.[2] For initiation of combustion, Blackwood and Bowden ascribe importance to the fact that the melting points of sulfur and of potassium nitrate are approximately 120° and 330°C, respectively. They adopt the reasonable view that for reaction to begin at least one of the components must melt and flow to achieve close molecular contact with another component. The observation that grit addition enhances impact ignition only if the melting point of the grit exceeds that of sulfur is interpreted as suggesting that the melting and flowing of sulfur alone can produce ignition at sufficiently high pressures. At lower pressures, in the vicinity of atmospheric, the fact that the heated-plate ignition temperature lies between 300° and 350°C may be interpreted as suggesting that some melting of potassium nitrate is required. In any event, the idea that ignition occurs at a local hot-spot within the powder is well-substantiated.[1]

Thermal decomposition was studied by measuring rates of gas evolution under isothermal conditions of elevated temperature, for black powder as well as its constituents, separately and in pairs.[1] These observations, coupled with measurements of product composition, led Blackwood and Bowden to propose a reaction mechanism that was consistent with these results and also with initiation measurements. Important steps in the initiation mechanism were suggested to include

$$2\,K\,NO_3 + S \rightarrow K_2SO_4 + 2NO \tag{2}$$

$$K\,NO_3 + 2NO \rightarrow K\,NO_2 + NO + NO_2 \tag{3}$$

$$2\,NO_2 + 2S \rightarrow 2SO_2 + N_2 \tag{4}$$

and

$$2K\,NO_3 + SO_2 \rightarrow K_2SO_4 + 2NO_2 \tag{5}$$

as well as reactions involving $H_2S$ formed from organic constituents of charcoal. Equations (4) and (5) might be viewed as a chain, with $NO_2$ and $SO_2$ as carriers, and with Eq. (3) as the initiation process. Equations (2) and (5) are exothermic, whereas the others shown are endothermic. Hot potassium sulfate (melting point 1080°C) was a major condensed product, formed directly by Eq. (2) and also through the sequence of Eqs.(3)-(5).

Streak and high-speed framing photography provided a considerable amount of revealing information on flame propagation in black powder.[1] At atmospheric pressure, the normal regression rate of a burning pellet 2 mm in diam was observed to be only about 0.4 cm/sec, whereas the spread rate through a collection of particles was approximately 60 cm/sec. Under confinement, where pressure could build up, the spread rate measured by streak photography reached about 2000 cm/sec at an estimated pressure of 40 atm.

Received July 31, 1975; revision received Nov. 6, 1975. This work was supported by the Product Assurance Directorate, Picatinny Arsenal, through Battelle Columbus Laboratories. The experimental work was performed by Shivadev K. Ubhayakar with apparatus available from research sponsored by AFOSR (monitored by B.T. Wolfson). The author wishes to thank J. Craig Allen and Marc M. Ibiricu for providing materials, information, and comments helpful to the study.

Index categories: Combustion in Heterogeneous Media; Fuels and Propellants, Properties of.

*Professor of Aerospace Engineering, Department of Applied Mechanics and Engineering Sciences. Associate Fellow AIAA.

Framing photography of sparse arrays and analysis of "smoke" deposits on glass strongly suggested that spread was produced by traveling hot sprays of molten salts, with melting temperatures between 550° and 750°C, and with particle sizes ranging from less than 1 $\mu$ to more than 10 $\mu$. Fragments burning only on one side also could be propelled to produce spread. This rapid spread is not observed in black powder composed of fine particles (< 100 $\mu$ in diam) when they are packed in close contact; in this case propagation resembles normal regression of the larger pellets. However, later information suggests that spread rates through matrices of 2-mm pellets are lower than spread rates through matrices of 300-$\mu$ pellets, thereby indicating that there is an optimum pellet size for maximum rate of spread. It seems logical that hot salts containing $K_2SO_4$ are agents in rapid spread.

Campbell and Weingarten[2] employed differential thermal analysis and thermogravimetric analysis of black powder and mixtures of its components, similar to those of Blackwood and Bowden, obtaining overall activation energies for initiation in the vicinity of 14 kcal/mole, except in the absence of sulfur, in which case the activation energy increased to roughly 30 kcal/mole. The results lend support to the mechanism given in Eqs. (2)-(5), and also suggest that Blackwood and Bowden tended to overemphasize the importance of reactions of sulfur with charcoal organics.

Detailed measurements of the normal regression rate of black powder have been made at reduced,[3] elevated,[4] and very high[5] pressures. From results shown in Fig. 1, it is seen that the pressure exponent of the burning rate decreases as the pressure increases. The exponent appears to approach unity at very low pressures, but at higher pressures an increase in pressure by four orders of magnitude produces a rate increase of barely one order of magnitude. Although different segments of the curve can be assigned different slopes to suggest the existence of transition pressures at which the slope changes abruptly, the data in total are equally consistent with the illustrated continuous variation in slope.

Because of the complexity of black powder, a theoretical explanation of Fig. 1 is difficult to obtain. A model has been developed[6-8] in which the deflagration rate is controlled by processes occurring in a zone having a temperature in excess of 1000°K, much higher than temperatures typically prevailing during ignition. Carbon particles are viewed as being swept off the surface by gaseous products of reaction of sulfur and potassium nitrate, then burning in this two-phase flow by a surface reaction with gaseous oxidizer, primarily oxygen. The predicted dependence of the burning rate $m$ on the pressure $p$ and on the carbon particle diameter $d$ is $m \sim p^k/d^\ell$, where the exponents $k$ and $\ell$ range from ½-1, depending on whether the carbon combustion is diffusion-controlled or reaction-controlled. The functional dependences are not in excellent agreement with the data in Fig. 1, and Novozhilov[9] has estimated that the predicted burning rate lies well below that observed experimentally. These objections have been disputed,[10] but approximate agreement with data is achieved[10] only through rather extreme assumptions of complete carbon combustion to $CO_2$ in pure oxygen, derived from $KNO_3(\ell) \rightarrow KNO_2(\ell) + \frac{1}{2}O_2(g)$, with only small amounts of further vaporization or decomposition of $KNO_2$. Moreover, for the (sulfurless) model system studied,[10] predicted temperature sensitivities and dependences on $d$ do not agree well with experiment. Therefore, it seems quite possible that the model is inappropriate and that the deflagration rate is controlled by reactions occurring at lower temperatures in condensed phases.

The present work does not help much to clarify the normal regression mechanism. Instead, some new experimental observations, primarily relevant to initiation of combustion and to flame spread are given, based on techniques of high-speed cinemicrography and scanning electron micrography. Also, certain models of flame spread through matrices of pellets of black powder are outlined, as derived from the information summarized in the preceding, and from the new observations.

## II. Experimental Results

Black powder pellets with manufactured sizes in the vicinity of 0.5-3 mm were studied, and often were crushed to provide particles having sizes between 50 and 500 $\mu$. All tests were performed on single particles in air at atmospheric pressure. Three types of ignition were investigated, viz., laser ignition, spark ignition, and ignition by a heated wire. In the former case, a pulsed neodymium glass laser, described by Law,[11] was employed (maximum output 1 J, delivered in 0.2 msec). A particle was suspended on a fine glass fiber in the focal planes of the laser and of a framing camera; a timing circuit triggered the camera, backlighting, and laser, and the burning sequence was recorded at framing rates between 10,000 and 20,000/sec. In the case of spark ignition, the same methods of support and observation were employed, now at framing rates in the vicinity of 5000/sec; the spark fired repeatedly at irregular intervals. For hot-wire ignition pellets were supported away from solid surfaces on a pair of stretched nichrome wires through which a dc current was passed to provide heating; photographic recording was accomplished at framing rates comparable to those for spark ignition.

Typical sequences for laser ignition are shown in Fig. 2; the first is backlighted, whereas the second and third are not. In the first strip is seen the particle supported on the fine vertical fiber, the development of intense and largely one-sided combustion, cessation of combustion, and motion of the extinguished particle out of the field of view. Initiation of combustion coincides with the onset of the laser pulse; the wavelength of the laser light is such that it does not expose the film. The most intense burning always occurs on the side of the particle facing the laser, and extinguishment of combustion follows soon after termination of the laser pulse. The

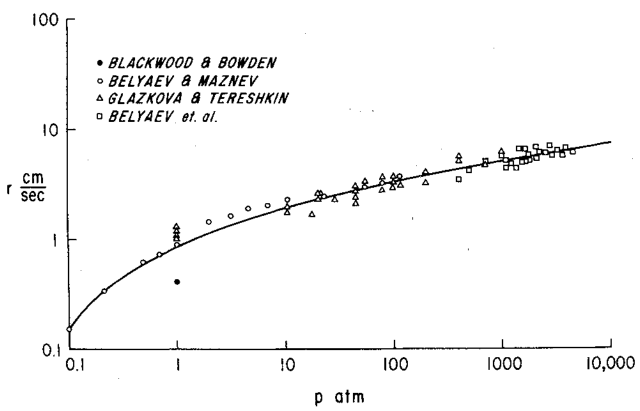


**Fig. 1 The normal regression rate of black powder as a function of pressure at 25°C.**

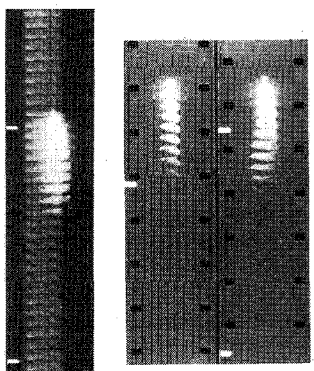

**Fig. 2 Laser ignition of black powder. The magnification is 0.72 on 16-mm film; marginal light markings occur at 1-msec intervals; approximate particle dimensions in hundreds of microns, left to right, are 8 × 8 × 5.5, 3 × 3.5 × 1, 6 × 6 × 1.2.**

particle moves in a direction opposite from its burning side. It should be emphasized that the activity visible in the film is combustion, not a laser-heating phenomenon. The laser intensity was kept to a minimum; with a small reduction in intensity, the particle failed to ignite. Irradiation of the probe alone, or of a carbon particle on the probe, produced much lower levels of exposure of the film at the same laser intensity.

The occurrence of extinguishment requires discussion. For purposes of comparison, laser ignition tests were made with particles of smokeless powder, and it was found that in this case a much less intense, spherically symmetrical flame developed, but again was extinguished upon cessation of the laser pulse. Extinguishment for this material has been studied previously.[12] Essentially, if the radiant pulse is either too intense or too brief, the heated layer at the surface of the propellant is too thin to sustain burning after the external energy source is removed. From boundaries determined for this extinguishment region for double-base formulations,[12] it is evident that extinguishment is to be expected in the present experiment with smokeless powder. Apparently the same situation prevails for black powder. In spite of this, it seems unlikely that the combustion phenomena observed during irradiation depend strongly on the energy input from the laser. While the burning occurs, it is so much more active for black powder than for other materials that its characteristics probably are not affected appreciably by external stimuli.

The long one-sided flame visible in the first strip of Fig. 2 was observed to occur over the entire size range of particles tested. Especially for the larger particles, bright streaks that move away from the surface are visible. These streaks, and the flame, may be seen more clearly without backlighting, as shown in the second and third strips of Fig. 2. The streaks must represent tiny but rapidly moving hot particles, possibly burning fragments of the parent particle, or else hot salts.

There are two different ways to obtain meaningful velocities from the photographs. One is to measure the initial rate of expansion of the luminous flame away from the particle of black powder. The other is to measure the lengths of the streaks and to divide by the exposure time of the frame (typically on the order of 1/40,000 sec). Both methods give velocities of approximately the same magnitude, on the order of 5000 cm/sec. This is very much larger than the flame-spread velocity (60 cm/sec) measured by Blackwood and Bowden[1] at atmospheric pressure; it even exceeds the spread rate they found (2000 cm/sec) after acceleration under confinement to 40 atm. The velocities obtained here may be interpreted as velocities of motion of individual particles that are responsible for flame spread, but not as spread rates, since spread represents an averaged effect of many particles. The fact that the streaks are much longer than those occasionally observed with smokeless powder, for example, suggests that black powder is much more efficient in transferring flame to adjacent particles.

A striking observation is the perpetual maintenance of one-sided burning for black powder. Flame spread along the surface of a black-powder particle appears to be very slow compared with that of a smokeless-powder particle, for example. This suggests that the black-powder spread mechanism is primarily from particle to particle, rather than along the surfaces of individual particles.

Figure 3 compares scanning electron micrographs of particles of black powder before and after laser irradiation. The crushed black powder is quite angular beforehand, and the high magnification shows that it contains many small crystals of widely varying sizes. After irradiation, the particle appears much smoother, showing definite evidence of liquid formation during combustion. The microcrystals are less pronounced but still visible in the high magnification after burning. A few craters appear to be present after combustion, possibly marking local sources of gas generation. Cratering and bubbling is much more evident in corresponding micrographs for smokeless powder. There seems to be no indication in these micrographs or in the motion pictures that the burning mechanism involves carbon combustion in a gaseous oxidizer, but there appears to be definite evidence for the occurrence of surface reactions in a liquid layer.

Although Blackwood and Bowden[1] report that there is no ignition by a spark, Fig. 4 demonstrates that in some instances a spark can initiate fleeting combustion. The intermittent spark is visible as a sharp, wavy streak in a few of the frames. The combustion generated by the spark is qualitatively similar to that produced by the laser pulse. The burning is not self-sustained; the reason for extinguishment probably is similar to that operative with laser ignition. The black powder can be consumed nearly completely with repeated sparks. The tendency for the particle to move away from the spark, observed by Blackwood and Bowden, also was found to occur often in the present tests.

With hot-wire ignition, in contrast to the buring produced by other methods of ignition, combustion of the particle proceeded to completion, probably because of a greater amount of heating of the particle prior to ignition. Well before completion of burning, the particle drops off its supporting wires and moves out of the field of view of the camera. Point ignitions again are achieved, in this case at a contact between a wire and the particle. There is a rapid production of a long hot streak of reaction products, emanating from the ignition point. This is similar to the streaks observed with laser ignition. Although the lower framing rates prevented accurate measurement of hot-particle velocities, the data are consistent with speeds previously quoted for laser ignition. In addition, burning of the particle from the hot-spot, with very little spread to the rest of the surface, is characteristic of the combustion process. Therefore, the combustion mechanism appears to be independent of the mode of ignition.

In summary, the present experiments support the idea that black powder is very efficient for producing flame spread by mechanisms that involve direct transfer of hot particles. They also suggest that lateral spread of flame along the surface of a single particle of black powder is slow, and under conditions of close packing might be a rate-limiting step.

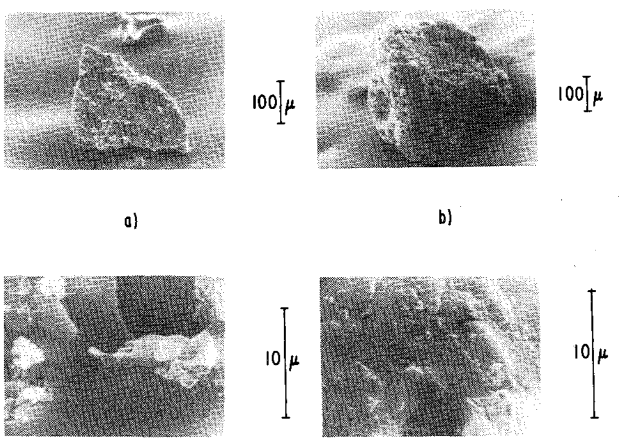


**Fig. 3 Scanning electron micrographs of black powder before and after laser irradiation.**

## III. Gas-Like Model for Flame Spread through a Matrix

If it is agreed that travel of hot salt particles through the black-powder pellet mix is responsible for the flame-spread process, then the problem of predicting the spread rate becomes the problem of predicting the rate of progression of hot particles. The paths that these particles must traverse through the gas is so tortuous that the progression rate cannot be obtained directly from the particle velocities. A difficult

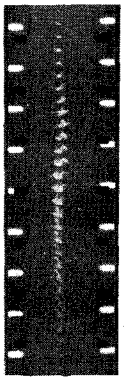

Fig. 4 Spark ignition of black powder (magnification 0.3).

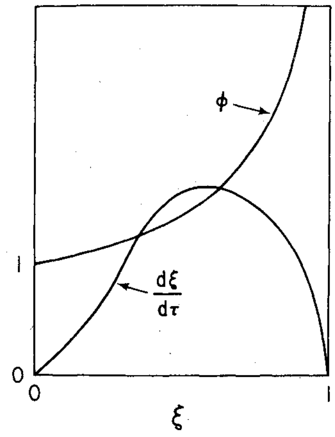


Fig. 5 Schematic illustration of theoretical spread rate and pressure as functions of the distance of the reaction front from the point of ignition.

statistical problem arises. There is at least one simplifying assumption that bypasses the statistical problem and which may be correct in limiting cases. This is the assumption that, on the average, the hot salt particles progress through the propellant at the same rate as the hot gaseous reaction products. With this assumption, spread rates may be calculated by considering only gas flow, and a gas-like model emerges.

It is relevant to ask under what conditions the model may tend to be valid. If the hot particles always moved with the same velocity vector as the local velocity vector of the gas, then the model would be correct. This condition clearly is not attained in the experiment just reported, since the calculated normal gas velocity is less that 500 cm/sec, while the observed particle velocities reach 5000 cm/sec. However, high pressure and small particle size (e.g., small constituent particle sizes in the manufacture of the material, provided that hot salt particle sizes are directly related to constituent particle sizes) tend to favor rapid velocity equilibration between gas and particles; therefore, for suitably produced black powder, the assumption may be good at high pressures. Also, it appears that if the packing is very close and the pellets are highly irregular, so that the path is quite tortuous, the particles that travel in nearly straight lines and do not follow the gas, very often will collide with solid surfaces, and therfore make slow progress through the charge, possibly no faster than the gas. Sufficiently high tortuosity and low porosity, therefore, also can favor the model.

For simplicity, the approximation of a spatially constant pressure throughout the chamber will be introduced. This should be viewed as a first step warranting later improvement. The approximation tends to be best at high porosity, and it is unclear whether it is consistent with the aforementioned restrictions.[13] Therefore, the present model must be viewed as speculative. An alternative model can be defined, in which there is a strong quasisteady pressure gradient, with high pressure prevailing in the burning portion of the matrix and low pressure in the nonburning portion, the resistance of the bed impeding the gas flow and supporting the pressure gradient. Such a model should be amenable to analysis but is not developed herein. There has been some previous work along these line.[14,15]

Consider a chamber of volume $V$ and length $L$, packed with pellets of black powder such that the void fraction is $\epsilon$ (the ratio of the volume not occupied by the powder to the total volume of the chamber). At time $t=0$ ignition will occur at one of the chamber $x=0$, and flame will propagate through the chamber to the other end $x=L$. The volume of gas in the chamber $\epsilon V$ is composed of two parts, the original gas (subscript 1) and gaseous reaction products (subscript 2). If it is assumed that the original gas is compressed isentropically, then at any given time its volume is

$$V_1=\epsilon V(p_0/p)^{1/\gamma} \tag{6}$$

where $p$ is chamber pressure, $p_0$ is the initial pressure, and $\gamma$ the specific heat ratio for the original gas. Neglecting the decrease in pellet volume during the spread process (a reasonable approximation), the volume occupied by product gases will be

$$V_2=\epsilon V-V_1 \tag{7}$$

The product gases are treated as ideal, with mean molecular weight $\bar{W}$ and flame temperature $T_2$. Here both of these quantities will be taken as fixed constants. The poorest approximation is constancy of $T_2$, which will increase as $p$ increases and be different for different elements of the product gas. However, estimates on adiabatic compression suggest that the approximation will be reasonable perhaps up to a pressure of the order of 100 atm. With the given approximations, the density of the product gas is

$$\rho_2=p\bar{W}_2/R^\circ T_2 \tag{8}$$

where $R^\circ$ is the universal gas constant.

The mass of the product gas is $\rho_2 V_2$, and the time rate of increase of this mass is determined by the burning rate. Let $m$ be the normal burning rate (mass per unit area per second) of a particle of black powder. This quantity is the product of the regression rate $r$, shown in Fig. 1, with the density of black powder $\rho_p=1.75$ g/cm$^3$. If $\mu$ denotes the surface area of the collection of pellets per unit chamber volume, then a mass balance gives

$$(d/dt)(\rho_2 V_2)=m\mu(V_2/\epsilon) \tag{9}$$

in which the final factor is the chamber volume occupied by flame at any given time.

Define a nondimensional pressure as $\varphi=p/p_0$ and a nondimensional time as

$$\tau=tm_0\mu R^\circ T_2/(\epsilon p_0\bar{W}_2) \tag{10}$$

where $m_0$ is the value of $m$ at $p=p_0$. Put $m=m_0 f(\varphi)$, where the function $f(\varphi)$ can be obtained from Fig. 1. Equations (6)-(9) may then be used to show that

$$(d/d\tau)[\varphi(1-\varphi^{-1/\gamma})]=(1-\varphi^{-1/\gamma})f(\varphi) \tag{11}$$

The integral of Eq. (11) gives the pressure-time history

$$\tau=\int_1^\varphi\left[1-\left(\frac{\gamma-1}{\gamma}\right)\varphi^{-1/\gamma}\right]\left[\left(1-\varphi^{-1/\gamma}\right)f(\varphi)\right]^{-1}d\varphi \tag{12}$$

The spread rate $dx/dt$ can be obtained from the relationship

$$\xi\equiv x/L=V_2/\epsilon V \tag{13}$$

From Eqs. (6) and (7), it seen that in Eq. (13)

$$\xi=1-\varphi^{-1/\gamma} \tag{14}$$

A nondimensional rate of spread then is found to be from Eq. (11)

$$(d\xi/d\tau)=\xi(1-\xi)^{\gamma+1}f/[1+(\gamma-1)\xi] \tag{15}$$

A schematic illustration of the dependence of spread rate on flame position, as predicted by Eq. (15), is shown in Fig. 5. Also shown is a curve for the nondimensional chamber pressure.

A number of aspects of this theoretical result on spread rate deserve comment. First, it is seen that theoretically the rate begins at zero because the initial volume of burning pellets is zero. Of course, this is unrealistic, because initially there will be a finite volume of burnt gas. Moreover, the assumption that the hot salts move with the gas is unlikely to be realistic at the instant of initiation. A portion of the curve near $\xi = 0$, therefore, should be excluded in Fig. 5.

Shortly thereafter, the model predicts a linear increase in velocity with position. This is caused by the continuously increasing volume of burning powder, under conditions such that the normal regression rate remains approximately constant; it is a direct effect of hot-gas motion. During this early-time period, the distance time formula is simply

$$\xi = e^{\tau} - 1 \tag{16}$$

which has a linear growth for small $\tau$ and an exponential growth for large $\tau$. Later, if the effect of $f$ exceeds that of $(1-\xi)^{\gamma+1}$, the velocity increases more rapidly than linearly with $\xi$, i.e., the flame travel is greater than that given by Eq. (16), because of the increase in normal regression rate with increasing pressure. This result (from Fig. 1) causes $f$ to increase with $\xi$, thereby tending to produce increased acceleration. This effect is likely to be present in real matrices as well as in this simplified model. A rough way of extending Eq. (16) to account approximately for this effect is to write

$$\xi = e^{f\tau} - 1 \tag{17}$$

although in reality

$$\int_0^{\tau} f d\tau$$

should appear instead of $f\tau$, when $(1-\xi)^{\gamma+1}$ is neglected.

As the flame approaches the end of the matrix, the model predicts that the spread rate begins to decrease; eventually the rate is predicted to go to zero and the pressure to infinity. This effect is physically incorrect and is caused by breakdown of a number of assumptions of the model at late times. First of all, the assumption of constant $T_2$ becomes invalid. Secondly, the model has assumed that pellets occupy the entire chamber, but typically there is additional free gas volume. An improvement in the model can be effected by artificially increasing $L$ to account for this excess volume and by employing the present results only up to a value of $\xi$ less than unity, say $\xi_f$. In this case, $\xi_f$ will be the ratio of the free volume in the matrix to the total free volume. The model is likely to break down if $\xi \gtrsim 0.5$.

Although the model is one-dimensional as stated, there is no difficulty in applying it to charges of arbitrary shape. In the general case, $\xi$ is the ratio of the free volume subtended by the spreading flame to the total free volume of the charge. Instead of giving a velocity or linear spread rate, the model then gives a rate of increase of volume, without determining the shape of the burning volume.

Perhaps the most important result of the model is its qualitative prediction of the dependence of a spread time on design parameters. This prediction is given by Eq. (10). The nondimensionalization is such that $\tau$ is of order unity. Therefore according to Eq. (10), the spread time varies as

$$t \sim (\epsilon p_0 \bar{W}_2)/(m_0 \mu R^\circ T_2) \tag{18}$$

In order to reduce the spread time, one may decrease the void fraction, increase the surface-to-volume ratio of the black powder (e.g., use smaller pellets), increase the flame temperature, decrease the mean molecular weight of reaction products, or increase the ratio of the normal regression rate to the pressure. Most of these predicted dependences are physically reasonable over a fairly wide range of conditions.

## IV. Random Walk with Multiplication for Flame Spread

The worry in any gasdynamic model is that the hot particles may not follow the gas motion. The opposite extreme is that in which each hot particle travels with a fixed constant velocity, say of magnitude $v$, independent of the gas motion. Since experimental observations suggest that the particle velocity is not related to the gas velocity, it would seem reasonable to assign each hot particle a constant velocity, provided that the gas pressure is not too high, the particle is not too small, and the distance the hot particle travels is not too great (i.e., the packing is not too loose). This velocity might be produced either by the rapid burst of combustion-produced gas at the surface of the pellet when the particle is generated or by continued gas production in the wake through continuing combustion of the particle as it travels. Of course, there will be a distribution of velocities among hot particles, but for the purposes of discussion the distribution can be approximated as a delta function.

The particle velocity $v$ will not be identical with the flame spread rate, because the hot particles are obstructed in their travel by the the black powder pellets. One might assume that the particles are emitted in random directions, and that they travel an average distance $\delta$ before encountering another pellet. The value of $\delta$ will depend on the pellet size and the degree of packing. It would appear that $\delta$ is likely to increase with increasing pellet size, probably proportionally, but that $\delta$ will be apparently smaller than the size of a typical pellet.

Given $v$ and $\delta$, and given that hot particles travel in random directions, there exists a basis for a spread model based on a three-dimensional random walk. Particles may be viewed as moving in a straight line for a distance $\delta$, stopping to select a new direction at random, and then again moving straight for a distance $\delta$, etc. The random walk in three dimensions is well known,[16] but its visualization in the present problem is more difficult. It usually is assumed that the entire three-dimensional space is available to the particle. In the present case only the free volume is available; at each step approximately half of the $4\pi$ solid angle is excluded from the selection of direction by the presence of the black powder pellet on which the particle is generated. It should be easy to devise geometrical arrangements in which this exclusion strongly influences the character of the random walk. However, it also should be possible to hypothesize sufficiently randomly oriented surfaces of black powder for the process to be viewed as an ordinary random walk occurring in the free volume only.

There are aspects of the ordinary random walk that are not consistent with the existing knowledge on flame spread. A Gaussian density function results, and the distance traveled by a particle is known to be proportional to the square root of time $x \sim t^{1/2}$. Thus, the effective macroscopic velocity of the particle decreases as time increases, $x/t \sim 1/t^{1/2}$. This would suggest, contrary to experiment, that the spread rate is greatest at the time of initiation. The discrepancy implies that the conventional random walk is insufficient for describing the spread process.

In order to circumvent the difficulty, one might try to allow $v$ to increase with pressure (i.e., with time), reasoning that it should increase with increasing normal regression rate. However, this approach does not seem very promising; for example, it is unlikely to produce agreement with the experiments of Blackwood and Bowden at atmospheric pressure. A better approach is to recognize that after a hot particle ignites a point on the surface of a pellet, that point usually emits many (not one) hot particles, which travel in different random directions (see, for example, Fig. 2). The model that suggests itself then is one of a random walk with

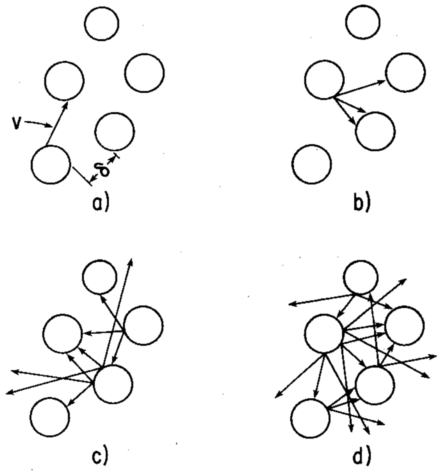


**Fig. 6 Schematic model of random walk with multiplication.**

multiplication. At each step, instead of one particle leaving the point in a random direction, a number $n>1$ of particles leave the point in random directions. This type of multiplication will modify the dynamics of the random walk and physically could be expected to produce an effective macroscopic velocity that remains constant or increases with time.

The model is illustrated schematically in Fig. 6 for the case $n=3$. The four parts, a), b), c), and d) show the travels that occur at four successive time steps. From the point at which the first particle impinged, three particles emerge in b). From each of the three new impingement points, three more particles emerge in c). It is seen that intensities of combustion would increase rapidly, as observed experimentally.

A three-dimensional random walk with multiplication apparently has not been analyzed in the literature. The mathematical problems involved would be quite interesting. The problem might well be tractable and might admit steady-state traveling-wave solutions corresponding to a constant rate of flame spread. The mathematical problem will not be attacked here; attention is restricted to qualitative aspects of the results.

A characteristic diffusion coefficient for the model is $\alpha = v\delta$. A representative spread velocity then would be $\alpha/\ell$, where $\ell$ is a characteristic distance. Without further analysis, it is unclear what the appropriate identification of $\ell$ is. It might be expected that $\ell$ will exceed $\delta$ and also exceed the representative pellet size; perhaps $\ell$ would be of the order of the diameter or length of the pellet matrix. The spread rate $v\delta/\ell$ would then be appreciably less than $v$. If 5000 cm/sec is representative of $v$ (Sec. II) and 60 cm/sec is a characteristic spread rate,[1] then $\delta/\ell$ would be of order $10^{-2}$.

The time for flame spread, predicted by the model, would be of order

$$t \sim L(\delta/\ell)/v \tag{19}$$

where $L$ is the length of the matrix. If $v$ is proportional to $m$, and if $\delta$ is proportional to $\epsilon/\mu$, then Eq. (19) agrees with Eq. (18) in at least two respects. There would clearly appear to be other respects in which the two equations differ. Further study of the random walk with multiplication would be of interest.

## V. Conclusions

Combustion of black powder is a complex process, as is the mechanism by which flames spread through a porous matrix of the material. During combustion there is a liquid layer on the surface of a pellet of black powder, and hot particles, a few microns in diameter, are emitted at high velocity (up to 5000 cm/sec) from the surface. These particles may be composed only of potassium salts, or may contain burning carbon as well. The hot particles probably are very efficient in producing rapid flame spread from pellet to pellet in a porous matrix. On the other hand, on a continuous surface of black powder, the rate at which flames spread from ignited to unignited regions would appear to be slow, judging from high-speed photography of burning particles ignited on only one side.

Hot-wire ignition of pellets of black powder results in continued burning leading to nearly complete consumption of the propellant. However, both pulsed-laser and spark ignition result in a brief period of combustion, followed by extinguishment. It is believed that this is because these latter ignition techniques produce too shallow a heated layer at the surface of the material.

Theoretical analyses of flame spread through a matrix of black powder are in a primitive stage of development. It seems likely that at a sufficiently high porosity, a model involving a random walk of hot particles, with multiplication of the number of traveling particles at each stop, may be proper; however while at a sufficiently low porosity a gasdynamic model of some type may be preferable. A simplified gas-like model predicts that the spread time is directly proportional to the void fraction of the matrix, and is inversely proportional to the ratio of surface area to volume of the pellets, the flame temperature, and the ratio of the normal regression rate to the pressure. Further theoretical work seems warranted on the random-walk model and on a gasynamic model that admits spatial gradients of pressure. Also, experiments on flame spread through matrices would be of interest, for the purpose of ascertaining functional dependences that can be checked against theory.

Further detailed experimental work on the combustion of black powder would be of interest. It should be possible to measure ignition times associated with the impingement of hot salt particles on the surface of the nonburning propellant, rates of flame spread along continuous surfaces of the material (e.g., by use of either large pellets or tightly packed, fine powder), and motions in the gas of the hot particles generated by the surface burning process. Such information would contribute to our understanding of both the normal-regression and the flame-spread aspects of black-powder combustion.

## References

[1] Blackwood, J.D. and Bowden, F.P., "The Initiation, Burning and Thermal Decomposition of Gunpowder," *Proceedings of the Royal Society of London* A213, 1952, pp. 285-306.

[2] Campbell, C. and Weingarten, G., "A Thermoanalytical Study of the Ignition and Combustion Reactions of Black Powder," *Transactions of the Faraday Society*, Vol. 55, 1959, pp. 2221-2228.

[3] Belyaev, A.F. and Maznev, S.F., "Dependence of Burning Rate of Smoke-Forming Powder on Pressure," *Doklady Akademiia Nauk SSSR* Vol. 131, 1960, p. 887.

[4] Glazkova, A.P. and Tereshkin, A.A., "Relation Between Pressure and Burning Velocity of Explosives," *Zhurnal Fizikii Khimii*, Vol. 35, 1961, pp. 1622-1628.

[5] Belyaev, A.F., Korotkov, A.I., Parfenov, A.K., and Sulimov, A.S., "The Burning Rate of Some Explosive Substances and Mixtures at Very High Pressures," *Zhurnal Fiziki i Khimii*, Vol. 37, 1963, p. 150.

[6] Bakhman, N.N., "Transfer of Dispersed Particles by the Gas Current in the Combustion of Powders," *Doklady Akademiia Nauk SSSR* Vol. 129, 1959, pp. 824-826.

[7] Leipunskii, O.I., "Dependence on Pressure of the Rate of Combustion of Black Powder," *Zhurnal Fiziki i Khim*, Vol. 34, 1960, pp. 177-181.

[8] Novozhilov, B.V., "The Burning Rate of a Model Two-Component Powder Mixture," *Doklady Akademiia Nauk SSSR* Vol. 131, 1960, p. 1400.

[9] Novozhilov, B.V., "Theory of Combustion of a Model Mixture of Black Powder," *Zhurnal Fiziki i Khim*, Vol. 36, 1962, pp. 1803-1806.

[10] Zakharov, V.M. and Klyachko, L.A., "Concerning the Burning Rate of a Model Composite Propellant," *Fizika Goreniya i Vzryva* Vol. 8, 1972, pp. 15-26.

[11]Law, C.K. and Williams, F.A., "Combustion of Magnesium Particles in Oxygen-Inert Atmospheres," *Combustion and Flame*, Vol. 22, 1974, pp. 383-405.

[12]Ohlemiller, T.J., Caveny, L.H., DeLuca, L., and Summerfield, M., "Dynamic Effects on Ignitability Limits of Solid Propellants Subjected to Radiative Heating," Fourteenth Symposium (International) on Combustion, The Combustion, The Combustion Institute, Pittsburgh 1973, pp. 1297-1307.

[13]Gough, P.S., personal communication, Montreal, May 1975.

[14]Kuo, K.K., Vichnevetsky, R., and Summerfield, M., "Theory of Flame Front Propagation in Porous Propellant Charges under Confinement," *AIAA Journal*, Vol. 11, April 1973, pp. 444-451.

[15]Gough, P.S., "Flow of a Compressible Gas through an Aggregate of Mobile Reacting Particles," Ph.D. thesis, Department of Mechanical Engineering, McGill University, Montreal, Dec. 1974.

[16]Papoulis, A., *Probability, Random Variables and Stochastic Processes*, McGraw-Hill, New York, 1965.