Chapter: 01

Explosives – General

1.1 Introduction

Over the last twenty years or so the term “Energetic Materials” has gradually replaced the traditional expression of “powder, explosives and solid propellants for civil and military use”. This change in terminology did not come about by chance, but instead reflects the increasingly important role of “materials” in the design and use of solid propellants for rocket motors and of explosives for military warhead. After the incident of 9/11, the word explosive has got a dramatic role in the life of a common citizen. Everyone in the world is trying to get familiar with explosives and their behavior. It is of dire need to know the basics of this volatile material along with advance studies on the physical behavior, structural changes and kinetic parameters of most high explosives. An extensive research has been carried out worldwide in the past extending from bulk synthesis, to engineering and materials science, to the microscopic study of molecular dynamics and structure (i.e., molecular level understanding of these systems) and much more is expected in the near future. So in the most common terms, an explosive is defined as a substance, which when suitably initiated either by friction, impact, shock, spark, flame, heating, or by simple application of an energy pulse, undergoes a sudden/ rapid chemical reaction thereby producing a very large amount of heat with exertion of high pressure on surrounding medium. Energetic materials consist in general a broad group of compounds and compositions pertaining to explosives, propellants and pyrotechnics [1]. Explosives commonly require some stimulus like a blow or a spark to provoke them in order to liberate their energy for the change which produces the explosion, but the stimulus which "sets off" the explosive does not contribute to the energy of the explosion. The various stimuli to which explosives respond and the manners of their responses in producing explosions provide a convenient basis for the classification of these interesting materials [2].

1.2 Explosive Constituents

The majority of the substances which are classed as chemical explosives generally contain Oxygen, Nitrogen and oxidizing elements (fuels) such as Carbon and Hydrogen. The oxygen is generally attached to nitrogen, as in the groups NO and NO_2. The exceptions to this rule are Azides, such as Lead Azide (PbN) and nitrogen compound such as Nitrogen Tri-iodide and Azoimide (NH, NI), which contain no oxygen. In the event of a chemical reaction, the nitrogen and oxygen molecules separate and then unite with fuel components as shown in equation 1.1.

$$2C_7H_5N_3O_6 \longrightarrow 7CO + 5H_2O + 7C + 3N_2\uparrow$$

Equation: 1.1 Decomposition of Trinitrotoluene (TNT)

During the reaction large amount of heat and energy are liberated, generally accompanied by high pressure. The heat given out during the reaction is the difference between the heat required to break up the explosive molecule into its constituent elements and the heat released on recombination of these elements to form CO_2, H_2O, N_2, etc. [3].

1.3 **High Explosives**

High explosives are substances which are safe to handle, their shelf life is long and their density is high. Similarly propagation of the explosion for high explosives is very rapid [4]. High Explosives are the most powerful energetic materials exploding at a supersonic rate of decomposition. Their velocity of explosion ranges from 3,000 to 9,000 meters per second also called as detonation velocity or velocity of detonation (D). High explosives are generally employed in military warheads, mining, demolition, and various other military applications. These detonate under the influence of the shock of a suitable primary explosive. High Explosives being more powerful and brisant, sensitive to fire and shock with extremely high rate of decomposition can be identified for their specific physical characteristics and chemical properties and not by merely seeing a substance with combustion characteristics. A substance may be extremely reactive chemically but perfectly stable in the absence of anything with which it may react. Similarly A substance may explode readily by a slight shock, but it may be stable if left to itself. Another may require shock of a powerful detonator for explosion and may be subject to spontaneous decomposition. Energetic materials overlap somewhat into mainly three classes based on the behavior of a number of them to nature of stimuli to which they are subjected and by the manner in which they are used. A high explosive differ from low explosive in that it must , in general, be initiated by the shock of a blasting cap (shall be discussed separately). When low explosive begin its combustion, the burning travels from particle to particle because of the granular form of the explosive. This results in the deflagration of the material. High Explosive detonates, which has been described as instantaneous combustion. When a blasting cap is detonated in a high explosive, it delivers an extremely sharp shock to the explosive. This shock breaks the bond of the molecules of the chemically bonded explosive material and oxidizers. The disruption of the molecules is transmitted as a shock wave radiating outward in all directions from the point of initiation. This internal shock wave is known as a detonation wave, and it causes each molecule to rupture. This molecular rupture increases wave speed making it reach its maximum speed in a short span of time. Regulations concerning the manufacture and use of explosives appear complicated, but their necessity is obvious. Experience and goodwill are however always essential to ensure the smooth running of the system and thus public safe.

1.4 **Types of Explosions**

Explosion is a sudden and rapid release of gases from a confined space followed by high temperatures, pressure, violent shock and bang. For an explosion phenomenon rapid release of gases is the primary condition. Three basic forms of explosions are:

- Mechanical Explosion
- Chemical Explosion
- Atomic Explosion

1.4.1 **Chemical Explosion**

An extremely violent conversion of a solid or liquid explosive compound into gaseous form with a much greater volume than the reactants from which they were produced. Generally an explosive slab generates about 10,000 to 15,000 times greater volume than the original volume of the explosive on detonation. These gases expand very rapidly, achieving different velocities of detonation ranging around 8 km (5 miles) per second. Similarly 3000^{o}C to 4000^{o}C of temperature is generated during detonation of a solid which generates large amount of heat and gas. Detonation takes place in microseconds with a loud noise and shock. Chemical explosives are also used extensively in nuclear devices such as missiles.

1.5 **Deflagration (Rapid Combustion)**

A subsonic or merely a rapid form of combustion propagating through thermal conductivity is called as deflagration or simply a slow form of deflagration. The most popular form of deflagration is ordinary fire. Other forms are flames combustion and explosion which are technical forms of deflagration. Internal combustion engine (ICE) of an automobile is also a form of deflagration or rapid combustion where combustible fuel is mixed with adequate amount of air. On compression, spark plug ignites the mixture of fuel and air. Ignition temperature is reached which results in a rapid combustion or deflagration. Mainly a combustion, deflagration and detonation are differentiated on the basis of the speed of the burning action. In engineering term a deflagration is controllable combustion process but detonation is not.

1.6 **Detonation (Instantaneous Combustion)**

Detonation is a supersonic shock wave with a rapid chemical reaction occurring just behind the shock front. The propagation wave velocity is greater than the speed of the sound of unreacted explosives in which it is travelling exothermically [5]. All types of military based explosive whether in solid, liquid or reactive gaseous form undergo detonation process [6]. Solid and liquid explosives have greater velocity of detonations than gaseous explosives having clearer resolution for the wave system to develop. Detonation is also a form of instantaneous combustion because during detonation there is a time interval required for the simultaneous and complete combustion of explosive particles. Velocity of this "instantaneous combustion" is called as velocity of detonation designated as "D". Experimental values of D for various high explosives have been calculated using VOD meter and observed to ranging from approximately 2,743 m/s (9,000 ft/s) to over 8,382 m/s (27,500 ft/s). The highest possible velocity of an explosive will always result into a complete detonation with a high order detonation whereas a low order detonation is either incomplete detonation or complete detonation at lower than maximum velocity. Following factor or combination of factors are considered as the main cause for the possible low order detonation:

- Initiator (blasting cap) of inadequate power
- Corrosion or deterioration of the explosive charge
- Bad contact between blasting cap (initiator) and the explosive charge
- Porosity or exudation in the explosive charge
- Formation of cavities and discontinuity in explosive
- Cracking and base separation of the explosive

1.7 **Effects of an Explosion**

Effect of an explosion of a military high explosive depends largely on the type of explosive compound, its filling capacity and on the energetic binders (if used) which contribute to the conversion reaction. The effect of an explosion is also directly linked to the energy and density. As we know that velocity of detonation and detonation pressure increases with increasing the initial density of the explosive charge and vice versa. The main parameters that are used to determine the effect of an explosion are detonation velocity, detonation pressure and the resulting capability to accelerate metals. As a general rule we can see that petroleum fuels usually have high potential energy as compared to the explosives but the later releases high rate of energy which produces greater volume of blast pressure. For example Trinitrotoluene (TNT) has a detonation velocity of 6940 meters per second compared to 1680 meters per second for the detonation of a pentane-air mixture, and the 0.34 meter per second stoichiometric flame speed of gasoline combustion in air. During explosion or detonation of an explosive charge, extremely violent heat is generated along with formation of gaseous products thereby converting solid explosive charge into much more stable components. This process that occur in about 0.001 second, will produce three primary effects and several other associated secondary damaging effects on the surrounding medium [7]. The three primary effects produced are blast pressure, fragmentation, incendiary and thermal effect.

1.7.1 **Blast Pressure Effect**

This effect is directly related to the pressure build up on detonation of explosive where heat is liberated and the hot gases are travelling at enormous speed. The whole process takes place in micro seconds. According to the latest study on detonation it is assumed that the process occurs in approximately 1/10,000 second (100 µs). Simultaneously the expanding gases exert pressures of about 635 metric ton (700 tons) per square inch on the surrounding medium. The pressure build up will compress the atmospheric air and cause the expanding gases to move away from the detonation point at velocities of up to 11,265 km (7,000 mph). Hot expanding gases (weighing tons) move away in a circular form like a shock wave and produce devastating result on the surrounding objects. Pressure wave loses its power while its move away detonation site and ultimately die down. Such a pressure wave is defined as blast pressure wave. Two distinct phases (positive pressure phase and negative phase) are developed by the blast pressure wave which will exert different types of pressures on the medium. Although negative phase is less powerful than positive pressure phase but lasts for more than three times of the positive pressure phase. In general, the blast pressure effect is considered to be the most powerful and damaging effect of all the other known effects produced by detonation of explosive charge.

1.7.2 **Secondary Blast Pressure Effects (Reflection, Focusing, and Shielding of the Pressure Wave)**

Just like other reflecting objects (light waves or sound waves) a blast pressure waves will bounce off reflective surfaces causing a scattering or focusing effect of the pressure wave. In open air detonation process, a blast pressure wave will dissipate in the open air and will lose its power and velocity much faster than in confined place. Since reflection of the blast wave off the medium surfaces reinforce the actual waves by overlapping it and is a pressure wave, hence it exerts physical pressure on the medium surface. A blast pressure wave may also be concentrated on a medium surface while acting as a parabolic reflector. The same phenomenon can be seen in sound waves which are focused and directed towards a target point. Shielding (self-explanatory) occurs when the blast pressure wave strikes against a static object. During close window detonation, various new and off course strange effects have been observed due to shielding or reflection. One such unusual effect happens where complete wall is damaged or blown out but hanging mirror on the opposite side of that wall is still intact to the wall surface.

1.7.3 **Fragmentation Effect**

Terrorist favored technique where fragmentation effects are desirable using conventional explosive bomb or casing. In this technique various kind of nails, ball bearings or fence staples are mixed inside the explosive filled casing or bomb or may be placed on the outer surface to achieve shrapnel effects. An internal design of explosive filled jacket with ball bearing nails and other metal parts with desirable fragmentation effects are shown in the Figure 1.1.

Figure: 1.1 Picture showing explosive filled suicide jacket.

If an explosive is filled in a metal tube and is closed from both ends by placing a detonating device at one end. On initiation of the casing, it will be observed that not only a blast pressure wave but also shrapnel like fragments of the casing or bomb do indeed travel at supersonic speed taking part in creating optimum damage to the targeted object. Each fragment of the casing is expected to travel at a measured velocity of 822.96 m/s (2,700 ft/s) which is approximately equal to the speed of a conventional military rifle bullet and reach a few feet from the point of initiation of the bomb or explosive filled casing. Each shrapnel like fragment will be directed to travel in a straight line from the point of initiation until their flight is obstructed either by reduction in velocity or striking the target object. Further these fragments will either ricochet or become fixed. It must be noted that on detonation of the explosive charge inside the casing or bomb, hot expanding gases produced will act on the casing material making it widen in size to about one and one-half times its original size depending upon material strength before it breaks into various shrapnel like fragments. Also it is assumed that nearly half of the energy released by the detonation of the high explosive filled bomb or casing is utilized in breaking the material of the casing and shattering the fragments to some distance apart whereas rest of the energy is used in propelling the shrapnel like fragments. Consequently, the use of shrapnel like fragments inside the explosive filled casing or bomb produces optimum damage on the target by rupturing, puncturing, or creating holes inside the target material. After the blast or detonation of the high explosive filled casing or bomb, each shrapnel like fragment will have a pointed, stretched and narrow configuration due to extremely high heat and pressure build up on the place of detonation. In case the same bomb or casing is filled with a low powered explosive (Black powder etc) and detonated, larger sized material fragments are produced which broad peak, blunt and thick in configuration. Each fragment of the casing material or enclosed bomb serves the same objective and achieves the desired effects on the target object like normal fragmentation.

1.8 **Composition and Behavior of Chemical Explosives**

Explosives are the chemical compound which when suitably initiated decomposes rapidly forming new stable substances with the liberation of enormous heat and energy and build up pressure rise in the surrounding medium. Detonation or explosion of an explosive is a self-propagating process that develops automatically within the explosive molecules converting few of the energy into shock waves and loud noise. Generally population could be more vulnerable to the high risk of subtle health effects once exposed to high explosives than injury by detonation [8]. A chemical explosive therefore needs to contain enough oxygen for thermal decomposition and fast combustion process. For oxygen deficient explosive materials additional substance is added to provide enough oxygen for the maintenance of the thermal decomposition or detonation process and this added substance is called as Oxidizer. The oxidizer supply oxygen by decomposing under heat. Nitrates, Chlorates, Perchlorates, Permanganates, transition metal Oxides, Peroxides and other unstable high oxygen content molecules, all can be used for military high explosives [9].

1.9 Explosive Mixtures

Since oxidizer are mixed in high explosives through melt casting, pressing or other filling techniques, the deflagrating substances are blended with oxidizer mechanically and the resultant mixture is known as Explosive mixture[10]. For all the propellants or low explosive manufacture (specially used in rifles cartridge case or pistol rounds filling), mechanical blending techniques are adopted. In general propellants or low explosives are combustible materials that burn rapidly to produce gases in order to perform mechanical work, such as rocket propulsion. If normal blending of the mixture is not possible for oxidizer and low explosives, water is added to form a paste with fine particles. This is done to avoid any rupture or breakage of the solid explosive mixture when dry during storage, transportation or even during fire.

1.10 Explosive Compounds

High explosive compounds are blended chemically so that fuel (combustible material) and oxidizer are tightly bonded. On the other hand mechanical blending does not suffice the requirement and is unreliable for high explosives. For the formation of nitroglycerin, glycerin is chemically blended into nitric acid where it is poured slowly for uniform mixing and thorough chemical blending to achieve strong elemental bonding.

1.11 Applications of Explosives

It is the difference in velocities of explosives that differentiate between low explosive material and high explosive compound. High explosive produces shattering effect on the target object being highly powerful whereas low explosive on the other hand simply produces pushing or heaving effect due to lower rate of expanding gases. It is therefore quite important for the designer to select an explosive based on the effects desired. Both commercial and military high explosives differ greatly from one another and are therefore applied accordingly. Another most widely used application of the military high explosive (including Composition B) is the shaped charge, where shrapnel and directed effects are desirable on the target material [11].

REFERENCES

[1] Organic chemistry of explosives by Agrawal Jai Prakash., R. D. Hodgson. John Wiley and Sons, 2007.

[2] The Chemistry of Powder and Explosives, Volume-II, 1943, By TENNEY L. DAVIS, Ph.D Emeritus Professor of Organic Chemistry Massachusetts Institute of Technology Director of Research and Development National Fireworks, Inc.

[3] The Chemistry of Explosives by Akhavan, J. 2^{nd} edition (2004).

[4] Military High Explosives by Jörg Mathieu* and Hans Stucki. ,Chimia 58 (2004) 383.389 © Schweizerische Chemische Gesellschaft ISSN 0009.4293.

[5] Explosives Engineering by Cooper, Paul W., Wily-VCH (1996) ISBN 0-471-18636-8.

[6] Fickett and Davis, 'Detonation', Univ. California Press, (1979).

[7] www.securitdriver.com–articles-explosive, Forces of Improvised Explosive Devices. Cited on 19-03-2011.

[8] Dissolution rates of three high explosive compounds TNT, RDX, and HMX., Chemosphere, Volume 47, Issue 7, May 2002, Pages 725-734 by Jason C. Lynch, James M. Brannon, Joseph J. Delfino.,

[9] Principles of Explosive Behavior. Army Materiel Command Pamphlet 706-180, April 1972.

[10] www.ejercitobolivia.mforos.com/JEOGRAFIA NAUTICA de BOLAVIA-1879.

[11] Explosives by Kohler, J., Meyer, R. VCH - Verlages., Weinheim., FRG, 1993.

Chapter: **02**

Properties Of High Explosives For Military Applications

2.1 General Description

Numerous compounds are explosives, however the number of compounds that can be used militarily is relatively small. Some are used for commercial applications while other high performance high explosives are used extensively for military purposes. High explosives are kept in storage condition for different lifespan depending upon the degradation and performance of high explosives. Particular tests are conducted before hand to identify various properties of the high explosives for optimum characterization. These preliminary tests are necessary before filling to avoid any problems during storage, transportation or even in the field fire area. For universal standards on military high explosive formulation, data from conducted tests are compared to the standard explosive. The relative rank is then used to determine possible applications. Modern military warfare demands current military munitions must function accurately and reliably and produce desired effects on the target. Furthermore an explosive charge must be safe in storage, handling, transportation and use [1].

2.2 Physical Properties of High Explosives

Military high explosives are intended to qualify few of the under mentioned physical properties for their optimum utilization.

2.2.1 Availability and Cost

Military high explosives need to be cheap, easy in synthesis, and their raw material should be abundantly available. In addition, manufacturing process of all military explosives particularly low explosives (being more sensitive to the action of shock, friction and spark) must be reasonably simple and safe [2].

2.2.2 Sensitivity

One of the most predominant factors in determining a military high explosive is their relative sensitivity to various actions on their exposure. Primary explosives are highly sensitive to heat, shock and readily initiate on exposure to mechanical or electrical friction, heat, or spark.

On the other hand, high explosives need explosive train to be completed for their detonation. The term sensitivity covers many aspects like impact, friction or heat.

2.2.3 **Brisance and Power**

The brisance and power of an explosive determine its applicability for specific purposes. For example a bursting charge must be more brisant and comparatively less powerful but a ditching charge needs to be more powerful and less brisant.

2.2.4 **Stability**

Military explosives must be able to withstand long periods of storage under unfavorable conditions. Storage conditions ranges from extreme heat and humidity in the tropics to the cold of arctic regions. Normal encountered environmental temperature range varies between - 40 to +70°C. Since explosive material tends to decompose rapidly at high temperature, therefore all standard military explosives may be considered to have a high degree of stability at temperature extremes [3]. An explosive compound containing nitrogen groups will rapidly decompose if exposed to the ultraviolet sun rays, hence its stability can be adversely affected. Similarly a number of explosive materials are highly sensitive to electric spark or flash which can make them unstable. Static or other electrical discharge may be sufficient to inspire detonation under some circumstances. Therefore electrical grounding of the operator is an important element of safety while working in electrical environment.

2.2.5 **Density**

Density is an important consideration when choosing an explosive. Explosive charge with a maximum energy density for higher performance is considered to be most suitable. In general, the greater the density of the explosive, the greater is the energy available and so greater will be the detonation velocity of the charge [4]. However same is not true in case of some of the metallo-organic primary explosives where density is increased by the presence of mercury or lead but energy of the explosives remains the same. Density of a particular explosive compound can be expressed in terms of specific gravity. Specific gravity is the ratio of density of explosive charge to the density of water at STP (Standard Temperature and Pressure). Commercial explosives have specific gravity ranging from 0.6 to 1.7 grams per cubic centimeter. For hard rock blasting or mining purposes where fine fragmentation or deep borehole is required, high density explosive charge is usually employed as shown in figure

2.1. But in case of sandy rock or easily fragmented area where fine fragmentation is not intended, an explosive charge with low density will suffice the requirement. Explosive density is also extremely important when working in damp and wet environmental condition as lower density charge with a specific gravity of less than 1.0 will not sink in water.

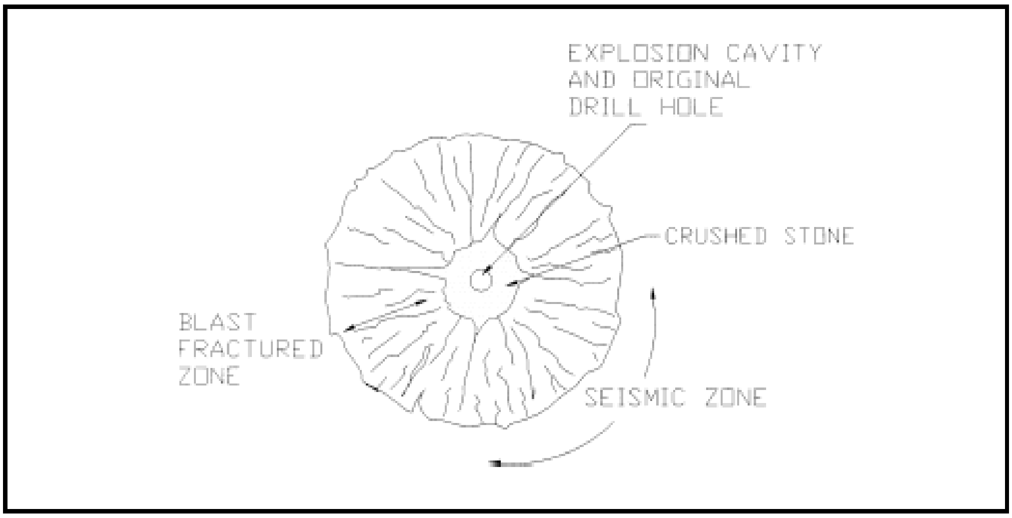

Figure: 2.1 Mechanics of Rock blasting.

2.2.6 **Hygroscopicity**

Most of the explosive charge when in humid environment suffers from corrosion, deterioration or degradation which ultimately reduces its sensitivity, strength and detonation velocity. The introduction of moisture into an explosive charge is therefore highly undesirable. Hygroscopicity determines explosive tendency for the moisture absorption. Moisture not only affects explosives adversely by acting as an inert material that absorbs heat when vaporized but also causes initiation of a chemical reaction within the explosive material. Reduction in sensitivity, strength, and velocity of detonation causes discontinuity of the explosive mass. Exudation is a most common example of moisture ingress where explosive ingredients creep out of the munitions joints or screw threads and ultimately results into fire, toxic or possible explosion hazard. Stability of the charge is also affected by the presence of moisture contents as it accelerates decomposition of the explosive. For all of these reasons, hygroscopicity must be kept to a bare minimum in military explosives [5].

2.2.7 **Volatility**

Volatility is the property of an explosive material which shows readiness with which a substance vaporizes. Increasing the volatility of an explosive charge will cause rapid increase in the pressure buildup and ultimate separation of ingredients in composite explosive. Since safety concern demands reduction in volatility of the explosive compound, therefore a military high explosive must be least volatile and more energetic.

2.2.8 **Reactivity**

Explosive reactivity with munitions casing is highly undesirable from safety and performance point of view. A military explosive must therefore be non-reactive to foreign material. One of the reasons is that reaction so produced will accelerate the rate of decomposition in the presence of moisture and hence liberation of gaseous products, loss of power and loss of sensitivity will result. When the explosive is to be loaded in contact with or mixed with another explosive or binder, reactivity between ingredients must be minimized.

2.2.9 **Toxicity**

Many high explosives such as MNT (Mononitrotoluene) are highly toxic in nature due to their chemical structure. Since the effect of toxicity may vary from a mild headache to serious damage of internal organs. Nitro compounds are particularly poisonous. Similarly Nitrobenzene, known as "oil of mirbane," may be absorbed through skin or its vapors may be inhaled through breathing. Even careless wearing of clothing containing nitrobenzene contents has also been reported to cause death. Any explosive of high toxicity is therefore unacceptable for use in military service as human life is directly exposed to its contents during filling, storage, transportation and firing [6].

2.2.10 **Environmental Impact**

Explosive materials are mostly undesirable substance from environment point of view as it contaminates surrounding area where manufacturing, filling, formulation or even demolition takes place. Extensive use of the explosives in military warfare (both conventional and unconventional) is also responsible for the global warming issue. Advances in the field of energetic materials demand that rapid measures must be taken to eliminate the chances of explosive contamination of the environment.

2.2.11 **Demilitarization**

A military explosive should have favorable demilitarisation characteristics. It is considered to be appropriate, if it is easily recovered from military munitions for re-utilization. In this way all hazardous environmental effects can be minimize. Similarly bulk storage of the military high explosive can be avoided. A modern military explosive, such as PBX (plastic bonded explosive) is an excellent example of such explosives, where thermally sensitive binder is used. During recovery process, PBX is heated to a safety temperature wherein binder decomposes and explosive material may be completely recovered for reloading and re-utilization [7].

2.3 **Other Properties Of Explosive**

In order to achieve explosive charge with an optimum performance, many predictions can be made in blast design and formulation besides above mentioned physical properties. Other desired properties include density, detonation and borehole pressure, water resistance, and fume class. Different explosive substances have different properties due to varying condition and methods of manufacture, filling and formulation [8].

2.3.1 **Detonation and Borehole Pressure**

Detonation pressure increases with increase in density of explosive charge and vice versa. Similarly detonation pressure is directly proportional to the detonation velocity. The detonation pressure is more dependent on detonation velocity than specific gravity. Detonation pressures of high explosives range from 10 to more than 140 Kilo bars (l Kilo bar is equal to 14,504 psi). An explosive with high density should not cause any borehole rupture or deterioration.

2.3.2 **Water Resistance**

Modern warfare demands military high explosives to be water resistant and should not deteriorate or lose their sensitivity on exposure to water or even moisture contents. Sensitivity is a measure of explosive detonation on the action of spark, friction or heat etc. In case explosive is handled in dry condition, water resistance is of no significance. In the event of firing where quick firing is imminent and borehole is wet, an explosive with water resistance characteristics is considered to be most appropriate to use. Meanwhile if the firing period extends and water is expected to penetrate through the borehole, “very good” to excellent” water resistant explosive is required. Higher density explosives have linear range of fair to excellent water resistance. On the other side low densities explosives possess little or no water resistance characteristics. A blast showing brown nitrogen oxide fumes means that particular explosive has deteriorated from exposure to water while in storage or during firing.

2.3.3 **Fume Class**

Commercial explosive once detonated produces CO_2, N_2 gas along with water vapors. Also few other undesirable poisonous gases such as CO and nitrogen oxides are formed during the process. These bi-product gases are known as fumes. Each explosive substance has a different fume class as compared to others based on the nature and quantity of the undesirable gases produced during detonation. For explosives compound producing smaller amount of undesirable and unfavorable fumes are rated in a better class and vice versa. Although fume class gets a lower consideration as compared to other properties of high explosives, but once in confined space better fume class is important. Environmental safety measures demand high explosives with greater fume class when detonated, since CO gradually destroys the brain and central nervous system and nitrogen oxides immediately form nitric acid in the lungs [9].

2.4 **Types of explosives**

Explosives comes in a vast variety ranging from low to high explosives based on their difference in explosive power, brisance, heat and sensitivity, gaseous product and many more. Generally two major classes of service explosives are commercial and military purpose explosives. Commercial explosives are designed to be less powerful than military high explosives but they contain blasting and combustible materials such as ammonium dynamite, gelatin dynamite, NG based dynamite, ANFO, dry blasting agents binary explosives etc. In contrast, military high explosives are specifically designed to give tactical and/or strategic results on detonation with rapid decomposition, violent liberation of gaseous product, enormous heat and shock and high pressure. They are used to create devastating effects like brisance, shattering or explosion on target material. In some cases, high explosives are formulated to give penetration effect such as shaped charge filling of an anti-tank (A/Tk) round.

2.4.1 **Commercial explosives**

Commercial explosives are manufactured world over in different methods although their basic formulation is the same. Few of the most common commercial explosives are:

2.4.1.1 **Blasting Caps**

Blasting caps are extensively used for blasting the main charge. Blasting caps are made from copper or silver material and are small cylindrical in shape. They are filled with small amount of sensitive but powerful explosive. Like all other explosives blasting caps should not be handled as slight mishandling can set it off [10]. Blasting caps are of two types i.e. mechanical and electrical. A mechanical or non-electric blasting cap is initiated by the help of safety fuze. Since black powder core the cap gets wet during storage or transportation, therefore two caps per blast at demolition site are used. On the other hand, electrical caps are initiated by the help of heat passing through electrical wire that extends out the end. Electrical wires are twisted or shunted so that cap is not set off by stray electrical current, which can be found even through static charge produced by human body (Figure 2.2). Other types of currents are called as EMR (Electromagnetic Radiation). For safety reasons all types of caps should be kept isolated during handling, storage and transportation.

Figure: 2.2 Electric Blasting Caps.

2.4.1.2 **Safety Fuze**

A safety fuze is used to gain a particular time delay after initiation of the explosive train. A safety fuze has black powder core covered by a solid waterproof jacket of black or orange colour. One of the ideal characteristics of the safety fuze is that it can burn in water but are not used in wet conditions (Figure 2.3).

Figure: 2.3 Burning Safety Fuze.

As in older safety fuze black powder core use to burn slowly but modern caps have shock tubes which detonate instead of burning and special type of initiator are used to produce shock instead of flame (Figure 2.4).

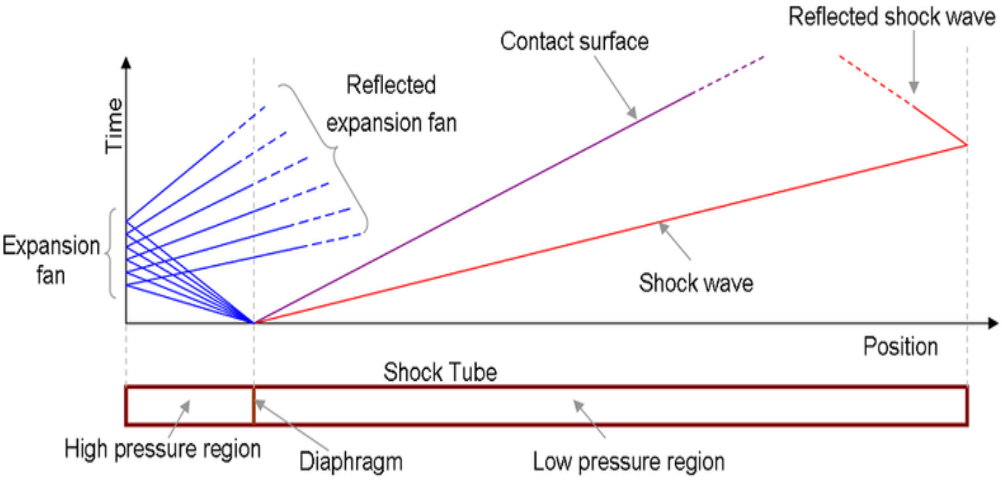

Figure 2.4 Different waves formed in a shock tube (With permission from the author) [11].

2.4.1.3 **Detonating Cord**

A detonating cord is quite similar to that of safety fuze in appearance. It has a white core of powerful explosive that detonates about four miles per second. For blasting of multiple charges simultaneously, a detonating cord is used (Figure 2.5).

Figure: 2.5 Reinforced detonation cord filled with Pentaerythritol Tetranitrate (PETN).

2.4.1.4 **Boosters**

Boosters are the materials used to increase the blasting power of a commercial explosive. Blasting caps are fitted inside the boosters to provide low power shock wave. Boosters come in a variety of sizes and colour but all types have hole at one end to take the blasting cap or detonating cord.

2.4.1.5 **Dynamite**

Dynamites are of two types i.e. Nitroglycerine and Ammonium dynamite. NG dynamite consist of nitroglycerine (nitro) mixed with sawdust or gray clay like filler. The nitro on setting at the bottom, emanate out of the stick and crystallizes. Such exudation causes the sticks to adhere to each other. On the hand separation of the sticks causes detonation. Old dynamite is extremely dangerous to handle being unstable. In contrast ammonium dynamite contains high percentage of ammonium contents mixed with other filler.

2.4.2 **Military Explosives**

There are two broad categories of military explosives covering primary explosives and secondary high explosives based on the difference in their rate of decomposition. Primary explosive burn rapidly (or deflagrate) whereas secondary explosive are the main charge in any warhead, bomb or munitions which detonate.

2.4.2.1 **Primary Explosive**

A primary explosive is the one where small amount of energy is required for their initiation. An explosive of these types is low powered and extremely sensitive to external stimuli such as impact, friction, heat, static electricity, or EMR. As a common rule, primary explosives are said to be more sensitive than PETN. Primary explosive are so sensitive that it can reliably be initiated by normal hammering, whereas PETN can usually be initiated in this manner, so this is only a very broad guideline. Primary explosives are mainly used to detonate less sensitive secondary high explosive (main bursting charge). Primary explosives are filled in blasting caps usually in milligrams to transmit shock wave across the explosive train. Few of the examples of primary explosives are:

- Lead Azide
- Lead Styphnate
- Mercury Fulminate
- Nitroglycerin
- Silver Azide
- Sodium Azide
- Tetrazine

2.4.2.2 **Explosive Booster or Intermediary**

This is a slightly larger amount of more powerful and less sensitive explosive which amplifies low power shock wave from primary explosive to detonate main bursting charge. In other words, a booster is a bridge between primary explosive and secondary explosive because an initiator only cannot detonate the main charge. Most commonly used chemical booster is Tetryl CE (Composition Exploding) but has now been superseded at places by other compositions such as small pellets of pure PETN or RDX.

2.4.2.3 **Secondary High Explosives**

Secondary high explosive differs greatly from other classes mainly on the basis of explosive power, force, liberation of heat and pressure on surrounding materials. A secondary high explosive is rated according to its detonation velocity in either confined or unconfined state. Detonation velocity is the speed with which shock wave travel through unreacted explosive [12]. Mostly explosive power is prominent once detonated in confined area. The detonation velocity of an explosive is directly related to initial density, initial ambient temperature and pressure, particle size, charge diameter, and degree of confinement. Decreased particle size, increased charge diameter, and increased confinement all tend to increase the detonation velocity. Unconfined velocities are generally 70 to 80 percent of confined velocities. Few of the military high explosives are:

- TNT
- RDX
- Composition B
- HMX
- TATB

REFERENCES

[1] Explosives, Propellants and Pyrotechnics Brasseys Volume- 2. Bailey A and S.G. Murray.

[2] Army Research Office. Elements of Armament Engineering, Part-1. Washington, D.C.: U.S. Army Material Command, 1964.

[3] Explosives, Propellants and Pyrotechnics by Brasseys Volume-2. Bailey A and S.G. Murray.

[4] Explosives Engineering by Cooper, Paul W., Wily-VCH (1996) ISBN 0-471-18636-8.

[5] Safety and Performance Tests for Qualification of Explosives. Commander, Naval Ordnance Systems Command., NAVORD OD 44811.Washington, D.C. GPO, 1972.

[6] Weapons Systems Fundamentals. Commander, Naval Ordnance Systems Command. NAVORD OP 3000, Volume -2, 1st Rev. Washington, D.C. GPO, 1971.

[7] Military Explosives, Departments of the Army and Air Force. Washington, D.C. 1967.

[8] Performance Properties of Commercial Explosives by J.N.Johnson, C.L.Mader, S. Goldstein 1983.

[9] www.ime.org/dynamic.php., cited on 23-04-2011.

[10] Explosives identification guide (2004).2nd Edition by Mike Pickett.

[11] User: Mythealias/ My References 2. Cited on 23-04-2011.

[12] Explosives Engineering by Cooper, Paul W. Wily-VCH (1996). ISBN 0-471-18636-8.

Chapter: 03

Munitions Disposal Techniques

3.1 Demilitarisation

All military organizations of the world keep a large inventory of munitions to support their tasks, both in operational missions and in training purposes. Munitions are liable to undergo disposals process due to one or may be in combination of other issues such as deterioration (through ageing), obsoleteness (due to development of new weapon system) and/ or being declared surplus to the requirements (due to changes in the requirements) throughout their life cycle. A huge stock pile of the surplus, obsolete and unserviceable munitions not only lead to a costly action financially but also require a large storage area. Safe and cheap disposal technique for such munitions is an important aspect. Advances in demilitarization were precipitated by the end of the Cold War. This led to dramatic reductions in force levels and increases in the demilitarization of stockpiles. High explosive like RDX, HMX and TNT are most common environmental pollutants. These explosive materials can undergo biotransformation with soil microorganisms and drift through soil subsurface, thereby contaminating groundwater [1]. Demilitarisation is an increasingly important technique of munitions management where these obsolete munitions can be demilitarized i.e., disposed of in accordance with all legal and regulatory requirements and policies relating to safety, security and the environment [2]. The process of disposal is being shaped by a number of factors. One of the notable factors is the increasingly stringent environmental regulation restricting and modifying these methods. The disposal of obsolete/ surplus munitions by open air burning or open detonation is the most widely known technique but its usage is restricted nowadays due to environmental problems. Many alternative procedures are currently under development for the reclaiming and reutilization of obsolete / unserviceable munitions. The present work also includes solvent based recovery of RDX and TNT from Composition B based munitions.

3.2 Factors for the disposal of obsolete and unserviceable munitions

Following factors are responsible for the quick disposal of obsolete, surplus or unserviceable munitions.

- Environmental Hazards.
- Economic Effects.

- Safety Concerns.
- Time issue.

3.2.1 **Environmental hazards**

Energetic materials being one of the most hazardous chemical substances not only pollute the environment but also leave adverse effects on the human life. In general conventional munitions have a continuous impact on the environment during all levels of their life cycle i.e. during production, while in use and on de-militarisation [3]. Some of the most chronic diseases like tuberculosis, cancer, kidney failure etc. are very common example. Extensive field work in demolishing these undesirable energetic materials still probe danger to the healthy environment, since the toxic fumes and gases contaminate surrounding of the disposal pit. Similarly industrial treatments for the disposal of explosives have only minimized these effects but not thoroughly treated. Few of the most commonly used demilitarization techniques for the disposal of undesirable munitions can be considered to be following [4]:

- Demolition
- Incineration.
- Oxidation and Biodegradation.

Demolition is a simple and widely practiced technique but because of numerous hazards being produced by this technique, it has been banned in a number of developed countries by the environmental regulators. Most dominant hazards of open demolition include air emissions, residual material (either energetic or toxic materials such as heavy metals) and loud noise. Residual material may cause ground water contamination and challenge personnel safety. On the other hand, incineration provides a means of treating emissions and a controlled industrial process. There are various types of incineration systems that are already in use for the disposal of unserviceable munitions [5]. Similarly oxidation and biodegradation creates a similar range of environmental hazards to incinerators. Noise can be an issue but is not generally worse than other industries. Furthermore any process involving water will produce waste water. This can be reduced by closed cycle reclamation systems but explosives contaminated water is still a major issue. Such methods of disposal are highly undesirable from environmental point of view because they contribute greatly to the pollution of the environment in many ways.

3.2.2 **Economic Effects**

Besides few of the inherent problems associated with human life and environment, other issue of unwanted munitions can be storage and handling this volatile and dangerous energetic material. Since financial constraints in Pakistan cannot afford huge stock of unserviceable and surplus munitions requiring additional manpower and storage, a significant amount of surplus munitions are regularly destroyed every year through various techniques mentioned earlier. Similarly a significant amount of munitions are destroyed each year due to deterioration or obsoleteness. To curtail such a huge spending modern munitions are need to be designed to give best reutilization even after completing shelf life. Similarly during conventional method of incineration for the disposal of these undesirable munitions, a large amount of fuel is required for the heating of the incinerator and hence cost effects become too heavy to afford.

3.2.3 **Safety Concerns**

Undesirable munitions pose severe threat to the living organism specially human beings. Degraded or deteriorated munitions are more liable to spontaneous combustion that can lead to deflagration to detonation phenomenon or sudden blast. Storage of deteriorated or unserviceable munitions can be costly and potentially hazardous for munitions that have reached the end of their service life. Similarly all those individuals working on the care and preservation, transportation and disposal of these volatile materials are directly exposed to accidental initiation of highly sensitive explosive munitions. Besides, human suffer greatly due to open detonation where relatively high levels of undesirable NO_x , acidic gases, particulates and metal waste are being produced.

3.2.4 **Time Issue**

Since modern warfare demands high standards of training and accurate response within defined time period, therefore, storage and handling of highly undesirable or unserviceable munitions can jeopardize the time schedule. Modern munitions are required to incorporate demilitarisation processing issues. Since munitions with rapid disposal characteristics will eventually save the time, which are utilized in handling, transportation and demolition of said munitions.

3.3 Steps involved in demilitarisation

The demilitarisation process of conventional munitions consists in general the following steps:

- Transport to the demilitarisation site.
- Unpacking from transportation packages
- Disassembly
- Removal of energetic materials
- Destruction or demolition
- Resource recovery and re-utilization.

3.3.1 Transport to the demilitarisation site

All undesirable and unserviceable munitions are disposed-off at specified demolition grounds normally at safe distance from local population. This is done primarily to safeguard human beings and other living organism from dangers posed by degraded munitions. Transportation of these deteriorated munitions is carried out according to the well-defined Standard Operating Procedure to avoid any accidents during transportation. Mostly munitions carrying trucks or specialized vehicles are used for transportation.

3.3.2 Unpacking from transportation packages

After safe transportation of munitions to the demolition site, these are unloaded from the vehicle in an organized manner and unpacked from transportation packages for further disposal.

3.3.3 Disassembly

It is the removal of all energetic materials and other components from munitions to disarm it by means other than detonation and combustion [6]. Munitions that are incorporated with fusing arrangement are disassembled at the repair and dismantling facilities made for the purpose. In case the same facility is not available, alternate method for the field disassembly is carried out at demilitarisation site with appropriate tools. The under -study munitions (containing Composition B explosives) have also been disassembled with the help of a breakdown machine which will be discussed later. One of the specific disassembling machines is shown in figure 3.1

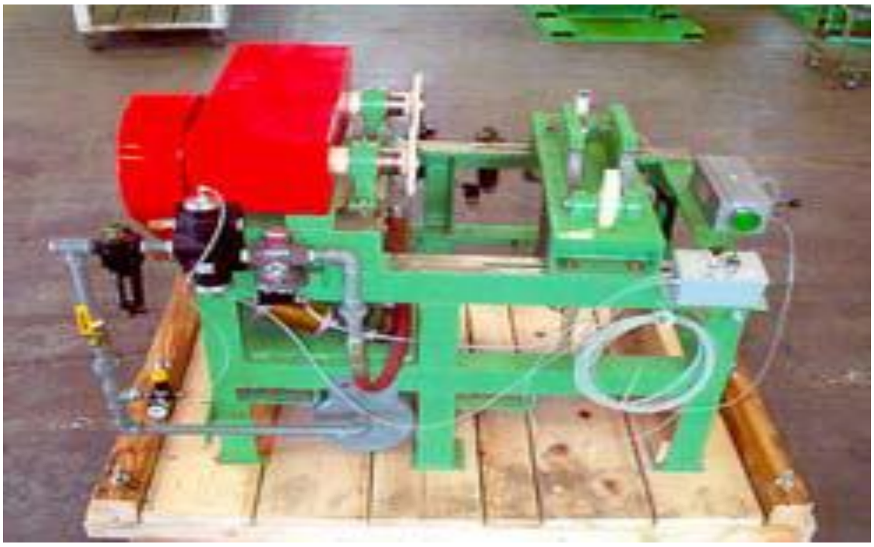

Figure: 3.1 APE 1002M3 Two spindle defuzing machine.

3.3.4 Removal of energetic materials

The most important aspect of this research is to utilize recovered explosive components separated from unserviceable munitions containing Composition B explosive so that the same can be further formulated into a commercial explosive substance. This will not only result into the reduction of military budget but will also contribute to the overall environmental safety concerns. The present research is also being carried out on the recovered explosive materials such as RDX and TNT from Composition B based munitions. One of the current military munitions such as 106 mm Recoilless Rifle unserviceable round has been selected which is an anti-tank round incorporated with Point Initiating Base Detonating (PIBD) fuze.

3.3.5 Open Burning and Open detonation (OB/OD)

One of the most widely applied disposal techniques for the demilitarisation of munitions is Open Burning and Open Detonation (OB/OD). Nearly all types of unwanted or surplus conventional munitions containing military high explosives were previously destroyed through Open Burning and Open Detonation. This was one of the easiest methods for the disposal of unwanted munitions where least technical handling was required. However, stricter environmental protection regulations have made this technique quite impractical owing to its adverse side effects. Much of the research efforts are concentrated now days on the complete recovery of the energetic materials and other components from undesirable munitions. Figure 3.2 shows open detonation technique used for the disposal or destruction of 155 mm High Explosive filled munitions [7].

Figure: 3.2 Open detonation of 155 mm HE Shells.

3.3.6 **Resource Recovery and Re-utilization**

After the successful recovery of complete explosive materials and other components (like paraffin wax and binders if mixed) from deteriorated munitions, metal casings or shell bodies are collected for subsequent disposal. These metal parts or scrap can be recycled in recovery plants if possible or may be sold in the civil market for the re-utilization of the same for other task after thorough machining. This process can only be adopted in case authorized organization can recycle the metal parts into specific molds other than military designs and casing so that irregular usage of the casing can be avoided. On the other hand, recovered energetic materials can be utilized for commercial applications after necessary formulation or even these chemical compounds can be utilized for energy based projects. Thus these highly energetic materials can be converted for other specific purposes like fertilizers or conversion into commercial chemicals for civil and military applications. A schematic layout of the above mentioned steps for the demilitarization of undesirable or degraded munitions is shown in the figure 3.3.

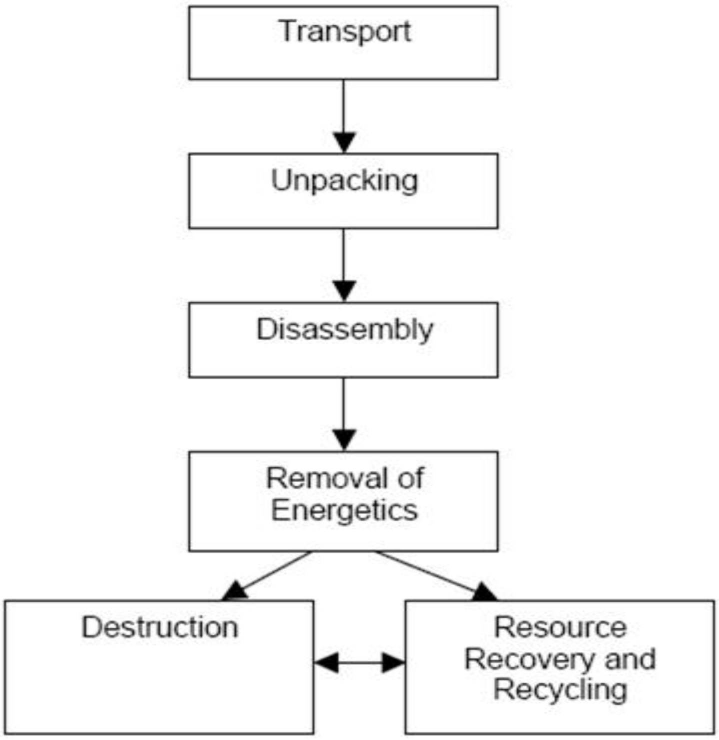

Figure: 3.3 Schematic layout of demilitarisation process.

All munitions have a finite lifetime. They can reach the end of their lives through ageing processes or deterioration. These munitions may also become obsolete by developments in weapons systems or surplus due to changes in requirements. Other factors include their disposal due to international treaties and agreements.

3.4 **Dumping**

Dumping was one of the common disposal technique used in the past. It was considered scientifically safe with the opinion that the explosive content of munitions would degrade quickly making them safe. The environmental effects of these volatile materials were totally ignored. However, field experience has made it clear that the degradation of munitions pose a safety hazard for very long periods of time even after dumping.

3.5 **Sea Dumping**

Although sea dumping of undesirable munitions was continued until 1972, when it was immediately banned through 1972 UN Convention on the Human Environment in Stockholm which lead to the 1972 UN Convention on the Prevention of Marine Pollution by the Dumping of Wastes and Other Matter (London Convention) [8] . The ban was imposed formally on 30 August 1975. Similarly the London Convention contained a ‘black’ list of banned wastes and a ‘grey’ list of wastes requiring special care but did not specifically ban sea dumping of munitions.

3.6 **Demolition**

Although similar in technique to open detonation but demolition is considered to be least hazardous than open detonation as the environmental effects on surrounding air are less than former. In demolition unserviceable munitions are laid in a regular pattern under a well-defined underground pit where typical high explosive train is incorporated to provide sufficient shock wave to the main charge. Although tough in regards to digging a deep underground pit but safety to the human life is considered to be more in this technique. Some of the inherent hazards involve atmospheric pollution and more dangerous situation in case of a blind. Environmental protection regulation demand least adoption of these techniques for the disposal of unwanted and unserviceable munitions where alternate methods of decanting and recovery can made utilized.

3.7 **Typical High-Explosive Train**

Most commonly used three step explosive train consist of a safety fuse filled with gun powder, a non-electric blasting cap or detonator and primer CE. Since burning of gun powder in the safety fuse would produce a flame which is sufficient enough to detonate the blasting cap or detonator. The detonation wave would be transferred to main bursting charge through flash instantaneous detonating containing PETN filling. It is not always the same explosive train to be adopted as some of the explosives are insensitive to the detonation wave produced by detonator and would eventually require an intermediary or booster like Tetryl CE to detonate the main high explosive charge. In short, an explosive train is an excellent arrangement of explosive according to their sensitivity and power. In case of any breakage or interruption in the explosive train, detonation of the main charge will not occur. A typical three step explosive train is shown in figure 3.4.

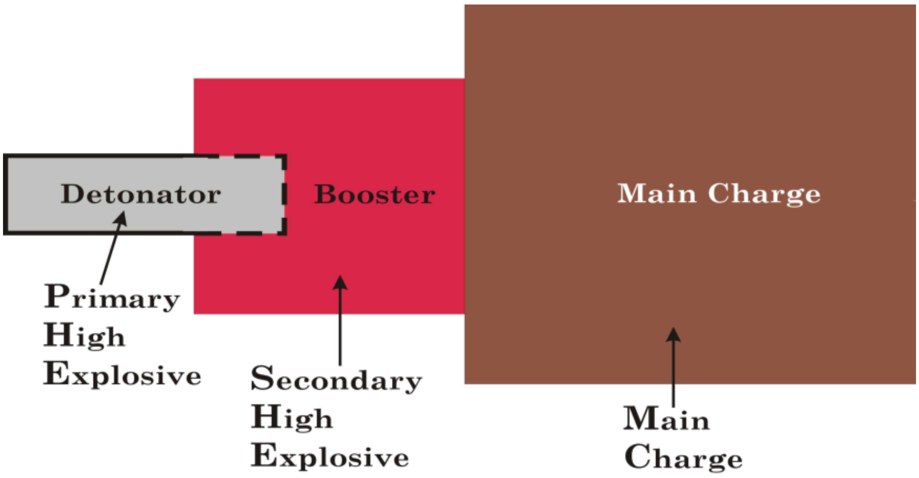

Figure: 3.4 Typical three steps Explosive Train.

An explosive train with complete demolition stores and explosive filling is described in table 3.1 below.

Table: 3.1 Type of demolition stores with their explosive components and purpose.

S.No	**Item used**	**Explosive filling**	**Purpose**
1.	Safety Fuze	Gun Powder	Flash Carrier
2.	Detonator	Lead Azide, Lead Styphnate and Mercury Fulminate	Detonation wave producer
3.	Fuze Instantaneous Detonating	Pentaerythritol Tetra Nitrate (PETN)	Detonation wave carrier
4.	Primer Composition Exploding (CE)	Tetryl	Detonation wave enhancer
5.	Plastic Explosive (PE-3A)	RDX 87% Wax 11%, Lecithin 1%	Main bursting charge/ explosive

3.8 Separation of RDX and TNT from Composition-B based munitions

In the past, open burn/ open detonation have been used to dispose of undesirable munitions, however these methods fail to meet the challenges of lowering the waste by-products in a cost effective manner [9]. Since all other techniques for the de-militarisation of unserviceable and unwanted munitions lead to a variety of environmental pollution and safety hazards, solvent-based recovery of explosive materials and other components from munitions is considered to be quite useful technique for the disposal of said munitions. Stable energetic materials recovered from unserviceable munitions are considered to be easily separated and reloaded. On the hand, solid propellants which may have a limited shelf life require significant degrees of processing prior to recycling [10]. Present study is primarily focused on the separation of RDX and TNT from unserviceable Composition B explosives (60/40), so that the same can be reutilized for commercial or other valuable purposes. A detailed experimental work along with solvent based disposal technique used for the separation of recovered RDX and TNT from unserviceable Composition B explosive is described in chapter no 5.

REFERENCES

[1] Detection of explosives and their degradation products in soil environments., Journal of Chromatography A, by A. Halasz, C. Groom, E. Zhou, L. Paquet, C. Beaulieu, S. Deschamps, A. Corriveau, S. Thiboutot, G. Ampleman, C. Dubois, Jalal Hawari., Volume 963, Issues 1-2, 19 July 2002, Pages 411-418.

[2] www.thefreedictionary.com/demilitarization.Cited on 26-04-2011.

[3] Demilitarisation of munitions reuse and recycling concept for conventional munitions and rocket propellents by Victor H, Baryakhtar and Theo Rosendorfer (1997).

[4] Review of Demilitarisation and Disposal Techniques for Munitions and Related Materials by Josh Wilkinson, Duncan Watt .Cited on 6-05-2011.

[5] Literature review on demilitarization of munitions by Isabelle Poulin DRDC Valcartier. Cited on 5-04-2011.

[6] Demilitarization of military munitions and explosive ordnance items, PNP circular no 12 series of 2008.

[7] United States munitions demilitarization, conventional ammunition demilitarization capabilities.US Army Defense Ammunition Centre. Cited on 17-02-2011.

[8] http://www.mod.uk/NR/rdonlyres/52954E9D-A12E-4DB8-85D5A5AC8EFB45C/0/bd_ backgrd.doc. Cited on 13-01-2011.

[9] Reclaiming RDX and TNT from Composition B Containing Military Shells by Kym B. Arcuri, Duane A. Goetsch, Steven J. Schmit, Paul L.miller. US 6,777,586 B1, August.17,2004.

[10] US military explosives, TM 9-1300-214, 1984.

Chapter: 04

Thermal Analysis Techniques

4.1 General

Rapid changes that occur during thermal decomposition of various energetic materials have led to the invention of thermal analysis techniques. Thermal analysis consists in principal of different techniques used to measure physical and chemical properties of a substance as a function of temperature. During thermal analysis techniques, material substance is subjected to a controlled temperature program. In thermal analysis techniques, the sample and reference material are subjected to uniform heating rate and any temperature difference that develops between them is recorded. In other cases, physical or chemical property change in the sample material is observed during controlled heating rate. Various types of thermal events such as Melting point, boiling point, thermal decomposition, sublimation, glass transition temperature, double decomposition, phase changes etc. can be easily observed during thermal analysis techniques. All types of explosives can be characterized very effectively using any suitable thermal analysis technique as it can determine explosive behavior on decomposition such as endothermic or exothermic. The same results can be further utilized in finding various kinetic parameters like enthalpy change, order of reaction and the most valuable information on activation energy.

4.2 Types of Thermal Analysis Techniques

Thermal analysis may be carried out in a variety of techniques where sample is kept under controlled temperature range along with reference material and sample properties are keenly observed. Initial starting conditions (input data) are given to the system for the desired effects to be achieved. Most widely used techniques for the thermal analysis are given as under [1].

4.2.1 Differential Thermal Analysis (DTA)

Differential thermal analysis (DTA) is a techniques that involves heating (or cooling) a test sample and an inert reference material under identical conditions and recording any temperature difference which develops between them.

4.2.2 **Differential Scanning Calorimetry (DSC)**

DSC is quite similar in use to DTA except that the peaks in DTA thermogram represents a difference in temperature between sample and reference, whereas the peaks in DSC thermogram represents the amount of electrical energy supplied to the system to keep sample and reference material at the same temperature. DSC is often used for the study of heat capacities and kinetics of explosive reaction in the absence of phase changes, whereas DTA combined with TGA is mainly used for the thermal analysis.

4.2.3 **Thermo-gravimetry (TG)**

This technique gives valuable information of sample mass change as a function of weight loss with respect to change in temperature or time. This weight loss can be further utilized in finding various kinetic parameters of the sample.

4.2.4 **Thermo-mechanical Analysis (TMA)**

This technique is used to measures various mechanical properties of the sample on heating.

4.2.5 **Thermo-magnetometry (TM)**

Technique is quite similar in use to TMA, however this technique is mainly used to measure magnetic properties of the sample.

4.2.6 **Thermo-particulate Analysis (TPA)**

TPA gives information on the evolution of particles on heating.

4.2.7 **Emanation Thermal Analysis (ETA)**

Evolution of radioactive gas from a sample is mainly observed during ETA technique.

Thermal analysis being the most reliable source of determining various chemical, physical and mechanical properties of a sample material can be effectively used to get a desired result on heating. Since energetic materials require thorough study on its thermal behavior and kinetic parameters therefore present study is mainly focused on utilizing TGA and DTA techniques which are further discussed in detail.

4.3 Differential Thermal Analysis (DTA)

Differential thermal analysis (DTA) being the most suitable technique for the analytical study of a sample is extensively used during research works. In this technique given quantity of a sample under study and a reference material are placed in separate pans depending upon the temperature limit for the measurement of the sample under study. A controlled heating rate is selected under controlled temperature program. Any difference in the sample temperature or reference material is then plotted as a function of temperature. Thermocouples provide useful information on the differential temperature which is recorded. Furthermore this difference in temperature between sample and reference material is plotted against time or temperature. The resulting curve is called as Thermogram. During heating of the system, any change in the chemical or physical properties of a sample observed is the result of a thermal event where heat is being evolved and subsequently temperature of the sample is raised above the reference material. This temperature rise will give an exothermic peak on the DTA plot. Conversely a process, which is accompanied by the absorption of heat, will cause the temperature of the test sample to lag behind that of the reference material, leading to an endothermic peak. Thermogram provides exothermic peak or endothermic peak of the sample relative to the inert reference. DTA curve is a useful tool in gaining information about the purity of the explosive sample as contamination of the explosive will cause a reduction in the melting point. Consequently the magnitude of the depression will reflect the degree of contamination. Similarly any phase change or reaction will give rise to an endothermic or exothermic peak. So a DTA curve may be helpful in determining different thermal events taking place in a test sample on heating such as melting, boiling, crystalline transitions, decomposition, glass transitions, phase transitions etc.

4.3.1 Properties of Reference material used in DTA

DTA technique being more sophisticated requires that reference material should possess following properties.

- It should be inert and stable during controlled heating rate which can be as high as 1550^{o}C. So a reference material should not undergo any thermal change over the operating temperature range.
- It should not react with thermocouple or holding pans of the system.
- It should have similar thermal conductivity and heat capacity to that of the sample under analysis.

Organic compounds such as TNT, RDX and TNB etc. are investigated with a reference material such as Octyl phthalate and silicone oil. Whereas alumina (Al_2O_3) and Carborundum are used as reference material for the investigation of inorganic materials.

4.3.2 **Apparatus used in DTA**

DTA apparatus comprises mainly of following items.

- Sample holder or pans with thermocouples.
- Controlled temperature programmer.
- Heating coils.
- Balance.
- Furnace.
- Inlet for Inert gas flow system.
- Thermo recording system.

During DTA, furnace plays a vital role by providing stable and sufficiently large heating zone. A furnace, therefore, is required to respond quickly to commands from controlled temperature programmer. Controlled temperature programmer is used to achieve constant heating rate throughout the investigation of the sample. The recording system gives actual information on the thermal events taking place during DTA. A diagrammatic layout of the DTA apparatus is shown in figure 4.1[2].

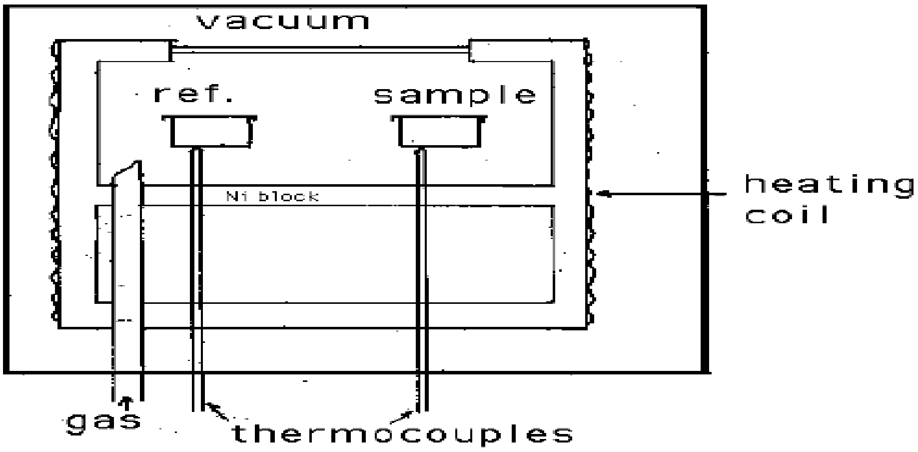

Figure: 4.1 Diagrammatic layout of a DTA apparatus.

4.3.3 **Conditions required for measurement of DTA Curve**

DTA technique involves constant heating process of the sample and reference material where heating rate is observed by the thermo couples. Thermo couples are attached to the end of the balance beams as shown in figure 3.1.Further the temperature difference between the sample and reference pan is detected and used for the measurement of thermal event taking place in the sample in comparison to the reference material. The recorded temperature difference is then plotted against linear temperature or time range to get the final DTA curve. Almost all the high explosive are exothermic in nature, therefore a sharp peak is shown for the exothermic event (decomposition) taking place in an explosive sample. On the hand melting points or boiling points of various high explosives give endothermic peak in the thermogram, for example, TNT. This shows that various endothermic or exothermic peaks obtained in the DTA curves are related to the nature of the sample material under analysis. Holding pans for the sample and reference material are supposed to be same, so that it does not affect the data obtained during DTA technique.

4.3.4 **Factors affecting Differential Thermal Analysis Curve**

DTA curve provides useful information about the sample under investigation. Mainly two types of factors are observed which can adversely affect the DTA curve [3]. These factors are related to the either sample characteristics or may be instrument being used.

4.3.4.1 **Sample related conditions**

The sample characteristics affect the DTA curve in the following manner.

- Particles size.
- Sample weight.
- Heat capacity and thermal conductivity of sample.
- Loading density.
- Crystalline state.
- Rate of decomposition.
- Activation energy of the sample.

4.3.4.2 **Instrument related conditions**

Instrument related factors are equally important in investigating a sample material to the best possible results. Following features may affect the final results of a DTA curve.

- Heating rate of the furnace.
- Atmospheric effects of the sample.
- Furnace shape and size.
- Sample holder or pan used.
- Shape and size of the sample holder.
- Balancing of the sample holder.
- Location of thermocouple.
- Investigation time.
- Degree of errors in the instrument data.
- Final response of the instrument.

Differential Thermal Analysis and Thermo-gravimetric Analysis techniques can be used simultaneously for the thermal investigation of an energetic high explosive. Since both the techniques are run under identical conditions, therefore resultant curves so obtained are utilized in determining the kinetic parameters of high explosives. The present study is primarily based on the simultaneous use of both TGA and DTA. In order to get a fair idea of both the techniques, thermo-gravimetery or TGA have been discussed in the subsequent paragraph.

4.4 **Thermo-gravimetric Analysis (TGA)**

Thermo gravimetric analysis (TGA) is a suitable technique for the measurement of explosive reaction. In TGA the test sample is placed on a balance inside an oven and heated at a desired rate and the loss of weight of the sample is recorded as a function of temperature. Such changes in weight can be due to evaporation of moisture, evolution of gases and chemical decomposition reaction i.e. oxidation[4].It is used primarily for the determination of composition of a substance and finds application in wide variety of fields ranging from analysis of plastic, rubber, minerals, ceramics and chemicals etc. In either case, useful data is obtained about the sample material which can be utilized further in determining other parameters of the sample such as thermal decomposition, stability, activation energy and order of reaction. The percentage weight loss is then plotted against given temperature rate. In thermo-gravimetric analysis, emphasis is given to the sample initial weight, linear heating rate, atmospheric medium and precision of the instrument used. Thermo-balance is used for the measurements of changes made in sample mass with temperature [5]. Thermo-balance is actually a combination of an electronic microbalance and a furnace along with associated temperature programmer. Microbalance is kept in close enclosed system for the controlled temperature environment. A graph of thermo-gravimetry usually consists of Y axis for the percentage (%) mass loss and X axis shows temperature (linear heating rate) or time.

4.4.1 Optimum conditions for TGA Curves

- Sample weight.
- Thin layer of sample.
- Sample holder or container.
- Inert gas flow (N_2, He).
- Suitable heating rate.

4.4.2 Typical TG curves

TGA curves with characteristic properties of the sample material are shown in figure 4.2.

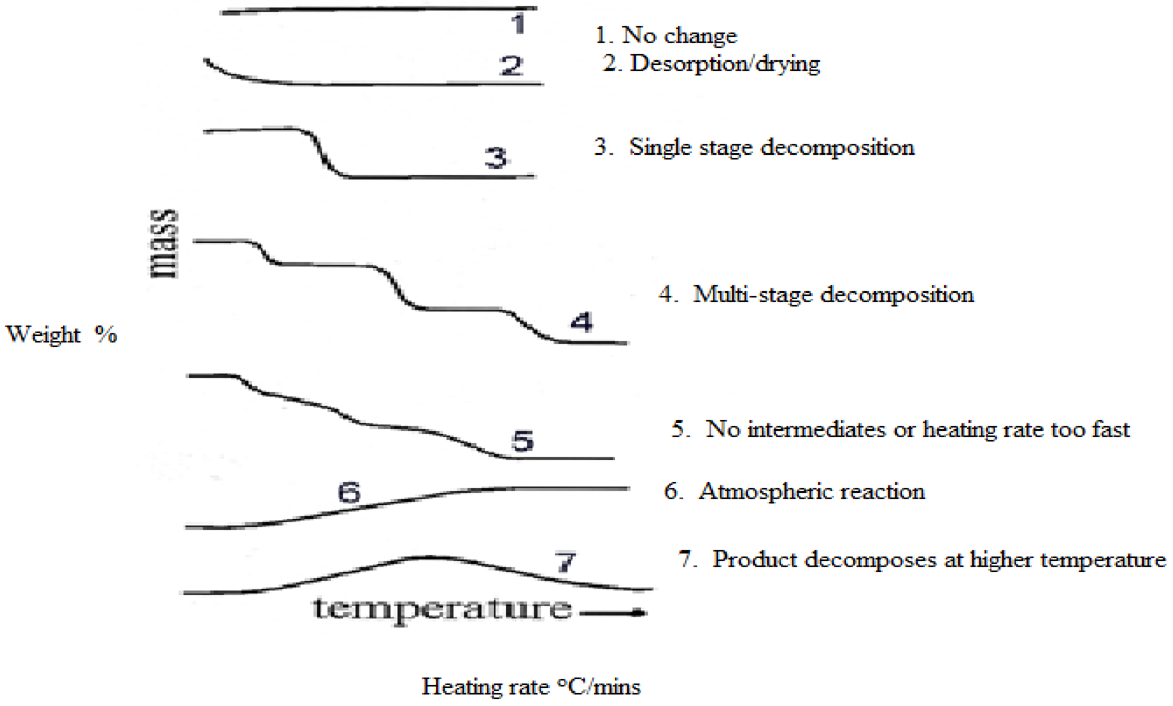

Figure: 4.2 Types of TGA Curves.

4.5 Working Principle of TGA

Both the microbalances containing sample and reference material provided with their respective driving coils. During DTA process, any change in the sample weight is closely monitored by the optical position sensors with a slit. The optical position sensor transmit an optical beam to the microbalances connected with driving coils and the current or data input is subsequently supplied to the driving coil so that the slit returns to its original position. Here the current supplied by the microbalance to the driving coils is proportional to the weight loss or weight gain. Therefore any change in the sample weight with respect to reference material can be detected immediately. Figure 4.3 shows working principle of TG equipment.

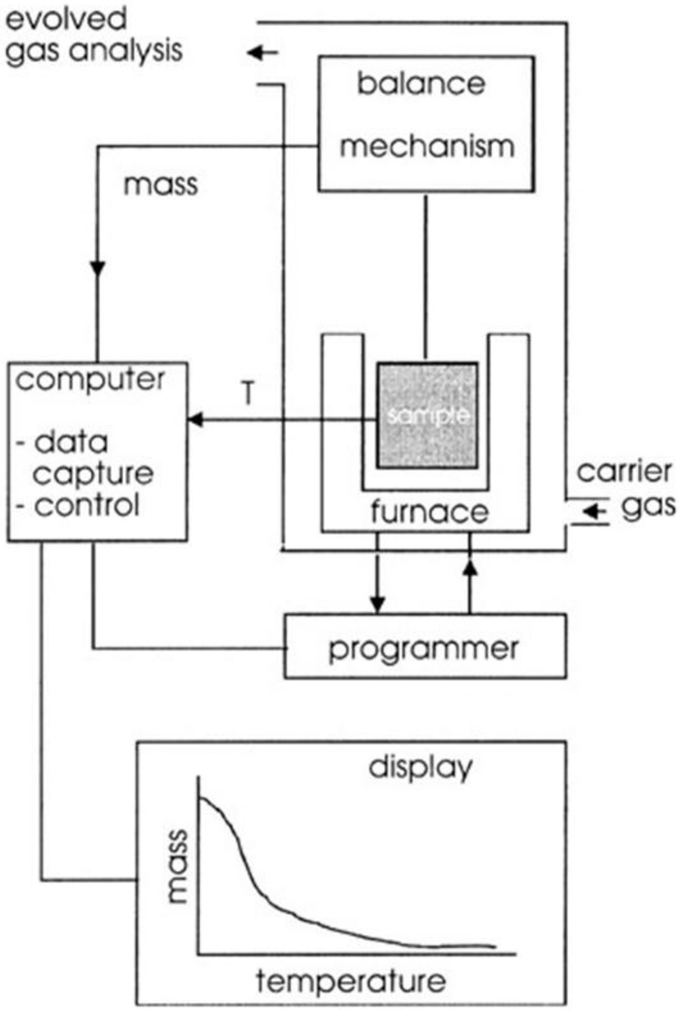

Figure: 4.3 Working principle of TGA equipment.

4.6 **Derivative Thermo-gravimetry**

Derivative Thermo-gravimetry commonly known as DTG is used to further simplify the results obtained from TGA. Since TGA determines the weight loss as a function of temperature or time, some of the weight loss curves may look alike. In order to obtain some other valuable information from the resultant weight loss curves, DTG is used to convert these curves into first derivative curve prior to the interpretation of the result. Unlike TGA where a continuous curve is obtained, DTG curve provides a series of peak. So the area under these peaks reflects the weight change of the sample. The derivative weight loss curve also provides useful information of the weight loss by indicating sharp peak which is a measure of prominent weight loss. In other words sharp peak shows maximum decomposition rate. Presently, both TGA and DTG are simultaneously used for the determination of sample characteristics such as decomposition, degradation temperatures, phase transformation temperatures, effect of moisture content on explosives material. Figure 4.4 shows TG and DTG curves with single stage decomposition and multiple stage decomposition.

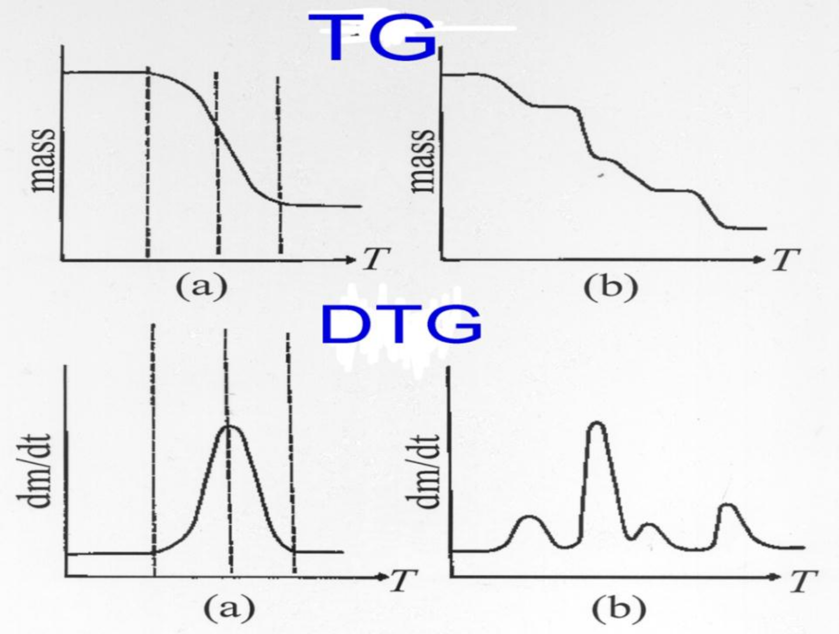

Figure 4.4 Diagram with different TG DTG curves.

4.7 Simultaneous Thermal Analysis

Simultaneous Thermal Analysis (STA) is a useful technique where both the DTA and TGA techniques can be applied to a sample analysis simultaneously in a single instrument [6]. One of the noteworthy points is that the sample is subjected to a common heating program along with other initial input data. In simultaneous thermal analysis technique, both the curves for a single sample are obtained at one time i.e. a curve for the differential temperature versus sample temperature and another curve for sample weight loss as a function of temperature. The combination of these two curves is quite useful in analyzing the sample in a short time. Sometimes third curve may also be seen for DTG. This additional TG derivative curve makes this combination very effective tool for the sample analysis. Simultaneous TG/DTA also measures heat flow besides weight changes in a sample material as a function of temperature in a controlled environment. Simultaneous measurement is quite useful if the interpretation of the results is simplified and complimentary data confirms each other. Simultaneous thermal analysis technique also provides information about endothermic and exothermic events which do not involve any weight loss such as melting, crystallization and those involving weight losses such as decomposition. Simultaneous TGA/DTA curves are shown in figure 4.5, where the sample is subjected to a common heating rate under controlled environment. Here both the TGA and DTA curves are plotted against same temperature range.

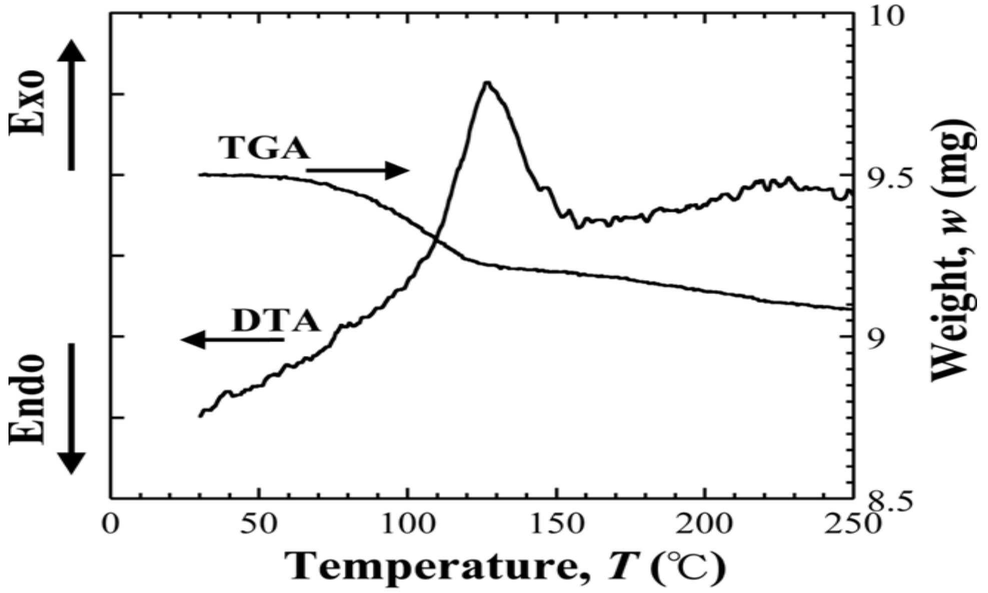

Figure 4.5 Simultaneous TGA/DTA Curves.

The present work has been performed with simultaneous TG/DTA technique for the study of thermal behavior of various high explosives along with determination of their kinetic parameters such as activation energy and order of reaction.

4.8 **Measurements of Kinetic Parameters**

Kinetic is the study of the rate of change of chemical reaction. These reactions can be very fast such as detonation of high explosives, medium like dissolution of sugar in water or even very slow like rusting of iron. In explosive reactions the rate is extremely fast and is dependent on the temperature and pressure of the reaction and the concentration of the reactants [7]. In the present research work kinetic parameters of various high explosives have been measured using curve fitting program. Results from simultaneous TG /DTA have been interpreted so that accurate data is obtained about the kinetic parameters such as activation energy, order of reaction and enthalpy etc. These parameters have been determined using one of the methods discussed as under.

4.8.1 Methods for the measurement of Kinetic Parameters

Literature finds various methods for the measurement of activation energy, order of reaction and enthalpy of explosive material. Few of the most commonly known methods are:

- Doyle Method.
- Coats and Red fern Method.
- Horowitz and Metzger Method.
- Free man and Carroll Method.
- Newkirt Method.

Although all of the above methods are quite accurate and reliable in use , however present study for the calculation of different kinetic parameters (especially activation energy) of various high explosives have been carried out with help of Horowitz and Metzger Method (Curve Fitting Program). So Horowitz and Metzger method used for the calculation of activation energy of various high explosives shall be discussed here in detail. In order to pursue further with study on kinetic parameters, reference temperature is determined initially and will call it Ts. At this temperature, rate of decomposition of the sample as well as its weight loss are maximum. We can determine reference temperature Ts with the help of following relationship.

$$\mathbf{Ts = Wt / Wo = 1/e}$$

Where

Ts = Reference temperature.
Wt = Sample weight at any given temperature T.
Wo = Sample initial weight.
e = exponential.

Second step will help in calculating **ɵ** (theta) from the Ts.

$$\mathbf{\theta = T - Ts}$$

Where,

T is the sample temperature at weight Wt.

By plotting **ɵ** against **ln ln Wo/ Wt**, we get a straight line. The gradient or slop of the straight line obtained in above mentioned equation is actually derived from

$$\mathbf{Slop = Ea / RTs^2}$$

Where,

Ea = Activation Energy

R = Universal Gas Constant (8.314 J K^{-1} $mole^{-1}$).

From the above relationship we can get the value of the activation energy.

REFERENCES

[1] Introduction to Thermal Analysis techniques and applications by Brown Michael E 1988.

[2] Thermal analysis techniques by H. K. D. H. Bhadeshia, University of Cambridge, Materials Science & Metallurgy. Cited on 20-4-2011.

[3] Thermal Methods of Analysis by Wisley W.M. Wendlandt 1964.

[4] Explosive Ordnance and Engineering, Thermodynamics, by Akhavan J. MH 190B. Ext 2324.

[5] Thermal Methods of Analysis by Wisley W.M. Wendlandt 1964.

[6] http://en.wikipedia.org/wiki/Thermal_analysis. Cited on 30-4-2011

[7] Explosive Ordnance and Engineering, Thermodynamics, by Akhavan J. MH 190B. Ext 2324.

Chapter: 05

Experimental Work

5.1 General

As discussed in the previous chapters, extensive research work on the characterization and demilitarization of unserviceable or unwanted explosives is in practice world over. Since bulk of the unserviceable munitions is lying in various ammunition depots of Pakistan Army which needs to be disposed-off in the most appropriate manner, so that environmental hazards along with other risks to human life are diminished. Similarly surplus munitions present a problem in relation to its guard, storage, care and preservation where most of the available manpower is utilized. Secondly rapid advancement in the field of energetic materials requires that Pakistan Army should extend its research and development on energetic materials. In order to resolve this challenging task, NUST has offered a full time research program for the Army. It was considered appropriate to exploit this opportunity and conduct a thorough research on the re-utilization of unserviceable and surplus munitions. The present work is primarily focused on the same project and is carried out in the field laboratories available at School of Chemical and Materials Engineering (SCME), NUST. Research work is conducted in a sequential order which is discussed here in detail.

5.2 Preliminary Arrangements

General Headquarters was formally approached for the arrangements regarding provision of unserviceable or undesirable munitions, so that requisite samples could be recovered from the said munitions. After deliberate efforts, final approval was obtained for the collection of samples from various ammunition depots including POFs Wah. Some of the general steps involved in streamlining the present research work are discussed in detail.

5.2.1 Issuance of Explosive Samples

Military high explosives are the most difficult commodity in regards to its availability especially in LIC (Low Intensity Conflict) environment. Also handling, transportation and storage of these highly volatile and sensitive compounds pose a serious threat to one’s life besides being a classified and controlled item, therefore all possible security measures were taken to avoid any untoward incident. Both serviceable and unserviceable military high explosives samples were analysed and examined for their comparative behavior and characteristics. Mainly Composition B, RDX and TNT samples were analysed during present research work. The samples were issued from various Ammunition Depots including POFs Wah

5.2.2 **<u>Sample Collection</u>**

After formal approval from General Headquarters, explosive samples were collected from following Ammunition Depots and Ordnance Depots:

- Central Ammunition Depot Havelian.
- Ammunition Depot Okara.
- POFs Wah.

Unserviceable TNT samples were collected from CAD Havelian, whereas unserviceable Composition B samples were collected from Ammunition Depot Okara. POFs Wah was only approached for the provision of small quantity of serviceable samples of TNT, Composition B and RDX.

5.2.3 **<u>Dismantling Procedure</u>**

All the explosive samples were made available after deliberate efforts, however much complex mechanism was adopted for the recovery of unserviceable RDX and TNT from Composition B explosive. Composition B explosive is mainly filled in HEAT (High Explosive Anti-Tank) round containing PIBD (Point initiating Base Detonating) fuse. These rounds are specifically filled with Composition B explosive charge to give high penetration effect along with optimum destruction on the target material. As the HEAT rounds are much more complicated (due to PIBD fuse arrangements) to dismantle than other munitions in service, special arrangements for the dismantling of these unserviceable munitions was made. Literature survey reveals that HEAT rounds can be dismantled only if suitable breakdown machine with adequate safety arrangements is available. Unfortunately properly designed machines with specified protection materials are not available in the Ammunition Depots. Therefore complete dismantling was carried out manually in the most responsible way under the supervision of a specialized Ammunition Technical Officer and minimum required manpower (Figure 5.1).

Figure: 5.1 Dismantling of 106 mm HEAT Round.

An unserviceable round of 106 mm Recoilless Rifle was selected out of unserviceable munitions lot (1976), held at Ammunition Depot Okara. A schematic layout of 106 mm RR HEAT Round is shown in Figure 5.2 below.

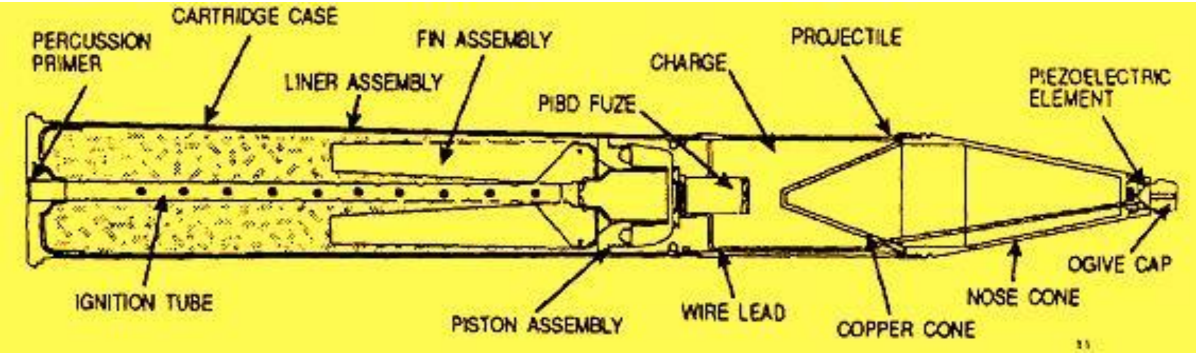

Figure: 5.2 Schematic Layout of 106 mm RR HEAT round M344A1 [1].

The whole operation was conducted in extreme safety and security environment as per the general instructions laid down in available secret official documents. After the complete dismantling operation of the HEAT round into cartridge case and shell body, separation of unserviceable explosive Composition B from shell body was carried out. Since most of the melt-cast shell fillings are recovered through thermal decanting process, however the same process was not possible in case of 106 mm HEAT round containing Composition B (RDX/ TNT/ Wax) filling. The reason behind this is that Composition B explosive compound is a mixture of RDX/ TNT and Paraffin Wax in a proportion of 59.5/39.5/ 1 percent respectively.

RDX cannot be recovered by conventional thermal decanting process due to very close difference in its melting and ignition temperature (RDX melts at 204.1°C and its ignition temperature is 213°C) [2]. Subsequently manual technique for the recovery of explosive materials was adopted with the help of non-ferrous tools. The operation was considered quite safe and secure for retrieval of unserviceable explosives material. Figure 5.3 to Figure 5.7 show stepwise recovery of various parts in complete dismantling operation.

Figure: 5.3 Recovery of PIBD fuse with Fin Assembly from 106 mm HEAT Round.

Figure: 5.4 106 mm HEAT Round filled with Composition B Explosive and Wire lead.

Figure: 5.5 Removal of Ogive head from 106 mm HEAT Round.

Figure: 5.6 Piezo-electric elements at Ogive head.

Figure: 5.7 Dismantled parts of 106 mm HEAT Round.

After the successful dismantling and recovery of complete explosive materials, arrangements were made for the safe transportation of these military high explosives from Ammunition Depot Okara to the School of chemical and Materials Engineering (SCME), NUST. Table 5.1 below gives a detailed description of all other explosive samples collected from CAD Havelian and POFs Wah, along with their physical characteristics.

Table: 5.1 Physical properties of Military High Explosives

Explosive	Status	Melting point ^{o}C	Ignition Temperature ^{o}C	Density (g cm^{-3})	VOD (km s^{-1})	Received From
TNT	Serviceable	82.8	234.9	1.65	6.9	POF Wah
RDX	Serviceable	204.1	213	1.82	8.7	POF Wah
Composition B	Serviceable	-	-	1.65	8.05	POF Wah
Composition B	Unserviceable	-	-	1.65	-	Ammo Depot Okara
TNT	Unserviceable	80.9	240	1.65	-	CAD Havelian
RDX Separated	Unserviceable	204.1	213	1.82	-	SCME Lab
TNT Separated	Unserviceable	80.9	240	1.65	-	SCME Lab

5.3 Purpose of the present research work

Almost all the conventional methods for the disposal of unserviceable or undesirable munitions have led to a number of accidents worldwide involving initiations of munitions by impact/shock aboard ships, aircrafts carriers and munitions train [3]. Similarly many precious lives have so for been sacrificed during clearance and disposal of these unserviceable or undesirable munitions. One of the noteworthy incidents took place in demolition ground, Ammunition Depot Nowshera, on 07 July, 1991 (10:15 a.m.), where an Army Officer and three other soldiers have sacrificed their precious lives and embraced shahadat during the demolition of unserviceable munitions. Besides, many more were left with partial or complete disability. Simultaneously bulk disposal of unserviceable munitions at demolition ranges have severely polluted the surrounding environment [4]. These conventional disposal techniques are not only perilous but are wasteful, where highly energetic materials are destroyed without being utilized. To avoid theses menace, alternate methods are required to be formulated for the demilitarization of energetic materials in a most environmentally-friendly manner [5]. The present work is based on complete separation of RDX and TNT from unserviceable Composition B explosive, which is a feasible, safe and relatively cheap method with very little waste generation. Also this method is quite acceptable by Environment Protection Act.

5.4 Separation of RDX and TNT from Unserviceable Composition B Explosive

Solvent-based separation of technique for the disposal of unserviceable Composition B explosive material has attracted the most interest. Since melt-cast loading of Composition B explosive is more economical and suitable process for mass production and filling into munitions. Composition B explosive is a mixture of RDX and TNT with trace amount of Paraffin Wax, where RDX and TNT are added in a definite proportion to suit the final product. In order to separate RDX and TNT from unserviceable Composition B explosive sample through solvent-based technique at laboratory level in terms of solubility of RDX and TNT in gram per 100 grams solvent at different temperature was studied [6] .Table 5.2 and 5.3 shows solubility of both RDX and TNT in various solvents respectively.

Table: 5.2 Solubility of RDX in gram per 100 grams of Solvent.

Solvent Type	Solubility
Water	0.006 (25 ^{o}C)
Butyrolactone	14.0 (25 ^{o}C)
Ethyl acetate	1.5 (20 ^{o}C)
Ethanol	0.11 (20 ^{o}C)
Diethyl ether	0.055 (20 ^{o}C)
Chloroform	0.008 (20 ^{o}C)
Toluene	0.02 (20 ^{o}C)
Benzene	0.05 (20 ^{o}C)
Dimethyl sulfoxide	41.0 (25 ^{o}C)
Acetone	8.2 (25 ^{o}C)

Solvent Type	**Solubility**
Dimethylformamide	37.0 (25 °C)
Acetonitrile	5.5 (25 °C)

Table: 5.3 Solubility of TNT in gram per 100 grams of Solvent at 25°C.

Solvent Type	**Solubility**
Water	0.02
Carbon disulfide	0.63
Carbon tetrachloride	0.82
Ethanol	1.5
Diethyl ether	3.8
Chloroform	25.0
Toluene	67.0
Benzene	88.0
Dimethyl sulfoxide	128.0
Acetone	132.0
Dimethylformamide	142.0

From Table 5.2 and Table 5.3 [7], it is evident that chloroform being the most important and relatively cheap solvent can be used for the separation of RDX and TNT along with Paraffin Wax from unserviceable Composition B explosive sample. Although TNT is best soluble in dimethylformamide but the same solvent cannot be used as RDX is also soluble in it. Similarly other solvents were not used based on the solubility of RDX and TNT solubility difference. Chloroform being the only solvent where TNT is almost completely soluble, whereas RDX shows no significant solubility in chloroform.

5.4.1 <u>**Apparatus Used for the Separation Of RDX and TNT from unserviceable Composition B explosive sample**</u>

- Analytical Balance
- Water Bath (Digital Constant Temperature Tank HH-4)
- Beakers (500/250 ml)

- Graduated cylinder 250 ml
- Pipette 10 ml
- Simple glass funnel
- Separating funnel
- Mechanical stirrer
- Water bath
- Thermometer
- Clamp stand

General layout of the apparatus used for the separation of RDX and TNT from unserviceable Composition B explosive sample is shown in figure 5.2.

Figure: 5.8 Apparatus used for experimental work.

5.4.2 **Chemical Used**

- Chloroform Solvent - 1 litre (Quantity used in total)
- Unserviceable Composition B Explosive sample - 10 grams
- Distilled Water - 3 Litres (For washing/ separation)

5.4.3 **Procedure**

The separation of RDX and TNT from unserviceable Composition B explosive sample was carried out in several steps which are discussed as under:

5.4.3.1 **Step-1**

- Whole apparatus (only glass wares) were washed with distilled water to remove any impurities present on the surface of the apparatus.

- A small quantity of the unserviceable Composition B explosive sample was ground into a porcelain mortar so that powdered explosive sample can be effectively separated into individual ingredients.
- 200 ml of chloroform, measured with help of graduated cylinder was added into 10 grams of unserviceable Composition B explosive powdered sample (calculated on analytical balance) in a separating funnel.
- The mixture was well shaken so that chloroform solvent is uniformly mixed with powdered Composition B explosive sample.
- After thorough mixing of the sample into chloroform solvent, mixture was placed on a clamp stand so that RDX and TNT layers can be formed based on the difference in solubility of explosive components into chloroform solvent.
- The mixture was allowed to remain stationary on the clamp stand for about one hour so that mixture gets completely separated in two different layers in chloroform solvent.
- Once two distinct layers were formed, lower layer of RDX particles containing slight impurities was drained off through the base hole in the separating funnel and poured into empty beaker.
- Figure 5.3 shows initial stage formation of RDX and TNT layers in chloroform solvent during the experimental work.

Figure: 5.9 Experimental work in progress

5.4.3.2 Step-2

- The separated RDX particles containing trace amount of TNT/ paraffin wax were mixed with 100 ml of pure chloroform solvent in second separating funnel, so that, further purification of RDX particles could be made possible by dissolution of TNT into fresh amount of Chloroform solvent.
- Simultaneously, TNT solution containing trace amount of RDX and paraffin wax in first separating funnel was kept in place so that the same could be further purified to get pure TNT free from any impurities.
- RDX particles mixed with fresh amount of chloroform in step-2 were again shaken well for uniform mixing of TNT and paraffin wax into chloroform solvent and then allowed to stand for yet another one hour.
- After one hour, two layers were formed in the separating funnel, thus helping to remove RDX particles from the mixture into a beaker.
- Chloroform solvent containing TNT particles were poured into first separating funnel.

5.4.3.3 Step-3

- After repeating the process (for six times) of separating RDX particles from mixture in a repeated addition of chloroform solvent in different proportion and allowing the mixture to stand for one hour, one hour, 30 minutes, 15 minutes, 10 minutes and 10 minutes respectively, the precipitated RDX particles were placed in open air for drying.
- Since chloroform rapidly evaporates at room temperature if kept in open atmosphere for some time, dried particles of white crystalline RDX were found.
- White crystalline powdered RDX sample free from any impurities and completely dried was further analysed through TG/DTA technique, so that its thermal behavior and other kinetic parameters could be determined.

5.4.3.4 Step-4

- In this step, TNT particles mixed with paraffin wax and chloroform solvent in first separating funnel were put in a beaker so that TNT particles along with paraffin wax could be easily separated from chloroform by heating the solution in water bath at temperature between 25^oC to 65^oC.
- The process was keenly monitored and after a short while, the chloroform solvent completely evaporated near 62^oC thus leaving behind TNT particle and paraffin wax at the bottom of the beaker.
- A mixture of TNT particles and paraffin wax so obtained was further washed with distilled water in a separating funnel.
- The mixture of distilled water, TNT and paraffin wax in separating funnel was shaken well and then allowed to stand at clamp for a while so that TNT and paraffin wax could be separated from each other based on the difference in their gravity in water.
- Since TNT is completely insoluble in water, it settled down at bottom whereas paraffin wax being lighter than water was observed at the top.
- The same process was repeated several times until paraffin wax was completely separated from pure TNT crystals.
- Brown TNT crystals free from paraffin wax and other impurities were then dried at room temperature, so that the same could also be analysed thermally

by simultaneous TG/DTA technique and its activation energy could be calculated with the help of Horowitz and Metzger method.

5.5 State of the unserviceable munitions with Pak Army

Just like all other professional Armies of the world, Pak Army is keeping huge stockpiles of unserviceable or undesirable munitions. These munitions not only pose a serious threat by prolonged storage accommodations but also their undue maintenance and conventional disposal is a cumbersome task. Pakistan Army has disposed-off approximately 1931.300 M/Tons of unserviceable munitions from 1 July, 2010 to 30 June, 2011. The present state shows that nearly 689 M/ tons of these unserviceable or undesirable munitions are awaiting disposal through normal conventional method of demolition. This will not only have adverse effects on environmental pollution but will cost huge budgetary deficit through their maintenance, transportation and wastage of highly energetic materials.

5.6 Safety Precautions

- Good order and scrupulous cleanliness being pre-requisite for protection against hazards while handling explosives and pyrotechnics.
- Removal of spillage of chemicals and explosives.
- Work should be done behind protection wherever feasible.
- Use of protection/safety screens in tests where heat is employed or produced.
- Ensure all reasonable safety for unwatched overnight tests.
- Inspection of electrical equipment to determine that it is in order.
- The quantities of explosives and pyrotechnic powders shall be limited to bare minimum.
- Residues from tests shall either be removed from the working place or rendered in-offensive.
- During the preparation of samples, pay attention to the risk of ignition when grinding and sifting.

5.7 Heating

- Many stability tests and other examinations involve heating under varying conditions. All such operations must be carried out in apparatus designed to ensure complete guarantee against uncontrollable temperature rise.

- When explosives are submitted to heating tests, ignition and /or violent decomposition of the sample must be considered. Protection gear must be used while heating the samples.

5.8 Static Electricity

- Static electricity is a particular hazard in laboratory work with explosive compounds.
- Minimize the production of electrical charges by avoiding insulating material in dress.
- Avoid even slight friction.
- When working with primary explosives, equipment used should be connected with ground.
- Fix Lightening conductors on Labs working on explosives.

5.9 Other Safety Aspects

- Explosive residues must not be mixed with other refuse nor removed by flushing them down the sink but they shall be chemically destroyed at the laboratory or collected at a central point of disposal e.g. by burning.
- Bulk unserviceable explosives and explosives-devices shall be destroyed at designated ranges under the supervision of trained manpower.
- Explosive residues generally are more delicate to handle than pure explosives because impurities can catalyze decomposition which may become uncontrollable. Hence residues warrant special caution in handling.
- Mixing together different residues should be avoided.
- Non-metallic (preferably plastic) components with suitable scrubbers be employed in exhaust fans.
- Any type of electrical sparking especially in exhaust fans, near explosive storage containers, explosives handling /equipment must be avoided.
- For the fabrication, machining, sieving etc. of explosives charges, lathes, milling machines and other requisite equipment must be remotely controlled.
- For dismantling of explosives devices for subsequent analysis, special tools etc. be designed and all operations must be preferably remotely controlled.
- Presence of bare minimum number of personnel is ensured while working with explosives.

REFERENCES

[1] http://www.gunbroker.com. Cited on 05-05-2011

[2] Explosives, Propellents and Pyrotechnics by Bailey A, S. G. Murray. Volume-2, 1989.

[3] Synthesis, characterization and thermal studies of 2-oxo-1,3,5-trinitro-1,3,5-triazacyclohexane.,N.Sikder et al./journal of hazardous materials A96 (2003) pp.109-119.

[4] Recovery of TNT and RDX from Bulk Composition B Explosives, US patent no.US 7,423,187 B1 Sep. 9, 2008.

[5] Separation of RDX from Composition B via a supercritical fluid extraction process by Jeffrey B. Morris, published in proceedings of 1997 JANNAF safety & Environment Protection Subcommitte Meeting,CPIA Pub. 647, Volume-1.March 1997, pp.283-290.

[6] Analysis of explosives by Alm, A., Dalman, O., Frolen-Lindgren, I., Hulten, F., Karlsson, T., and kowalska, M. (1978), FOA report C-20267-DI, national Defence research Institute: Stockholm.

[7] Modern methods and applications in analysis of Explosives (April 1996), Jehuda Yinon., Shmuel Zitrin. ISBN: 978-0-471-96562-6.

Chapter: 06

Results and Discussions

6.1 General

Energetic materials are highly volatile and dangerous compounds during handling, transportation, storage or even during field utilization. The danger becomes greatest once particular munitions are declared unserviceable, degraded or deteriorated. One of the main reasons for these eminent dangers may be its thermal behavior like thermal stability or sensitivity. A high explosive seldom initiates under ordinary circumstances unless appropriate explosive train is provided or confined for a longer period of time. But in case of unserviceable explosive materials, one cannot give guaranty for its stability at extreme temperature or under varying conditions. The present study is aimed at finding out thermal behavior and other kinetic parameters like activation energy of different high explosive both in serviceable and unserviceable conditions, so that comprehensive results are obtained beforehand. TG/ DTA tests were conducted in Chemical laboratory of SCME, NUST, on available facility for each explosive sample. Results so obtained were further interpreted to get optimum characterization and calculation of kinetic parameters of different military high explosives. These results are further discussed in detail.

6.2 Thermal study of the explosive samples

Before carrying out any particular test for the analysis of explosives samples, Perkin Elmer Diamond TG/DTA instrument available at SCME laboratory was run without explosive sample using ceramic crucible, so that any impurities inside the ceramic crucible can be removed. The test was run at temperature limit between 25^{o}C to 1200^{o}C at the heating rate of 10^{o}C/min which is nearly extreme temperature limit. Impurities present in the ceramic crucible if any, were completely evaporated. Once the instrument was ready to use, thermal studies of Composition B, RDX and TNT samples (both serviceable and unserviceable recovered) were carried out for simultaneous thermal analysis.

6.2.1 Initial conditions

All the explosive samples were analysed using similar set of initial conditions (except sample weights) called as input data. These conditions were set as under:

Temperature Limit	-	$25^oC \pm 5^oC$ to 550^oC
Sample Heating Rate	-	10^oC per minute
Medium	-	Purging N_2 (Inert gas)
Crucible	-	Ceramic pan

6.3 Results

The results of the thermal studies have been discussed separately for DTA and TGA. These are described as under.

6.3.1 Test No.1 (Recovered Unserviceable Composition B Explosive Sample)

6.45 ± 1 mg of unserviceable Composition B explosive sample recovered from 106 mm RR HEAR round has been analysed using following details:

6.3.1.1 DTA Curve

The thermal behavior of unserviceable Composition B explosive sample has been observed within a temperature range of 29^oC to 550^oC. The DTA curve of unserviceable Composition B explosive sample exhibits an endothermic peak at 80.71^oC, which corresponds to the melting of TNT under controlled temperature range as shown in figure 6.1 below. The next exothermic peak that appears to be quite sharp and pointed at temperature of 249.6^oC, corresponds to the thermal decomposition of RDX.

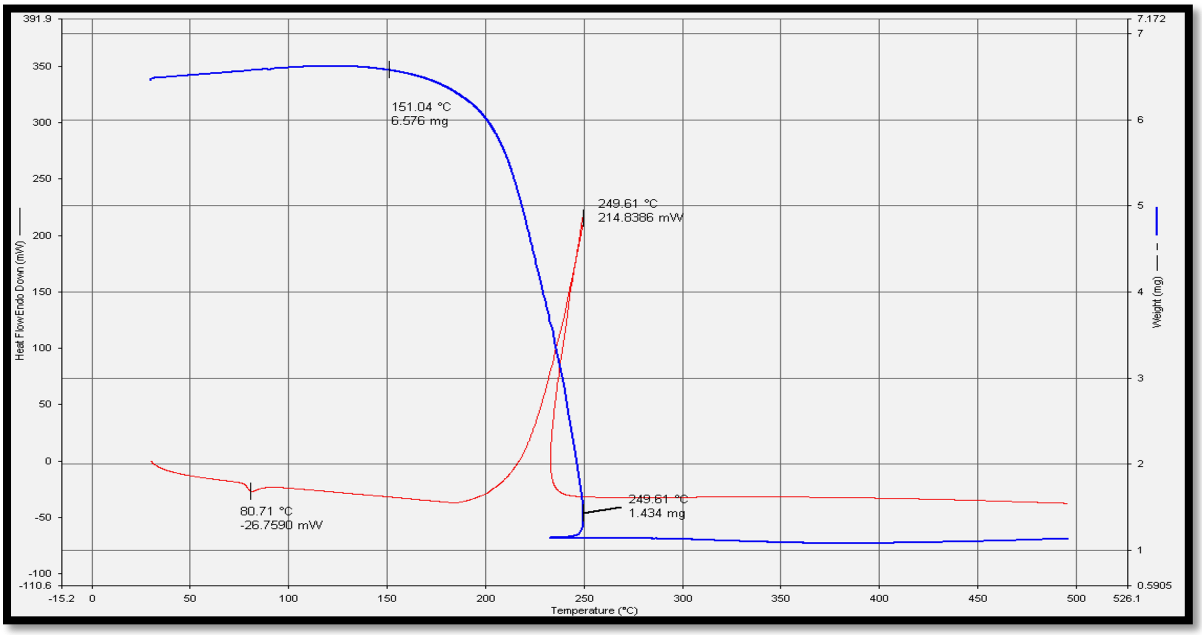

Figure: 6.1 Typical TG/ DTA Curve of Unserviceable Composition B explosive sample.

6.3.1.2 **TG Curve**

Figure 6.1 also shows a TG Curve for recovered unserviceable Composition B explosive sample. TG curve indicates a single stage decomposition of unserviceable Composition B explosive sample during entire thermal event. The weight loss appears to start at 151.04 ^{o}C and ends at 249.61^{o}C . The rate of sample mass loss was observed to be slow between the temperature range of 151.04-200^{o}C but becomes rapid afterward. The total weight loss over the temperature range 151.04-249.61^{o}C could found to be near 97%.

6.3.1.3 **Kinetic Parameters**

An important kinetic parameter like activation energy of unserviceable Composition B explosive sample have been determined from the TGA curve so obtained, with the help of Horowitz and Metzger Method. This is a curve fitting software based method which gives quite accurate data from the given curves. A graph used for the calculation of activation energy is shown in figure 6.2 below.

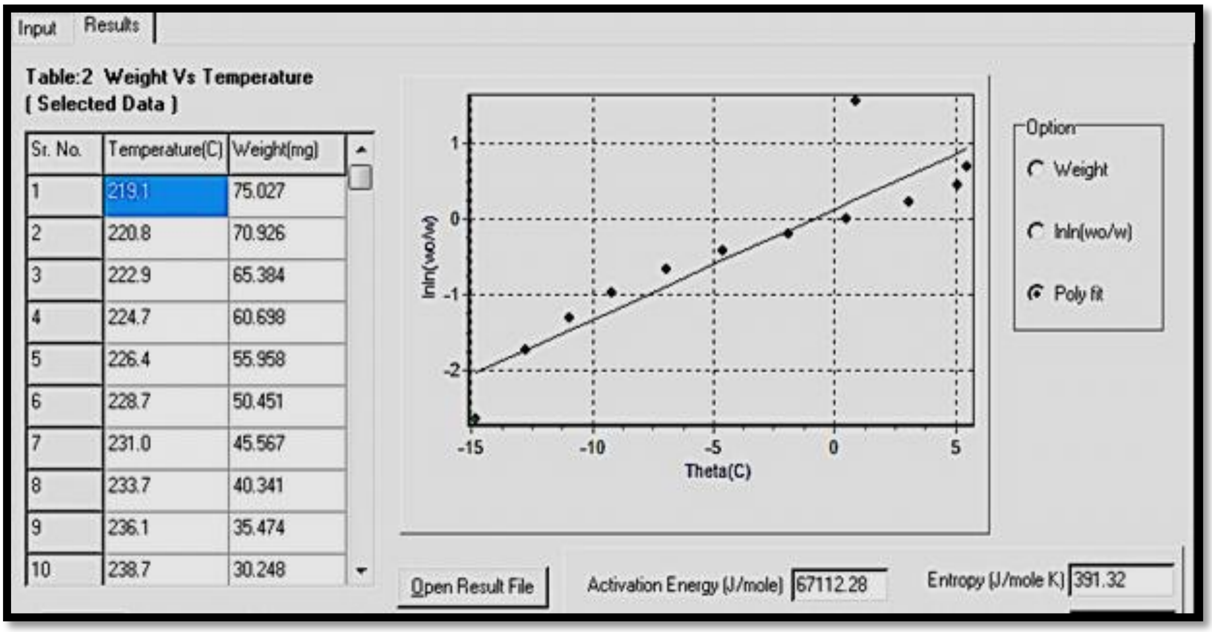

Table:2 Weight Vs Temperature
(Selected Data)

Sr. No.	Temperature(C)	Weight(mg)
1	219.1	75.027
2	220.8	70.926
3	222.9	65.384
4	224.7	60.698
5	226.4	55.958
6	228.7	50.451
7	231.0	45.567
8	233.7	40.341
9	236.1	35.474
10	238.7	30.248

Option
○ Weight
○ lnln(wo/w)
● Poly fit

Activation Energy (J/mole) 67112.28

Entropy (J/mole K) 391.32

Figure 6.2 Graph for the calculation of activation energy of recovered unserviceable Composition B explosive sample.

This graph shows that activation energy of unserviceable Composition B explosive sample under non-isothermal condition as specified above is 67.1 KJ/mole.

6.3.1.4 **Discussion**

TGA and DTA results of energetic materials along with the activation energy and rate of decomposition of different military high explosive samples are identified under non-isothermal condition. A comparative statement is made of both serviceable and unserviceable explosive samples to understand how storage condition or presence of impurities affects their thermal behavior. From figure 6.2, thermo-gravimetric study of unserviceable Composition B explosive sample shows a single stage decomposition of the explosive sample which has started from 151.4^{o}C with a peak maxima at 249.61^{o}C. Similarly DTA curve shows that unserviceable Composition B sample exhibited an endothermic peak at temperature of 80.71^{o}C, corresponding to the melting of TNT and an exothermic sharp peak at 249.61^{o}C,which could be ascribed to the decomposition of RDX in the mixture under controlled temperature program. Since melting point of RDX (204.1^{o}C) is very close to its ignition temperature of 213^{o}C [1], a separate peak was expected in a temperature range of 204.1-213 ^{o}C. However no distinct peak was observed in the DTA curve above, which means that the system already contained sufficient heat energy due to melting of TNT for the immediate decomposition of RDX to take place without its melting or ignition and hence a new feature of RDX curve was observed in the Composition B explosive mixture.

6.3.2 **Test No.2 (Serviceable Composition B Explosive Sample - POF Lot)**

This test was conducted with 6.60 mg of serviceable Composition B explosive sample received from POFs Wah, under controlled temperature program. Few of the analysis of the conducted test are:

6.3.2.1 **DTA Curve**

Thermal behavior of serviceable Composition B explosive sample has been observed within a temperature range of 25^{o}C to 550^{o}C. In this particular sample, The DTA curve exhibits an endothermic peak at about 84.18^{o}C, which is actually the melting point of TNT in the mixture as shown in figure 6.3. Simultaneously an exothermic sharp peak of narrow width at temperature of 251.5^{o}C corresponds to the thermal decomposition of RDX.

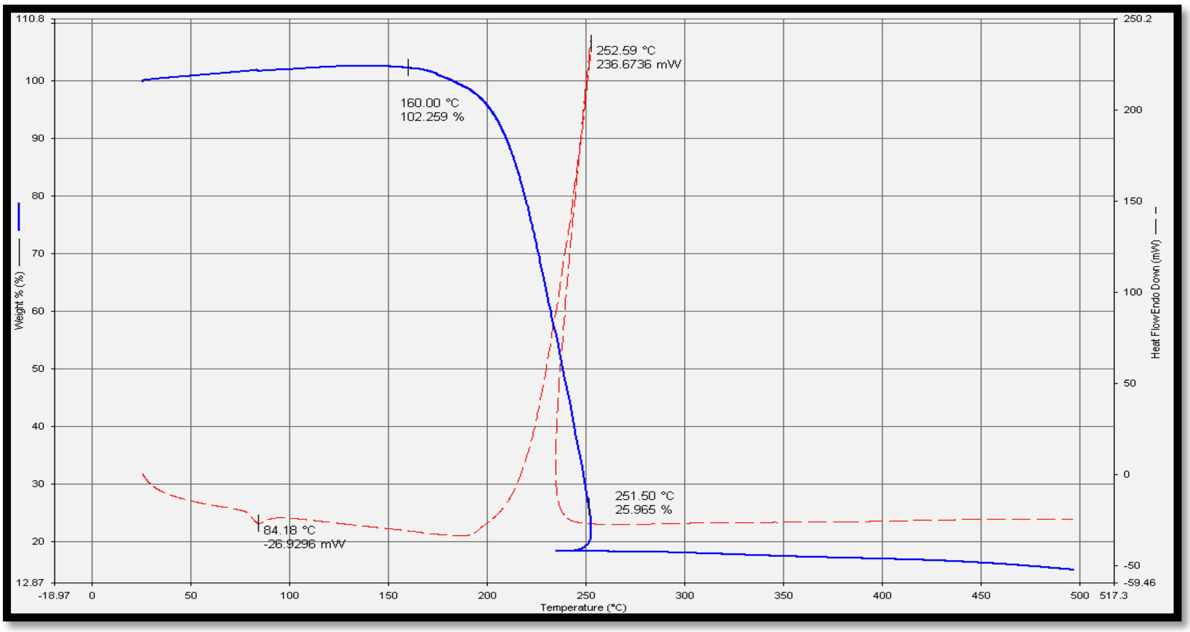

Figure: 6.3 Typical TG/DTA Curve of serviceable Composition B explosive sample.

6.3.2.2 **TG Curve**

TGA Curve for the serviceable Composition B explosive sample is also shown in the figure 6.3. Thermo-gravimetric curve shows that the decomposition of serviceable Composition B explosive sample takes place in a single step. TGA curve also show that the weight loss of the sample started from 160°C and completed at the peak maximum of 251.50°C. This shows that decomposition of serviceable TNT takes place between 160-251.50°C, unlike unserviceable Composition B explosive sample where decomposition occurred between temperature range of 151.04-249.61°C.

6.3.2.3 **Kinetic Parameters**

Activation energy of the serviceable Composition B explosive sample has been calculated from the TGA curve using previously mentioned curve fitting software method. The results so obtained are given in figure 6.4 below.

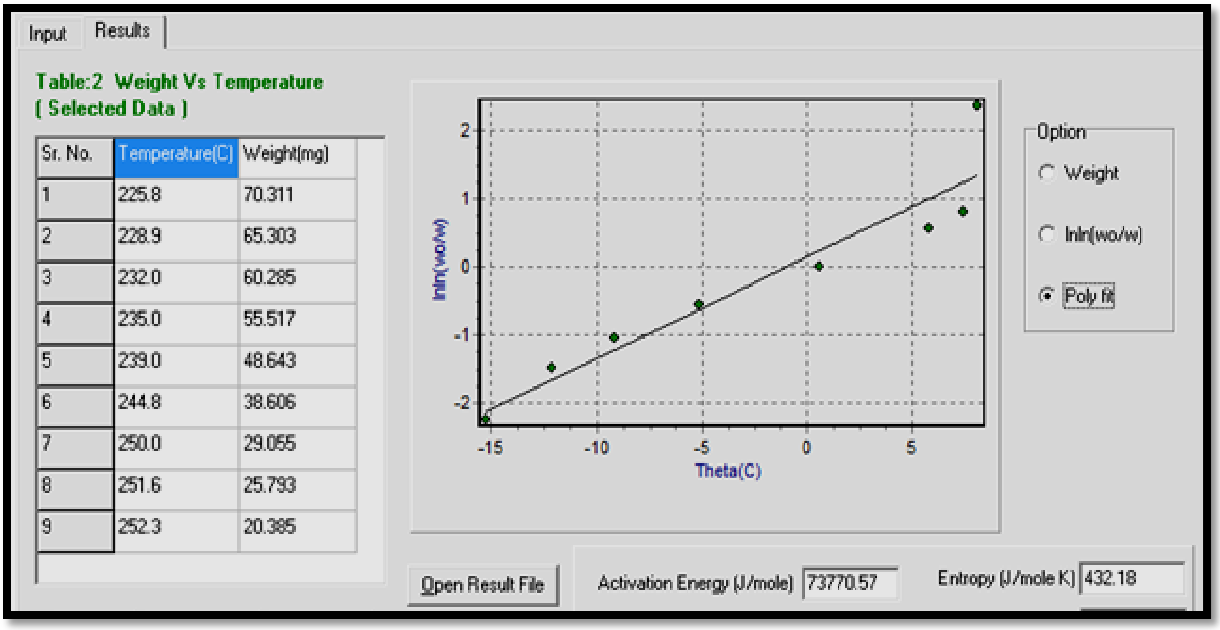

Table:2 Weight Vs Temperature
(Selected Data)

Sr. No.	Temperature(C)	Weight(mg)
1	225.8	70.311
2	228.9	65.303
3	232.0	60.285
4	235.0	55.517
5	239.0	48.643
6	244.8	38.606
7	250.0	29.055
8	251.6	25.793
9	252.3	20.385

○ Weight
○ lnln(wo/w)
● Poly fit

Activation Energy (J/mole) 73770.57
Entropy (J/mole K) 432.18

Figure 6.4 Graph for the calculation of activation energy of serviceable Composition B explosive sample – POF Lot.

From the graph it is evident that the activation energy of serviceable Composition B explosive sample under non-isothermal condition has shown to be 73.7 KJ/mole. In case of unserviceable Composition B explosive sample, activation energy was calculated to be 67.1 K J/mole.

6.3.2.4 **Discussion**

From the comparison of both these unserviceable and serviceable Composition B explosives samples, it is assumed that the decomposition of unserviceable lot has started earlier than the serviceable explosive Composition B lot. This means that with the passage of time explosive sample starts losing its characteristic value and may degrade due to absorption of moisture contents or other impurities. Similarly it has been noted that the activation energy of the unserviceable explosive has lowered with time, which means that the unserviceable Composition B explosive sample has become more sensitive and less stable than serviceable explosive lot. On comparing the results with the literature value, it has also been noted that the values of activation energy so obtained from above mentioned techniques are in quite agreement to the available data [2]. Another aspect of the analysis gave valuable information about the RDX behaviour in both the explosive Composition B samples where only the decomposition peak of RDX was shown without its melting or ignition temperature peak due to immediate effects of TNT melting point. From the above two results it could also be determined that decomposition of RDX in unserviceable Composition B started earlier than in serviceable Composition B explosive sample. This could be primarily because of the filling defects or other environmental conditions.

6.3.3 **Test No.3 (Separated Unserviceable RDX Explosive Sample)**

In order to carry out TG/DTA of separated unserviceable RDX explosive sample, 6.8 mg of said explosive sample was analysed under controlled temperature program. The results of TG/DTA are summarized as under.

6.3.3.1 **DTA Curve**

The thermal behavior of separated RDX explosive sample has been determined within a temperature range of 29^{o}C to 550^{o}C. The DTA curve of unserviceable RDX explosive sample exhibits an endothermic peak at temperature of 203.5^{o}C, which corresponds to the melting point of RDX explosive sample. The next DTA event could be determined as the exothermic decomposition of RDX shown as broad peak at temperature of 254^{o}C.

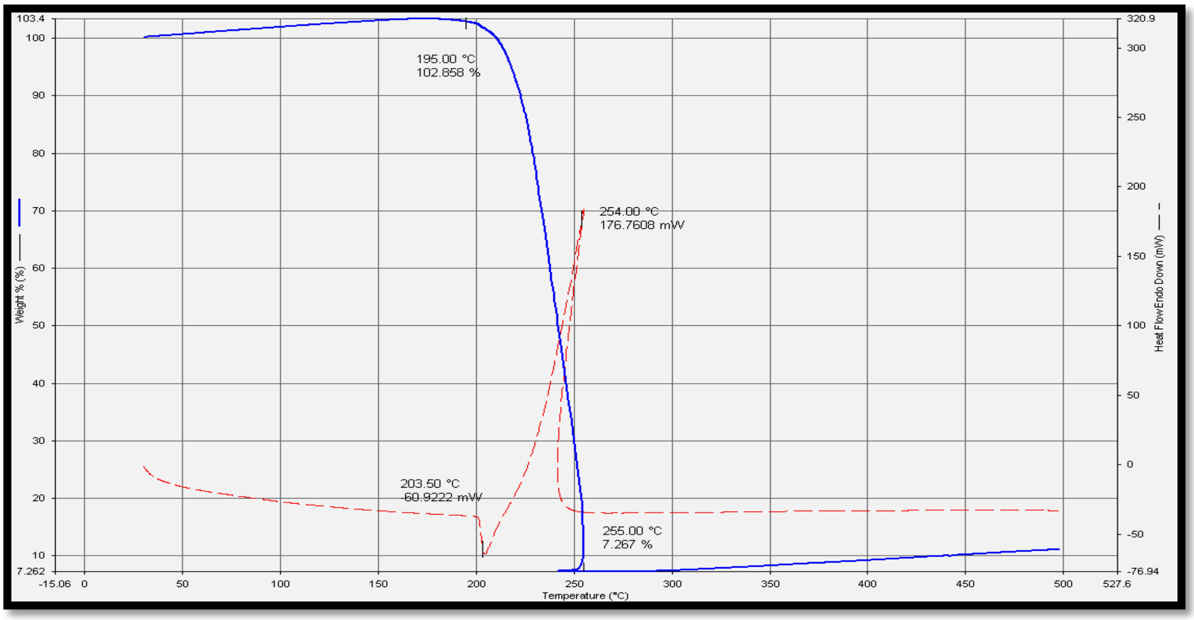

Figure: 6.5 Typical TG/ DTA curves of Unserviceable RDX explosive sample separated from Composition B.

6.3.3.2 **TG Curve**

TGA curve for the separated RDX explosive sample is also shown in figure 6.5. Thermo-gravimetric curve shows that the thermal decomposition of unserviceable RDX explosive sample occurs in a single stage. Here the loss in mass of the sample started from 195^{o}C. The rate is slow between 195-203.50^{o}C. But suddenly becomes very rapid and decomposition ends at 255^{o}C.

6.3.3.3 **Kinetic Parameters**

Activation energy of the RDX sample under analysis has been calculated using curve fitting software based Horowitz and Metzger method. The graph as shown in figure 6.6 indicates that the activation energy of the separated RDX sample under non-isothermal conditions is 75.5 KJ/mole.

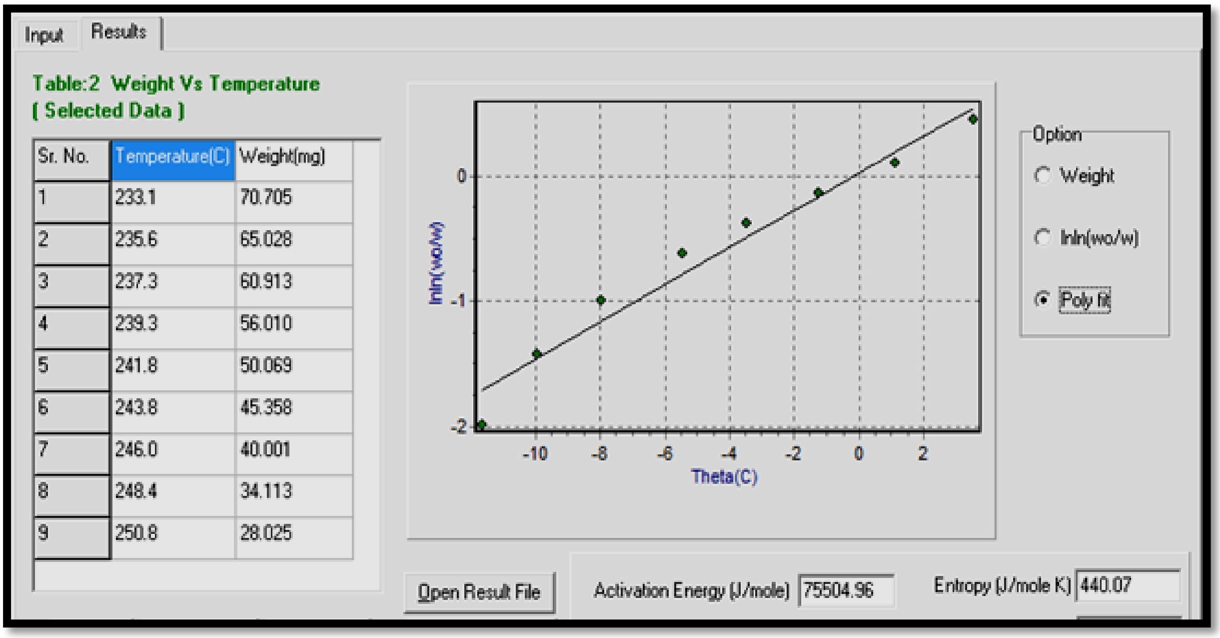

Table:2 Weight Vs Temperature
[Selected Data]

Sr. No.	Temperature(C)	Weight(mg)
1	233.1	70.705
2	235.6	65.028
3	237.3	60.913
4	239.3	56.010
5	241.8	50.069
6	243.8	45.358
7	246.0	40.001
8	248.4	34.113
9	250.8	28.025

Option
○ Weight
○ lnln(wo/w)
● Poly fit

Activation Energy (J/mole) 75504.96

Entropy (J/mole K) 440.07

Figure 6.6 Graph for the calculation of activation energy of separated unserviceable RDX explosive sample.

6.3.3.4 Discussion

The separated RDX explosive sample has been subjected to thermal analysis in order to study its thermal stability and to find out other kinetic parameters like activation energy. From figure 6.5, two curves have been identified for DTA and TGA of the sample under investigation. From DTA curve it has been observed that separated unserviceable RDX explosive sample started melting at the temperature of 203.5^{o}C, which is an endothermic decomposition of the sample. Simultaneously a broad exothermic peak at the temperature of 254^{o}C corresponds to the thermal decomposition of RDX sample under study. It has also been observed that pure RDX sample clearly exhibited an endothermic peak for its melting point which was not indicated in the DTA curve of Composition B explosive samples. Similarly Thermo-gravimetric study of the separated RDX explosive sample depict that thermal decomposition of the sample took place between a temperature range of 195-255^{o}C.

6.3.4 Test No.4 (Serviceable RDX Explosive Sample –POF Lot)

Serviceable sample of pure RDX received from POF Wah was analysed for its thermal behavior and kinetic parameters in comparison to the separated unserviceable RDX explosive sample. For the purpose, 6.73 mg of pure RDX sample was analysed under controlled temperature program and simultaneous TG/DTA curve were obtained which are discussed below.

6.3.4.1 **DTA Curve**

The thermal behavior and kinetic parameters of pure serviceable RDX explosive sample has been determined using above stated condition where the sample was analysed within a temperature range of 29^{o}C to 550^{o}C. Here the DTA curve of serviceable RDX explosive sample shows an endothermic peak at approximately 204.60^{o}C, which is clearly the melting point of a serviceable RDX. Similarly an exothermic intense peak for the decomposition of Pure RDX explosive sample has been observed at temperature of 250.40^{o}C. Since the rate of decomposition becomes extremely rapid after melting point of the sample under investigation, therefore no visible peak is obtained for the ignition of RDX.

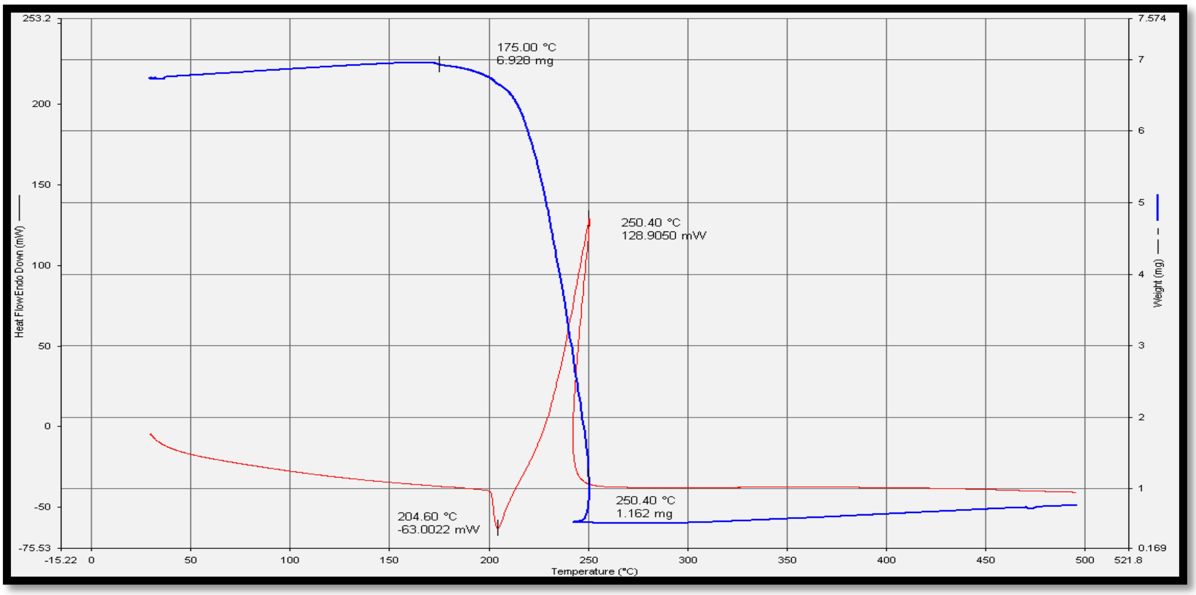

Figure: 6.7 Typical TG/ DTA curves of serviceable RDX explosive sample- POF Lot.

6.3.4.2 **TG Curve**

Thermo-gravimetric study of pure RDX explosive sample shows that sample starts to decompose at 175^{o}C and remains moderate till 204.60^{o}C. Similarly it has been observed that the decomposition of serviceable RDX explosive sample attains a peak maximum at 250.4^{o}C where the thermal decomposition of the sample under study completes. Similarly it has been determined from the TGA curve that decomposition of pure RDX sample takes place in single stage.

6.3.4.3 **Kinetic Parameters**

After obtaining typical TGA curve of pure RDX sample, kinetic parameters of the sample have been calculated with the help of Horowitz and Metzger method. The activation energy of the pure RDX explosive sample has been calculated as 200 KJ/mole which is in agreement to the literature value of pure RDX. Figure 6.8 shows the calculated value for the activation energy of pure RDX sample under investigation.

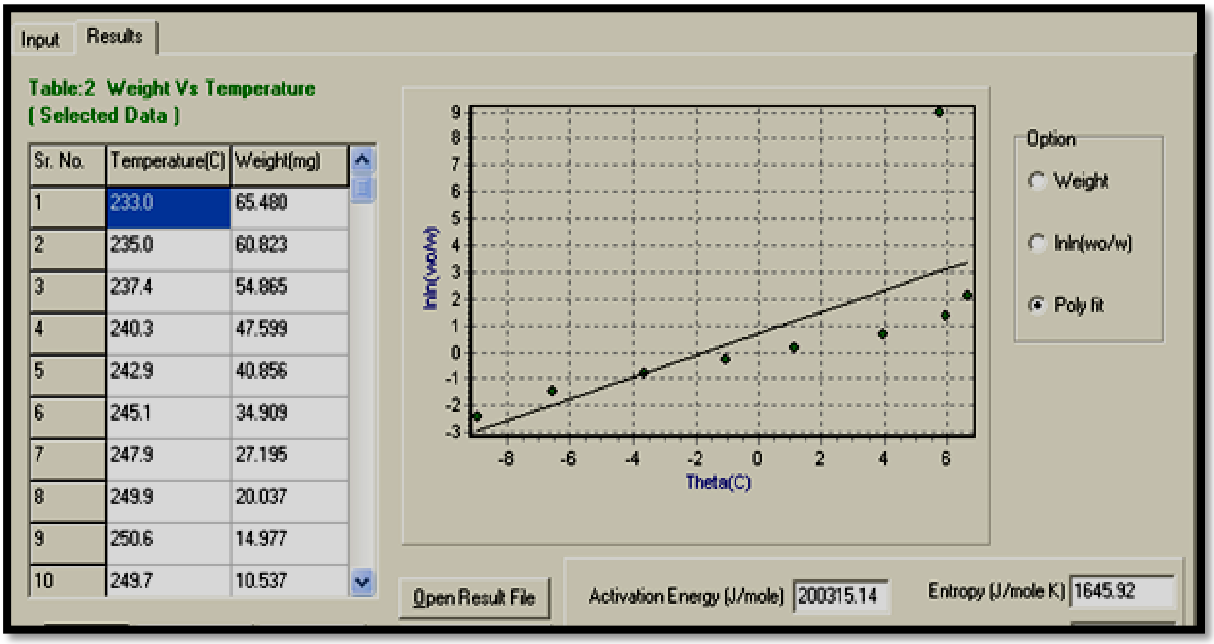

Table:2 Weight Vs Temperature
(Selected Data)

Sr. No.	Temperature(C)	Weight(mg)
1	233.0	65.480
2	235.0	60.823
3	237.4	54.865
4	240.3	47.599
5	242.9	40.856
6	245.1	34.909
7	247.9	27.195
8	249.9	20.037
9	250.6	14.977
10	249.7	10.537

○ Weight
○ lnln(wo/w)
● Poly fit

Activation Energy (J/mole) 200315.14

Entropy (J/mole K) 1645.92

Figure 6.8 Graph for the calculation of activation energy of serviceable RDX explosive sample.

6.3.4.4 **Discussion**

After comparative study of both the serviceable and unserviceable RDX explosives samples, it has been observed that the activation energy of serviceable RDX explosive sample is 200 KJ/mole [3], whereas activation energy of separated RDX explosive sample is calculated as 75 KJ/mole. This clearly shows that separated RDX explosive sample has become more sensitive and thermally unstable with the passage of time. This is primarily because of the presence of any impurities during filling, formulation in the Composition B explosive mixture or may be due to moisture ingress inside the munitions during long storage life. This has ultimately led to the degradation or deterioration of the RDX explosive melt-cast with TNT in Composition B explosive mixture. It has also been observed that decomposition of separated RDX sample started decomposing at relatively later stage as compared to the serviceable lot. It means the sample could contain some other impurities which have shifted the decomposition of RDX from 175°C in pure RDX sample to 195°C in separated RDX explosive sample. Thus the presence of impurities greatly affects the thermal behaviour and kinetic parameters in any particular explosive mixture. Comparison of both samples clearly indicates that the thermal decomposition of RDX explosive is highly exothermic in nature with single step decomposition reaction. Also the behavior of RDX decomposition in a Composition B explosive mixture is quite different then in pure form. As RDX was observed to decompose immediately after the melting of TNT in composition B explosive samples and its melting or ignition temperature was overrun. On the other hand, separate peaks for the endothermic and exothermic decomposition of RDX were obtained during the DTA of pure RDX samples.

6.3.5 **Test No.5 (Separated Unserviceable TNT Explosive Sample)**

6.5 mg of unserviceable TNT explosive sample separated from Unserviceable Composition B explosive has been analysed as under:

6.3.5.1 **DTA Curve**

The thermal behavior of unserviceable TNT explosive sample has been observed within a temperature range of 25°C to 550°C. The DTA curve of unserviceable TNT explosive sample exhibits an endothermic peak at 82.3°C, corresponding to the melting point of TNT under non-isothermal conditions as shown in figure 6.9. The next endothermic broad peak has been shown at temperature of 240.1°C, which shows an endothermic decomposition of TNT sample.

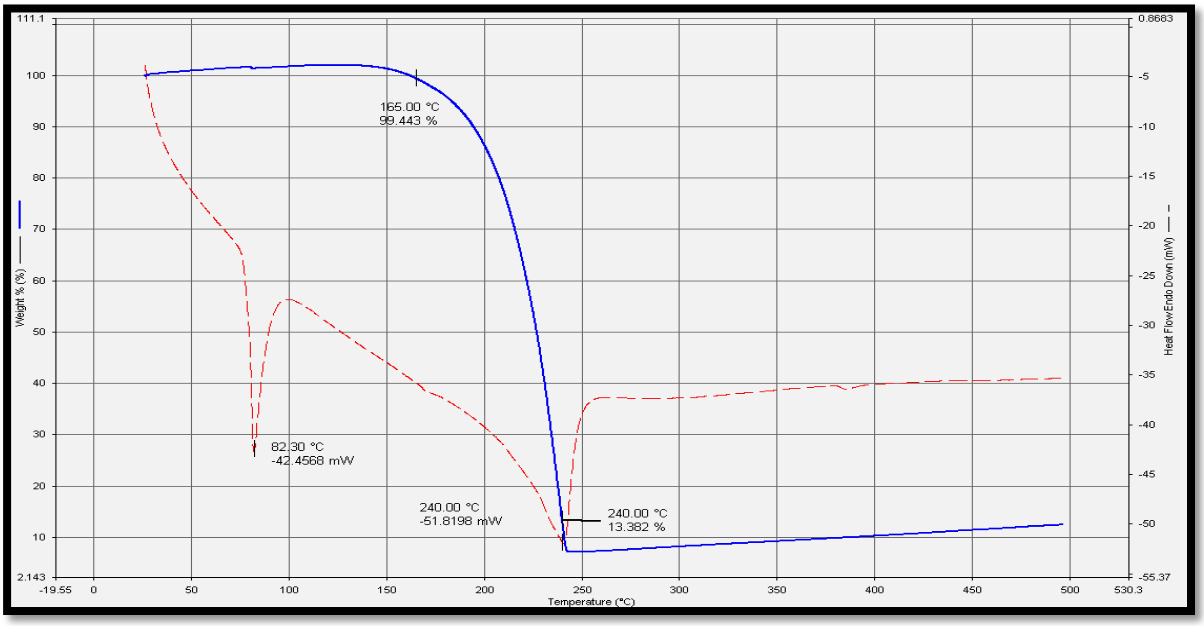

Figure: 6.9 Typical TG/ DTA Curve of Unserviceable TNT explosive sample.

6.3.5.2 **TG Curve**

Figure 6.9 also shows a TGA Curve for recovered unserviceable TNT explosive sample. The endothermic decomposition of unserviceable TNT explosive sample starts near 165^{o}C and completes at 240^{o}C. The total weight loss over the temperature range of 165-240^{o}C was found to be 97%. TGA curve also indicate that the thermal decomposition of unserviceable TNT explosive sample under investigation is a single stage reaction.

6.3.5.3 **Kinetic Parameters**

Activation energy of unserviceable TNT explosive sample has been determined directly from the TGA curve so obtained, with the help of Horowitz and Metzger Method. A graph used for the calculation of activation energy is shown in figure 6.10 below.

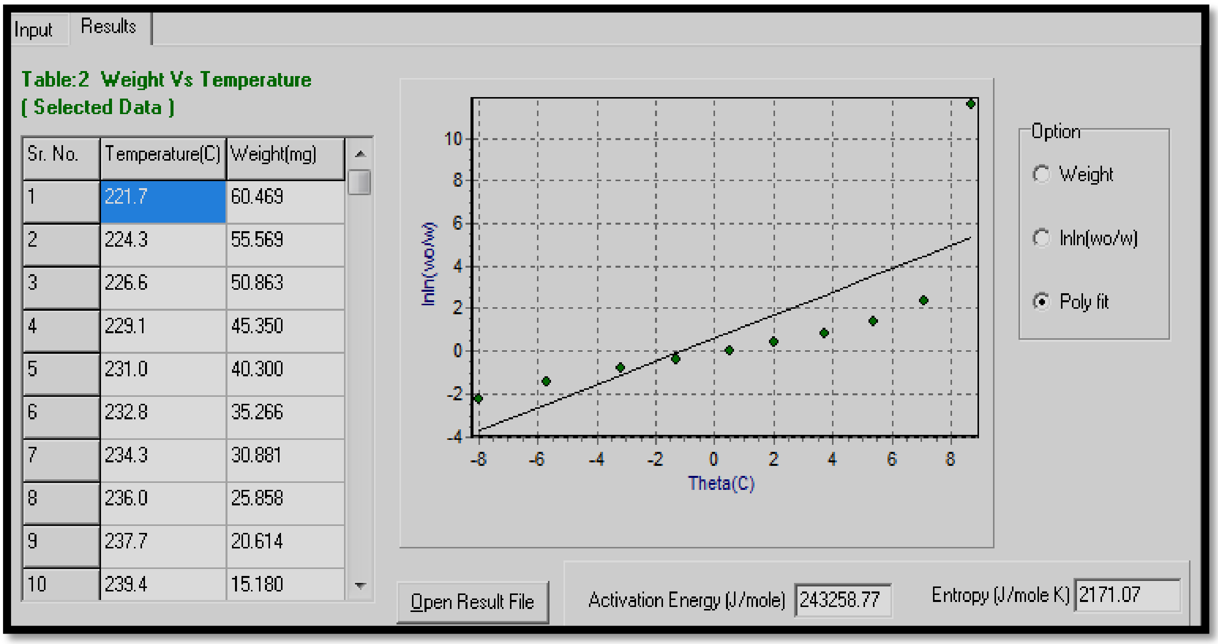

Table:2 Weight Vs Temperature
(Selected Data)

Sr. No.	Temperature(C)	Weight(mg)
1	221.7	60.469
2	224.3	55.569
3	226.6	50.863
4	229.1	45.350
5	231.0	40.300
6	232.8	35.266
7	234.3	30.881
8	236.0	25.858
9	237.7	20.614
10	239.4	15.180

Option
○ Weight
○ lnln(wo/w)
● Poly fit

Activation Energy (J/mole) 243258.77

Entropy (J/mole K) 2171.07

Figure 6.10 Graph for the calculation of activation energy of separated unserviceable TNT explosive sample.

This graph shows that activation energy of unserviceable TNT explosive sample under controlled temperature program is very large i.e. 243.5 KJ/mole.

6.3.5.4 **Discussion**

From the resultant data obtained from TG/DTA technique and Horowitz and Metzger method, it has been observed that unserviceable TNT explosive sample under long storage life has attained an activation energy of 243.5 KJ/mol which is quite large as compared to the literature value for the serviceable TNT i.e. 222 KJ/mole [4]. Also a single stage decomposition of the separated unserviceable TNT explosive sample has been observed from the TGA curve.

6.3.6 **Test No.6 (Serviceable TNT Explosive Sample – POF Lot)**

A pure sample of 6.52 mg of serviceable TNT received from POFs Wah has been investigated and thoroughly studied for their thermal behavior and kinetic parameters within a temperature range of 30^{o}C to 550^{o}C. Further interpretation of the results obtained is given below.

6.3.6.1 **DTA Curve**

The thermal behavior and thermal stability of well-known pure TNT has been observed with the available method. The DTA curve of serviceable TNT explosive sample exhibits an endothermic peak at 82.81^{o}C, which is the melting point of TNT under controlled temperature program as shown in figure 6.9 below. The next broad peak, as shown in figure 6.9, is an endothermic peak indicating the thermal decomposition of pure TNT explosive sample. The decomposition of the sample completes at 234.98^{o}C.

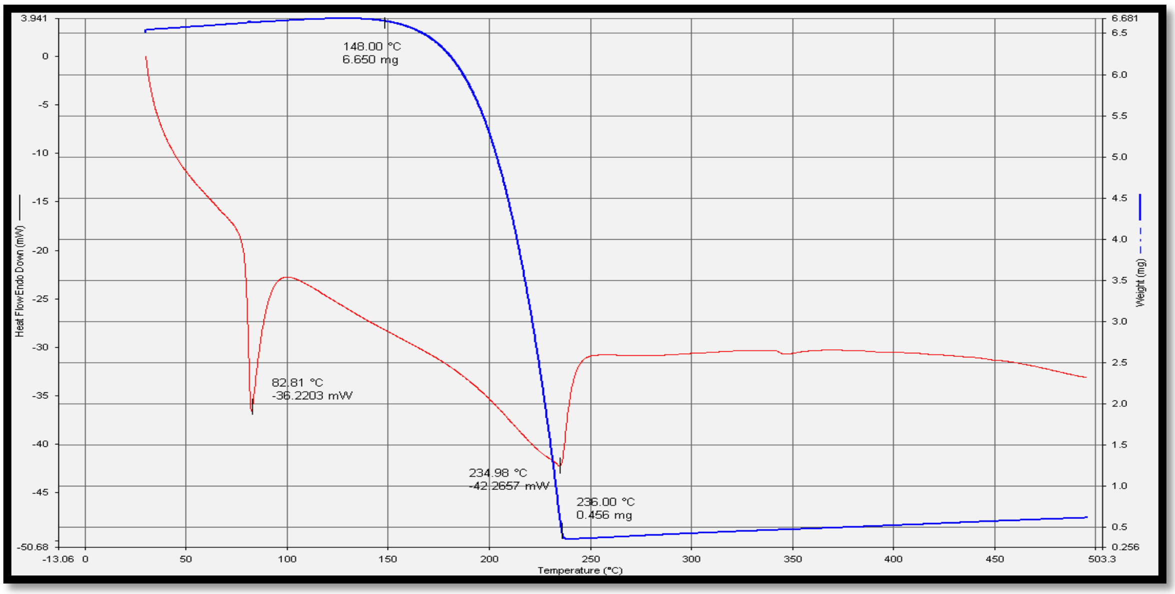

Figure: 6.11 Typical TG/ DTA Curve of serviceable TNT explosive sample – POF Lot.

6.3.6.2 **TG Curve**

Thermo-gravimetric curve for the serviceable TNT sample has been observed as shown in figure 6.11. From TGA curve it has been determined that thermal decomposition of serviceable TNT explosive sample occurs in a single stage between temperature range 148^{-} 236^{o}C. Similarly TG curve indicates that around 95% weight loss of serviceable TNT sample occurs during the entire thermal event.

6.3.6.3 **Kinetic Parameters**

Kinetic parameter like activation energy of serviceable TNT explosive sample has been determined using Horowitz and Metzger method. Result from the TGA curve indicates that serviceable TNT explosive sample has activation energy of 222.1KJ/mole, which is in agreement to the available literature value. The same result has been shown in figure 6.12 below.

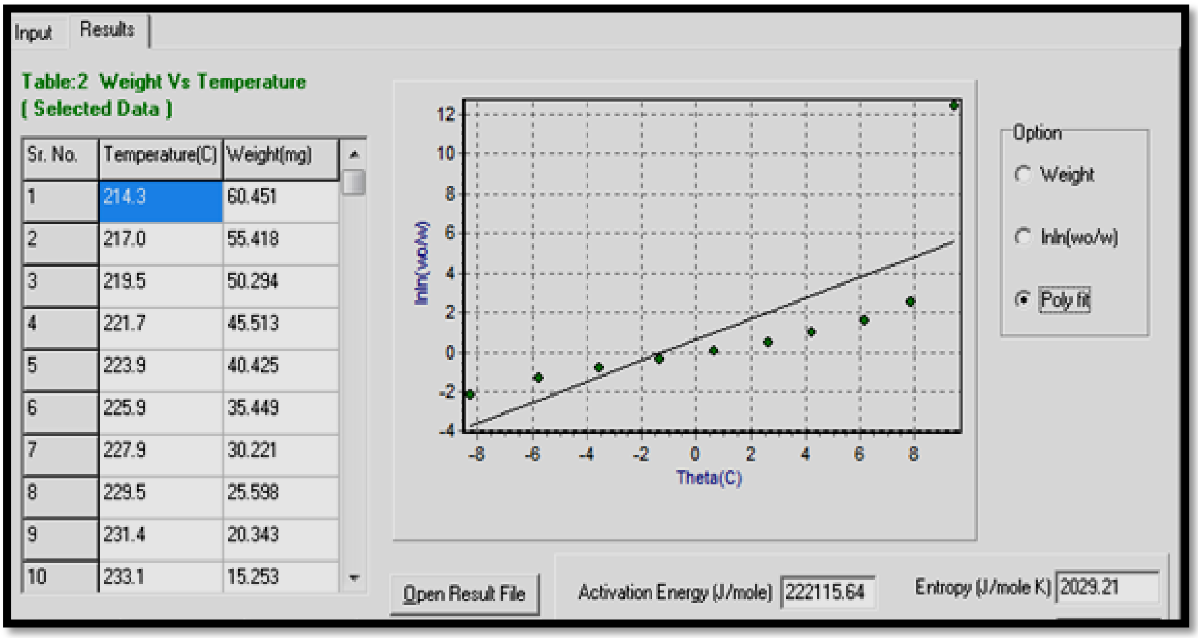

Table:2 Weight Vs Temperature
(Selected Data)

Sr. No.	Temperature(C)	Weight(mg)
1	214.3	60.451
2	217.0	55.418
3	219.5	50.294
4	221.7	45.513
5	223.9	40.425
6	225.9	35.449
7	227.9	30.221
8	229.5	25.598
9	231.4	20.343
10	233.1	15.253

Option
○ Weight
○ lnln(wo/w)
● Poly fit

Activation Energy (J/mole) 222115.64

Entropy (J/mole K) 2029.21

Figure 6.12 Graph for the calculation of activation energy of pure serviceable TNT explosive sample.

6.3.6.4 **Discussion**

From the comparative study of both the serviceable and unserviceable TNT explosive samples, it has been observed that pure serviceable TNT explosive sample has activation energy of 222.1 KJ/mole whereas unserviceable TNT explosive sample yield activation energy of 243.4 KJ/mole. It means that serviceable TNT will result into a better performance in regards to its thermal stability and sensitivity. Its rate of thermal decomposition and activation energy are well defined. Whereas unserviceable explosive compounds shows lots of variation in their thermal stability and sensitivity. This means that with the passage of time, moisture contents may have affected serviceability of the TNT and resulted into change of its chemical or physical properties such as increase in activation energy and stability. This increase in activation energy of the explosive charge has negative impact on its thermal sensitivity and stability because thermally stable compound are more difficult to detonate and may lead to a shell blind or dud during fire.

6.3.7 **Summary of the Results**

A summary of results obtained during the entire research work for the explosives samples investigated are given in table 6.1 below.

Table: 6.1 Summary of explosives result.

S.No	Explosive	M/ Pt (^{o}C)	Literature Value for M/Pt (^{o}C)	Calculated Ea (KJ/mole)	Literature Value for Ea (KJ/mole)	Decomposition Range (^{o}C)
1	Unsvc Comp-B	80.71	-	67.1	67$\pm$2% [#]	151.04 – 250
2	Svc Comp-B	84.18	80.9	73.7	66.7$\pm$3.6% [#]	160 – 252.59
3	Unsvc RDX	203.5	-	75.5	-	195 – 254
4	Svc RDX	204.6	204.1	200	199[*]	175 - 250.4
5	Unsvc TNT	82.3	-	243.5	-	165 – 240
6	Svc TNT	82.81	80.9	222	222[*]	148 – 236

Table 2 of Thermochimica Acta by J.-S. Lee, C.-K. Hsu 367-368 (2001) 371-374.

* Values obtained from Explosive Ordnance and engineering Thermodynamics by Akhavan J.MH190B. Ext 2324.

Thermal stability and sensitivity of any particular explosive are directly related to the kinetics and mechanism of thermal decomposition [5]. Besides, further investigation of weight loss and melting point of any explosive is equally important. After carrying out a detailed study of the different explosive samples, it has been revealed that most of the explosive substances lose their stability and sensitivity with the passage of time and are affected by the presence of impurities during melt-cast filling or may be due to moisture ingress during storage, transportation or even handling of the munitions. This may give rise to fire, toxic and possible explosion hazard [6]. Results from the TG/DTA technique calculated by Horowitz and Metzger method are quite accurate and show values for the explosive samples that are in quite agreement with the literature values. In case of unserviceable TNT explosive sample separated from Composition B explosive, increase in the activation energy of the TNT sample has been observed which could be related to the significant reduction in sensitivity and increase in thermal stability of the explosive. Since all explosives are designed to give higher performance coupled with adequate stability and sensitivity to various stimuli, therefore, larger variation in the increase of thermal stability could give another manifestation that the material may become too insensitive to initiate and could result into misfire or blind. Similarly lowering of the activation energy, as observed in case of unserviceable Composition B and separated RDX explosive sample, means that the explosive samples have become more susceptible to external shock/ friction or other means of stimuli. Thus the desired characteristics of explosive stability and sensitivity are compromised and may eventually lead to accidental initiation or fire of the munitions.

6.4 **Conclusion**

The present study on the various military high explosive samples has given better understanding and comprehensive knowledge on their thermal-cum kinetic parameters. After going through these tests, it is also clear that explosive sample gets deteriorated and degraded during long shelf life due to the presence of moisture contents and other impurities. Storage condition also dictates its serviceability and performance which means that adequate storage of the munitions and their proper handling may result into better performance and increase in the munitions life. Efforts to convert unserviceable explosive materials into vital energetic materials can be made with the help of available chemicals thereby decreasing budget deficit and may convert huge expenditure on the traditional explosive materials towards more demanding advance energetic materials. Simultaneously the explosive samples so separated can be easily formulated and converted into commercial explosives or even they may be used in other applications.

Since explosive filling, formulation and manufacture is a classified work throughout the world, therefore very little work on the subject can be found in the published literature. The present project on the separation of different explosive substance from a mixture and study of their thermal behavior and kinetic parameters has, therefore, significant value and School of Chemical and Materials Engineering, SCME, NUST has earned a unique status in this particular field.

6.5 **Problem faced/ Bottle necks**

- Procurement or timely availability of energetic materials/ raw materials and required chemicals.
- Up-gradation of laboratory facilities.
- Enhancement of the field laboratory facilities.

6.6. **Future Recommendations**

Following are suggested for the coming days.

- The present work for the separation of RDX and TNT from unserviceable Composition B explosive may be undertaken at pilot and industrial scale so that bulk quantity of the unserviceable explosives filled in various munitions held with Pakistan Army may be converted into commercial explosives.
- TG/DTA study may also be carried out on pyrotechnics and propellants to gain better understanding of their stability and re-utilization
- Various other related techniques like XRD, SEM, Bomb Calorimetry, Micro Calorimetry, Elemental Analysis, FT-IR, GC-MS, etc. may be employed for gaining better understanding of the science of energetic materials.
- Present work may be extended at PhD level to enhance further understanding of the energetic materials.

REFERENCES

[1] Explosives,Propellants &Pyrotechnics by Bailey A & S. G Murray. Volume- 2, Page-147.

[2] A study on the thermal decomposition behaviors of PETN, RDX, HNS and HMX by J.-S Lee et al./ Thermochimica Acta 392-393 (2002), pp.173-176.

[3] Explosive Ordnance and engineering, Therrmodynamics by Akhavan J. MH 190B. Ext 2324. Page-16.

[4] Explosive Ordnance and engineering, Therrmodynamics by Akhavan J. MH 190B. Ext 2324. Page-16.

[5] A study on the thermal decomposition behaviors of PETN, RDX, HNS and HMX by J.-S Lee et al./ Thermochimica Acta 392-393 (2002), pp. 173-176.

[6] Explosives, Propellants &Pyrotechnics by Bailey A & S. G Murray. Volume- 2, Page-156.