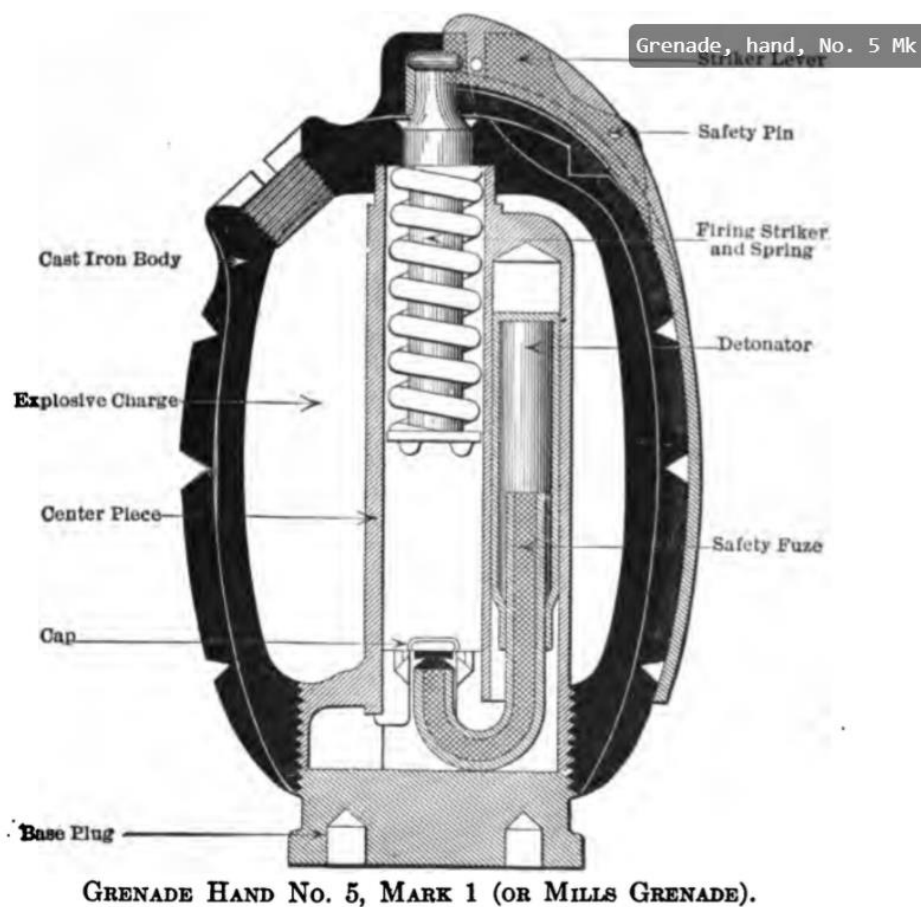


BSc (Hons.)/BEng (Hons.) Ordnance, Munitions and Explosives

ACDA4011 – Level 4 Chemistry OME Assignment



[1]

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Abstract

This report gives an insight into the underlying principles by which a fragmentation grenade (as on front cover) functions, both mechanically and chemically. The differences in the chemical properties of the different types of energetic substance, give a distinction between how they react when initiated, from the combustion of the pyrotechnic delay, to the deflagration albeit it rapid of confined black powder, the sensitivity to impact igniting primary explosive and the relatively insensitive, but much more powerful secondary explosive. The explosive train for such a device is intended to be impetus (firing striker), to Primer TW5 (Tetrazene + Paraffin Wax), which initiates the manganese, tin and bismuth oxide delay composition, this burns at a steady rate and provides enough energy to ignite the confined black powder cap which deflagrates rapidly enough to shock the nitroglycerine (secondary explosive) within the dynamite composition of the main charge. The high brisance of the dynamite causes the serrated outer shell of the grenade to shatter and sends fragments at high velocity in all directions, giving the main effect. The heat heats and exothermicities of the components and chemical, physical properties are also described.

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1. Introduction

1.1. The Problem

A report is required detailing the ignition train of a military hand grenade that is needed to achieve top level function as follows:

A simple explosive device will have a simple top level functionality

The ignition train of the device will be as follows:

Initiate ignition train, Provide time delay, initiate main effect, provide main effect.

For each phase in the grenades' ignition train the materials that may be considered for use must be described.

All reactions should have a balanced chemical equation, calculation for heat released, exothermicity and a description of the mechanism for energy release.

A description of the proposed ingredients and compounds chemical and physical properties should be given, as well as an indication of any characteristics, which might affect the long term performance of the product.

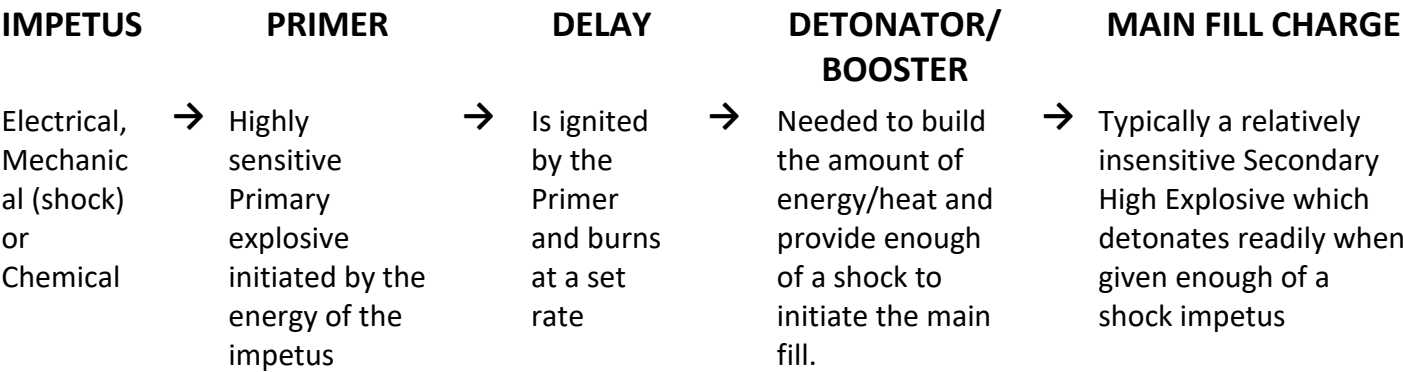
For the proposed energetic compounds the processes of manufacture and proposed methods of control for critical features must be outlined. [2]

1.2. Theory – Explosive Train

When attempting to light a fire not only do you need all three sides of the fire triangle (Fuel, Oxygen and Heat), but your fuel also needs to be in scale with the heat provided. This means that it would be very difficult to start a fire with a log and a match. The best approach therefore is to match the heat to the fuel, as each fuel burns a greater amount of heat is released to ignite the next large fuel source. So from a match to a log fire would go:

Match → Paper → Kindling → Log

In an explosives train a similar principle exists, in that each stage requires a larger amount of energy to initiate the next stage of the process, this is known as the Activation Energy (AE). The AE is provided by the process in the train before. A typical explosives train could be:



2. Method

2.1. Hand grenade function and design

Current designs of hand grenade will be researched and studied, to give an understanding of the ignition systems commonly utilised, in both foreign and domestic hand grenades. As well as, how the explosive or ignition train functions within a hand grenade.

The common types of both primary and secondary explosives used in hand grenade explosives train will be researched by way of literature review and will largely be sourced by electronic means (due to current COVID-19 restrictions inhibiting use of physical texts).

Data sheets will be used to ascertain figures for bond energies to allow calculation of Heats of Formation (ΔH) and exothermicity of the chemical compounds chosen for said device. These will also be used in combination with various databases to find information on the chemical and physical properties of such chemical compounds, in particular those properties that might affect the long term performance of the product.

Finally the processes by which the energetic materials selected for said device, are manufactured and possible methods for critical features could be controlled.

All citations and diagrams or pictures will be fully referenced in the reference section.

3. Results

3.1. Hand Grenade mechanisms

Research was carried out as described above and the following information attained:

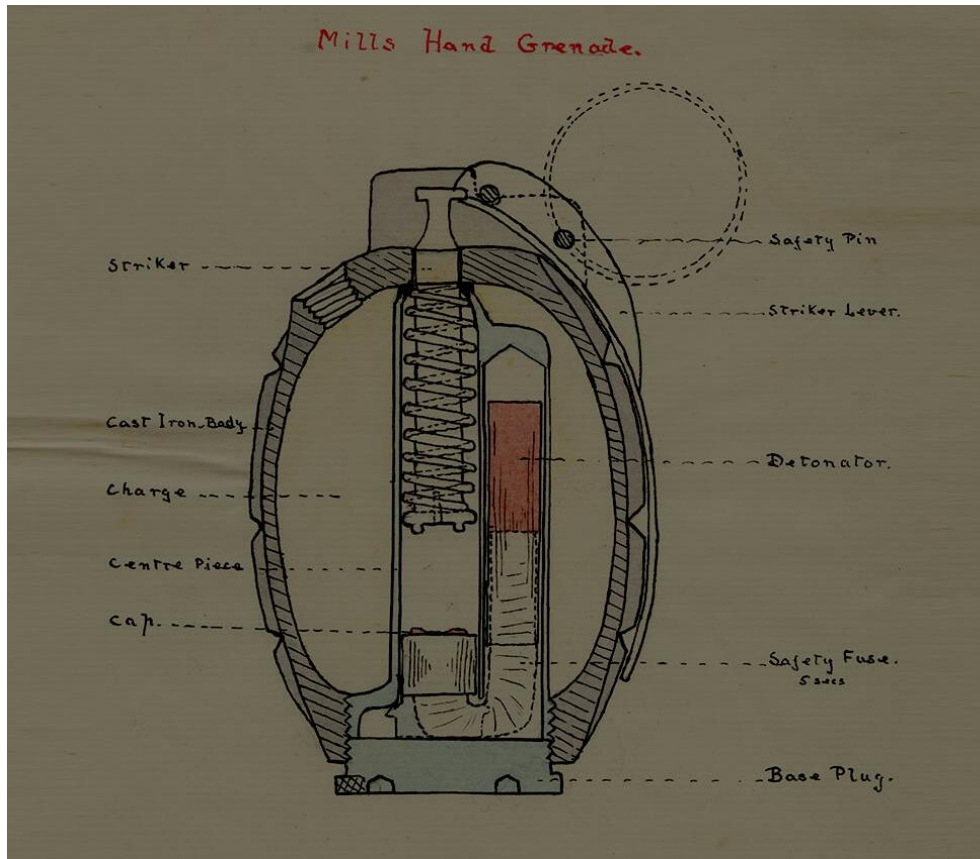


Figure 1: Example of Time delay Mills Grenade [3]

The common methods for hand grenade initiation/ignition sequence seem to be one which is initiated by a mechanical means i.e. a spring loaded striker which is released when the safety pin is pulled and the fly-away lever is released. This provides a shock impetus to a highly sensitive (i.e. low F of I) primer (Primary explosive) which is housed within a percussion cap. As the percussion cap is struck it detonates, providing enough heat and kinetic energy (by way of a shock wave) to ignite the safety Fuze or time delay composition. A typical setup can be seen above in Figure 1. the Mills Bomb or Mills Hand Grenade. [3]

The delay composition has a burn rate which typically allows a 4-5.5 second delay until the burn front reaches the detonator, again with sufficient heat and kinetic energy to initiate the detonator. The detonator then detonates causing an even larger amount of thermal (heat) and kinetic energy to be transferred to the relatively insensitive main charge or secondary explosive. An explosive with a high brisance or shattering effect is then used to produce a force on the outer skin of the grenade, typically the surface of which will be serrated or scored to aid fragmentation of the outer shell.

There are other forms of ignition such as electrical or chemical. The striker pin is then projected downward by the spring causing the striker pin to strike a percussion cap. The percussion cap detonating provides enough energy to ignite the time delay composition as above, meaning that there is enough

energy supplied to meet the activation energy (AE) requirements. The fuze composition is such that it provides sufficient energy to initiate the detonator i.e. the detonators activation energy (AE). The detonator can be a primary explosive that is very sensitive and as such does not require much of a stimulus to detonate and in doing so providing the AE required by the less sensitive secondary explosive which is the main fill or main charge. On detonation the main charge causes a lot of heat, gas, pressure, sound and light to be generated. This rapid expansion causes the case to fragment. The fragments of metal are projected in all directions at high velocity giving the grenade its' main effect.

So given the Mills Grenade as a typical example what are the different types of explosive that could be used typically for each stage of the initiation train?

3.2. Explosives

The properties of different types of explosive make them particular useful in different parts of the explosive train, dependant on the desired effect. According to Malcolm Fox and the chapter: *Initiating Explosives. In: Glossary for the Worldwide Transportation of Dangerous Goods and Hazardous Materials*. Different types of High Explosives' properties are as follows:

"Primary syn. initiator explosives, those most sensitive to heat, shock, electric spark, friction, and impact. They are usually high explosives such as the fulminates and lead azide, although lead azide may be sensitized with a small amount of lead styphnate.

Secondary explosives, those that do not easily go from deflagration to detonation, do not initiate electrostatically with ease, and require larger shocks to detonate. They include nitrocellulose, PETN, and desensitized nitroglycerine.

Tertiary explosives, those most difficult to detonate. They include extremely powerful high explosives like RDX and HMX." [4]

3.2.1. Primary explosives mixtures

The initiator part of the explosive train will be a primary explosive contained within a percussion cap, which when struck will ignite and start the train. The following are examples of some Primary explosives as given in *The Chemistry of Explosives by Jacqueline Akhavan* [5]:

- Mercury Fulminate
- Lead Azide
- Lead Styphnate
- Silver Azide
- Tetrazene
- TW5 (Tetrazene + Paraffin wax) [6]

3.2.2 Delay composition options

A pyrotechnic delay composition will burn for a predetermined amount of time from the point of ignition to end effect. These compositions can be divided into gassy and gasless compositions. Gassy compositions tend to be used in vented environments and gasless in more confined conditions. For gassy compositions such as black powder can be used. For gasless compositions mixtures of metal oxides or metal chromates with an elemental fuel can be used. Some examples of which are below [5]:

- Black powder (gassy)
- Tetranitrocarbazole and potassium nitrate (gassy)
- Boron, silicon and potassium dichromate (gasless)
- Tungsten, barium chromate and potassium perchlorate (gasless)
- Lead chromate, barium chromate and manganese (gasless)
- Chromium, barium chromate and potassium perchlorate (gasless)
- Bismuth oxide, manganese and tin (gasless) [7]

3.2.3. Detonator options

Dependant on the energy provided by the delay composition a detonator/booster may be needed to produce enough heat and perhaps more importantly shock, needed to initiate the relatively insensitive secondary explosive (main fill).

The main fill is normally a primary explosive (as in section 3.1.). Though if a gassy black powder is confined, the gas produced will push the burning front forward increasing the burn speed dramatically and giving the required shock for ignition of secondary explosives, such as nitroglycerine in Dynamite.

3.2.4. Secondary explosive options

The following are examples of secondary explosive that are given by *Jacqueline Akhavan in 'The Chemistry of Explosives' (2011)* [5]:

- | | |
|------------------|-----------------|
| • Nitroglycerine | • TATB |
| • Nitrocellulose | • HNS |
| • Picric Acid | • NTO |
| • Tetryl | • TNAZ |
| • TNT | • CL-20 |
| • Nitroguanidine | • Fox-12 (GUDN) |
| • PETN | • DNAN |
| • RDX | • FOX-7 (DADNE) |
| • HMX | • LLM-105 |

4. Discussion

4.1. Favoured options

4.1.1. Percussion Cap Primer composition

After reviewing the different options for grenade initiation it was decided that striker pin in combination with a percussion cap was a good method of initiation, which has been used for a very long time. Looking at the options for primary explosive (section 3.2 and 3.2.1.) it became apparent that the options were very toxic, all of which included heavy metals, apart from Tetrazene or 1-(5-tetrazolyl)-3-guanyl tetrazine hydrate.

The final option which was thought best suited to being used as a priming composition was a new invention called TW5 [6], this composition is a combination of Tetrazene and paraffin wax, as Tetrazene is too sensitive to be used on its own and therefore is used as a sensitizer much like Lead Styphnate. The advantages of this combination besides relatively lower toxicity is that in the TW5 composition the paraffin wax fills the boundaries between the tetrazene crystals, forming a protective layer and helps bind them together, which prevents friction between the crystals, helping to passivate the composition and allowing it to be pressed into shape for use in the percussion cap.

4.1.2. Delay Composition

As discussed in section 3 there are two main types of chemical delay which are used, these can be gassy and gasless. Gassy compositions tend to be used in pyrotechnics such as fireworks, where the gas can be vented to the outside while propagating the burn front. If a gassy black powder for instance is used in a confined space such as a grenade, it could burn very quickly, as the gas produced can push the burn front forward and although black powder does not undergo Deflagration to Detonation Transition (DDT) very readily it can provide a good shock due to the velocities achieved in confinement of about 1300m/s [8], but due to this velocity increase would probably not make a brilliant choice of delay, as it could burn too quickly. Therefore the choice of a gasless or metal (fuel) /oxidizer composition is better suited, such as, a mixture of Bismuth oxide, Manganese and tin, which gives a slow burning (gasless), delay composition.

4.1.3. Booster/Detonator and Main charge

As mentioned previously in sect 3 black powder can have a much higher velocity of deflagration if confined, therefore the explosive train can utilise the energy from the burn front of the delay composition to ignite a small cap of black powder, to ignite the main charge of dynamite as described here: "*Dynamite is detonated by lighting a simple cord fuse, which carries a flame to a small cap of low explosive black powder; the ignition of the black powder causes a shockwave to propagate through the nitroglycerine—initiating detonation.*" [9] This detonation causes a high brisance, the shattering effect causes the outer case of the grenade to fragment, sending high velocity metal fragments in all directions giving top level function.

4.2. Heat of Combustion/Detonation and Exothermicity

The Heat of Detonation of an explosive can be used to calculate the exothermicity of the explosive or kJ of energy per gram of explosive.

To calculate the Heat of Detonation the following steps are needed:

1. A balanced equation is needed for the detonation reaction, before the equation can be balanced the
2. Detonation products must be calculated.
3. K-W or modified K-W Rules must be used
4. To know which set of rules apply the Oxygen Balance (OB - Ω) must be calculated

The Heat of Detonation/Combustion (ΔH_d) = $\sum H_f(\text{Products}) - \sum H_f(\text{Reactants})$

Most direct enthalpy changes can't be easily measured for detonations i.e. route 1 above, but Heats of Formation can be, where the Heat of Formation is defined as:

Hess's Law:

The enthalpy change accompanying a chemical change is independent of the route by which the chemical change occurs.

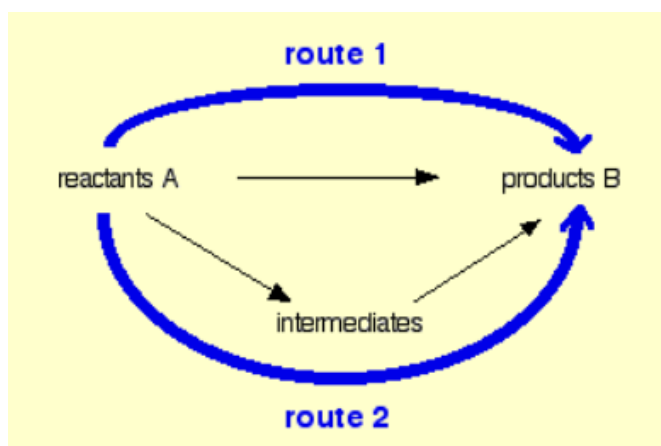


Figure - 2.0: Hess's Law and Hess's Cycle from ChemGuide.co.uk [10]

Oxygen Balance (OB - Ω) = $\frac{([d-(2a)-(\frac{b}{2})] \times 1600)}{M_r}$, when the generic formula for the explosive compound is in the format: $C_aH_bN_cO_d$ and M_r = molecular mass (g mol^{-1})

Primer - Tetrazene

Chemical formula: $C_2H_8N_{10}O$

$$\text{Oxygen Balance (OB - } \Omega) = \frac{([1-(2 \times 2)-(\frac{8}{2})] \times 1600)}{188.152} = -59.53 \text{ to 2 d. p.}$$

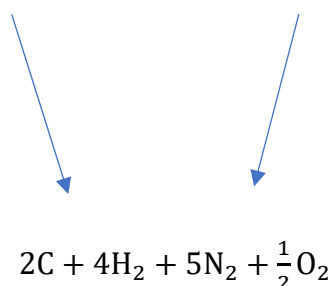
An Oxygen Balance of less (more negative) than -40 stipulates use of Modified K-W Rules, as follows:

Rule no.	Conditions
1	Hydrogen atoms are converted to water
2	If any oxygen remains then carbon is converted to carbon monoxide
3	If any oxygen still remains then carbon monoxide is oxidized to carbon dioxide
4	All the nitrogen is converted to nitrogen gas, N_2

As there is only one oxygen atom in a Tetrazene molecule, this limits the amount of hydrogen which can be converted into water, as such only 1 molecule of water can be formed taking 2 hydrogen atoms. 6 Hydrogen atoms are left to form 3 Hydrogen molecules. As there is no additional oxygen carbon cannot be converted to carbon monoxide let alone carbondioxide, so carbon remains as carbon (probably soot). Lastly all 10 Nitrogen atoms are converted to 5 Nitrogen molecules. As shown below:

Rule no.	Conditions	
1	Hydrogen atoms are converted to water	$2H + 1O \rightarrow H_2O$
2	If any oxygen remains then carbon is converted to carbon monoxide	$2C \rightarrow 2C$
3	If any oxygen still remains then carbon monoxide is oxidized to carbon dioxide	
4	All the nitrogen is converted to nitrogen gas, N_2	$10N \rightarrow 5N_2$

The resulting detonation equation is: $C_2H_8N_{10}O \rightarrow H_2O + 2C + 3H_2 + 5N_2$



Given the heats of formation as follows:

Substance:	Empirical Formula:	$\Delta H_f/\text{kJ mol}^{-1}$:
Tetrazene	$\text{C}_2\text{H}_8\text{N}_{10}\text{O}$	+189.12 [5]
Water	H_2O	-241.82 [11]

N.B.: All elements in their natural state have a heat of formation of 0 kJ mol^{-1} i.e. C, H_2 , N_2 and O_2 . Hess's Law and Hess Cycle give the following:

Heat of reaction, $(\Delta H) = \sum \Delta H_f(\text{products}) - \sum \Delta H_f(\text{reactants})$

So for Tetrazene the heat of reaction or heat of detonation, $\Delta H = -241.82 - (189.12) = -430.94 \text{ kJ mol}^{-1}$, to then calculate exothermicity in $\text{kJ g}^{-1} = \frac{\Delta H}{M_r}$, where $M_r = 188.152 \text{ g mol}^{-1}$. Therefore an exothermicity for Tetrazene = -2.29 kJ g^{-1}

Now that an example of the process has been shown all of the components in the explosive train will be shown in the table on the following page.

4.2.1. Table of Heats and Exothermicity

Part of device:	Substance:	Formula:	Molecular weight, (M_r) (g mol^{-1}):	Oxygen balance:	Type of K-W Rules applied :	Reaction equation:	Heat released (ΔH) (kJ mol^{-1}):	Exothermicity (kJ g^{-1}):
Percussion Cap Primer	Tetrazene	$\text{C}_2\text{H}_8\text{N}_{10}\text{O}$	188.152	-59.53	Mod.	$\text{C}_2\text{H}_8\text{N}_{10}\text{O} \rightarrow \text{H}_2\text{O} + 2\text{C} + 3\text{H}_2 + 5\text{N}_2$	-430.94	-2.29
	Paraffin wax (Hentriacontane)	$\text{C}_{31}\text{H}_{64}$	436.84	N/A Combustion	N/A	$\text{C}_{31}\text{H}_{64} + 47\text{O}_2 \rightarrow 32\text{H}_2\text{O} + 31\text{CO}_2$	-850	-1.95 [12]
Delay Composition	Bismuth oxide, manganese and tin (gasless)	$\text{Bi}_2\text{O}_3, \text{Mn Sn}$	$465.957 + (54.938 \times 5) + 118.71 = 859.357$	N/A	N/A	$\text{Bi}_2\text{O}_3 + 5\text{Mn} + \text{Sn} \rightarrow 2\text{Bi} + 2\text{MnO} + \text{Mn}_3\text{Sn}$ [7]	*-125.98	*-0.73
Detonator	Black powder	$\text{KNO}_3 + 3\text{C} + \text{S}$	$101 + 36 + 32 = 169$	N/A Deflagration	N/A	$2\text{KNO}_3 + 3\text{C} + \text{S} \rightarrow \text{K}_2\text{S} + \text{N}_2 + 3\text{CO}_2$	-1068.33	-6.32
Main fill/charge	Nitroglycerine	$\text{C}_3\text{H}_5\text{N}_3\text{O}_9$	227.087	+3.52	Normal	$\text{C}_3\text{H}_5\text{N}_3\text{O}_9 \rightarrow 3\text{CO}_2 + 2\frac{1}{2}\text{H}_2\text{O} + \frac{1}{2}\text{O} + 1\frac{1}{2}\text{N}_2$	-1414.40	-6.23

* Based on Manganese combustion [13]

5. Conclusion

The top level functionality of such a device depends critically on the components in explosive train having the right energetic output to initiate the next stage, by providing the right amount of energy both thermal and kinetic. This means that the Primary explosives need to be sensitive, but not too sensitive as to cause unintentional functioning. This is achieved by passivation of the tetrazene in TW5 by paraffin wax and the use of tetrazene to provide a substantially less toxic output.

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