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A Temperature-Profile Study of the Combustion of Black Powder and its Constituent Binary Mixtures

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Eine Untersuchung des Temperaturprofils beim Abbrand von Schwarzpulver und dessen binären Mischungskomponenten

Eine frühere thermoanalytische Untersuchung von Schwarzpulver mit kleinen Probemengen und langsamen Aufheizraten wurde erweitert auf eine Untersuchung des Schwarzpulvers unter den weniger kontrollierbaren Bedingungen der Anzündung und Verbrennung durch gleichzeitige Messung der Temperaturprofile und Abbrandgeschwindigkeiten.

Wird die Abbrandgeschwindigkeit in Abhängigkeit von der Zusammensetzung aufgetragen, ergeben sich konkav abwärtsverlaufende Kurven bei den verschiedenen Mischungen von Holzkohle mit KNO_3 (schwefelfreies Schwarzpulver) und bei Holzkohle/KNO_3-Mischungen mit unterschiedlichen Anteilen an Schwefel. Die Zusammensetzung der Mischung mit maximaler Abbrandgeschwindigkeit stimmt nicht überein mit der Zusammensetzung der Mischung mit maximaler Reaktionsenthalpie. Das Maximum der Temperaturen wurde registriert bei etwa 1400 °C. Es wurde gefunden, daß die Abbrandgeschwindigkeiten abnehmen mit zunehmender Teilchengröße der Bestandteile, mit zunehmender Kompaktierung der Mischungen oder, wenn inerte Füllmittel oder zusätzliche Brennstoffe zugemischt werden. Die Abbrandgeschwindigkeiten werden auch beeinflußt durch einen Feuchtigkeitsgehalt größer als 2%, ein Fehlabbrand tritt bei einer Feuchtigkeit oberhalb 15% ein.

Etude de l'évolution de la température lors de la combustion de la poudre noire en fonction de sa composition

Une étude thermoanalytique antérieure, effectuée sur de petits échantillons de poudre noire avec des montées en température lentes, a été étendue à la réaction plus difficilement contrôlable de l'allumage et de la combustion avec mesure simultanée des profils de température et des vitesses de combustion. Lorsqu'on représente la vitesse de combustion en fonction de la composition, on obtient des courbes concaves tournées vers le bas pour les différents mélanges de charbon de bois et de nitrate de potassium (poudre noire sans soufre) et les mélanges contenant à coté du charbon de bois et du nitrate de potassium, différentes proportions de soufre. La composition ayant la vitesse de combustion la plus élevée, n'est pas identique à celle présentant l'enthalpie de réaction maximale. La température maximale enregistrée est d'environ 1400 °C. On a constaté que les vitesses de combustion diminuent lorsque la taille des grains des constituants augmente, lorsque le mélange est plus fortement compacté ou lorsqu'on ajoute des composants inertes ou des combustibles supplémentaires. Une humidité supérieure à 2% influence également la vitesse de combustion; au-delà de 15% d'humidité, la réaction de combustion devient douteuse.

Summary

An earlier thermo-analytical study of black powder, using small sample masses and slow heating rates, has been extended to an examination of the behaviour of black powder under the less-controlled conditions of ignition and combustion, by simultaneous measurement of temperature profiles and burning rates.

Burning-rate against composition curves for various charcoal/KNO_3 mixtures (sulphurless black powder) and for charcoal/KNO_3 mixtures with various proportions of sulphur, were concave-down-type curves. The compositions of mixtures with maximum burning rates did not correspond with the compositions of mixtures with maximum enthalpy-of-reaction. Maximum temperatures of ~ 1400 °C were recorded. Burning rates were found to decrease with increasing particle size of the constituents; with increasing compaction of the mixtures, or when inert diluents or subsidiary fuels were added to the mixtures. Burning rates were also affected by moisture contents above 2%, and failure of burning occurred at $>15\%$ moisture.

1. Introduction

Black powder has a long and intriguing history[1–4] and the burning of black powder has been extensively studied[5]. This study complements a recent thermo-analytical study of black powder and its constituents[6]. The reactions which occur during thermal analysis at slow heating rates are not necessarily those which take place during the ignition and combustion of black powder, but thermal analysis does provide insights into the main factors which need to be taken into account in studying the combustion.

The black powder used in this and the previous study[6] was prepared by dry mixing of the ingredients or via a water-based paste[7]. The wet paste is non-explosive in bulk and is only dried as required.

Information on the burning of pyrotechnic compositions can be obtained through simultaneous measurement of burning rates and of temperature profiles[8–10] as the burning front of a column of pyrotechnic material passes a temperature sensor. In those few pyrotechnic systems where mass transport is negligible, the measurement of temperature profiles can be used to obtain quantitative kinetic and thermodynamic information[9,10]. The complex burning of black powder, which involves gaseous and molten intermediates and products, precludes a quantitative kinetic study, but the measurement of temperature profiles still provides useful qualitative and semi-quantitative information on the burning. The effects of varying factors such as compositions, particle sizes and the presence of additives of various kinds (including residual water in the paste), on the profiles and the burning rates can be readily examined.

2. Experimental

2.1 Techniques

Powdered samples of sulphur, KNO_3 and charcoal (moisture 4.5%, volatiles 16.0%, fixed carbon 77.2% and ash 2.2%) were supplied by AECI Explosives and Chemicals Ltd. Dry, sieved (<53 μm) powders were mixed by end-over-end tumbling in the presence of small rubber balls.

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Pastes were prepared by mixing the ingredients in a small planetary-type mixer, with a water-jacketed bowl for operation above room temperature. The pastes were spread thinly on glass plates and dried slowly at room temperature to try and avoid diffusive transport and crystallization of KNO_3. The dried samples were scraped off the plates, gently crushed in a mortar and sieved through a < 150 µm screen. These sieved powders were then further dried in an oven at 75 °C for 10 h.

Samples were burnt in a stainless-steel channel, 1-mm thick and $30 \times 6 \times 6$ mm^3 in internal dimensions. Thermocouples of platinum/10% rhodium, platinum wires (0.1 mm in diameter for rapid response) were inserted in slits cut 10 mm from one end of the channel. The thermocouples were electrically insulated from the channel with asbestos paper. Two additional slits, 3 mm from each end, were cut for recording burning times, by triggering of a timing circuit activated by infrared detectors.

Samples (~ 1 g) were loaded into the channel in layers and gently tamped. The filled channel, a stainless-steel lid and a metal spacer were positioned in a hydraulic press and pressed for one minute under a load of approximately 1 ton. Some samples were only lightly pressed manually using a wooden block. Unless otherwise stated, mixtures were hydraulically pressed.

Surface burning, commonly observed in propellant mixtures[11], in which a thin section of a mixture burns rapidly over the surface leaving the actual combustion front behind, was observed during the burning of black powder. After several trials, the surface burning was successfully inhibited when a solution of 20% "Genkem" glue in CH_2Cl_2 was applied, to the exposed surface of the packed column, followed by drying in an oven at 70 °C for 15 min. Temperature profiles for coated and non-coated mixtures were virtually identical.

Black powder could be ignited using a match-head, but the binary charcoal/KNO_3 mixture could not, so for uniformity all black powder compositions were ignited using a short starter increment of a 50% Mn/$KMnO_4$ composition.

Enthalpies of reaction were determined in inert atmospheres using a Perkin-Elmer DSC-2 differential scanning calorimeter and a 1314 Parr bomb calorimeter.

2.2 Recording system

The thermocouple output was fed via a low-noise D.C. amplifier and a fast (< 25 µs conversion time) 12 bit analog-to-digital converter to a South Western Technical Products 6809 microcomputer.

Software written in FORTH was used to monitor the thermocouple output and to commence data capture above a threshold set to 70 °C. Sampling intervals were from 1 ms to 65 ms with a maximum of 2048 data points.

3. Results

3.1 Burning of 12.5% charcoal/KNO_3 mixtures

Typical temperature profiles for hand-packed and pressed columns of this mixture are shown in Fig. 1. A rapid rise in temperature over 400 ms is followed by a noisy maximum temperature region (~ 1000 °C) over the next 2000 ms. The rise-time of the profile and the burning rate are inversely related[9,10]. The subsequent cooling curve shows some exothermic processes associated with the solidification of molten products. A significantly longer rise time to maximum temperature (up to 800 ms) as well as a lower maximum temperature (850 °C) was observed for pressed columns. The burning of pressed powders was, however, not always sustained.

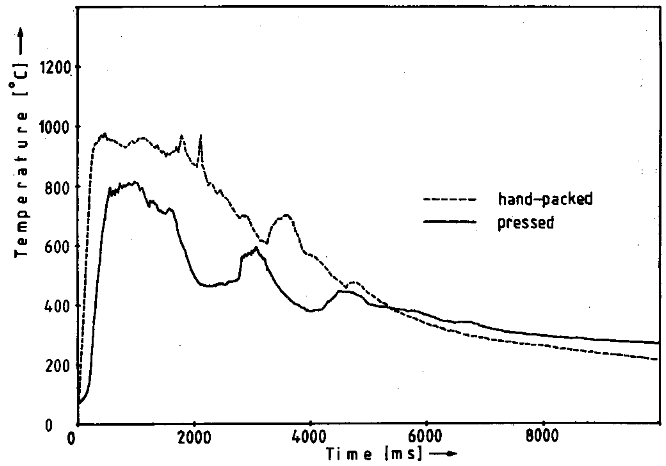

Figure 1. Temperature profiles of 12.5% charcoal/KNO_3 mixtures (pressed and hand-packed).

Discontinuities which occur on the slopes of profiles at approximately 420 °C to 440 °C, during the rise to maximum temperature, lie within the range of DTA ignition temperatures for binary charcoal/KNO_3 mixtures reported by Kirshenbaum[12].

The burning rates and profiles obtained for both pressed and hand-packed columns were not very reproducible. The molten slag formed may act as a partial seal during the reaction and may force the hot evolved gases forward ahead of the burning front, resulting in poor reproducibility. Burning rates were 0.16 ± 0.01 cm/s and 0.20 ± 0.01 cm/s, for pressed and hand-packed powders respectively. The enthalpy of reaction determined from bomb calorimetry was -2.75 ± 0.09 kJ/g and compares well with the value of -2.83 ± 0.20 kJ/g determined from DSC curves[6].

3.2 Other charcoal/KNO_3 mixtures

A plot of the burning rates of a range of compositions of the binary (sulphurless) mixtures against the charcoal content, for hand-packed and pressed columns, is shown in Fig. 2. Also

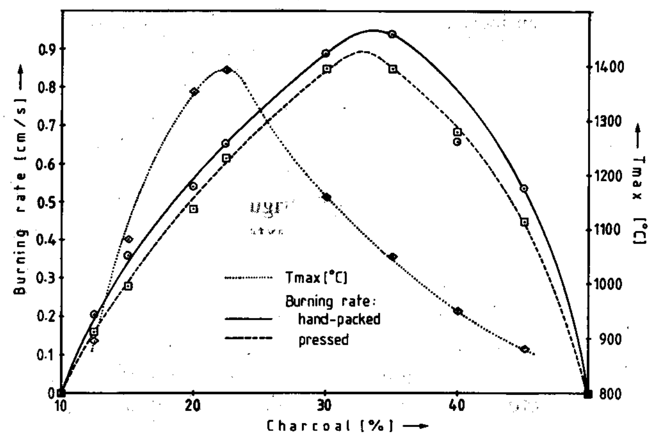

Figure 2. Burning rate and T_{max} against percentage charcoal for various charcoal/KNO_3 compositions.

shown is the maximum reaction temperature (without correction for heat loss).

Generally, hand-packed powders burned faster than pressed columns. The 10% charcoal compositions, both as loose powders and when slightly compacted, failed to ignite. Slightly compacted 50% charcoal mixtures were ignited, but a self-propagating reaction could not be sustained. Smoke emitted from the unburnt end of the channel indicated permeability of the column.

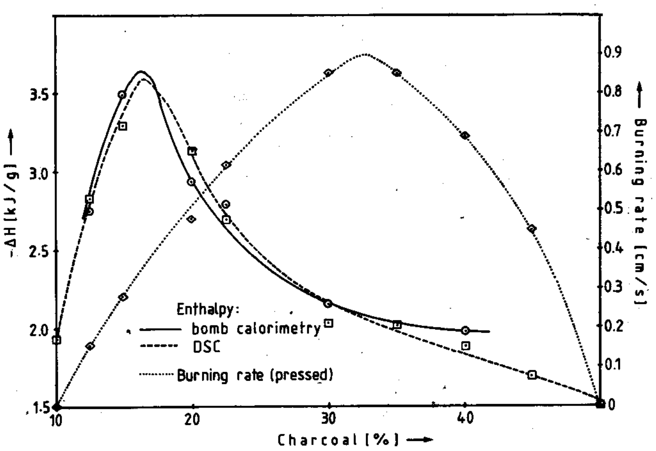

Figure 3. Enthalpy of reaction against percentage charcoal for various charcoal/KNO_3 compositions.

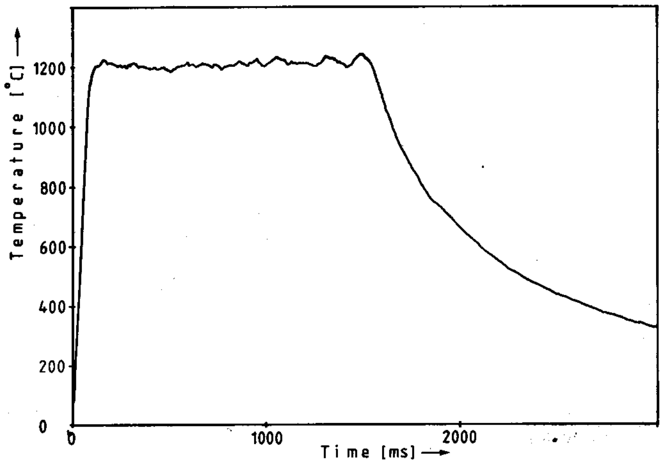

Figure 4. Temperature profile of the ternary mixture over 3000 ms.

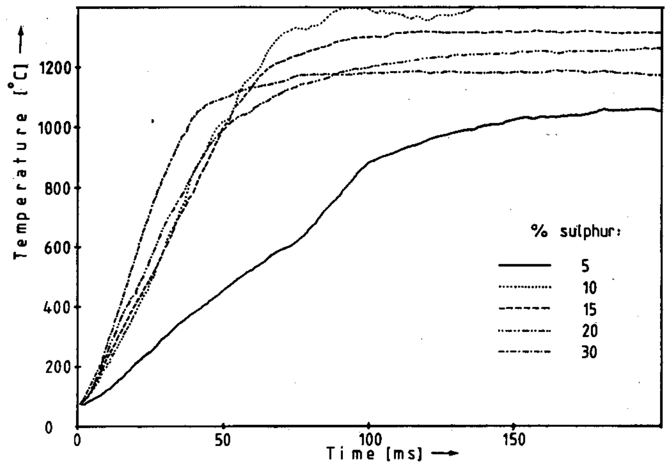

Figure 5. Temperature profiles of pressed ternary mixtures containing various proportions of sulphur.

A plot of the enthalpy of reaction (from bomb calorimetry and DSC) and burning rate (pressed) versus % charcoal is shown in Fig. 3. The maximum enthalpy of reaction occurs at 16.5% charcoal. The composition at which ΔH is a maximum is usually taken as corresponding to the stoichiometric composition of fuel to oxidant. 16.5% charcoal corresponds to a fixed carbon content of 12.8%. Urbanski(13) reported that a stoichiometric mixture of KNO_3 and charcoal contained 87.1% KNO_3 and 12.9% charcoal (volatile content not specified) and evolved −3.26 kJ/g. The reaction was proposed to be

$$5\,C\,(s) + 4\,KNO_3\,(l) \rightarrow 2\,K_2CO_3\,(s) + 3\,CO_2\,(g) + N_2\,(g)$$

The maximum ΔH values obtained from DSC and bomb calorimetry (approximately −3.39 kJ/g and −3.51 kJ/g, respectively) compare reasonably well with the value obtained for the 12.9% charcoal mixture of Urbanski.

In Fig. 3, the maximum ΔH occurs at a much lower charcoal content (~ 16.5%) than that for the maximum linear-burning rate (~ 33.5%). This difference is expected(14) to be small for systems containing non-metal fuels, i.e. poor thermal conductors, and the maximum burning rate is expected to occur near the stoichiometric composition. The significant difference for the charcoal/KNO_3 system indicates that several factors such as the low melting point of the oxidant and the presence of gases may contribute to heat transfer in burning columns of this mixture, so that a relatively high burning rate is maintained despite the departure from stoichiometry. The burning rate decreases sharply after 35% charcoal and this may indicate that excess charcoal, a poor thermal conductor, impedes heat transfer during burning.

3.3 Burning of ternary mixtures

A typical temperature profile (over 200 ms) of a pressed mixture of dry black powder (Fig. 4), shows a rapid rise in temperature, followed by a relatively flat maximum temperature region (~ 1250 °C). Cooling occurs after 1600 ms. The rapid rise in temperature is seen to occur within 70 ms.

Burning rates for pressed and hand-packed colums were 0.83 ± 0.01 cm/s and 0.95 ± 0.01 cm/s, respectively. The enthalpy of reaction determined from bomb calorimetry was −2.84 ± 0.04 kJ/g. This decrease in burning rate with an increase in compaction of the powder is consistent with the observations made by Sasse(15).

3.4 Black powder with various proportions of sulphur

Profiles for binary charcoal/KNO_3 mixtures containing 0.25, 0.50, 0.75, 1.0 and 1.5 mass fractions of the 20% sulphur in pressed columns of black powder are shown in Fig. 5. From the profiles, the rise time to T_{max} is steepest for 15% sulphur. The maximum temperature (without correction for heat loss) shows that the hottest mixture contains 10% sulphur and a further increase in the sulphur content causes a decrease in the maximum reaction temperature.

Table 1. The Effect of Increasing Sulphur Content on the Burning Rate of Sulphurless Black Powder.

Sulphur [%]	Burning rate [cm/s]	T_{max} [°C]	Enthalpy of reaction, − H (bomb calorimetry) [kJ/g]	[kJ/mol] (of oxidizer)
0% h	0.20 ± 0.01	900	2.75 ± 0.03	243.5
p	0.16 ± 0.01			
5% h	0.39 ± 0.01	1020	3.35 ± 0.05	278.8
p	0.38 ± 0.01			
10% h	0.71 ± 0.01	1350	3.21 ± 0.02	252.2
p	0.56 ± 0.01			
15% h	0.94 ± 0.01	1300	2.92 ± 0.02	217.2
p	0.81 ± 0.01			
20% h	0.95 ± 0.01	1240	2.80 ± 0.04	201.0
p	0.83 ± 0.01			
30% h	0.79 ± 0.01	1140	2.59 ± 0.05	166.8
p	0.77 ± 0.01			

h = hand-packed, p = pressed.

The burning rates of these mixtures and the enthalpies of reaction obtained from bomb calorimetry are shown in Table 1.

Generally hand-packed powders had faster burning rates than pressed powders, but the temperature profiles obtained for pressed powders were more reproducible. A steady increase in the burning rate was observed reaching a maximum at approximately 18.5% sulphur and decreasing at higher sulphur contents.

The burning rates for pressed columns, the enthalpy of reaction and the enthalpy per mole of oxidizer (Q) are plotted against the % sulphur in Fig. 6. The maximum values for Q and ΔH occur at approximately 82.3% KNO_3, 11.8% charcoal and 5.9% sulphur and decrease at higher sulphur contents. The ΔH value for the stoichiometric ternary mixture is similar to that observed for the stoichiometric charcoal/KNO_3 mixture. The maximum burning rate occurs at 71.4% KNO_3, 10.2% charcoal and 18.4% sulphur and this composition does not correspond to the stoichiometric composition. The composition with the maximum burning rate is close to the composition of black powder (70% KNO_3, 10% charcoal and 20% sulphur) used in the manufacture of safety fuse. Thermal analyses[6] have shown that the exothermic pre-ignition reaction[16]

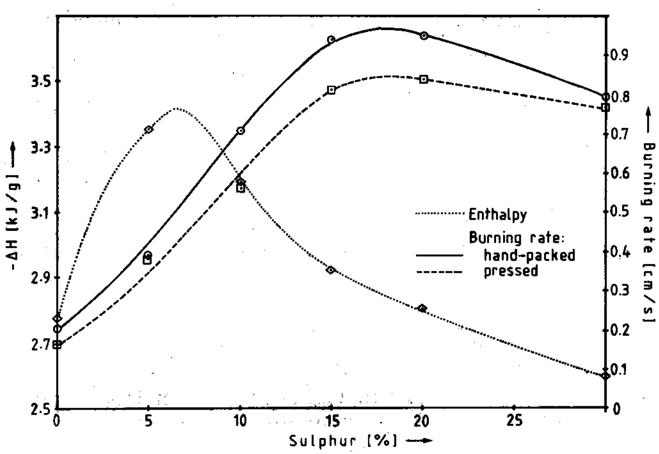

Figure 6. Enthalpy of reaction against percentage sulphur for ternary mixtures containing various proportions of sulphur.

between sulphur and KNO_3 which occurs at a lower temperature than the charcoal/KNO_3 reaction, lowers the DTA ignition temperature[12] of the ternary mixture compared to that of the binary mixture. This lowering of the reaction temperature of black powder is attributed[17] to a general fluxing effect[14].

The burning rate of the 12.5% charcoal/87.5% KNO_3 composition is increased by the presence of sulphur. Unlike the burning rate curve for the various charcoal/KNO_3 compositions, the burning rate curve for the ternary mixture is steeper at low% sulphur and the sulphur present in mixtures in excess of the stoichiometric composition maintains a relatively high burning rate despite the departure from stoichiometry. This is achieved possibly through an increase in the importance of the S/KNO_3 reaction or through improved heat transfer on forming a molten or gaseous sulphur phase[12].

3.5 *The effect of compaction*

Both the linear burning rates and the mass burning rates of samples of black powder, pressed to various densities, are given in Table 2.

The linear burning rate increased from loose powders to hand-packed powders, but a further increase in compaction, led to a decrease in the burning rate. This dependence of the burning rate on density was also observed by Sasse[15]. The mass burning rate (g/s) showed only an increase with increasing density in the range studied.

The density of commercial black powder varies over the range 1.60 g/cm³ to 1.80 g/cm³. Grained powders with low densities generally have faster burning rates, and powders with high densities have lower burning rates. The data in Table 2 indicate that the burning rates at densities between 1.66 g/cm³ and 2.12 g/cm³ are similar, so that density alone cannot account for the different burning rates of the columns.

Table 2. Variation in Burning Rate with Density.

Mixture	Linear burning rate [cm/s]	Density [g/cm³]	Mass burning rate [g/s]
Loose powder	0.44 ± 0.02	0.73	0.16
Hand-packed	0.95 ± 0.01	1.45	0.67
Pressed 1 ton	0.83 ± 0.01	1.66	0.67
3 tons	0.79 ± 0.01	2.06	0.79
5 tons	0.74 ± 0.01	2.12	0.76

3.6 *Particle sizes of individual constituents*

Burning rates were obtained for samples of black powder in which the particle-size ranges of either the charcoal or the KNO_3 were varied. The particle-size ranges of the other two constituents were kept within the usual 0 to 53-μm range.

The burning rates of hand-packed columns of the ternary mixtures in which only the particle size of charcoal was varied are shown in Table 3.

A maximum burning rate was observed at a mean charcoal particle size of approximately 25 μm and the burning rates generally decreased with increasing charcoal particle size. The largest decrease in the burning rate occurred for charcoal particle sizes from 25 μm to 100 μm. The samples containing charcoal particles of about 200 μm burn almost as slowly as the binary 12.5% charcoal/KNO_3 mixtures.

Table 3. Burning Rates of Black Powder with Increasing Particle Sizes of Charcoal.

Particle-size range [μm]	Mean particle size [μm]	Burning rate [cm/s]
0 to 38	15	0.84 ± 0.01
0 to 53	25	0.95 ± 0.01
0 to 300	55	0.41 ± 0.01
0 to 2000	200	0.17 ± 0.01

Table 4. Burning Rates of Black Powder with Increasing Particle Sizes of KNO_3.

KNO_3 particle-size range [μm]	Burning rate [cm/s]
0 to 53	0.83 ± 0.01
125 to 150	0.47 ± 0.01
150 to 180	0.42 ± 0.01
180 to 200	0.39 ± 0.01
200 to 250	0.37 ± 0.01
250 to 300	0.34 ± 0.01
300 to 355	0.29 ± 0.01
355 to 425	0.27 ± 0.01

Varying the particle size of KNO_3, while keeping the charcoal and sulphur particle-size ranges constant at 53 μm, affected the burning rate as shown in Table 4.

Temperature profiles for the above mixtures confirmed the above results in that the rise time to T_{max} increased with an increase in particle size of the KNO_3. The maximum temperatures varied between 1280 °C and 1400 °C, and generally increased as the particle size of the KNO_3 increased.

The profiles for the largest KNO_3 particles used (355 μm to 425 μm) showed an initially slow rise in temperature up to 400 °C, by which stage the KNO_3 melts and then there is a more rapid rise in temperature as contact between fuels and oxidant is improved.

3.7 Effect of water content

The water retained in black powder from its preparation as a paste is readily lost, under the conditions of thermal analysis, without any significant influence on the high temperature reactions. During the very much faster process of burning of black powder, any residual water may be expected to influence the burning rate. The role of water vapour in accelerating the rate of burning of certain pyrotechnic mixtures is well recognized[14], but higher moisture contents either have little effect or may retard the reaction. According to Conkling[18], the substantial variations in the burning characteristics of black powder from batch to batch are caused by a number of factors such as the purity of the constituents, the source of charcoal, the extent of mixing and also the moisture content of the mixture. In the traditional process for the manufacture of black powder[13,19], a small amount of water (~4%) is often used and is thought to give a saturated solution of KNO_3, within the matrix of the charcoal, leading to an enhancement of the reactivity of the grains[20]. Black powder with a moisture content of 1% is most readily ignited[21].

Known quantities of water were added to samples of "dry" black powder paste, which were stored at room temperature in sealed bottles for 1 to 2 days. The mixtures (except for that containing 15% water) were pressed in the usual manner and the surface coatings were left at room temperature to dry. The profiles (Fig. 7) showed an increase in the rise-time to T_{max} with increasing moisture content. The rise-time to T_{max} for the 15% moisture content was ~1000 ms. The ignition of this mixture was not always sustained. A plot of burning rate versus moisture content is shown in Fig. 8. A decrease in the burning rate is observed only after 2% moisture content. Mixtures containing 20% moisture failed to ignite.

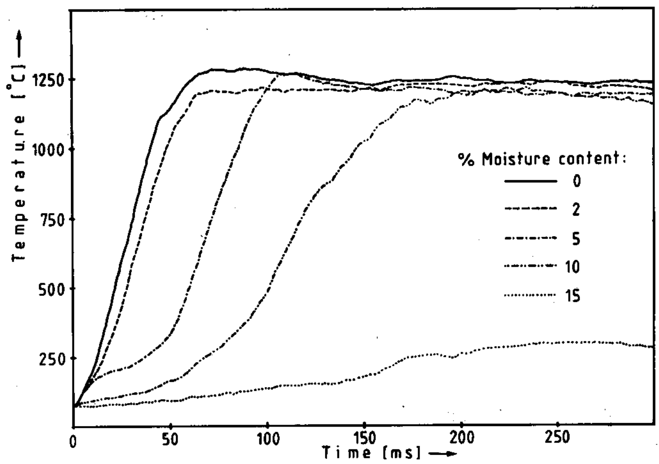

Figure 7. Temperature profiles of ternary mixtures with various moisture contents.

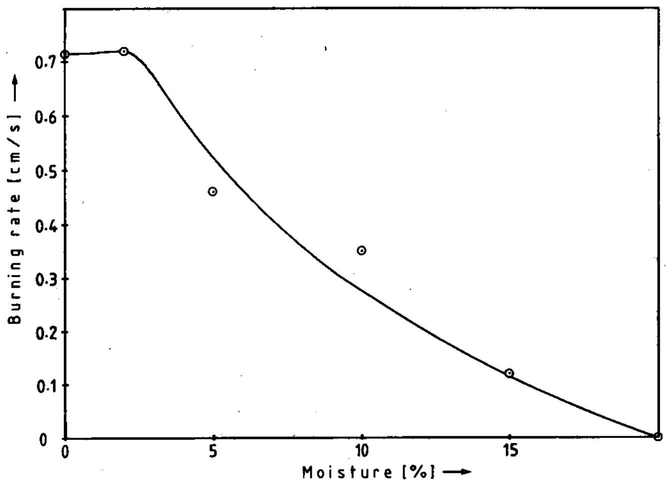

Figure 8. Burning rates of ternary mixtures with various moisture contents.

3.8 Deliberate modification of the burning rate

Grain size and/or density are used extensively to control the rates of propagation and burning of the traditional grained black powder. The factors which control the burning rate of black powder made from the paste are likely to be even more complex. Although control of the burning rate by varying the stoichiometry is always an option, the burning characteristics associated with a particular stoichiometry may not always be desirable in certain applications.

According to McLain[14], factors which alter the enthalpy of reaction, ΔH, and/or the ignition temperature, T_i, of pyrotechnic compositions, are expected to influence the burning rates. An empirical relation[14], the propagation index $P_I = \Delta H/T$ predicts that a high ΔH and a low T_i (i.e. high P_I) results in a faster-burning composition.

ΔH may be altered without a change in the black powder composition by changing the heat transfer characteristics during burning by incorporating inert thermal insulators into the mixture[14], or by inclusion of subsidiary fuels or oxidants.

3.9 Addition of inert diluents

Upto 10% by mass of two materials, kaolin light (B.D.H.) and HCl-washed sea sand (N.T. Laboratories), were added separately to black powder containing the usual mass percentages of the constituents. The estimated particle size for the kaolin was < 53 μm and 200 μm to 400 μm for sea sand. Only a slight decrease (~ 6% at the 10% addition) in the burning rate was observed for sea sand mixtures, but a more substantial decrease (~ 38%) was observed for mixtures containing 10% kaolin. The kaolin was shown to release ~ 6% water on heating and this water is thought to contribute to the decrease in the burning rate.

3.10 Subsidiary fuels

Many organic compounds, often used as binders, act as subsidiary fuels. With their low melting points they can have several effects: a general fluxing effect increasing contact between fuel and oxidant; a solvent effect on sulphur, preventing its loss by volatilization; and their general preliminary heating effect through providing an alternative low-temperature exothermic process. Addition of small amounts of a few rather arbitrarily-chosen, but readily-oxidizable organic compounds all showed the same trend to slower burning.

4. Discussion

4.1 Burning of black powder

Loose black powder grains burn several times faster than compressed single large grains. The burning of black powder may thus be considered to fall under two categories: one for loose grained powders and the other for single large charges. An important distinction was made by Blackwood and Bowden[22] between the rate of propagation, which is the rate at which reaction spreads from grain to grain, and the rate of burning, which is the rate at which individual grains are consumed. They showed that the burning of grained powder is accompanied by sprays of hot molten droplets (500 °C to 700 °C) of potassium salts. These droplets impinge on unburnt grains and induce localized ignitions. The rate at which individual grains are consumed is 0.4 cm/s. The spread rates of the sprays were ~ 60 cm/s which corresponds to the propagation rate of black powder[22]. Spray velocities[23] of 130 cm/s and[5] up to 5000 cm/s have also been reported.

When confined in steel tubes (4 mm i.d.), propagation rates of 1500 m/s were reported for sulphurless powders[24]. The rate of propagation for ternary mixtures (~ 500 m/s) is lower than that of binary mixtures[24]), so the presence of sulphur slows down the rate of propagation. Although high propagation rates may be obtained for grained powders, it appears that the size of the grain also limits the rate of propagation; rates of ~ 170 m/s were reported for coarse grains and ~ 650 m/s for finer grains[24].

Propagation of burning in fine powders (< 100 μm)[22] and in large single grains[17] is much slower than in grained powders and the rate of propagation corresponds to the burning rate[22]. The burning occurs from a "face"[22], that is "burning takes place only on exposed surfaces and the rate at which the surface regresses normal to itself into the powder grain is the same at all points"[21]. Hahn *et al.*[23] have noted that a considerable decrease in the explosive properties of black powder is observed when grained powders are ground to a fine powder. Although molten sprays are observed[15], these sprays are not responsible for the propagation of burning of fine powders. When grained powders are confined in tubes, burning rates of ~ 1 cm/s have been reported[22]. Similar burning rates are observed in safety fuse[16, 18].

5. Conclusions

Despite the turbulence created by molten and gaseous products, which may cause movement of the thermocouple during burning, the temperature profiles obtained for the burning of black powder were fairly reproducible. To obtain reproducible measurements of burning rates, the exposed surface of the columns had to be coated to inhibit the transfer of flame along the exposed surface.

Of the various binary compositions possible from the constituents of black powder, only charcoal/KNO_3 mixtures show self-sustaining combustion. The stoichiometric composition of fuel to oxidant for charcoal/KNO_3 mixtures lies at ~ 16.5% charcoal and the maximum burning rate occurs at ~ 33.5% charcoal. The charcoal contained 77.5% fixed carbon[6].

The burning rates of ternary black powder mixtures with various sulphur contents increased with increasing sulphur content up to 20% sulphur and decreased thereafter. The maximum burning rate occurred close to the composition (70% KNO_3, 10% charcoal and 20% sulphur) used for the manufacture of safety fuse. The burning rates for the blasting composition (75% KNO_3, 15% charcoal and 10% sulphur) were faster, than those, measured under similar conditions for the safety-fuse composition. Measured enthalpies of reaction were similar despite the differences in composition.

Factors other than composition which affect the burning rate of black powder may be summarized as follows:

(1) An increase in compaction produces a decrease in the linear burning rate (cm/s) but an increase in the mass burning rate (g/s). Similar observations[28] led to the conclusion that the rate-controlling reactions of black powder occur in the condensed (i.e. liquid and solid) phase. The maximum reaction temperature (1250 °C) is, however, sufficient to cause the sublimation or vaporization of most intermediates and products.

(2) Materials with poor thermal conductivities, e.g. sea sand and kaolin, decreased the burning rate of black powder. The decrease observed for kaolin-containing samples was greater than that for samples containing sea sand and this may arise from the water present in the kaolin.

(3) The addition of subsidiary organic fuels decreased the burning rate.

(4) Variation of the mean particle size of charcoal had a much greater effect on the burning rate than that of varying the KNO_3 particle size. A substantial variation in the burning rate (as much as 80%) can occur over a small range (50 μm) in

the mean particle size of charcoal. The smaller effect observed for KNO_3 is to be expected because of the low melting point of KNO_3 and the participation of molten KNO_3 in the reaction.

(5) It is difficult to remove the last traces of water from black powder prepared from the paste without affecting the mass ratio of sulphur. The residual water may thus contribute to the decreased burning rate of the black powder paste. For black powder with water contents ranging from 0 to 20%, a reduction in the burning rate only occurs above a 2% moisture content but the burning rate then decreases with increasing moisture content and burning fails beyond 15% moisture.

(6) Electron micrographs of pastes showed that recrystallization of KNO_3 and growth of these KNO_3 crystals occurs. Further growth will also occur on cooling and drying of the paste. This increase in KNO_3 particle size will thus decrease the burning rate of the resulting powder.

The main factors which arise for consideration from this study are:

- the prevention of the escape of sulphur vapour from the reacting system. Burning rates depend upon the presence of sulphur and thus can range from 0.77 cm/s (for an excess of sulphur) to 0.16 m/s for "sulphurless" black powder.
- the presence of residual water in the powder. This could have a marked influence on the burning rate (0.72 cm/s for the driest powders to failure at 15% H_2O).
- KNO_3 transport in aqueous solution from the paste to the surroundings during drying. The KNO_3 content of the black powder is thus non-uniform giving different burning rates at different distances from the core of the burning column.

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