

# THE INITIATION, BURNING AND THERMAL DECOMPOSITION OF GUNPOWDER

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[Plates 3 to 6] {I do not have these plates. /djh/}

This paper describes an experimental study of the initiation of burning in gunpowder and of the way in which this develops and grows to explosion. There is evidence that initiation is due essentially to the formation of local hot spots; these may be formed by the adiabatic compression of air pockets, by the friction of grit particles and in other ways. The necessary temperature for these hot spots is remarkably low (*ca.* 130° C) but it is sufficient to melt the sulphur. It is suggested that the formation of a liquid phase is important and that the process starts with the reaction of molten sulphur with the oxyhydrocarbons present in the charcoal. These oxyhydrocarbons which can be extracted from the charcoal with a suitable solvent, melt at a low temperature and can also provide a liquid phase. A high pressure is necessary before these reactions can proceed at a sufficient rate.

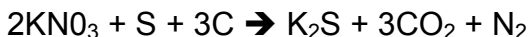
A study is made of the way in which the initial reactions develop until the heat evolved is sufficient to start the main reaction, which is the oxidation of carbon by potassium nitrate. There is evidence that the acceleration of the initial reaction which leads up to the rapid burning is controlled by the oxyhydrocarbons present in the charcoal. High-speed camera studies show that the gunpowder grains themselves burn comparatively slowly in a layerwise fashion and suggest that the rapid propagation of the reaction from grain to grain is due to the emission of a hot spray of molten droplets of potassium salts.



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## INTRODUCTION

Gunpowder is made by grinding together a mixture of potassium nitrate, sulphur and charcoal in the stoichiometric proportions to satisfy the equation



The finely ground ingredients are pressed into a cake and this is broken up and screened to produce grains of various sizes. Gunpowder has been the subject of considerable investigation. Violette (1848) determined the temperature at which gunpowder could be ignited. The monumental paper by Noble & Abel in 1875 which dealt mainly with the process of burning and with the explosive force developed in gunpowder is a major contribution. Debus (1882) made some observations on the mechanism of burning, and a more thorough examination of this, especially the part played by sulphur, was made by Hoffman in 1929 and this was extended by Watanabe in 1933. In recent times Oza & Shah (1943) have studied the chemical reactions between potassium nitrate and charcoal, and Huff & Moore (1944) have examined the impact and thermal sensitiveness of gunpowder.

Although gunpowder is a complex system it is an interesting one, since it apparently consists of three solid phases which must interact. The mechanism both of its initiation and of its burning is still obscure. Some recent studies of other explosives (Bowden, Mulcahy, Vines & Yoffe 1947; Bowden & Gurton 1948; Bowden & Yoffe 1952) have shown that their initiation is essentially due to the formation of local hot spots, and the growth of explosion from these centres of initiation has been followed. A study has now been made of the birth and growth of explosion in gunpowder in an attempt to see whether some simple physical picture of the process involved could be obtained. The work falls into three main parts. The first is a study of the initiation of gunpowder, the second of the growth of explosion and the third deals with the chemical processes involved in the early stages of decomposition.

## PART I INITIATION

It is well known that gunpowder can be initiated by impact, and a typical value for the impact energy required is 2 Kg falling through 60 cm, (12 x 10<sup>4</sup> g cm) (Huff & Moore 1944). It may also, of course, be initiated by heat (Violette 1848; Huff & Moore 1944; Hoffmann 1929). However, the mechanism responsible for initiation is not understood, and the first part of this paper describes an experimental investigation of the process and of the factors contributing to sensitiveness.

### *Sensitiveness to simple impact*

The apparatus used for impact was the same as that used by Bowden & Gurton (1949). The anvil was a 1 in. steel roller held on a large block of steel; the striker was another steel roller  $\frac{1}{2}$  in. diameter. Throughout the experiments the weight of the steel ball dropped on the striker was 1800 g. The first experiments were carried out using a fine gunpowder (150 mesh) which was spread as a thin continuous film on the anvil. The powder was dried, since a very small amount of moisture will reduce its sensitivity. A drop of 125 cm (impact energy  $22 \times 10^4$  g cm) was necessary to give 100 % initiation. It was noted that at heights below this there was evidence that melting of the sulphur took place and that there was a marked tendency for the powder to flow under impact even with films as thin as 0.1 mm.

With grained powders, that is, powders in the form of small rotund grains of approximately 12 to 25 mesh, an increase in sensitiveness was found. With the larger grained powder (12 mesh) a drop of 70 to 80 cm gave 100 % initiation. With the smaller grains (25 mesh) this was obtained with a drop of 50 to 60 cm. (Impact energy ca.  $10 \times 10^4$  g cm.) The distribution of the sample was of importance here, since if the anvil was completely covered with grains it would be equivalent to a thick layer of powder and the energy of the blow would be absorbed in crushing and compressing the powder. With large grains of 12 mesh three or four grains only, placed centrally on the anvil, were used, and with the smaller 25-mesh grains eight to ten grains were spread over the anvil. This appeared to give the most consistent results. Figure 1, plate 3, shows how initiation takes place at a point, and propagation spreads with erosive burning to the edge of the powder. The increased sensitiveness of grained powders suggested that air may be entrapped in the grains and compressed during impact and experiments were carried out to test this.

The fine powder was spread on the anvil in the form of a small ring, since, as earlier work has shown, this leads to the entrapping of an air space in the centre. The impact sensitiveness immediately showed an increase, and drops of about 55 cm (impact energy  $9.9 \times 10^4$  g cm) were effective in producing 100 % initiation. These results are almost the same as those obtained for grained powders and the crushing of the grain powders was examined. The first step was to determine whether air could be included during the slow crushing of grains, and for this purpose grains were crushed by a steel surface forced against a glass plate. By this means the process could be observed as the pressure was applied, and some pictures showing three stages in the process are shown in figure 2, plate 4. It is clear that air can easily be entrapped under these conditions. In order to see whether this was also true under dynamic conditions an investigation was carried out by means of high-speed flash photography. For this purpose a flash tube having a repetition frequency of 2000 c/s was used. This was an integral portion of the Pulse Modulator, type 64, and is a spark gap in an argon-filled envelope. This is pulsed from an electronic pulser giving pulses of  $1 \mu$ s duration. Using this in conjunction with a drum-camera, a sequence of silhouette pictures of grains being crushed between glass plates could be

obtained. The apparatus is shown in figure 3, and several sequences taken with this apparatus are shown in figure 4, plate 3. The crushing of the powder has been achieved in  $1/2000$  s, and as the pressure is released the compressed air pocket can be seen expanding and finally bursting from the side. Slight erosion caused by the escaping gases can also be seen. In these experiments a low-impact energy was used, since the armour glass anvils would not stand the full impact. For this reason initiation occurred only rarely. It seems clear that sudden compression of entrapped gas can take place when grained powders are used. Very fine powders showed no signs of the formation of air pockets unless they were spread as an annulus.

#### *Impact in the presence of grit*

If a height of drop is used at which no initiation is obtained under normal conditions and grit is added, gunpowder can be initiated. This occurs, for example, with a drop of 40 cm. (impact energy  $7.2 \times 10^4$  g cm). There are three factors here that appear to be of importance: the melting-point of the grit, its hardness and its crystalline form. The first of these is by far the most important.

When grit is used, it is essential that the size of the grit particle shall be comparable to that of the powder tested. If a very fine-grain powder is used with a large piece of grit, then energy will be used in crushing the grit before effective crushing of the powder has taken place. On the other hand, if large grains of powder are used with very small pieces of grit they will become embedded in the crushing powder before they themselves are crushed and initiation will not take place. If the powder and grit are of comparable size so that they are crushed simultaneously, initiation occurs readily and appears in all cases to take place at or near the piece of grit. A series of flash photographs given in figure 5, plate 4, shows that initiation appears to start at or very near the grit particles. This is shown also in a macrograph of the anvil given in figure 6, plate 4.

The melting-point of the grit is of interest and the initiation efficiency as a function of a melting point of the grit is shown in table 1.

TABLE 1. EXPLOSION EFFICIENCY OF GUNPOWDER IN THE PRESENCE OF VARIOUS GRITS AT AN IMPACT ENERGY OF  $7.2 \times 10^4$  G CM

grit added	M.P. (° c)	hardness (Mohs scale)	initiation %
none	—	—	0
ammonium sulphate	100	2 to 3	0
ammonium acetate	114	3	0
zinc octa, cosanoate	130	2	20
ammonium thiocyanate	150	2	30
ammonium nitrate	170	2 to 3	60
potassium thiocyanate	173	2	50
selenium	175	3	60
silver rutrate	212	3	100
potassium nitrate	334	2	100
sodium bromate	381	2	100

It can be seen that a lower melting-point limit of approximately 130° C is reached where grit particles no longer sensitize the gunpowder. This corresponds approximately to the melting-point of sulphur (120° C), and as previously stated there is evidence that sulphur will melt and flow plastically under the condition of impact used.

Sulphurless gunpowders show a marked contrast in their behaviour with grit. When the melting-point of the grit exceeds 334° C (which is the melting-point of potassium nitrate) 100 % initiation can be obtained. With grits melting just below initiation, burning and thermal decomposition of gunpowder this temperature the explosion efficiency decreases, and with such a grit at 212° C the efficiency fell to 20 % (see table 2).

TABLE 2. EXPLOSION EFFICIENCY OF SULPHURLESS GUNPOWDER IN THE PRESENCE OF VARIOUS GRITS AT AN IMPACT ENERGY OF  $12.66 \times 10^4$  G CM

grit added	M.P. (° C)	hardness (Mohs scale)	initiation %
none	—	—	0
selenium	175	3	0
silver nitrate	212	3	20
sodium acetate	324	2	30
potassium nitrate	334	2	60
cadmium iodide	388	2	100

The results with sulphurless powders are not quite so clear-cut as with normal powders, but it is apparent that much higher hot-spot temperatures are necessary. If the melting-point of the grit exceeds that of the potassium nitrate the efficiency is 100 %.

The effect of hardness has been examined using minerals the melting-points of which are all in excess of 1000° C. No definite correlation with hardness was observed. Very hard materials such as carborundum may be less effective owing to the difficulty of producing multiple fractures in the grit particle itself. There was some evidence that very soft said very hard minerals are less effective than those of intermediate hardness. There was also an indication that minerals of cubic habit, such as galena, halite and sodium bromide, were less effective.

#### *Artificial hot spots*

These experiments suggest that in normal gunpowder, a hot-spot temperature of 130° C or more can induce reaction in a normal gunpowder. In order to simulate this, experiments were carried out with heated strikers. The strikers were heated in a small furnace and transferred to the impact apparatus. By heating the strikers to a standard temperature (400° C) and measuring the surface cooling it was possible to estimate the temperature of the striker at the moment of impact. It was found that if the temperature of the striker was approximately 170° C at the moment of impact the explosion efficiency was 60 % when the height of fall was 40 cm, (impact energy  $7.2 \times 10^4$  g cm). With unheated strikers no initiation occurred at this impact energy.

In order to localize the effect of the hot spot so that a closer parallel could be obtained with grit, a striker was constructed having a small copper centre wound with Nichrome wire. This was housed in a steel striker of the same diameter as those normally used. The effect of this was to make a flat striker with a spot of hot copper in the centre approximately 0.05 cm in radius. The surface temperature of the copper tip could be maintained constant, and results obtained with this apparatus confirm those obtained with grit. If the temperature of the copper spot was 175° C the explosion efficiency was 60 %; at higher temperatures, e.g. 220° C, it was 100 %. With a cold striker no initiation occurred. It should be emphasized that simply placing a film of gunpowder on a metal surface heated to 200° C will not cause initiation. Impact or confinement is apparently necessary for the hot spot to become effective (see later for the effect of pressure).

#### *Sensitiveness to friction*

In the friction experiment tests it is necessary that samples be rubbed between two surfaces in such a manner that the effects of impact can be neglected. The type of apparatus used for this was the same in design as that used by Bowden & Gurton (1949). Here, the material was confined between a fixed steel surface

and a sliding steel plate. A load could be applied before sliding so that the sample is under pressure and a heavy falling pendulum strikes the slider and drives it along, thus moving one steel surface relative to the other. In most of the experiments the weight of the pendulum was about 2 kg and the drop 70 cm, the applied load was ca. 500 Kg. No initiation occurred.

When grit was included with the powder, the same negative result was obtained even with the most severe conditions available on this apparatus. A check test with RDX and PETN showed that these materials could readily be initiated with quite low loads and sliding speeds. The residue of gunpowder left on the slider after test consisted of a hard shiny compact film of powder which was not readily ignitable. Score marks could be seen on the two metal surfaces when a hard grit had been used. It is clear that gunpowder is remarkably insensitive to friction.

#### *Initiation by hot wire*

Since heat appears to be the main factor in causing initiation of gunpowder a brief study of the initiation by heat is of interest. For this purpose an apparatus was used in which gunpowder could be maintained in contact with a hot wire and the time to ignition measured. The apparatus consisted of a small spiral of constantan wire surrounded by a glass tube 25 mm long and 6 mm internal diameter. This was housed in a Perspex block, and the ends of the wire spiral were connected to stout supports and to an external circuit. The current through the wire could be adjusted by means of a rheostat. The effects of heat loss have not been considered here, since the tests were designed to be comparative only.

The behaviour of three powders of different grain size is shown in figure 7. It can be seen that as the current is increased the time to ignition decreases and that, at short times of ignition, the distinction between the different powders disappears. If the energies are calculated for each delay time from the equation  $E = i^2rt/4 \cdot 18$ , where E is the energy in calories, i the current in amperes, r the resistance in ohms and t the time in seconds, and are extrapolated to zero time, then a limiting value of  $4 \times 10^8$  ergs is obtained.

Some interesting features were noticed during the experiment. If the delay to ignition was longer than about 60 s, then the chances of obtaining an ignition were remote, but if ignition did occur it was accompanied by violent decomposition. This same held true for all long delay times. As the time became shorter, the violence of decomposition became less and at times of the order of a few seconds, the powder merely 'puffed' off as if burnt in the atmosphere. When prolonged initiation, burning and thermal decomposition of gunpowder heating of the powder took place, sulphur was volatilized from the powder and condensed on the cooler walls of the glass tube.

#### *Effect of pressure*

The effect of pressure on initiation seems to be of importance, since pressure is developed during the burning of gunpowder and may influence the ignition of unreacted powder. Also, during impact, high pressures are developed and their effect on ease of initiation may be important. By applying an external gas pressure to the hot-wire apparatus, this could be tested. The wire coil and glass tube were placed in a steel vessel which could be filled with argon from a cylinder to any desired pressure up to 90 atm. Some preliminary experiments on this apparatus showed that as the pressure was increased, the conductivity of the gas increased very rapidly and the wire coil cooled. To overcome this, a series of blank experiments was carried out using a dummy powder and the current adjusted at each pressure until the resistance of the wire remained constant. The effects of convection in this apparatus appeared to be small and, by suitable adjustment, the temperature of the wire could be kept reasonably constant.

Having determined the conditions of experiment, gunpowder was substituted, fine powder (150 mesh) being used throughout, and the delay to ignition determined as a function of the pressure, the temperature being maintained constant. The results are shown in figure 8. It can be seen that there is a large initial drop in delay over the first 30 to 40 atm, and that when 70 atm is reached, the delay is of the order of the time required to heat the wire to its full temperature. The temperature of the wire at atmospheric pressure is approximately 300°C.

If these results are compared with those for initiation with a hot wire, the analogy is apparent. Increasing the pressure while maintaining the temperature constant has a similar effect to increasing the temperature while maintaining the pressure constant. Both decrease the delay time for ignition.

#### *Ignition by Spark*

Some experiments were carried out on spark initiation. The method used was to charge a condenser to a high potential and then to discharge it near gunpowder. By this means a spark of very short duration of the order of  $10^{-5}$  s could be produced, the inductance in the circuit being kept to a minimum. When this experiment was carried out with grained or with fine gunpowders, it was found that the powders were scattered and the spark did not effectively touch them. This is because the resistance of the powder is higher than that of the ionized air. When fine powder was confined as a plug in a glass tube of 4 mm internal diameter and the plug was of a thickness less than the breakdown gap for the condenser, initiation could be obtained with potentials of 4 kV and a capacity of 1.2  $\mu$ F. Various voltages and capacities were used, and minimum energy required for initiation was of the order of  $10^8$  ergs in all cases. The initiation of grained powders could not be achieved even when the grains were held in a tube and higher capacity was used; again the spark by-passed the grains. This high resistance of the particles suggests that the surface of the grains may be coated with a layer of sulphur.



## PART II. BURNING AND THE PROPAGATION OF BURNING

This part will describe an experimental study of growth of the explosion. A distinction may be made between the rate of grain burning, that is to say, the rate at which the individual grains are consumed and the rate of propagation, that is, the rate at which the reaction spreads from grain to grain. Comparatively little work on this has been published. It is well known that the rate of propagation is dependent on pressure (Andrev 1945), and Kast (19 13) has measured the rate of propagation in glass tubes. A study both of the burning of the grains and the propagation has been made by high-speed flash photography and by moving-drum camera techniques.

### *Experimental*

A simple method of obtaining a measure of grain burning and of propagation in gunpowder is by the streak method. In this method, the powder is placed above a narrow slit 0.1 mm. wide, and the image of this slit is focused on to the drum of a drum camera. The general experimental arrangement was similar to that used by Bowden *et al.* (1947) for study of high explosives. By covering the slit with gunpowder and igniting it in the centre, a wedge-shaped light trace could be obtained from which the grain burning rate and propagation rate could be calculated provided that the magnification and the speed of rotation of the drum were known.

This method is only useful in measuring the duration of light output and the rate at which it is changing. Any phenomena not emitting actinic light would not be observed. In order to obtain some information on the processes not emitting light, use was made of shadow photography. Here, a series of pictures was taken with the gunpowder silhouetted against a light source. The sample to be photographed is placed near the condenser lens on the camera side, and the image of this object is focused on to the camera drum. On the other side of the condenser lens is mounted the light source at such a distance that it will converge at the camera lens. A Trigatron tube (CV 85) was used as a light source; this is the spark gap of a Pulse Modulator, type 64, used for pulsing a magnetron. The unit consists of a multivibrator supplying pulses at a repetitive rate from 400 to 2000 c/s. These pulses are shaped electrically and applied to the spark gap as 1  $\mu$ s pulses with a sharp 'ring'. The spark gap is triggered, and charged condensers in a delay line are discharged across the main gap. The output of light lasts only 1 to 2  $\mu$ s provided the output of the unit is terminated in a non-reactive load of 70 ohms. The spark gap itself is housed in a glass envelope filled with argon at 3 atm. and containing a small amount of oxygen to assist de-ionization. Suitable adjustment of some of the components of the multivibrator allow the unit to be pulsed up to approximately 8500 c/s before unreliable operation of the spark gap becomes serious. This increase in operating frequency also requires a change in the delay line and increase in the

capacity of the power supply. In the following experiments repetition rates are only 500 to 1000 c/s. Some hundred pictures could be taken in sequence showing stages in the burning of gunpowder. Visible light is given out by the powder once reaction is well established, and this tends to obscure the pictures in the later stages of burning and appears as a white streak on the pictures.

#### *Burning of gunpowder at atmospheric pressure*

Experiments were carried out on a grained gunpowder (12 to 25 mesh) and also on very fine powder (150 mesh). A typical trace for a normal grained gunpowder (dry) is shown in figure 9, plate 5. The duration of the light trace (that is, the length of the trace along the vertical axis) is a measure of the duration of grain burning. The angle of the trace gives a measure of the rate of propagation. The rate of propagation is reasonably constant, but for a thick layer of powder there is a tendency for the propagation rate to increase slightly as it proceeds. The mean of a number of experiments showed that the rate of propagation for the powder was *ca.* 60 cm/s. If we assume an average size for a particle is 2 mm diameter and assume them to be spherical, the rate of grain burning (i.e. the rate at which individual grains are consumed) was *ca.* 0.4 cm/s.

When a very fine powder (150 mesh) was used the rate of propagation was much slower. A sulphurless grained powder or a powder containing 1 % moisture also gave a slow rate of burning.

#### *Influence of pressure*

Some experiments were carried out with grained powder to investigate the influence of gas pressure on the burning. The powder was spread as a thin layer on the bottom of a horizontal glass tube which was connected to a large reservoir so that the Pressure remained reasonably constant during the burning. The Powder was ignited at one end by a hot wire. In this apparatus the powder could be burnt either at reduced pressure or at pressures of a few atmospheres. It was found that as the Pressure was reduced below 1 atm the amount of light evolved decreased and considerable unburnt residue was left. When the pressure was reduced to 16 cm Hg, it was possible to produce ignition, but in all cases the burning of the grains failed to propagate.

When the Pressure was raised above 1 atm the burning rate of the grains increased and the propagation showed a very marked acceleration. The behaviour in air at 2 atm is shown in figure 10, plate 5. The grain burning is much faster and it accelerates. Also the propagation, which again begins at a few centimetres per second, accelerates very rapidly at *ca.* 760 cm./s. In an atmosphere of nitrogen Or Of argon the behaviour was similar. At a Pressure of 3 atm the acceleration was still more marked.

The next series of experiments was carried out in closed tubes so that the pressure could build up to a high value (about 30 to 50 atm). When the tube is packed with grains so that the Pressure is rapidly built up the acceleration is very marked (see figure 11, Plate 5). Toward the end, the grain burning rate has accelerated to about 9 cm/s and the propagation rate to about 2000 cm/s.

### *Silhouette studies of burning grains*

By Placing grains on a glass surface in a line with a definite distance between each grain, it was Possible, by ignition of one grain, to secure propagation along the line of grains (see figure 12, plate 5). For grains of 12 mesh (12 mm diameter) the maximum distance between grains for complete propagation was approximately 6 mm. For grains of 25 mesh (1 mm, diameter) it was less than, 1 mm.

It was observed that, around a burning grain, a very fine film of residue was obtained. Microscopic examination of this residue showed that it consisted of minute crystals and small globules of solid material which were mainly potassium carbonate and potassium sulphate. This residue was spread around a grain, was thickest near the grain and became sparse at a distance of a few millimetres. This suggests that propagation may be caused by a fine spray of residue in the molten state.

A more precise method of studying these effects is to use the apparatus described above and photograph burning grains in silhouette. The grains are placed on a thin brass platform, separated from each other by a small gap and one grain is ignited by a hot wire. Figure 13, plate 6, is a series of frames showing a grain burning. It is the last of several grains and is fully alight. It will be seen that it is burning in a layerwise fashion. It will also be seen that the rate of consumption of the grain is somewhat greater in the horizontal direction than it is in the vertical direction. This is due to the vertical movement of the hot gases. By careful measurement the burning rate can be calculated and a mean value is approximately 0.4 cm/s, which is in reasonable agreement with the streak results.

If the process is observed at a lower magnification the method of propagation can be seen. Figure 14, plate 6, shows a series taken at somewhat lower magnifications. In each case the first grain has been ignited and is burning. A non-luminous reaction zone can be seen spreading out from the reacting grain, and when this reaches the next grain it starts reaction in the grain. There is an appreciable delay (some milliseconds) before sufficient light is evolved to affect the photographic emulsion.

A determination of the melting-point of the mixtures of the salts generally found in the solid products of combustion of gunpowder shows that these mixtures must be at a temperature of 550 to 750° C to be in the molten state. Since they appear as a fine spray, they will cool and solidify quickly, but provided their

temperature is in excess of about 500\* C we may expect them to produce immediate reaction in a grain of gunpowder. This fine spray was collected on a cold glass plate and examined in the microscope. The majority of particles were very small (from 1 to 10  $\mu$ ), but a num of them were appreciably larger. The rate at which the cloud of spray spreads is quite fast and is about 50 cm/s at atmospheric pressure. It is interesting to note that this corresponds with the observed rate of propagation in the streak photographs. Once a grain has reacted it can spread its own reaction zone and produce reaction in another adjacent grain. In a number of pictures it was observed that very small fragments of powder of the order of 0.1 mm diameter may be broken away from the main grain and fly through the air with a velocity of 15 m/s. These small particles were burning, and they cause initiation of another grain a considerable distance ahead of the reaction front. Frequently a whole grain, ignited at a point, will behave as a small rocket and shoot away from the reaction zone (see figure 12, plate 5). Thus it is possible for propagation to appear uneven due to grains being ignited ahead of the normal reaction front. The preburning in streak photographs is due to this.

#### *Fine gunpowder*

In the preceding description of results, no particular mention has been made of fine gunpowder (150 mesh), and this is because the burning of this substance is so different from that of grained powders. Propagation of the fine powder is much slower and it always bums from a face; in fact, the rate of propagation corresponds to the rate of burning. When confined in tubes, even lightly, it tends to bum from one end only and the light output is very weak. The. rate of propagation is of the order of 1 cm/s and approximates to that found for normal safety fuse. This contrast is striking. If rapid propagation is to occur it is apparently necessary to have an open space between the grains so that the hot flying spray can be effective. In a densely compacted powder this cannot occur and the rate of propagation is governed by the rate of burning.

### PART III. THERMAL DECOMPOSITION

It is well known that mixtures of potassium nitrate, charcoal and sulphur will react exothermically with the production of a large volume of gas. These reactions have formed the basis of extensive studies; one of the earliest and most thorough is that of Noble & Abel. These workers examined the products but did not formulate a reaction to explain the steps in the process. The more recent contributions have been referred to earlier in the paper.

It appears that the presence of sulphur promotes reaction, and this has been attributed by Hoffman (1929) to the formation of hydrogen sulphide at about 150°C from sulphur and organic matter present in the charcoal. This hydrogen sulphide, he suggests, reacts exothermically with potassium nitrate above 280°C to form potassium sulphate. It. is clear from the figures of Noble & Abel that the

amount of potassium sulphate formed is a function of the oxygen content of the charcoal and not of the hydrogen content which only varies between 2 and 4 %. It is also clear from experiment that the most reactive gunpowders are those made from charcoal, the carbon content of which falls within quite narrow limits. We shall see that reaction rate appears to be related to the organic materials present in the charcoal as well as to the presence of sulphur, and the suggestion put forward by Hoffman may require modification. Very little attention appears to have been given to the preliminary reactions which appear to control the behaviour of the gunpowder, and a study of these will be described in this section.

### *Experimental*

A convenient method of following the reactions is by measurement of the amount of gas evolved as a function of time. Since gunpowder is never called upon to burn in *vacuo*, it was decided to study the reaction at atmospheric pressure and an inert gas such as argon was used. The apparatus consisted of a reaction vessel and a silicone heating bath which could be raised to surround the reaction vessel. A ground-glass joint attached the vessel to a gas burette and liquid-air traps as required. The bath was electrically heated and thermostatically controlled and with the aid of a stirrer the temperature can be kept to within  $\pm 1^\circ$  C up to  $300^\circ$ C.

The sample (0.1 g of powder) could be introduced into the reaction vessel, the whole apparatus evacuated and filled with argon and the mercury level in the gas burette adjusted to zero at atmospheric pressure. The bath was then raised into position, the time noted and readings taken. Blank experiments were carried out at each temperature in order to correct for expansion of gas in the apparatus. By this means a series of volume-time readings could be made at various temperatures and the gas evolutions compared. The gases evolved could be drawn from the apparatus and identified, and, in some cases, estimated.

### *Ingredients*

The three ingredients, potassium nitrate, sulphur and charcoal, are all stable at temperatures below  $300^\circ$  C. Potassium nitrate does not undergo any physical change and is stable even at  $410^\circ$  C. Sulphur melts at  $120^\circ$  C but does not undergo any further change and is not appreciably dissociated; its vapour pressure rises steeply with temperature. Charcoal, which has been prepared by carbonization at temperatures of about  $350^\circ$  C, shows no detectable gas evolution or change of physical state. Of these three substances charcoal is the only one which is not a chemical of high purity. It consists essentially of a lightly carbonized soft-wood such as alder and contains, in addition to free carbon, a number of complex organic materials. These organic substances have not been fully identified but may be high homologues of aliphatic acids, ketones, alcohols and aldehydes and phenols. The amount and nature of these materials changes

as the temperature of carbonization changes. In general, it is found that the oxygen content of the charcoal changes in proportion to the carbon content, the hydrogen content remaining between 2 and 4 %. Experiments showed that these organic oxyhydrocarbons could be extracted with a solvent. When the solvent was removed by evaporation a tarry residue was obtained which had reducing characteristics. This tarry extract was solid at room temperature but could readily be melted.

#### *The system potassium nitrate + sulphur*

Experiments were carried out on mixtures of these materials. When they are mixed together by grinding to a fine state, no reaction occurs. If they are heated, gas evolution begins at a temperature of 250° C and is slow but continuous. As the temperature is raised, the gas evolution is increased but is still of the same form. Some typical results are shown in figure 15. The gases evolved during heating are oxides of nitrogen, first nitric oxide and then nitrogen dioxide. If the temperature is raised above the melting-point of potassium nitrate (334° C sulphur dioxide can be detected quite readily although it cannot be detected at lower temperatures. A small amount of potassium sulphate and potassium nitrite is formed in the solid residue.

#### *The, system sulphur + charcoal*

Intimate mixtures of sulphur and charcoal begin to evolve gas at a temperature of 250° C. As the temperature is increased, the amount of gas evolved per unit time is increased and the gas consists almost wholly of hydrogen sulphide. After heating for a period of some minutes, depending on the temperature, the gas pressure showing the effect of carbon content of the charcoal.

evolution begins to decrease until finally it ceases and prolonged heating produces no further change. Some results for three different charcoals are shown in figure 16. During this process a large proportion of the sulphur volatilizes on to the cooler part of the apparatus, but some still remains in the sample even about 290° C, and there should be ample sulphur present for reaction to continue. As the carbon content of the charcoal is increased, the amount of gas evolved decreases. It is clear that the hydrogen sulphide must be formed by a reaction of sulphur with the oxyhydrocarbons present in the charcoal. If this material is extracted with acetone in a Soxhlet a dark brown tarry residue is obtained. If the acetone is evaporated off and the residue mixed with sulphur and heated to 290° C a strong gas evolution can be obtained. The gas is hydrogen sulphide. When the argon in the apparatus was replaced with hydrogen no change in reaction rate could be found, and the hydrogen sulphide formation cannot be due to hydrogen chemisorbed on the surface of the charcoal. The substitution of graphite for charcoal initiation, burning and thermal decomposition of gunpowder resulted in cessation of gas evolution and the volume in the apparatus remained constant. Both these experiments show that

the hydrogen for hydrogen sulphide formation comes from chemical reaction with the oxyhydrocarbons usually present in the charcoal.

### *The system charcoal + potassium nitrate*

Mixtures of this type are known as sulphurless gunpowders and they can burn with much the same vigour as a normal gunpowder. When such a powder (70 %  $\text{KNO}_3$  30 % charcoal) is heated, gas evolution commences at a temperature of  $270^\circ\text{C}$  and increases in rate as the temperature is increased. Typical results are shown in figure 17.

Once again the carbon content of the charcoal is important, and when the carbon content is increased to 95 %, the charcoal appears to become activated. It can physically adsorb large volumes of gas, and during the early stages of reaction this adsorption of the gas takes place, causing a shrinkage in volume. However, with 70 % carbon charcoal a steady but diminishing gas evolution occurs, and once again nitric oxide and nitrogen dioxide can be detected. After prolonged heating, the rate of gas evolution becomes very slow and finally ceases.

If the argon in the apparatus is replaced by oxygen, a vigorous reaction takes place which often, at higher temperatures, results in explosion. If explosion does not take place, the rate of gas evolution again decreases as the time of heating becomes longer. With high carbon charcoals, the adsorption effect is much more noticeable, a very considerable shrinkage in volume taking place. Hydrogen in the apparatus has again no effect on the rate of reaction.

### *The gunpowder system*

When a mixture of the three ingredients is heated in an argon atmosphere, gas evolution begins at approximately  $250^\circ\text{C}$  and gradually decreases in rate as the reaction proceeds. When the temperature is raised, the reaction rate is increased, and at a temperature of approximately  $280^\circ\text{C}$  a remarkable change takes place (see figure 18). Gas is evolved for the first 5 min, and then the volume remains practically constant for another 15 min. After this time accelerated evolution of gas takes place over a time of approximately 2 min. The rate of gas evolution then decreases, and after a few more minutes it practically ceases.

As the temperature is increased, above  $280^\circ\text{C}$ , the rate of gas evolution is increased and the delay before the accelerated decomposition sets in becomes smaller. Finally, a temperature is reached (ca.  $300^\circ\text{C}$ ) where gas evolution starts strongly, accelerates and brings about explosion. Explosion generally follows in a comparatively short time if it is going to occur at all. When accelerated decomposition does occur it is preceded by an induction period where the gas evolution rate falls almost to zero, and it thus suggests that secondary reaction is

taking place in the gas phase. If the logarithm of the induction period is plotted as a function of the reciprocal of the absolute temperature, a straight line is obtained indicating that a monomolecular reaction is taking place.

Grained gunpowder behaves in a similar manner to a fine powder except that slightly higher temperatures are needed. There is another factor, however, which has considerable effect on the production of the accelerated reaction, and this is the carbon content of the charcoal. The above experiments refer to a normal gunpowder containing a 70 % carbon charcoal. Other experimental powders with charcoals of different carbon contents were made and tested in a similar manner. The results are shown in figure 19. It can be seen that the accelerated reaction occurs most strongly with the 70 % carbon charcoal and to a less extent with the 77.5 % carbon charcoal. With 65 % carbon there is only an indication of acceleration, and with 53 and 95 % carbon charcoal there is no sign of accelerated reaction. An optimum carbon content of 69 to 70 % is required to produce maximum acceleration.

#### *Self-heating effect*

It was observed that the behaviour of a gunpowder sample was dependent to some extent on the amount taken. Throughout the experiments samples of 0.1 g were used, and when the sample was reduced to 0.05 g it was found that the accelerated decomposition could no longer be obtained. Since no change was apparent in the nature of the sample, it was thought that this might be due to self-heating, and some experiments were carried out with samples of varying size. The use of larger samples of 0.15 g led invariably to explosion when the accelerating period was reached, even at temperatures at which 0.1 g did not explode. In order to show this more clearly, a thermocouple (platinum platinum--rhodium of 0.003 in. diameter) was introduced into the powder and the temperature rise measured. With samples of 0.15 g the rise in temperature due to self-heating was quite marked--the temperature of the bulk powder rose 7° C in 10 min and then explosion occurred.



### *Products of decomposition*

During the thermal decomposition of gunpowder under these conditions the principal gases evolved in order of appearance are hydrogen sulphide, nitric oxide and nitrogen dioxide. Hydrogen sulphide begins to come off as soon as the sample has reached a temperature above ca. 250° C, and nitric oxide also comes off very early in the process. Nitrogen dioxide does not appear in any observable quantities until the accelerated reaction sets in. At this stage all the hydrogen sulphide had disappeared and the gases consist mainly of nitric oxide and a trace of nitrogen dioxide. Up till the time gas evolution practically ceases in the induction period, hydrogen sulphide is the only gas evolved in estimable amounts, and after 5 min heating at 290° C, 70 % of the gases are still hydrogen sulphide. However, when accelerated reaction is due to set in, all the hydrogen sulphide has gone. During this induction period potassium sulphate is progressively formed and also a small .but detectable amount of potassium nitrite. No potassium sulphide is formed at any stage in these reactions, and sulphur dioxide could not be detected. The powder residue after accelerated reaction had occurred would still bum quite vigorously; in fact, it appeared to bum more vigorously than the original powder.

### *Organic materials present*

The exact nature of these materials is, as yet, unknown, but they belong in all probability to the classes of substances mentioned above. A solvent extract of these materials was made from a 70 % charcoal, evaporated to dryness and was added to a charcoal containing a 95 % carbon, in an amount sufficient to produce the equivalent of a 70 % carbon charcoal. This charcoal was then made up into gunpowder, said it was found that the resultant powder now behaved like one made from a 70 % carbon charcoal. Rapid acceleration and decomposition was observed, and it would appear that the initial behaviour is determined by this extract. This active ingredient occurs in greatest abundance in a 70 % carbon charcoal. The extract is solid at normal temperatures and melts between 80 and 120° C, so that at temperatures above 120° C it may be considered as a liquid.

### Discussion

#### *Initiation*

The experiments described in part 1 suggest that the initiation of gunpowder is usually brought about by the formation of a local hot spot. When the initiation is caused by impact it would appear that hot spots can be readily formed by the adiabatic compression of entrapped air. The higher sensitivity of the coarse - grained powder supports this view. The crushed grains can easily entrap air; compression of air pockets formed in this way may be detected by photographic methods. When a very fine gunpowder is used the impact sensitivity is very much lower, but as the experiments show, if the powder is distributed so that air

can be entrapped it again becomes sensitive. Further evidence that the initiation is local is provided by the examination of the anvil and striker after impact. The erosive burning frequently begins at a point and spreads out in channels from this (see figure 1, plate 3).

The experiments with grit particles lend support to this view. Again it is found that the initiation begins at, or very close to, the grit particle. The experiments with grits of varying melting-points axe striking and suggest that the hot-spot Initiation, temperature necessary for initiation may be as low as  $130^{\circ}$  C. This is very much lower than the hot-spot temperature required for most other explosives, which is in the region of  $400$  to  $500^{\circ}$  C. The correspondence of this temperature with the melting-point of sulphur suggests that the formation of a liquid phase may be an important factor in the initial stages of the reaction. If a sulphurless gunpowder is used this limiting temperature of the hot spot appears to be considerably higher, and it is found that the explosion efficiency is 100 % when the melting-point of the grit particle exceeds that of potassium nitrate ( $334^{\circ}$  C). It is clear that with a substance like gunpowder any reaction in the solid phase is necessarily very slow. Once a liquid phase is formed this difficulty no longer arises, and it would seem that the formation of molten sulphur can play a major part in the early stages of initiation. The effect of impact can melt the sulphur and cause it to come into intimate contact with the potassium nitrate and with the organic material in the charcoal. If sulphur is absent from the powder it is apparently necessary to melt the potassium nitrate before rapid reaction can start easily. Once sufficient heat has been liberated and the reaction has started it becomes primarily the oxidation of carbon by potassium nitrate; here different considerations apply, and at the high temperatures and pressures obtaining this may be a gas solid interface reaction. It is the early stage of the process that we are discussing here.

A single grit particle of appropriate size can initiate the explosion. During impact this is crushed and the broken fragments rub over one another, so producing a hot spot. Melting-point is the determining factor, but if the particles are too soft they axe less effective. The experiments with the heated anvil or with an artificial copper hot spot axe in harmony with the grit experiments and again indicate that reaction can begin if the local temperature is raised above the melting-point of sulphur. This temperature,  $130^{\circ}$  C, is much lower than the recognized ignition temperature of gunpowder (Violette, for example, quotes an ignition temperature of  $300$  to  $350^{\circ}$  C). Experiment shows that if a film of powder is placed on a metal plate heated to about  $200^{\circ}$  C it does not ignite. It would seem that in order to secure reaction at the low temperature a high pressure is also necessary. Calculations show that under the conditions of these experiments the average pressure during impact was of the order of 150 atm, and the local pressures were probably considerably higher. As the hot-wire experiments show, a high pressure will lead to rapid reaction at comparatively low temperature. The effect of pressure may be twofold. It may increase the reaction rate on a purely kinetic basis, and it may produce conditions which are very favourable for reaction.

Gunpowder is a heterogeneous mixture, and the charcoal component will not change its physical state appreciably under impact. The structure of the charcoal is such that fluids can flow into the small interstices in the mass and under pressure. When one or more of the other components is in the form of a liquid, such flow becomes possible. Intimate contact and rapid chemical reaction can then occur.

### *Burning and propagation of burning*

It is clear from the experiments described in part II that both the rate of burning (that is, the rate at which an individual grain of gunpowder is consumed) and the rate of propagation (that is, the rate at which the reaction is carried from grain to grain) are both very dependent upon pressure. At atmospheric pressure the rate of burning of a normal-grained gunpowder was about 0.4 cm/s. The rate of propagation along a line of grains was of the order of 60 cm/s. If the pressure is reduced below atmospheric both the rate of burning and of propagation decrease rapidly, and at pressures below a quarter of an atmosphere the grains fail to burn.

An increase in pressure produces a remarkable change in both burning rate and propagation rate. Even a pressure of 2 atm can produce a propagation rate twice that observed at atmospheric pressure, and when the pressure is increased to 20 to 30 atm both the burning rate and the rate of propagation increase by a factor of 15. The light output is short and highly actinic, showing that a much higher temperature has been reached. This behaviour is consistent with the view that the actual burning process is occurring primarily at a gas-solid interface. The study of individual grains indicates that they burn from the surface inwards in a uniform manner. The grains usually do not disintegrate, and there is no evidence of a reaction occurring inside the grain. The major reaction between charcoal and potassium nitrate apparently takes place close to the surface of the grain and not inside it.

There is evidence that the propagation from grain to grain is due primarily to the emission of a fine hot spray of molten particles (potassium salts). These particles are projected on to the neighbouring grains and ignite them. The fact that the expanding cloud round the burning grains is opaque supports the view that it consists of solid or liquid particles and is not simply hot gas. This is confirmed by the experiments where they are collected on a cold plate. Subsidiary experiments showed that it was difficult to ignite the powder by merely allowing hot gases to impinge on the grains.

### *Thermal decomposition*

The thermal decomposition of gunpowder at temperatures below the ignition point of the powder provides some interesting information on the processes which control the reaction rate in the burning of gunpowder. It is clear that several reactions can proceed concurrently since charcoal + sulphur mixtures evolve hydrogen sulphide and potassium nitrate + sulphur mixtures evolve nitric oxide and nitrogen dioxide. Since graphite + sulphur mixtures and graphite + potassium nitrate mixtures evolve practically no gas, the reactions which proceed with the charcoal in the early stages do not involve reactions with elemental carbon. There is some reason to believe that the surface nature of the charcoal will play some part in the reaction, since deposition of potassium nitrate in the interstices of the charcoal plays an important part in promoting reaction. However, this is a physical effect and is bound up with the ease with which the potassium nitrate and organic material in the charcoal can be brought into contact.

Since the potassium nitrate will not be liquid at temperatures below 334° C, and since the hydrocarbons, although liquids above 120° C, will be adsorbed or absorbed in the charcoal, it is necessary to have the potassium nitrate dispersed throughout the charcoal by means of solution during milling. The sulphur, when melting at 120° C, will form a liquid phase so that contact and rapid reaction can occur. The production of at least one liquid phase is apparently essential to this initial reaction, and gunpowder mixtures are quite stable at temperatures below the melting-point of sulphur.

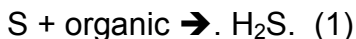
Although gas evolution increases with the increasing organic content of the charcoal, the conditions required to produce optimum reaction rate are critical and require the presence of both sulphur and some of the oxyhydrocarbons. No matter what the carbon content of the charcoal, accelerated decomposition cannot be produced in a sulphurless powder. In some respects the sulphur appears to

behave as a reducing agent, producing, among other things, potassium sulphate. In the early stages of the reaction it is itself being reduced to hydrogen sulphide by the organic material in the charcoal. This does not imply that these materials are themselves reducing agents, since normal saturated aliphatic hydrocarbons will produce hydrogen sulphide with sulphur when heated. These organic materials, though apparently saturated, will, however, readily decolorize potassium permanganate solution, and it is possible that they also possess reducing characteristics.

The work of Hoffmann has led to the assumption that the reactions involved are the formation of hydrogen sulphide by reaction of the sulphur with organic material above 150° C and then, at temperatures above 280° C, the exothermic reaction of hydrogen sulphide and potassium nitrate to form potassium sulphate. While potassium sulphate is formed during the induction period, there is always

a considerable excess of hydrogen sulphide, and if reaction does occur, it is not, strongly exothermic nor very rapid. It has been shown that the accelerated reaction does not in fact begin until the hydrogen sulphide has been used up.

It would appear from the evidence obtained that the reaction proceeds in several steps. As the temperature is increased these steps will become shorter and reaction will be faster. Since these reactions may also involve gases, the effect of pressure will also be important. The first reaction which takes place is the formation of hydrogen sulphide, thus



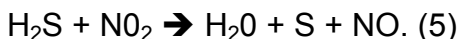
At the same time reaction proceeds between the organic material and the nitrate with the production of nitrogen dioxide:



Also, reaction can proceed between the sulphur and potassium nitrate with the formation of nitric oxide and nitrogen dioxide:



It is suggested that nitrogen dioxide then reacts with the hydrogen sulphide to produce nitric oxide and regenerate sulphur:



This would explain the disappearance of the hydrogen sulphide and the apparent cessation of gas evolution. This reaction (5) proceeds until all the hydrogen sulphide has been used up. When this is so, nitrogen dioxide can again appear, and since sulphur is still present reaction can occur with the production of nitrogen:



The sulphur dioxide could immediately react with potassium nitrate to produce potassium sulphate:



Experiment shows that no nitrogen dioxide is in fact liberated at this stage and that potassium sulphate is formed. Reactions (5) and (6) are both endothermic, but reaction (7) is strongly exothermic. This reaction (7) can therefore produce

the heat necessary to promote the decomposition and to lead on to the burning of the powder.

It should be emphasized that the work described in this section applies essentially to the early stages of thermal decomposition. Once the reaction gets under way and sufficient heat is evolved the process usually referred to as the burning of gunpowder can take place. This is primarily the oxidation of carbon by potassium nitrate. In the early stage of decomposition which we have been discussing here it would again seem that the production of a liquid phase is important. This liquid phase can apparently be produced by the organic material in the charcoal as well as by sulphur.

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#### REFERENCES

- Andrev, K. K. 1945 C.R. *Acad. Sci. U.R.S.S.* 49, 427.  
Bowden, F. P. & Gurton, O. 1949 *Proc. Roy. Soc. A*, **198**, 337, 350.  
Bowden, F. P., Mulcahy, M. F. R., Vines, R. G. & Yoffe, A. 1947 *Proc. Roy. Soc. A*, **188**, 291, 311.  
Bowden, F. P. & Yoffe, A. D. 1952 Initiation and growth of explosion in liquids and solids. *Cambridge Monographs on Physics*. Cambridge University Press.  
Debus, H. 1882 *Liebigs Ann.* **212**, 257; 213, 15.  
Hoffmann, K. A. 1929 S.B. *preuss. Akad. Wiss.* 509, 193, 432.  
Huff, W. & Moore, R. 1944 *Rep. U.S. Bur. Min.*, no. 3782.  
Kast, H. 1913 *Spring u. Zundstoffe*, p. 1025.  
Nobel, A. & Abel, F. 1875 *Phil. Trans.* 165, 49.  
Oza, T. & Shaho S. 1943 *J. Indian Chem. Soc.* **20**, 261, 286.  
Violette,— . 1848 *Ann. Chim. (Phys.)*, (3), **23**, 475.  
Watanabe, S. 1933 *Bull. Inst. Phys. Chem. Res. Japan*, **12**, 884.

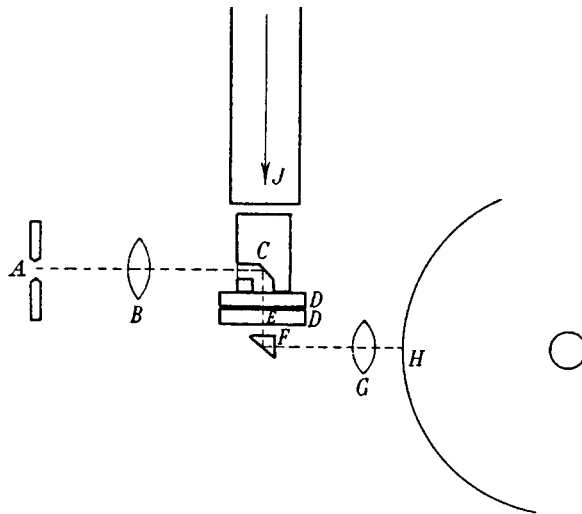


FIGURE 3. Apparatus used for flash photographic study of crushing of grains of gunpowder. *A*, flash tube; *B*, condenser lens; *C*, striker with prism; *D*, glass anvils; *E*, gunpowder grain; *F*, prism; *G*, camera lens; *H*, camera drum; *J*, guide tube for dropping weight.

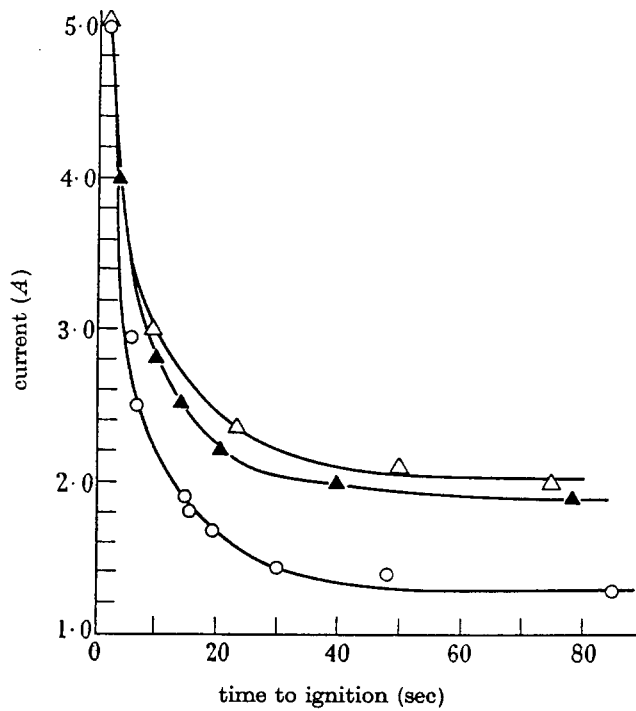


FIGURE 7. Curves showing the relationship between current flowing in a wire surrounded by gunpowder and the delay to ignition. ○, 150 mesh powder; ▲, 25 mesh grains; △, 12 mesh grains.

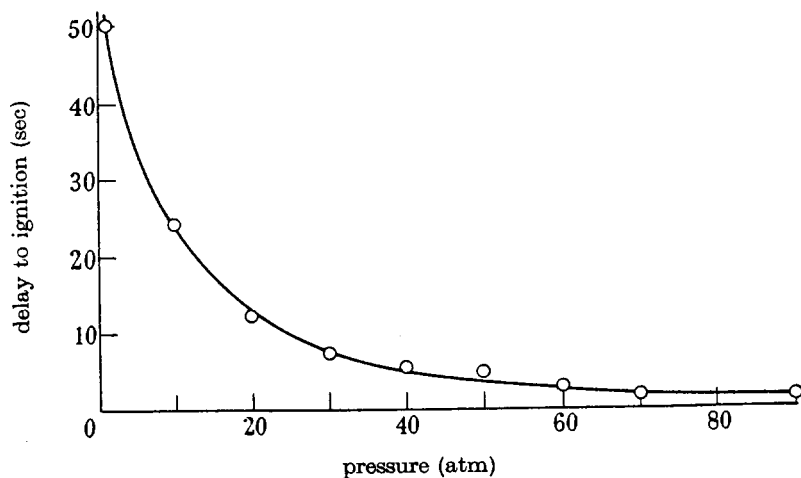


FIGURE 8. Curve showing the relationship between ambient pressure and delay to ignition at a constant temperature of *ca.* 300° C. A minimum delay of 1.2 s (the time of the wire to attain temperature) is reached at 70 atm.

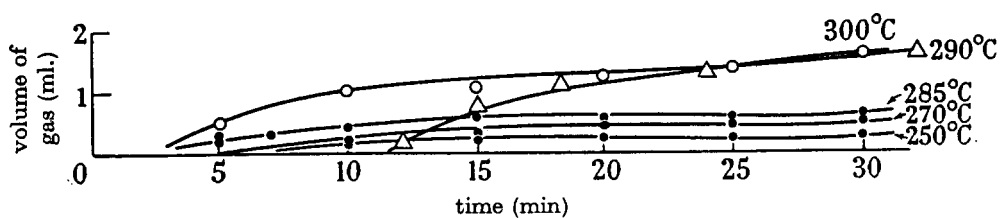


FIGURE 15. Gas evolution from a mixture of potassium nitrate and sulphur at atmospheric pressure at temperatures between 250 and 300° C.

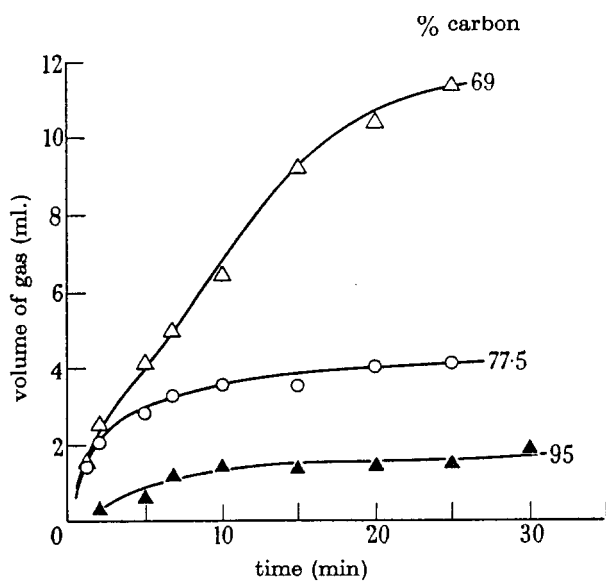


FIGURE 16. Gas evolution from mixtures of charcoal and sulphur at 290° C and atmospheric pressure showing the effect of carbon content of the charcoal.



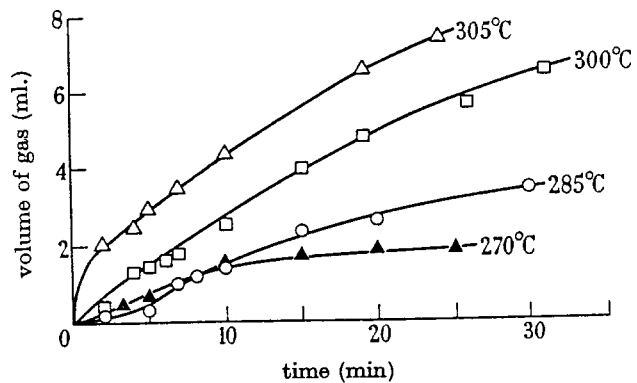


FIGURE 17. Gas evolution from a mixture of 70 % potassium nitrate and 30 % charcoal, at atmospheric pressure at temperatures between 270 and 305° C.

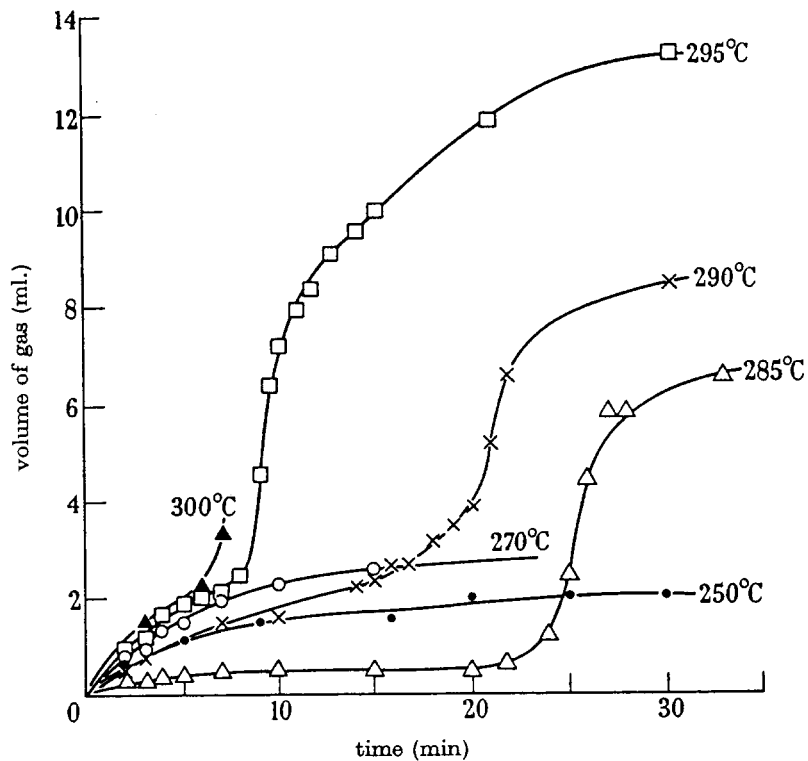


FIGURE 18. Gas evolution from normal gunpowder containing 70 % carbon charcoal, at atmospheric pressure and at temperatures between 250 and 300° C.

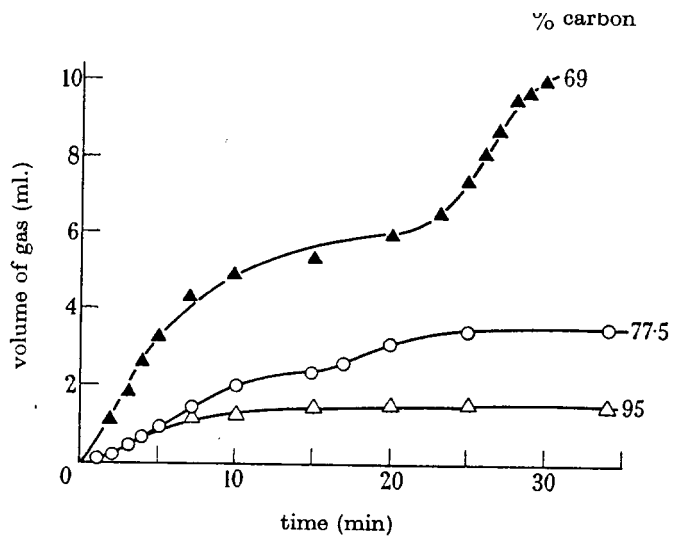


FIGURE 19. Gas evolution from gunpowders containing three different charcoals. Evolution is at atmospheric pressure and 290° C. The acceleration and evolution are a maximum for charcoal containing 69 % carbon.