CHAPTER 5
INITIATION OF EXPLOSIVES

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5 INITIATION OF EXPLOSIVES

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5.1 AWARENESS SUMMARY

In the practical application of explosives there is a requirement to start the explosive event by a reliable method of initiation. This could be initiation to a burning reaction, for example for gun propellants, rocket propellants or pyrotechnics, or initiation to detonation for high explosive charges. In either case energy must be imparted to the explosive such that the chemical reaction of explosive molecules or explosive mixture is caused to occur at such a rate it becomes self-propagating, that is it continues through the explosive charge. All of the methods described below that are capable of causing ignition or detonation of a charge will cause the explosive to be raised in temperature since the chemical reaction of explosion will increase its rate rapidly as temperature increases as shown in Figure 5-1. The methods of energy input are deliberate for practical initiation system; however, they also will be relevant to the potential accidental initiation of explosives.

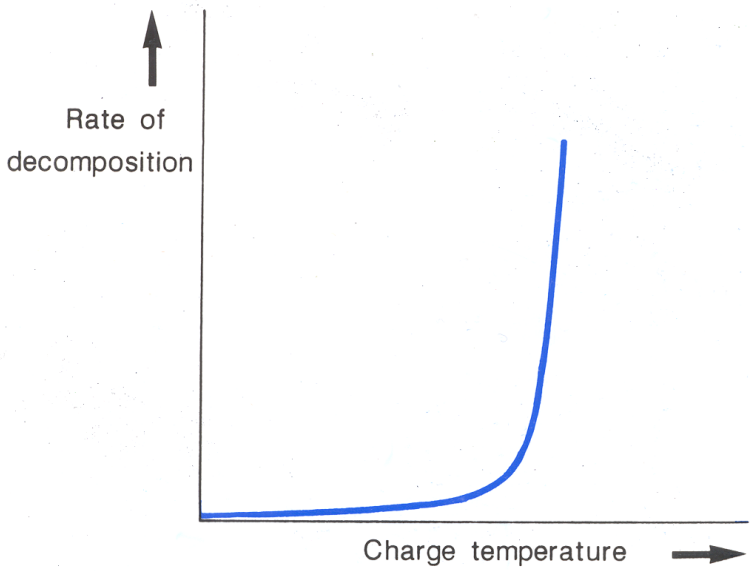


Figure 5-1 Rate of explosive reaction vs temperature

5.1.1 Initiation to Burning

5.1.1.1 Direct heat

If an explosive is heated, for example on a metal plate, at some point it will achieve a temperature at which ignition will occur. This would not be practical in a munition but is relevant to safe handling of explosives. Raising the temperature of a small sample of explosive at 5 °C per minute until ignition is

seen provides a Temperature of Ignition (T of I) (link to 20.10.2.3) for that explosive (Table 5-1). If an explosive is heated much more slowly, then this value can reduce by several 10s of degrees.

Table 5-1 Some Temperature of Ignition Values for Common Explosives

Explosive	Temperature of Ignition* (°C)
Nitrocellulose	187
Nitroglycerine	188
RDX	204
PETN	205
TNT	240
HMX	273

* Heated at 5 °C per minute

5.1.1.2 Flame

This is an obvious method of producing high temperatures and is used often for igniferous ignition, e.g. for igniting propellant. The source of the flame is either a pyrotechnic or primary explosive and temperatures well in excess of 10,000 °C can be produced. The explosive to be ignited is raised in temperature by heat conduction from hot gas products and often hot particles. The flash of flame must have sufficient time to raise the explosive to its ignition temperature.

5.1.1.3 Percussion

If an explosive material is struck and compressed it is possible for hot spots to be created in the explosive by adiabatic compression. That is if a trapped pocket of air is rapidly compressed it is raised in temperature. This is the mechanism used in small arms percussion caps (Figure 5-2) (link to 6.2.2.4) where the hammer of the weapon hits the cap causing an indentation, which compresses the cap composition.

This is an example of hot spot formation (link to 5.3) within the explosive that is being ignited. These hot spots create centres of ignition that grow and coalesce to ignite the whole charge. If the cap composition is pressed too much in production then a significant number of the small air pockets are lost as the density increases. This can cause failures of percussion caps known as ‘dead pressing’ where the round fails to fire when hit by the hammer.

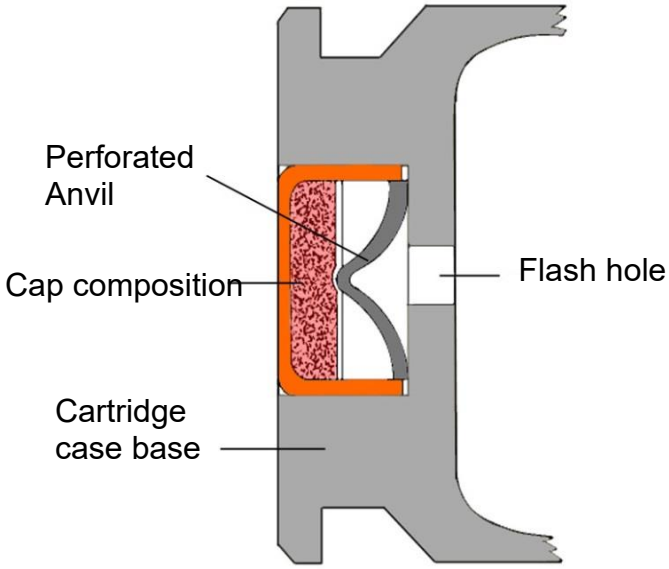


Figure 5-2 Small arms percussion cap assembly

5.1.1.4 Friction

The ability of friction to create increases in temperature is a well-known phenomenon. From a safety perspective this is important if bare explosive could experience friction such as walking on spilled explosive. For gritty explosives such as pyrotechnics this is a particular risk as they are generally powdered materials either in final form or during manufacture.

A practical use of friction as a method of ignition is the striking of match fuze and also the stab igniter (

Figure 5-3) will have a large element of friction in the mechanism causing ignition. As the striker needle enters the stab sensitive composition friction heating will occur between the composition and the sides of the angled needle point. There may also be an element of compression.

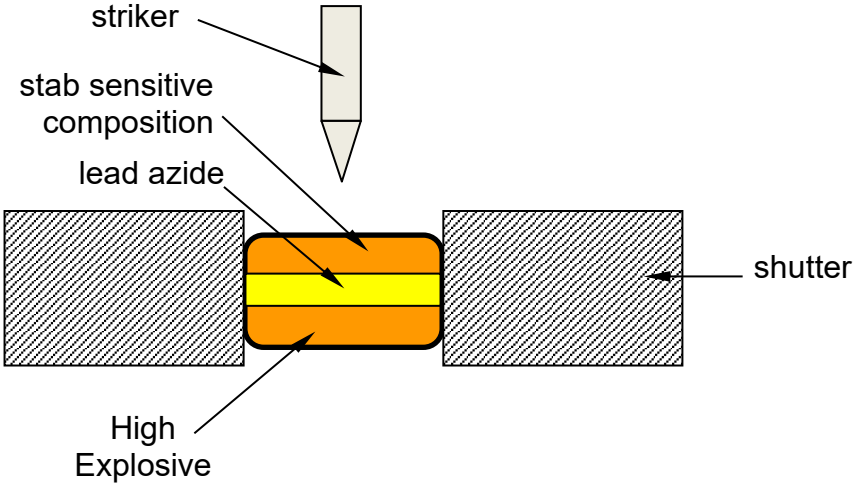


Figure 5-3 Stab initiation system

5.1.1.5 Electrical bridgewire

Passing a current through a wire that has resistance will cause it to heat. A common method to produce a flash of flame that can then be used as a source of ignition is the electric match-head. A bridgewire embedded in a primary explosive ignites when a current is passed through the wire, the ignition mechanism is simply the large temperature produced in the electrically heated wire (link to 6.2.2.9).

5.1.1.6 Static discharge

The most potent static discharge is lightning, which has a core temperature of around 15,000 °C, which clearly has the potential to initiate explosion reactions. Much lower energy static discharge also has the potential to ignite explosives. The discharge spark is in essence a highly localised source of energy, which creates a hot spot.

5.1.1.7 Conducting composition

Some primary explosive compositions contain graphite powder and when pressed in to a pellet will have conducting pathways created by particles of this conducting material. If a current is passed through the pellet there will be high resistance at points where the particles touch causing hot spots to be created and thus ignition of the explosive (link to 6.2.2.8).

5.1.2 Initiation to Detonation

5.1.2.1 Burning to detonation

Certain primary explosives such as lead and silver azides on ignition will immediately increase their rate of decomposition until burning transitions to a shock wave, which is to detonation. This is the most common method of creating a detonation in munitions. As the initial flame front moves through the

explosive it creates an ever increasing pressure and temperature ahead of it until the velocity exceeds the speed of sound at which point it detonates through the rest of the explosive.

Lead and silver azide will undergo this transition even unconfined and in small quantities such as tens of milligrams. Many explosives if confined can also undergo burning to detonation, which poses a hazard from munitions containing explosive in heavy metal casing such as artillery and mortar ammunition.

5.1.2.2 Donor-acceptor shock to detonation

An explosive charge that is undergoing detonation can, when in close proximity, detonate another charge. Factors that affect the success of this shock transfer are:

- Detonation shock pressure of the donor charge
- Sensitivity of the acceptor charge
- Any barrier between the two charges

As the shockwave from the donor enters the acceptor it will create an intense pressure wave that can create hot spots through compression of voids as for percussion initiation but in a more extreme manner. Other mechanisms such as shear forces add to the heat deposition and this forms a shockwave in the acceptor explosive. The intensity of the pressure wave entering the donor will depend on the detonation pressure of the donor explosive and anything that could reduce it such as a barrier, which can be a solid or indeed just air.

Figure 5-4 shows how the intensity of a detonation shockwave is affected by a barrier and by the sensitivity of the acceptor. When the stable shockwave in the donor enters a barrier it immediately begins to fall in pressure. As it enters the acceptor it begins to create energy release in the acceptor that then begins to produce a stable shockwave in the acceptor until it reaches the stable velocity of detonation and therefore stable detonation pressure.

If the acceptor has low sensitivity the shock pressure may fall significantly before it begins to accelerate to the stable condition. The thicker the barrier the lower the shock pressure entering the acceptor for a given donor shock pressure.

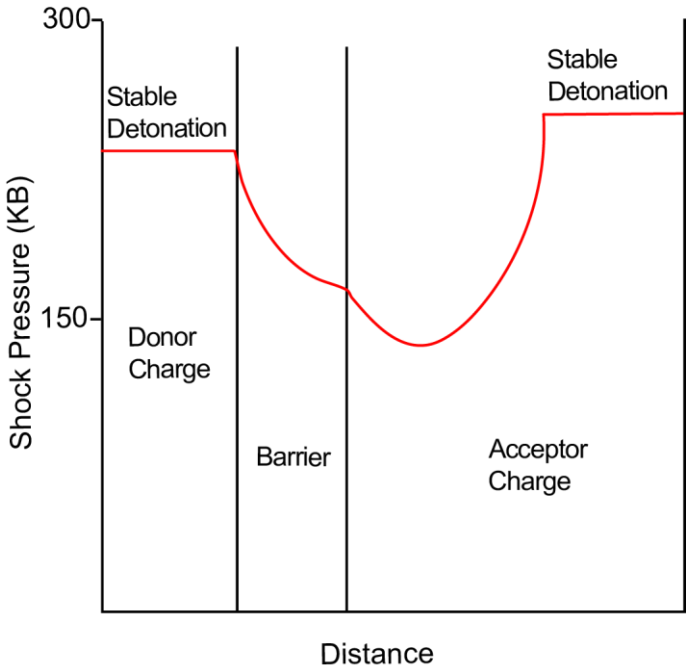


Figure 5-4 Shock pressure within a donor/barrier/acceptor

5.1.2.3 High velocity impact

Usually high velocity impact such as fragments and bullets do not directly shock an explosive to detonation. When a munition detonates in a bullet or fragment impact test the explosive content first initiates to burning but under heavy confinement of the munition casing detonates through deflagration (burning) to detonation transition. This occurs so rapidly the munition appears to detonate on impact.

In an Exploding Foil Initiator (EFI) type detonator, high velocity impact can be designed to create a detonation. A bridgewire sandwiched between two pieces of thin plastic is subject to a very large current delivered in less than a microsecond. This causes the bridgewire to explode firing a small fragment of the plastic at very high velocity in to a secondary booster type explosive with a sensitivity that allows the impact to form hot spot energy deposition and cause a shock wave to be created (link to 6.3.4.8).

5.1.2.4 Exploding bridgewire (EBW) detonator

As with the EFI, in an EBW a bridgewire is subject to the same electrical conditions with the wire embedded in a secondary booster type explosive. The bridgewire explodes with such violence it creates a shockwave in the booster explosive that transitions it to a self-sustaining shockwave in the explosive (link to 6.3.4.7).

5.2 INITIATION THEORY

5.2.1 The Effect of Temperature on Energy Distribution

One of the successes of quantum mechanics is in the definition of temperature. All materials possess energy in their structure, even at absolute zero a small amount of energy is retained in atoms and molecules. This energy resides in the electrons in their atomic orbitals around the nucleus, kinetic energy, whole linear motion (translation) of the particle, as well as vibration of chemical bonds, rotation of parts of the molecule around chemical bonds and the full body rotation of the molecule. In solids and liquids these atoms and molecules collide with neighbours with incredible regularity, 10^{13} collisions per second being common. Each collision allows for energy to be transferred between particles – one particle gaining energy the other losing it. In a system at a fixed temperature there will be a distribution of energy within the atoms and molecules, some particles possessing high energy, some low energy and the vast majority in the middle. Given the large number of collisions in the system the exact energy within a given particle will move up and down with time. The system is in a dynamic equilibrium.

The exact form of the energy-particle distribution depends on a large number of variables such as the mass of the constituent atoms, the number and strength of the bonds, internal symmetry of the molecule, the number of energy states which exist with the same energy level etc. This is the field of computational quantum mechanics.

If extra energy is added to the system the temperature increases the molecular level effect the frequency and violence of the collisions, vibrations and rotation increases. This causes a redistribution of energy between the molecules and within the molecules until a new dynamic equilibrium is reached. Figure 5-5 gives a schematic of the change caused by heating.

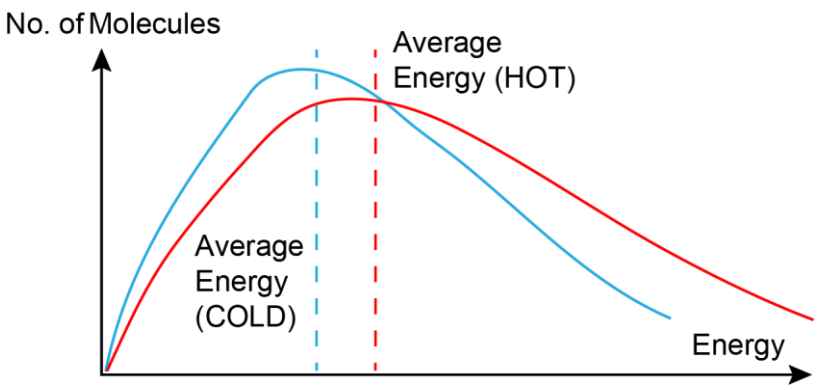


Figure 5-5 The effect of temperature on energy population

5.2.2 Bond-Breaking and Chemical Kinetics

If sufficient energy is accumulated in a molecule by collision, absorption of light/gamma rays/ cosmic rays, impact by high-speed particles etc. then it is possible that a bond can break. In many cases it is likely that the separated entities produced by the bond breakage recombine almost immediately. However, in some cases the separated entities form strong bonds with other atoms and molecules in the vicinity or undergo further fragmentation. This forms the basis of chemical kinetics.

Most chemical reactions start with an endothermic step, this means that energy has to be added to the molecule causing the initial bond breakage., Immediately after separation, the fragments are in a very high energy state. The fragments can lose energy by collision, the particles will lose a lot more energy by forming new bonds or by rearranging and fragmenting further. The energy released by this to other molecules can cause those molecules to fragment and so lead to a succession of chemical reactions. Reactions which give out energy are called exothermic and it is the balance between the endothermic and the exothermic reactions which determines the overall energy output. Figure 5-6 gives a schematic of the energy release for an exothermic reaction.

The easiest way to concentrate energy into a molecule is by heating it. If once, chemical reaction has started, sufficient energy is released this can cause the system to be self-heating. Effectively a positive feedback mechanism, building up the energy release rate to the phenomenal levels seen in explosives.

The energy required to take a molecule from its normal, standard temperature and pressure (298 K and 1 atmosphere) to the state where its weakest bond breaks is called the activation energy (E_{act}). The energy difference between the initial material and the final products is the energy that is available for doing other work. In most explosives this means a conversion from a solid or a liquid to a hot, high pressure gas which violently pushes against, fracturing and moving the surrounding material. Figure 5-6 gives a schematic idea of the energy thresholds and energy output.

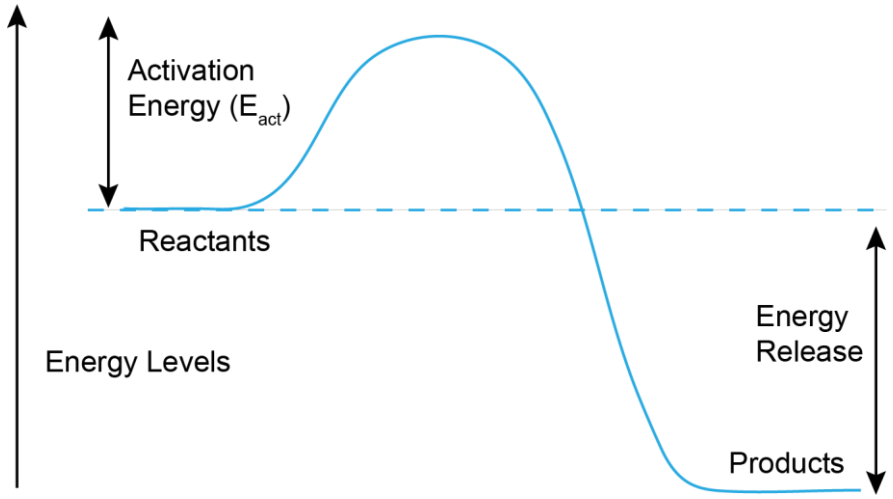


Figure 5-6 Energy balance from reaction in an exothermic chemical system

5.2.3 Boltzmann and Arrhenius

There are two fundamental equations used to understand this area of work. These were developed by Boltzmann and Arrhenius. Boltzmann considered the relative populations of a high energy state compared to a low energy state. The resulting equation has the form shown in Equation (5-1.

$$\frac{Nh}{Nl} = e^{(-\delta E/RT)} \tag{5-1}$$

Where *Nh* is the number in the high energy state and *Nl* is the number in the low energy state, δE is the energy difference between the two levels per mole of material, *R* is the gas constant and T is the temperature measured in Kelvin (K). Sometimes in Physics based texts the term *R* is replaced by *k*, the Boltzmann constant, in which case δE is energy per atom or molecule not per mole of reactant.

In this basic form the population of the lowest energy state is always higher than more energetic states. However, due to symmetry considerations, there may be several bonds which are equivalent, e.g. methane has 4 identical C-H bonds for example. The number of states with the same energy level is called the degeneracy and this often means that while there is one low energy state, there may be hundreds of higher energy states available resulting, at room temperature, in most molecules being at energy levels above the lowest energy state.

Arrhenius looked closely at chemical kinetics and discovered that, for a fixed reaction pathway, that the rate constant, a measure of the speed of transformation, was temperature dependant. While a complete exposition of this is beyond this text, it is useful to examine the dependencies within the Arrhenius equation (Equation (5-2)).

$$k(T) = A\, e^{(-Eact/RT)} \qquad (5\text{-}2)$$

Where k(T) is the rate constant at a temperature T, a value that links concentration to overall transformation rate. The term *A* is called the pre-exponential term. This encapsulates the frequency of impact of molecules against one another and the efficacy of that impact. Molecules have a structure and so the exact position of the impact on the structure is important. Overall the value of A varies from the low, $<10^{-6}$, showing that the overwhelmingly large number of impacts have no effect. Whereas some biological enzyme reactions have values so high it implies virtually every impact between the reactants results in reaction. The exponential term looks very similar to the Boltzmann relation. This not surprising, as the δE term is represented here as the activation energy i.e. the amount of energy that has to be concentred in the molecules to take it from the average state to the bond-breaking peak of the energy level diagram. T is the absolute temperature of the system. Processes with lower activation energy tend to occur more regularly than those with high activation energy, the higher the temperature the larger the number of molecules nearer the high-energy state.

For primary explosives e.g. Lead Azide, the activation energy is of the order 105 kj/mol and the value of A is 10^{11}. For secondary explosives the activation energies are generally larger, of the order 222 kJ/mol (for TNT) and collision factors are of the order 10^{22}. As the activation energy represents the energy needed to cause breakdown of the material this means that primary explosives require less stimulation to cause reaction. This agrees with the general fashion of rating primary as sensitive and secondary as less sensitive but this time in a quantitative fashion.

5.2.4 Frank-Kamenetskii Thermal Explosion Theory

In the 1930's the soviet scientist Frank-Kamenetskii investigated the thermal stability of energetic materials in a quantitative fashion. This work led to thermal explosion theory, which can be seen as a pre-cursor to hot-spot theory particularly with respect to energy balance.

Consider a solution of explosive in a solvent in an oven. It is relatively easy to vary the concentration of the explosive and strength of the heating i.e. the oven can be set to heat to a different temperature for each experiment. As the explosive heats up some of it will decompose into smaller molecules, releasing energy. This energy release will cause the solvent close to the decomposing energetic molecule to heat up. If there is a second explosive molecule near the decomposing molecule, this second energetic molecule will heat up and become more likely to decompose and so an escalation of temperature can occur locally then spreading to lead to increased and sustained reaction. However, if there are only a few or no energetic molecules in the vicinity of the decomposing energetic molecule then the energy released will spread into the general background level of the solvent molecules and effectively have no long

term effect. The important factor is the balance between heating caused by reaction and cooling based on the temperature of the surrounding solvent. This effect can be assessed in a more quantitative fashion by examining Figure 5-7 below.

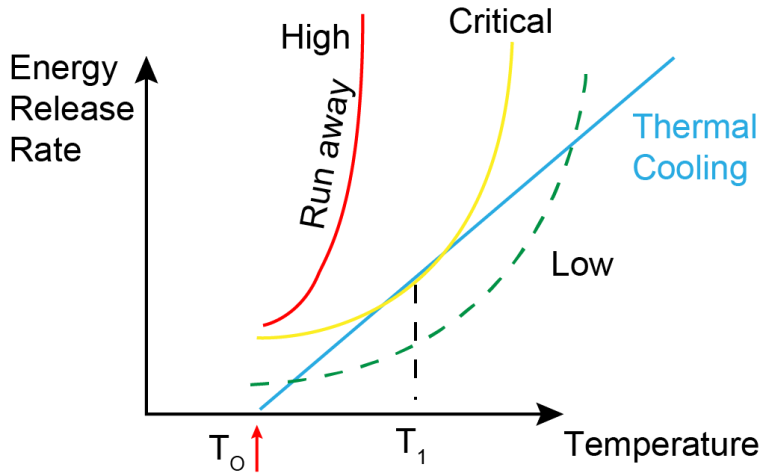


Figure 5-7 Energy balance for a heated explosive solution

In Figure 5-7 the three curves correspond to different concentrations of explosive, high, critical and low in an oven set a temperature T_0. These curves represent the energy output caused by the different concentration of explosive. The blue line represents thermal cooling. Newton developed a law of cooling which, simply stated, said that energy loss was directly proportional to the temperature difference between the hot body and the surrounding environment.

In the case of the high concentration of explosive it can be seen that the energy release rate is always above that of the thermal cooling line. This implies that the explosive solution will rapidly heat up and will 'run away' generally to an explosion. At the other extreme we have the low concentration, the green line, as it is heated and releases energy it raises the temperature. However, the cooling processes are very strong compared to the energy release. This means that at the point where the solid green curve meets the blue cooling line the rate of energy release is balanced by thermal cooling, so the system sits at a temperature slightly above T_0. The system neither heats nor cools from this temperature until the concentration of explosive, through decomposition, is reduced at which point the solution cools back towards T_0. The dotted green curve indicates where the temperature would have risen, in the absence of cooling.

For the critical concentration, decomposition causes the temperature to rise and as the temperature goes up so does the cooling rate. At this critical concentration a temperature is reached where the heating and the cooling are exactly balanced. Here the system is in a delicate balance, a slight increase in the energy release rate and the system will run away. The insight of Frank-Kamenetskii was to understand that not only were the rates of energy production and loss the same, but that the rates of change of energy production and energy loss were the same. Having the two sets of equations one balancing

the heat loss with heat production and the other the rate of change of those quantities allowed calculation of the time it would require for an explosive to heat to run away at a given oven temperature as shown in Equation**(5-3)**. The resulting calculations gave the results shown in Figure 5-7.

$$\tau = \frac{c_v R(T)^2}{AQ\ E} e^{E_{act}/RT} \qquad \textbf{(5-3)}$$

Where τ is the time to run away (or explosion), c_v is the heat capacity of the solution, basically the energy need to raise the temperature by 1 degree Celsius, A is the pre-exponential rate constant, Q is the amount of energy released from the reaction, T is the temperature of the oven, E_{act} is the activation energy. Looking at the form of this equation it is clear that a large value of activation energy means a long time to explosion, a large energy output means a shorter time, a large heat capacity means a longer time. By performing a series of experiments varying the temperature of the oven and measuring the time to explosion then values of A and E_{act} can be determined. This is useful as it allows insight into how much energy is required to cause extended reaction.

5.2.5 Thermal Values

In general, it is relatively easy to find tables of the thermal values of explosives in the literature. Safety databases will give values for flash point, spontaneous reaction etc. These values often seem to be very exact. However, as the discussion above shows the rate and extent of reaction is dependent on temperature and the molecules are distributed over a range of energies at any given temperature. This leads to a general approximation which works for a wide range of reactions ‘increasing the temperature by 10 ^{o}C doubles the reaction rate’.

Therefore, when reading data such as flash point or a phase change in a material there is a kinetic element to the value. Heating something slowly allowing time for reaction to build up may have equally aggressive consequences at a temperature below a stated value compared to plunging the explosive directly into a bath of material above the flash point. This can be thought of as a Frank-Kamenetskii style experiment: time to explosion depend on the heating rate.

As a consequence, when dealing with explosives the values for flash point or ignition point should be taken as a limit not to be approached and certainly violent explosion may occur of a munition is stored at a temperature below the flash point, for a long period of time.

5.3 HOT-SPOT FORMATION

In parallel with the work of Frank-Kamenetskii research was being conducted into friction and lubrication and calculations performed on the impact

phenomena of explosives. The energy deposited in the explosive sample was shown to be sufficient to raise the temperature by a few degrees or a few tens of degrees, very much lower energies than the levels required for a thermal explosion.

This resulted in the idea of hot-spots, areas in the material where energy was concentrated and exceeded the ignition threshold[1,2]. These areas were associated with heterogeneities in the structure of the explosive e.g. a bubble in liquids, a crack in an explosive crystal or the presence of a hard grit particle in a mixture. If the hot-spot was of sufficient size and concentrated sufficient energy, a so-called critical hot-spot, then it would grow, ultimately leading to ignition in the explosive. Many mechanisms were investigated of which six mechanisms were found to be capable of producing hot-spots of a critical size, these mechanisms are; bubble collapse, friction, shear band formation, fracture, visco-plastic work and electrical discharge. It must be remembered that while heterogeneities such as voids will cause energy to concentrate, not every heterogeneity will produce a critical hot-spot. Hot-spots which are too small or not sufficiently hot, will lose energy to the surroundings quickly and be thermally quenched: these are the sub-critical hot-spots. Research done by Bowden and Yoffe[1] was pivotal in this and they showed that the size, temperature and duration required to form a hotspot was of the order: size 0.1 - 10 µm, time duration 10 µs - 1 ms, temperature 700+ K.

In all cases the difference between critical and sub-critical hot-spots needs to be drawn. In the case of a critical hot-spot the reaction site is of sufficient size that the heat loss via thermal conduction is lower than the energy produced by the chemical reactions. Thus the temperature and reaction zones increase and extend into the bulk material. Sub-critical hot-spots are those for which, while chemical reaction may break out, the heat loss from the region is higher than the production rate from the reactions and thus the reaction is quenched.

In liquids, the conditions for critical hot spot formation have been extensively studied[3-8] and the size, duration and temperature required have been reasonably well-quantified. One advantage of a liquid or a single crystal of explosive is the inherent homogeneity of the system and relative ease of visualisation of the reaction front. However, many explosive systems are heterogeneous and energy concentration relies on interplay between the components.

Calculations[9] and experiments[10] on single cracks growing in individual energetic crystals show that the energy released from the crack tip is not sufficient on its own to cause sustained reaction. However, friction, caused by rubbing of the fracture surfaces against one another after crack growth, is an important mechanism in the production of hot-spots. These mechanisms are important in propellants as well as detonative systems[11].

5.3.1 Drop Weight Studies (Fracture, Friction and Pore Collapse)

A standard technique for sensitivity studies, the drop-weight is a system that allows long, low-level pressure pulses to be applied to small samples. In

combination with high-speed photography, photodiodes and stress transducers it is a powerful system for both qualitative and quantitative analysis of material response. The standard way of analyzing the output of a drop weight assumes the weight behaves as a rigid body and hence that one can simply apply Newton's laws of motion. This is used in determining the calibration of the drop weight force, by directly relating the measured force both to the deceleration of the weight also to position.

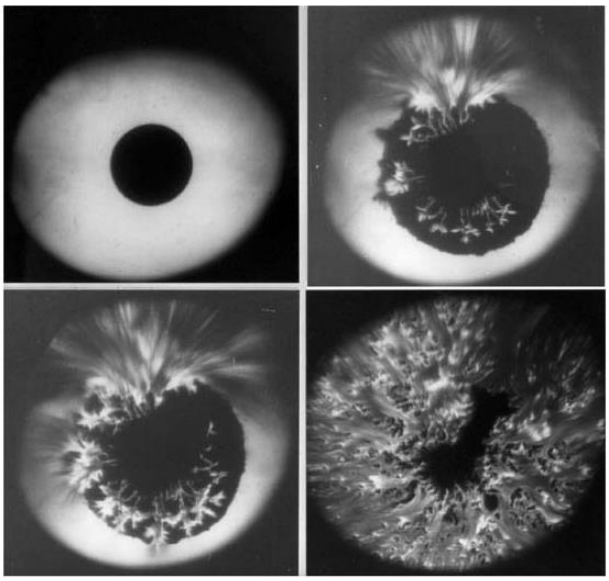


Figure 5-8 Ignition under impact of a thermite composition (Courtesy of Imperial College London)

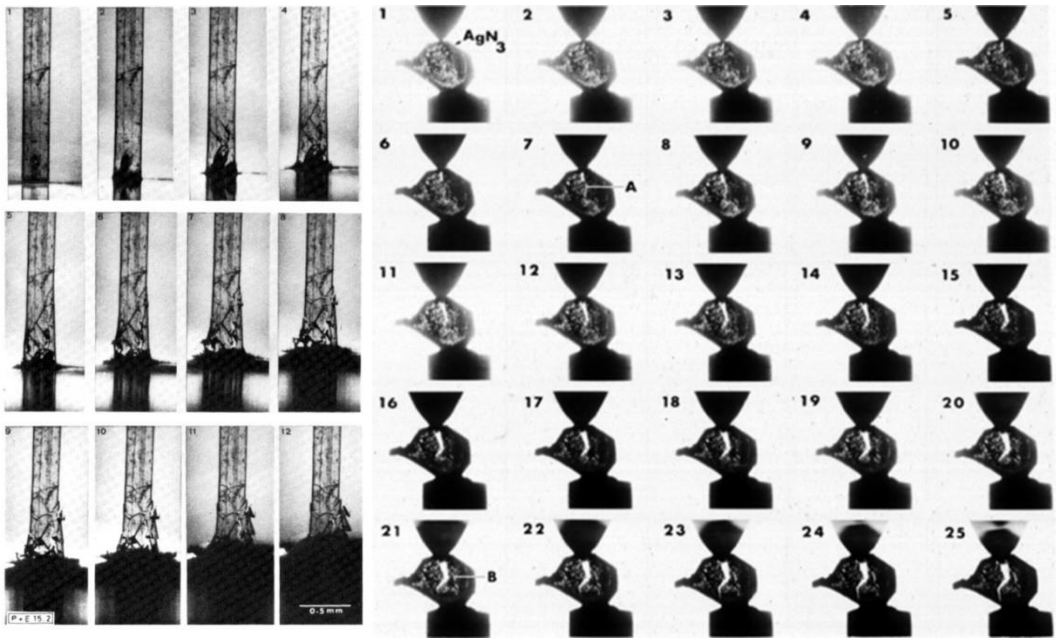
An example of a 'classic' high-speed photographic sequences obtained using this apparatus is given in Figure 5-8. Using transparent anvils images are taken along the impact axis. The top left image shows the disc of explosive before impact. The top right image shows the expansion, fragmentation and fracture of the sample. In the bottom left image there is an outbreak of reaction at the top of the sample, indicated by the jetting of hot, product gases. In the final image there is reaction throughout the sample. The time difference between these images was 10 ms. By varying the density of the sample, the grain size the contributions of the collapse of pores within the sample, the friction of grains against one another, and fracture of the grains can be studied.

5.3.2 The Relative Importance of Fracture

Fracture is often considered to be a principle cause of ignition. This can be the case but caution must be used. Figure 5-9(a) shows the effect of explosively loading a single crystal of silver azide, a sensitive primary explosive. The images were taken with an interframe time of 5 microseconds. The images show a crystal of silver azide, resting on a barrier of thin metal sheet which appears as a shadow line near the bottom of the image. A second crystal of silver azide is underneath and is initiated. The function of the metal sheet is to

stop hot reaction products from causing thermal explosion. Throughout the sequence it can be seen that the silver azide crystal shatters but does not otherwise react. In Figure 5-9(b) a single silver azide crystal is between the jaws of a loading device which crushes downwards into the crystal, breaking it. Although the fracture is moving at a high speed, again there is no reaction.

These results may seem counter intuitive, however, when the energy involved is calculated it is shown that the fracture energy released by an explosive crystal shattering is 40 mJ m^{-2}, which is not enough to cause much of a temperature rise. However, a tough polymer such as Perspex (polymethylmethacrylate) has a fracture energy of 250 J $m^{-2,}$ which is sufficient to cause critical hot-spots. This is important as if soft, rubbery polymer-bonded explosives are taken below their glass transition temperature then the strong, brittle polymer state will allow fracture to cause ignition.



(a) **(b)**

Figure 5-9 (a) fracture of a silver azide crystal by explosion, no reaction seen (b) fracture of a single crystal by knife edges, fast fracture but no ignition (Courtesy of Imperial College London)

5.3.3 Shear Bands

One mechanism which was not mentioned in the early studies is that of shear band formation. Here the impact on pressed powder pellets causes further compaction. However, this is followed by localised heating and fracture. These bands are formed when the area which is deforming becomes hot due to the concentration of mechanical stress, which softens the material in that area. This soft material becomes easier to distort and so deformation and motion and further heating occur along this surface. A similar process is found in some

metals and if the process is very quick with limited heat flow into the surrounding metal they are referred to as adiabatic shear bands.

Figure 5-10 shows a drop weight sequence for impact on to PETN. Initially the sample is opaque, however, during the impact the sample spreads and friction between the crystals leads to surface melting and fusing of the crystals. This makes the sample become relatively transparent. A reaction breaks out in the sample with the lines of reaction indicated by arrows on the frame marked as 0 µs. Reaction then builds along these lines in the later frames.

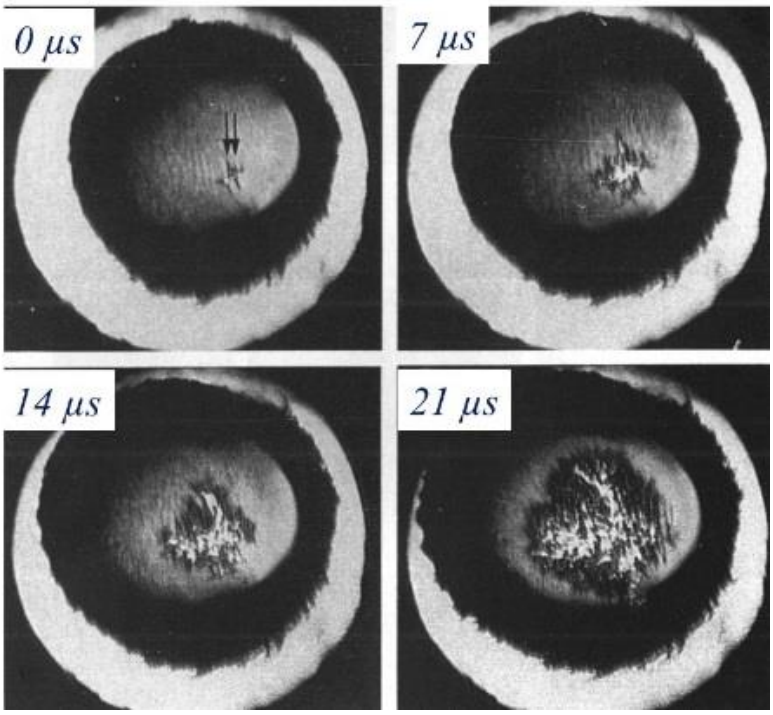


Figure 5-10 Impact on to a PETN sample (Courtesy of Imperial College London)

Figure 5-11 shows the results from using thermally sensitive film on the base of a sample of HMX that has been impacted. This was recovered after the impact and shows a series of lines indicating localized heating and evidence of shear band formation.

Figure 5-11 Shear bands seen on thermally sensitive paper recovered from a drop-weight impact on HMX sample (Courtesy of Imperial College London)

Figure 5-12 shows the initiation of a silver azide crystal under a shear load. Here, unlike in Figure 5-9(a), the crystal is loaded by the right hand side being pulled upwards and the other side being pulled downwards, without the crystal being allowed to rotate. Two fractures form in the crystal as indicated by the arrows in frame 3 and reaction builds up and spreads from those sheared surfaces.

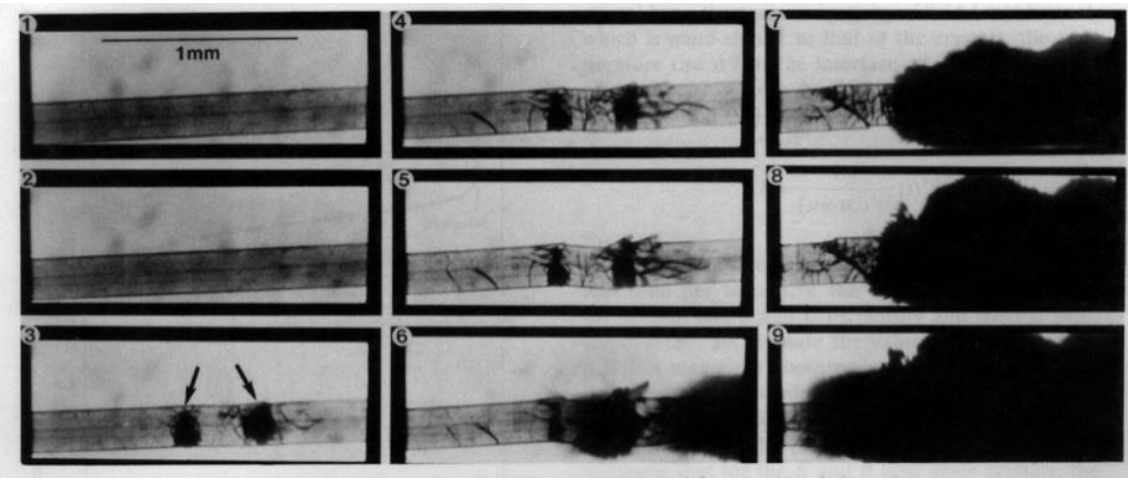


Figure 5-12 Silver Azide crystal showing initiation under shear loading (Courtesy of Imperial College London)

5.3.4 The Effect of Pressing Density

While five principal mechanisms of hot-spot formation have been identified the relative importance of these processes in a given sample is more difficult to quantify. The presence of additives, such as pressing agents, tends to reduce the effect of frictional heating, while PBXs with hard polymers tend to be susceptible to fracture.

One factor that clearly affects initiation mechanisms, particularly for powdered explosives and pyrotechnic compositions, is the pressing density. Figure 5-13 shows the level of light coming from samples of Ammonium Nitrate which have been struck by a high velocity copper plate. The level of light indicates the extent of reaction. As can be seen, the sample with 44% by volume of voids shows rapid build up to reaction. Those with 24, 17 and 11% void show much less light output. The extent of reaction drops with pressing density.

This result can be explained by considering the mechanisms. There are fewer pores in the sample at higher density and so pore collapse is reduced. Similarly, as the packing density is higher it is more difficult for crystal to move relative to one another, so friction is reduced. Pressing will also tend to break the crystals into smaller pieces so most crystals will have already have fractured slowly, so not allowing heating to be significant. Impact on these pre-fractured crystals does not allow for new surface to rub and shear against one another. Overall the incidence of heterogeneities favourable to hot-spot formation is reduced. This reduction in sensitivity is called ‘dead-pressing’.

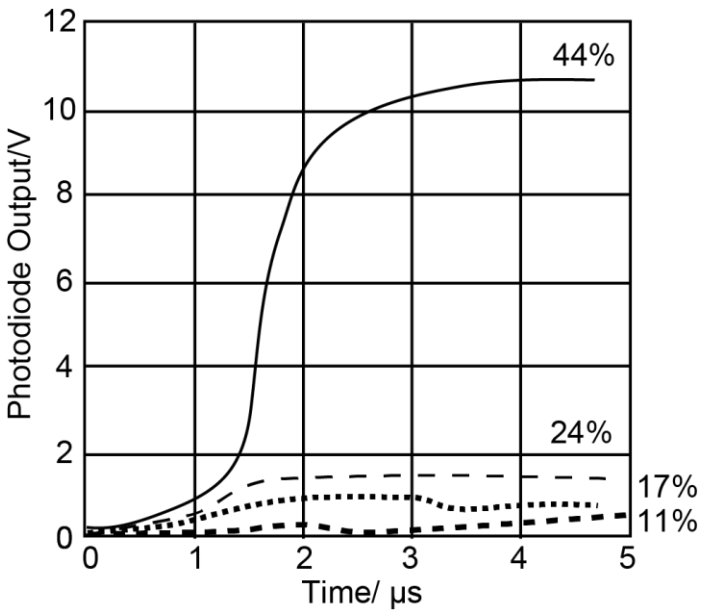


Figure 5-13 The effect of density on reaction breakout. The output of light from an impact on ammonium nitrate is shown. The lines correspond to the % volume of voids and pores in the sample

5.3.5 Bubble Collapse and Visco-Plastic Work

One of the most studied of the hot-spot mechanisms is that of bubble collapse[5-8]. This is understandable as it is easier to image voids in liquids compared to solids. The image in Figure 5-14 shows frames from a sequence showing the effect of a shock wave going across a single 3 mm void in a sheet of gelatin. It can be seen that the collapse is asymmetric with one side being forced across the bubble to strike the far side. There are a number of thermal processes occurring here. Firstly, there is the compression of gas in the void. This gives a flash of intense light as the temperature of the gas can reach several thousand degrees centigrade. While this sounds impressive, it must be remembered that the amount of gas in the cavity is limited and the total energy this represents can be quite small. A second mechanism is the local visco-plastic work going into the liquid around the cavity as it collapses. This can be significant and cause local heating. In this case the liquid becomes less viscous as it heats and so this may concentrate energy up to the point where the liquid becomes relatively inviscid. Finally, there is the energy of the impact of one side of the bubble against the other. This can be substantial, and lead to intense localized heating.

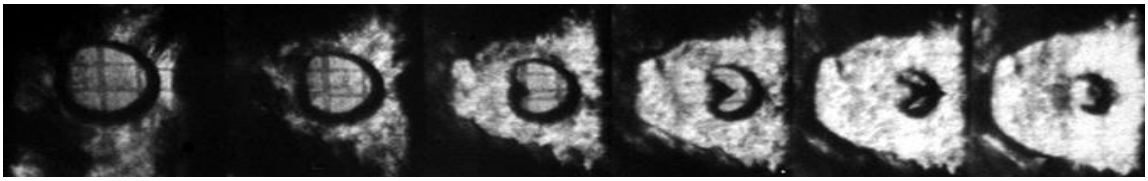


Figure 5-14 The collapse of a cavity in gelatine under shock wave loading (Courtesy of Imperial College London)

After the impact there will be turbulent mixing of the liquid and gas, thus stimulating further reaction. Overall, the combination of these three phenomena produces opportunity for a critical hot-spot to form.

5.3.6 Electrostatic Discharge

Electrostatic discharge can be an issue in dealing with some explosives and is widely recognized as an issue for pyrotechnics. This is an issue in some industries where static discharge in the presence of materials such as flour, dispersed in the air, can produce a fuel-air explosion (link to 9.4.1).

A non-conductive object can be charged by rubbing through a process known as triboelectrification. Typical examples of this occurring involve the removal of covers or packaging and manufacturing processes involving the relative movement of liquids and solids including particulates. The rate of charge generation will usually increase as the speed of the process increases. Corona discharge through the air provides the only charge limiting factor in continuous processes where no ground leakage paths exist. This allows very high potentials to be generated in processes such as the movement of a helicopter rotor through snowy air. The capacitance of an electrically isolated conductive object is typically dependent on factors such as its geometrical relationship to ground and its size. Overall, electrically isolated conductors are particularly

hazardous due to their ability to retain charge and release it all in a single incendive discharge.

From an electrostatic perspective the human body is regarded as a conductive object. The average human capacitance is around 150–500pF, which can charge to potentials of 5 to 25kV on an electrically isolated person. In the worst case, i.e., greatest energy, this means an isolated person could release a 156mJ spark. While this energy level is unlikely, a typical spark from an ungrounded person would be of the order of at least tens of millijoules. This quantity of energy could be generated from a simple action such as rising from a chair.

The incidence of electrostatic discharge increases during cold weather. This trend is difficult to quantify, but as the temperature falls so does the moisture the air can retain. This problem will be exaggerated within a warm room as the relative humidity will be lower for the same absolute humidity; essentially reducing the tendency of the air to produce a conductive film of moisture on clothing, casings, ground, etc. As a consequence, the resistivity of these surfaces will increase. This effect is exaggerated when dealing with the hydrophilic surfaces of natural materials, e.g., cotton and wood.

For materials such as lead azide[12] the semi-conductor characteristics of the material are cited as important in allowing current flow. The amount of energy absorbed by the material can be thought of as the simple current squared multiplied by resistance. PETN has been identified as a secondary material sensitive to spark initiation. This was shown to ignite at a voltage of 70 kV when the material was at 50% Theoretical Maximum Density (TMD).

For some materials like HMX the sensitiveness (link to 20.2.1) is dependent on grain size as shown in

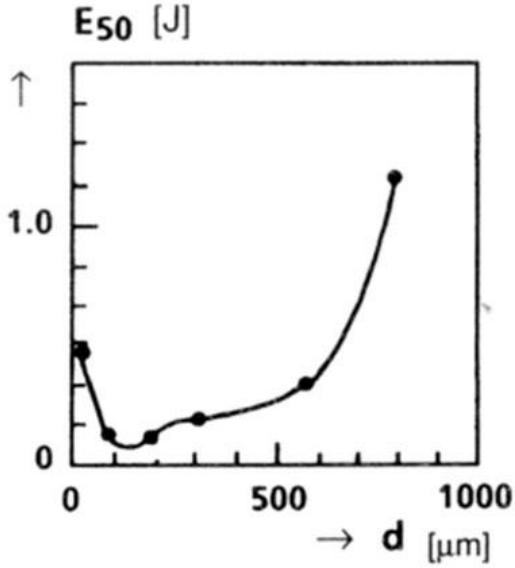


Figure 5-15. The sensitiveness increases as the grain size increases from 10 to 150 µm, remains fairly constant from 150 - 500 µm and finally rapidly decreases above 500 µm[13]. This variation is attributed to sharp grains with small contact

areas at the low grain sizes. At intermediate sizes the grains have truncated shapes and while the number of contact points is smaller they tend to be larger in area. At the higher grain size, the thermal conductivity of the system becomes important, tending to quench the hot-spots (link to 5.3) by thermal cooling[14].

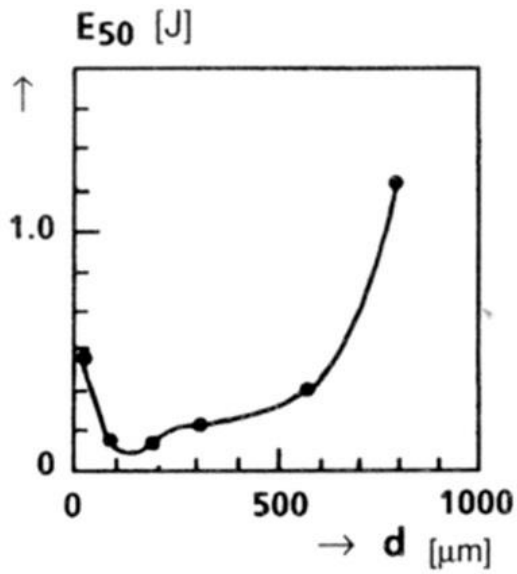


Figure 5-15 The sensitivity of HMX to electrostatic discharge with grain size

5.3.7 Hot-Spot Growth and Quenching

In Figure 5-16 the images of an impact of a flyer plate at 700 m s^{-1} on an 0.4mm thick bed of ammonium nitrate grains (150 – 210 µm) are shown causing hot-spots to be produced[15]. The exposure time of each image was 30 ns and the interframe time was zero. The increase and then decrease in light intensity from the hot-spots can clearly be seen in the sequence. Figure 5-17 shows the first two frames in detail where 2 areas are highlighted showing an area where hot-spots are growing an coalescing and another where the hot-spots are reducing and quenching. Other regions where the hot-spots are more widely spaced, towards the centre of the image, have died out. This appears to represent a distinction between critical and sub-critical hot-spots. Those hot-spots which are in proximity to one another link together possibly as a result of pressure pulses travelling between the hot-spots as a result of the production of product gases. Hot-spots which are more widely spaced tend to be quenched. In the third frame of Figure 5-16 the reaction front has spread to cover about 55% of the impact area. In the later frames the reaction moves away from the central zone where the ammonium nitrate has been consumed.

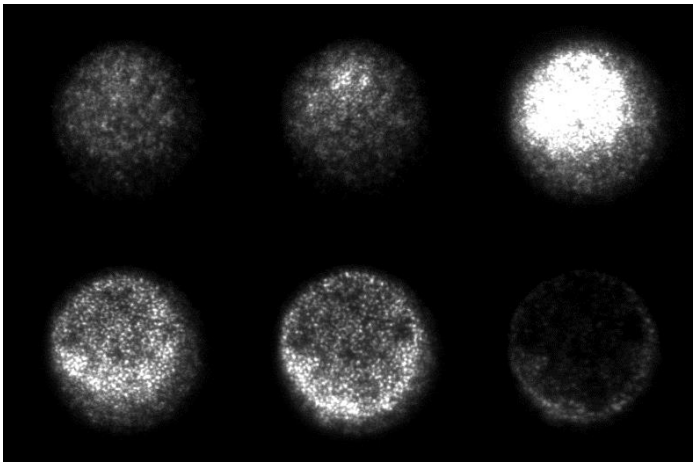


Figure 5-16 Hot-spot formation growth and quenching in ammonium nitrate struck by a flyer plate. Frames are in the order top left to top right, bottom top to bottom right. Diameter of the reaction zone viewed is approximately 8 mm (Courtesy of Imperial College London)

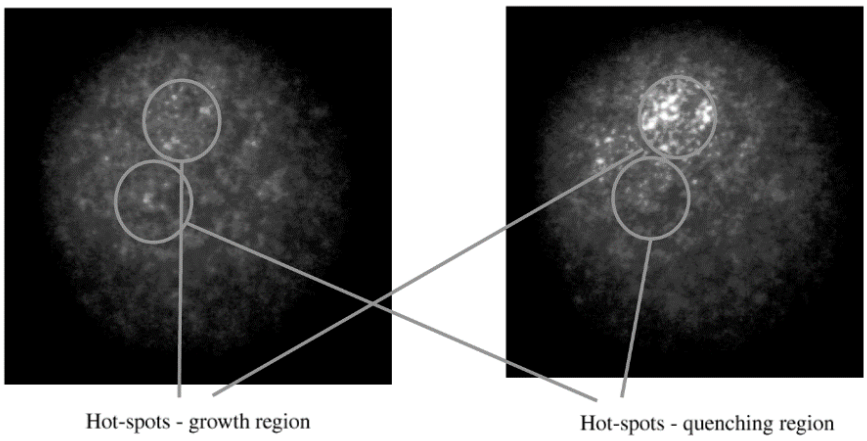


Figure 5-17 The first two frames of the sequence in Figure 5-16 (Courtesy of Imperial College London)

5.4 DEFLAGRATION TO DETONATION TRANSITION

One widely accepted mechanism for transition between deflagration and detonation (DDT) was described by McAfee et al[16-18]. Here, the critical hot spots lead to deflagration; this is associated with conductive burning at a rate of order 0.01 m s^{-1} though the energetic material. There is also a faster convective burning, caused by product gases forcing open channels either pre-existing in powder compacts or produced by impact. It has also been seen that slow cook-off can allow such channels to develop over timescales of hours. This convective burning happens at velocities of order 10 m s^{-1}. The pressure associated with the convection wave also caused the material immediately in front of it to become compacted, represented by the compaction waves shown

in Figure 5-18, this slows the rate of gas percolation, but allows pressure, temperature and pressure to increase rapidly. This confined burning presses against the surrounding material forming a dense plug of material that is pushed into unreacted material. This plug forms a considerable number of compressed hot-spots in the unreacted material which cause a rapid pressure build up and a shock to detonation transition (SDT). SDT is discussed in more depth in the next section. This transition has been studied experimentally[19].

The transit time between the deflagration and detonation depends on the density of the explosive, the degree of confinement and nature of explosive, so is highly variable and subject to the precise local conditions. The timescales for DDT is of milliseconds. A faster process which occurs for high-velocity impacts and stress is shock to detonation transition which occurs in microseconds. Shock to detonation also occurs when a detonating explosive is placed in contact with or in very close proximity to another explosive charge.

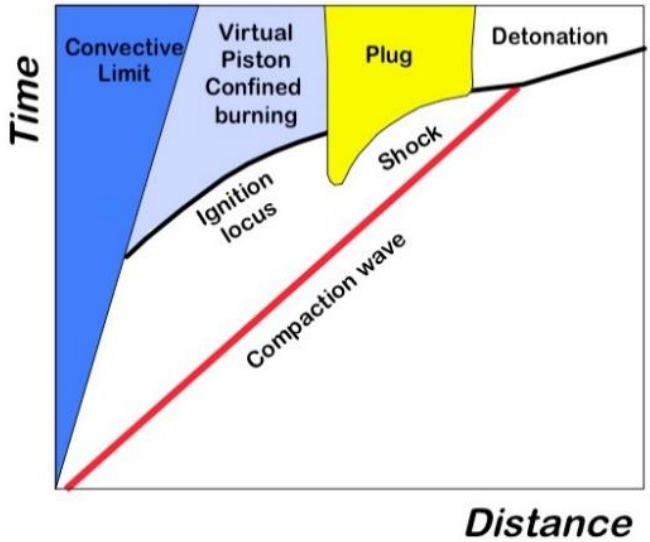
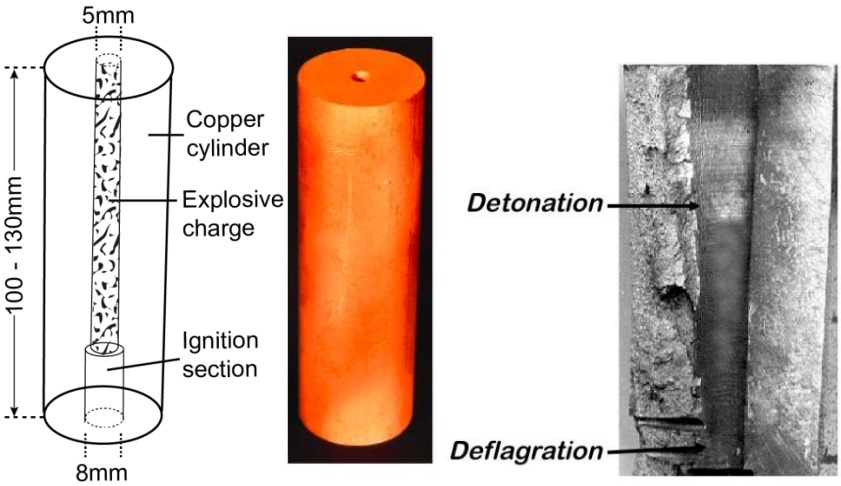


Figure 5-18 Schematic of overall process proposed by McAfee et al., along the centre line of a stick of explosive. Distance is the distance along the column from the ignition point

5.4.1 Deflagration to Detonation Studies

Amongst the simplest experiments are those, which heavily confine an explosive within a metal cylinder or square section bar in a 5mm diameter centrally drilled channel. The postmortem experiments use a cylinder of copper as shown in Figure 5-19(a). The result is seen in Figure 5-19(b) where physical evidence of the detonation can be seen.



(a) (b)

Figure 5-19 (a) Cylinder for use in post-mortem type experiments (b) visual evidence of the location where detonation begins (Courtesy of Imperial College London)

With the square steel bar a 1 mm wide polycarbonate window is laid along the length of the bar, which allows the event to be photographed with a streak camera. The window is thin enough that the level of confinement afforded by the steel is not overly compromised. This arrangement is shown in Figure 5-20.

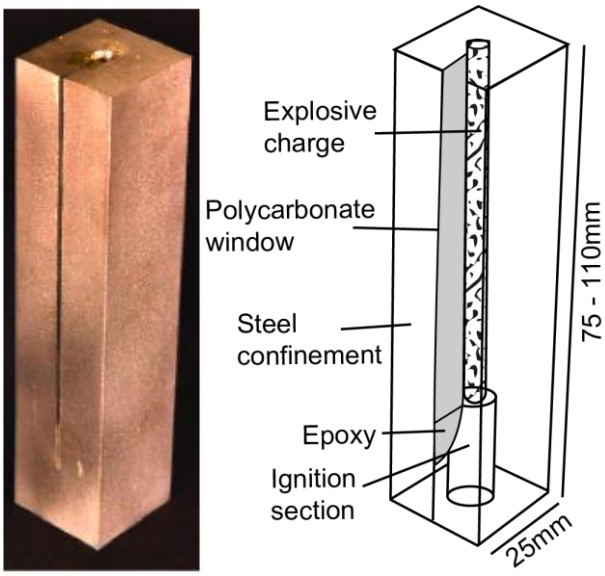


Figure 5-20 Square section bar showing the 1mm wide polycarbonate window (Courtesy of Imperial College London)

The type of data recorded from these experiments[20-22] is shown in Figure 5-21. The streak camera image shows convective burning B, the step from

deflagration to detonation D and the movement of the waves including a detonation wave F.

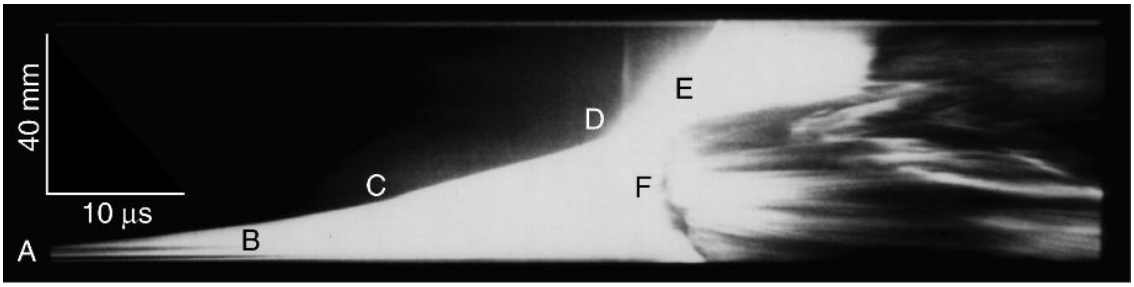


Figure 5-21 DDT event in ultrafine PETN[20] (Courtesy of Imperial College London)

5.5 SHOCK TO DETONATION TRANSITION

Shock to detonation transition (SDT) occurs in high-stress, shock wave environments. The process is effectively a thermal heating process. Shock waves are associated with rapid compression, high pressures and temperature rise. After a shock wave has passed over the material due to, for example, an impact or shock from another detonating explosive, the region around the impact zone is subjected to a temperature rise which allows reaction to start via the shock heating. Again this can be considered as the formation of a considerable number of hot-spots which each send out pressure waves which can coalesce to produce a large pressure pulse. Effectively, thermal explosion occurs after an induction time depending on local conditions. When the detonation wave breaks out it runs through material already compressed and heated by the initial shock thus causing super-detonation, detonation at a higher velocity than that normally associated with the material. Eventually the reactive shock overtakes the original shock to produce overdriven detonation in the lower density material. Ultimately, this settles to the 'normal' detonation velocity over some relaxation time and distance. This is shown in Figure 5-22.

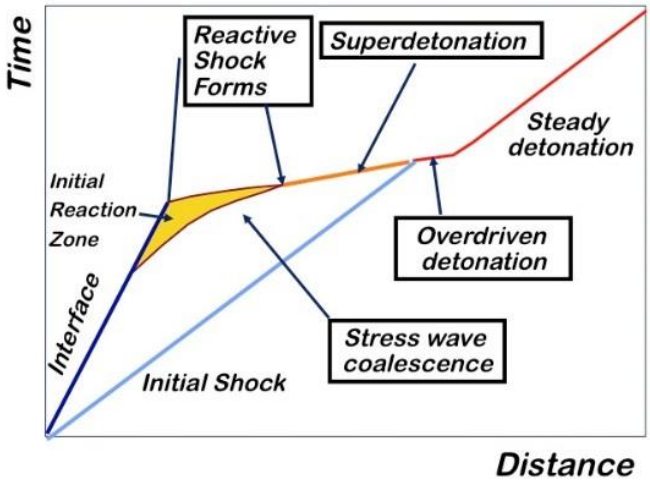


Figure 5-22 The process of Shock to Detonation Transition (SDT)

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