# HEMs: The Facet of Explosive Performance

# 4.1 Why Do Explosives Explode?

# 4.1.1 Spontaneity of Explosive Reactions

Why do explosives explode? We have seen in Chapter 2 that all explosives are basically metastable and they just wait for a trigger energy. Their explosive reactions—whether the explosive has a positive or negative heat of formation—are highly exothermic and evolve large volumes of gaseous products. Once the trigger energy is given, an explosive reaction proceeds spontaneously and no one can just stop it.

What decides spontaneity? All changes in nature, whether physical changes or chemical changes, are governed by two seemingly opposing forces, viz:

- 1. Tendency for minimum energy
- 2. Tendency for maximum randomness (freedom or disorder)

A boulder on the precipice of a hill tends to come down to minimize its energy content. It is too tense to have so much potential energy! A compressed gas in a cylinder tends to come out through the nozzle so that its molecules can go away from each other, enjoying complete freedom or randomness. They feel so congested and crowded within the cylinder! In thermodynamic parlance, the energy is referred by "H" (heat content) and the randomness or degree of disorder by "S" (entropy). However, often these two tendencies may oppose each other. To decide whether a process can take place spontaneously or not, both these tendencies are simultaneously taken into account at a given temperature "T", and a parameter called "Gibb's free energy" is introduced. G is defined as:

$$G = H - TS$$

At a given (constant) temperature, the changes in H, S, and G are then:

$$\Delta G = \Delta H - T\Delta S$$
$$-\Delta G = -\Delta H + T\Delta S$$

Ultimate criterion Tendency for spontaneity minimum energy  $(-\Delta H)$  maximum randomness  $(+\Delta S)$ 

Any system in nature tries to undergo a change resulting either in  $-\Delta H$  (release of energy) or  $+\Delta S$  (increase in disorder), or both. However, what happens if a change has opposing tendencies like  $(-\Delta H \text{ and } -\Delta S)$  or  $(+\Delta H \text{ and } +\Delta S)$ ? Substitute these values in the above equations and see the sign of  $\Delta G$ . If it is negative, the process takes place spontaneously. If it is positive, it does not. It all depends on the relative values of  $\Delta H$  and  $\Delta S$ . Let us take two examples of such opposing tendencies resulting in spontaneous changes:

#### 1. Endothermic dissolution ( $+\Delta H$ ) of salts in water:

The freedom of solvated ions in solution  $(+\Delta S)$  as compared to the "confinement" of the cations and anions in crystal lattice overshadows the endothermic  $(+\Delta H)$  effect to achieve a negative value for  $\Delta G$ .

#### 2. Polymerization reaction:

When a large number of monomer molecules result in a fewer number of macromolecules, their overall randomness  $(+\Delta S)$  is reduced. However, the high exothermicity  $(-\Delta H)$  of polymerization reaction overshadows this effect, resulting in a negative value for  $\Delta G$ .

An explosive reaction is both highly exothermic  $(-\Delta H)$  and involves the production of a large number of gaseous products  $(+\Delta S)$ , thus involving a large decrease in the values of free energy and making the process of explosion highly spontaneous.

# 4.1.2 The Kinetic Aspect of Explosive Reactions

For an explosion to occur, the reaction must be exothermic, large amounts of gases must be produced by the chemical reaction and vaporization of products, and the reaction must propagate very fast. If a chemical change is accompanied by a large decrease in free energy, i.e.,  $-\Delta G$ , does it mean that it can take place easily? Not necessarily. For example, a piece of coal burns in oxygen to form  $CO_2$  and water, and this exothermic burning should involve a large decrease in free energy. Even such "spontaneous" chemical changes need to be given an initial "activation energy"  $(E_a)$ , to "prepare" the reactants for instant chemical change. We have seen in Chapter 2 that even the so-called metastable explosives need to be given a "trigger energy" or activation energy to undergo explosive decomposition.

If this barrier of  $E_a$  does not exist, nothing will be stable on this earth, whether an explosive or a piece of coal! The difference may be that the value of  $E_a$  in the case of wood may be far more than that of an explosive. The less stable (or "metastable") explosive molecule X has all its bonds intact (See Figure 4.1) in its ground state. Once it is given the trigger or activation energy (by shock, heat, or impact), the molecule goes to the excited or activated state ( $X^*$ ) where certain bonds are preferentially broken (like the

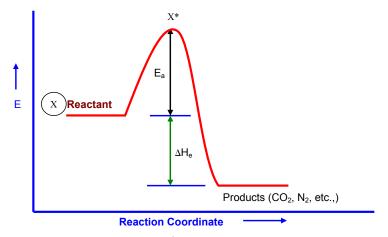


Figure 4.1
Activation Energy: A Need for a Chemical Reaction.

breakage of C– $ONO_2$  bond in nitric esters like NG). Having absorbed so much energy and having been mutilated like this, the molecule will no longer remain in that position but will immediately go to the lower energy state by degrading into stable products like  $CO_2$ , CO,  $N_2$ , etc., releasing large amount of heat.

The rate of such a reaction will depend mainly on two parameters viz. (1) the value of activation energy; and  $E_a$  (2) temperature of the reaction condition, as given by the Arrhenius equation for any chemical reaction:

$$k = Ae^{-Ea/RT}$$

where k = rate constant of the reaction

A = temperature-independent "Arrhenius constant" (or pre-exponential factor).

This equation shows that when temperature T increases or  $E_a$  decreases, the rate of the reaction increases exponentially, i.e., much faster than a linear relation (See Figure 4.2). If we take the logarithmic form of the Arrhenius equation, we get:

$$\log k = \log A - \frac{E_a}{RT}$$

A plot of log k against 1/T (Figure 4.3) gives, therefore, a straight line whose slope gives the value of  $-E_a/R$ , from which we can calculate the value of  $E_a$ .

 $E_a$  is an important parameter for an explosive. The lower the value of  $E_a$ , the higher is the sensitivity of the explosive for initiation.

Section 4.1.1 discusses the *thermodynamic* nature of explosives that have a huge "free energy advantage," whereas Section 4.1.2 talks about the *kinetic* aspect of explosives, i.e.,

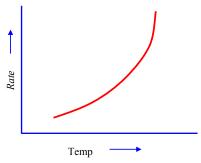


Figure 4.2

Exponential Increase of the Rate of a Reaction with Respect to Temperature.

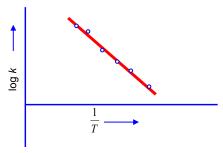


Figure 4.3

Plot of log k against 1/T.

how easily the explosive decomposition can take place with respect to the values of their activation energy and temperature.

# 4.1.3 Molecular Structure and Explosive Properties

The relationship between the molecular structure and the explosive property of a compound has been a matter of interest for quite some time. By the end of the nineteenth century, vant Hoff observed that nitration of certain compounds imparted explosive properties to the nitrated products. An increase in the number of nitro groups in a molecule caused an increase in the explosive properties. He stated: "It is atomic bonds of specific nature which generate the explosive character". In 1953, Plets proposed the concept of "explosophores" and "auxoploses" (similar to "chromophores" and "auxochromes" in the chemistry of dyes). Explosophores are certain specific functional groups that impart explosive properties to the molecules of the explosive compounds. Some of such groups are listed in Table 4.1.

 Nitro
 Nitrato

 —N+0 —O-N+0 

 Azo
 —N=N Azido
 —N-N±N

 Peroxido
 —Ö-Ö Perchlorato
 —O-Cl=O

Table 4.1: Structure of some of the explosophore groups.

Auxoploses are functional groups that modify or increase the explosive properties in a molecule. For example, the ease of initiation of picric acid (I) as compared to trinitrobenzene (II) appears to be due to either the activation of the benzene ring by the electron-donating hydroxyl group of (I) or the stabilization of the activated intermediate product of detonation by the -OH group. The hydroxyl group in (I) acts as an auxoplose.

Let us ask a basic question: Why are only certain functional groups like  $-NO_2$ ,  $-ONO_2$ ,  $-ClO_4^-$ , etc., explosive or metastable in nature? When a bond is formed between two atoms of different electro-negativities (ENs) (i.e., the tendency of an atom to attract the electrons to itself), the bond is strong; e.g., an O-H bond (wherein the EN of oxygen is higher than that of hydrogen) is strong and stable because of the dipole formed as shown below:

$$\delta - \delta + \delta - \delta +$$
O: H or O-H

If both of the bonding atoms have high EN values (the atoms lying toward the right of the periodic table of elements), their competition for electrons is so much that the bond formed between them is unstable (e.g., N—O as in nitrates and Cl—O as in perchlorates). Although N and Cl are highly electronegative atoms, a large positive charge (or oxidation

number) of 5+ and 7+ has been forced on these atoms in  $NO_3^-$  and  $ClO_4^-$ , respectively. Therefore, these  $NO_3^-$  and  $ClO_4^-$  groups badly look for electron donors to relieve this bonding stress. Carbon atoms within the same explosive molecule can oblige them to achieve this resulting in very stable products like  $CO_2$ , CO, and  $N_2$ . The well known Molecular Orbital Theory of bonding explains the relative instability of such groups and also groups such as azides.

$$-\overline{N}-N^+\equiv N$$

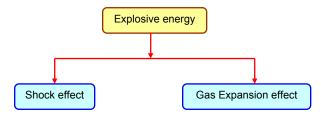
Closer insight into the mechanistic relationship between molecular structure and explosive properties of compounds became possible only after the development of spectroscopic techniques like X-ray photoelectron spectroscopy (XPS) and electron paramagnetic resonance (EPR), and theoretical treatments based on quantum mechanics, molecular shock dynamics, etc. The exact relationship between the molecular structure, shock sensitivity of the explosive compound, and the detonative decomposition is rather complex and is beyond the scope of this book. However, based on the extensive quantum chemical calculations and experimental techniques like High Speed Raman Spectroscopy, the following conclusions may be drawn:

- 1. The electronic structure of the explosive molecule plays a key role in its degree of shock sensitivity.
- 2. Only certain specific bonds in an explosive molecule are vulnerable to be broken by the shock energy causing explosive initiation, e.g., an N-NO<sub>2</sub> bond in a nitramine explosive like RDX.
- 3. The shock sensitivity appears to depend on the extent to which the polarity of these specific bonds gets reduced after they receive the shock energy. For example, why is RDX more "explosive" than nitroguanidine? To put it more scientifically, why is the shock sensitivity of RDX more than that of nitroguanidine? It has been found that the polarity of N-NO<sub>2</sub> bond is reduced by 55 and 22% in RDX and nitroguanidine, respectively, after they receive shock energy. It implies that N-NO<sub>2</sub> bond becomes more non-polar in RDX. A nonpolar bond gets more easily broken than a polar bond because in the latter, the electrostatic forces between the concerned atoms resist the breakage of the bond.
- 4. The decomposition of the molecules of an explosive compound does not occur immediately after the passage of shock front. Behind the front, the energy transmitted by the shock wave is received preferentially by certain molecules causing excitation in their vibrational and electronic energy levels. This excitation, which is a measure of the sensitivity of the explosive, triggers the initiation. It is only after sometime, probably a few nanoseconds, and the rest of the molecular population takes part in the "cooperative decomposition" process using the energy received from the shock-initiated molecules.

# 4.2 Two Aspects of Explosive Performance

# 4.2.1 Partition of Explosive Energy

When an explosive kept inside a drilled hole of a rock detonates, the rock goes to pieces. What causes this damage? Is it the shock or the gaseous mixture produced due to explosion, or both? We can divide the effects of "explosive energy" into two components viz. shock effect and gas expansion effect as shown below.



Components of energy released from an explosive

- Shock effect: It is the effect of high pressure detonation front on the target and the
  effect is proportional to the Detonation Pressure (P<sub>d</sub>) that depends on the velocity of
  detonation (VOD) of the explosive and its density.
- 2. Gas Expansion effect: It is the effect of high pressure gases produced on the target. We have seen in chapter 2 that this is equal to nRT<sub>o</sub> where "n" is the number of moles of the gases produced per gram of the explosive and T<sub>o</sub> is the detonation temperature. The explosive energy is therefore partitioned between shock and gas expansion.

In the above example of rock blasting, these two effects work in the following sequence:

- 1. The shock wave is the leader of the attack! The high pressure shock front (with pressures in the region of a few 100 kilobars) produces a highly intense compression through the rock.
- 2. This compression wave is followed by a rarefaction wave. During the phase of rarefaction, the pressure is below the atmospheric pressure and it creates tension (opposite of compression) through the rock.
- 3. The intense compression followed by tension causes plastic and elastic deformation of the material in quick succession, resulting in the cracking of the material.
- 4. The compressed gases waiting for such an opportunity and expand through these cracks to heave out the broken pieces.

It has been established that not more than 50% of the total explosive energy is through the shock, even in case of high VOD explosives. The share of credit between "shock" and

"gas expansion" factors for a damage exercise varies depending on the application, as below:

- 1. In certain applications like shaped charge ammunitions (to be discussed shortly), shock plays a predominant role rather than gas expansion.
- 2. In certain mining applications like coal mining, gas expansion effect is more important to heave out large chunks of coal, whereas a high VOD may be disastrous.
- 3. In many applications, as we have seen in the rock blasting case, both these effects work hand in hand.

## 4.2.2 Velocity of Detonation

VOD is the rate of propagation of a detonation in an explosive. It is a major index of the explosive performance. If the density of an explosive is at its maximum value (i.e., theoretical maximum density: theoretical maximum density (TMD)) the detonation velocity is characteristic of a given explosive. VOD of an explosive, however, depends on the following major factors:

#### 1. Loading Density ( $\Delta$ )

It is defined as the ratio between the weight of the explosive and the explosion volume, i.e., the space in which the explosive is detonated. If 10 g of RDX is loaded in an enclosed space of 20 cc, the value of  $\Delta$  will be equal to 10 g/20 cc = 0.5 g/cc. The higher the loading density, the higher will be the VOD for the simple reason that, a higher loading density ensures a larger quantity of the explosive per unit volume so that larger amount of evolved energy can sustain the detonation wave.

If  $D_1$  and  $D_2$  are the values of VOD of an explosive at  $\Delta_1$  and  $\Delta_2$ , the following empirical relation mostly holds true:

$$\frac{D_1 - D_2}{\Delta_1 - \Delta_2} = 3500$$

Marshall's formula gives the following relationship between VOD,  $\Delta$ , n (number of moles of gaseous products per gram of the explosive), and  $T_d$  (detonation temperature).

$$D(in m/s) = 430 (n T_d)^{1/2} + 3500 (\Delta - 1)$$

## Charge diameter

It we detonate a cylindrical column of explosive and measure its VOD, we will find that the velocity changes if we change the diameter of the column. VOD decreases as the diameter of the column decreases. This effect is caused by more energy losses to the peripheral sides of the column. When the diameter is large, the losses are small as

compared to what is produced at the wave front. However, losses become significant as the column diameter decreases.

Let us take a cylindrical column of an explosive with length L and diameter D. If E<sub>x</sub> is the energy produced per unit volume of the explosive during detonation and E<sub>v</sub> is the energy lost per unit area through its side surface, the percentage of loss of energy through the side of the column will be:

$$\frac{\text{the energy lost}}{\text{the energy produced}} \times 100\% = \frac{\left(\pi DL \times E_y\right)}{\frac{\pi D^2 L \times E_x}{4}} = \times 100\%$$

$$= \frac{4E_y}{DE_x} \times 100\% = \frac{k}{D}; (k = constant)$$

Since E<sub>v</sub> and E<sub>x</sub> are constants, this percentage loss is found to be inversely proportional to the column diameter. At lower diameters, the percentage loss of energy increases. Below a certain diameter that we call as the *critical diameter* of the explosive, the percentage loss is so much that the unsupported/unsustained detonation wave dies out. The critical diameter of an explosive depends on the type of explosive, its density of packing, inclusion of air bubbles, etc. It can be as small as about 0.5 mm in the case of an initiator like lead azide and as large as 100 mm in the case of less sensitive, low density ammonium nitrate.

The concept of "critical diameter" is made use of in the introduction of "detonation trap" during the manufacture of shock-sensitive NG. These traps whose diameters are less than the critical diameter of NG do not allow the shock wave to pass through them so that an accidental detonation in one part of the NG plant is not transmitted to the other parts.

#### 3. Degree of confinement

When the degree of confinement of an explosive increases, it increases its VOD.

#### 4. Strength of Initiation

The higher the strength of initiation of an explosive charge (e.g., by using a powerful detonator), the VOD of the explosive is higher and vice versa. Weak detonators are used to initiate industrial explosives to achieve a lower order of VOD. Measurements of VOD were earlier made by the good old "Dautriche method." Nowadays, "Pin Oscillography Technique" and "Streak Camera Techniques" are used for more accurate measurements.

# 4.2.3 Gas Expansion

Like the shock effect, the expansion work done by the gases is also an index of the energy of an explosive. As already mentioned in Chapter 2 (Section 2.3.9), this is called as the

"Specific energy" of the explosive. Sometimes, terms such as "strength" and "power" are also used.

Specific energy (f) is defined as the working performance per kg of an explosive. It can be calculated from the general equation of state for gases:

$$f = PV = nRT$$

If, for example, the adiabatic, isochoric flame temperature of RDX during the detonation is given as 2800 K, what would be its specific energy? One gram per mole of RDX (i.e., 222 g of RDX) explosively decomposes to give 9 mol of gaseous products (i.e., n = 9).

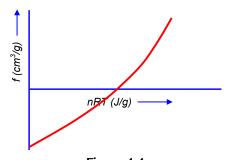
$$C_3H_6N_6O_6 \rightarrow 3CO + 3H_2O + 3N_2$$

Taking the value of R as  $8.314 \text{ J deg}^{-1} \text{ mole}^{-1}$ .

$$F = 9/222 \text{ mole } g^{-1} \times 8.314 \text{ J deg}^{-1} \text{mole}^{-1} \times 2800 \text{ deg.}$$
  
= 944 J/g : Specific energy of RDX.

This work performance parameter of all explosives can be experimentally determined. The old and still reliable method is by the Trauzl Lead Block Test. In this test, a known weight of the explosive is kept in a drilled hole of a solid lead block and sealed. On initiation of the explosive, the high pressure expanding gases increase the volume of the hole. The increase in volume is measured and this is a measure of "f" of the explosive that is reported in the units of cm<sup>3</sup>/g, i.e., the volume increase per gram of the explosive used. When we plot a graph of "f" obtained in this experiment against "nRT" values of different explosives, a nearly linear plot is obtained (Figure 4.4). The slight nonlinearity of the plot is probably due to our assumption that the high pressure gases behave ideally, which actually is not true.

Conventionally, picric acid is taken as the reference explosive to compare the power or strength of the explosives. Since  $n \propto V$  (volume of the product gases per g of the



**Figure 4.4**Work Performance (f) against nRT of Explosives.

Explosives	Power Index (%)	Explosives	Power Index (%)
Hexanitrostilbene (HNS)	108.7	Octogen (HMX, high melting explosive)	178.33
Nitrocellulose (NC)	131.09	Pentaeryhritol tetranitrate (PETN)	177.22
Nitroglycerine (NG)	164.49	Trinitrotoluene (TNT)	103.68

Table 4.2: Power index of a few explosives computed using LOTUSES.

explosive) and  $T \propto Q$  (cal val of the explosive), we can write nRT  $\propto QV$ , where QV is called the *characteristic product* of an explosive indicating its power. The power of an explosive is compared with that of a standard explosive like picric acid and expressed as "Power Index" as shown in the following example.

If we compare RDX with the standard explosive viz. picric acid, (Q = 1226 cal/g,  $V = 908 \text{ cm}^3/\text{g}$  for RDX, Q = 896 cal/g,  $V = 780 \text{ cm}^3/\text{g}$  for picric acid):

Power index = 
$$\frac{Q_{RDX} \times V_{RDX}}{Q_{PA} \times V_{PA}} = \frac{1226 \times 908}{896 \times 780} = 1.59 \text{ or } 159\%$$

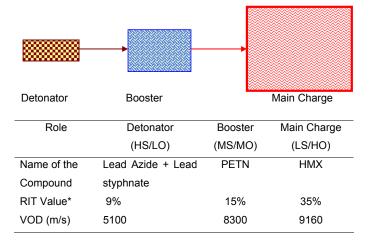
The power index of a few explosives was worked out using the LOTUSES software and is presented in Table 4.2, in which the volume of detonation gases were computed by Kistiakowsky—Wilson rules.

# 4.3 A Travel by Explosive Train

As mentioned in Chapter 1, "safety" and "reliability" are two vital requirements of any system containing explosives, including ammunitions. By "safety" we mean that the explosive should not go off when it should not go off. By "reliability" we imply that it should go off when it should go off! But explosives differ in their *sensitivity* to initiation by impact, friction, heat, electrical impulse, etc. as well as in their *output* in terms of shock intensity. To achieve our dual objective of safety of handling, transport, and storage on one hand and reliability of performance in an explosive-based system like an ammunition or an industrial explosive system on the other hand, we have to form a "train" of explosive system that contains (1) an initiating explosive of high sensitivity (HS) and low output (LO), like primary explosives; (2) an intermediary (also called booster) explosive of medium sensitivity (MS) and medium output (MO); and finally (3) the main explosive of low sensitivity (LS) and high output (HO). An example of such an explosive train is given in Figure 4.5 below:

# 4.3.1 Primary Explosives: "the engine starters in an explosive train!"

Primary explosives (or initiatory explosives) start the engine in the explosive train. They are highly sensitive to heat, friction, impact, shock, and electrostatic energy. They initiate



(\*RIT stands for the Relative Impact Test with respect to TNT as a standard explosive. It gives the height at which a given falling weight will initiate the explosive as compared to TNT. For a given falling weight, if TNT is initiated at 100 cm height, PETN gets initiated even at 15 cm height).

**Figure 4.5** An Explosive Train.

the next element or component in an explosive train (booster) that, in turn, initiates the main HE charge. Overall energy amplification from initiator to the main charge can be as high as about 10 million to one. The primary explosives are used in military detonators, commercial blasting caps, and percussion electric primers. They can be initiated electrically (e.g., "squibs"), mechanically (e.g., in stab detonators) or by shock from an exploding wire.

Only a few compounds can act as primary explosives to meet the military and industrial requirements in terms of sensitivity, output, ease of manufacture, cost, compatibility, and long-term storage stability. Mercury fulminate was the earliest one to be used, but is almost phased out now because of its poor storage stability. Some of the common primary explosives used today are lead azide, silver azide, lead styphnate, and lead dinitroresorcinate. Lead azide, although popular, has poor "flash pick-up" property and incompatibility with copper and brass used in ammunitions (due to the formation of dangerously sensitive copper azide during storage), and lead azide is normally mixed with lead styphnate to improve its flash sensitivity. Some important properties of three well-known primary explosives are given in Table 4.3.

Property	Mercury Fulminate	Lead Azide	Lead Styphnate
Molecular structure	O-N <sup>±</sup> =C <sup>-</sup> Hg O-N <sup>±</sup> =C <sup>-</sup>	N=N <sup>+</sup> =N <sup>-</sup> Pb N=N <sup>+</sup> =N <sup>-</sup>	O N O Pb <sup>2+</sup> . H <sub>2</sub> O
Molecular weight	284.6	291.3	468.3
$\Delta H_f (cal/g)$	+225	+340	-451
$\Delta H_e$ (cal/g)	355	367	370
Density (g/cc)	4.2	4.8	3.0
VOD (m/s)	5400	5300	5200
Relative impact test value (%TNT)	5	11	8
Static discharge (max energy for nonignition) (J)	0.07	0.01	0.001

Table 4.3: Properties of a few primary explosives.

## 4.3.2 Secondary Explosives: "the final operators of the explosive train!"

The secondary explosives are those with low or moderate sensitivity to initiation but with higher power or output. They include boosters as well as final HE charges. Most of them come under three categories viz.

- 1. aliphatic nitrate esters
- 2. aromatic nitro compounds
- 3. nitramines (aliphatic/aromatic/heterocyclic)

The details of the properties, preparation, and uses of these explosives will not be discussed in this section. Only certain salient points will be mentioned.

(1) *Aliphatic nitrate esters*: They are some of the most powerful explosives with high values of cal val, and also VOD. However, their stability is less than other classes of explosives because of the tendency of the C-ONO<sub>2</sub> bond to get hydrolyzed slowly, resulting in the formation of acids (HNO<sub>3</sub>/HNO<sub>2</sub>) that further catalyzes the decomposition.

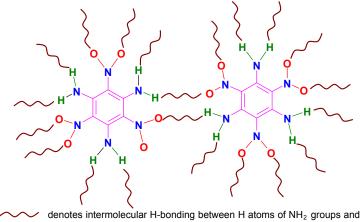
$$\begin{array}{c} \text{R} \longrightarrow \text{O} & \text{I} \\ \text{O} & \xrightarrow{\text{I}} & \text{I} \\ \text{O} & \xrightarrow{\text{I}} & \text{I} \\ \text{I} \\ \text{O} & \text{I} \end{array}$$

The most commonly known explosives of this category are NG, PETN, and NC. The properties of NG and PETN are given in Table 4.4.

(2) *Aromatic nitro compounds*: Aromatic nitro compounds are more stable than nitrate esters. All aromatic molecules are *resonance-stabilized* and the introduction of an electron-donating group like methyl groups ("hyperconjugation") further increases the ring stability as in the case of TNT, as shown below:

It requires more energy to destabilize such a resonance-stabilized ring, making such compounds more stable than the aliphatic explosives.

Very high thermal stability of triamino trinitrobenzene (TATB), which melts at about 350 °C, is attributed to an important additional factor viz. extensive network of hydrogen bonding as shown below:



denotes intermolecular H-bonding between H atoms of NH<sub>2</sub> groups and O atoms of NO<sub>2</sub> groups).

The important properties of two aromatic nitro compounds viz. TNT and picric acid are shown in Table 4.4.

(3) *Nitramines*: While nitric esters represent the O-NO<sub>2</sub> explosives and aromatic nitro compounds represent C-NO<sub>2</sub> explosives, nitramines represent N-NO<sub>2</sub> explosives. They can be aliphatic like nitroguanidine, aromatic like "tetryl" (2,4,6-trinitrophenyl methyl

Table 4.4: Properties of selected secondary explosives.

					Nitro-			
Property	NG	PETN	TNT	Picric Acid	Guanidine	RDX (Cyclonite)	HMX (Octogen)	Tetryl
Structure	$\begin{array}{c} H \\ H-C-ONO_2 \\ H-C-ONO_2 \\ H-C-ONO_2 \\ \end{array}$	C(CH <sub>2</sub> ONO <sub>2</sub> ) <sub>4</sub>	7 - 3	OH NO <sub>2</sub> NO <sub>2</sub>	H <sub>2</sub> N NH NO <sub>2</sub>	NO <sub>2</sub> H <sub>2</sub> C N CH <sub>2</sub> O <sub>2</sub> N N C N NO <sub>2</sub>	H <sub>2</sub> C CH <sub>2</sub> N CH <sub>2</sub>	- 
			-	•			NO <sub>2</sub>	NO <sub>2</sub>
Mol. weight	227.1	316.1	227.1	229.1	104.1	222.1	296.2	287.1
$\Delta H_f$ (cal/g)	-392	-402	-62.5	-225.7	-213.5	76.1	60.4	28.1
OB (%)	3.5	-10.1	-73.9	-45.4	-30.7	-21.6	-21.6	-47.4
$\Delta H_e$ (cal/g)	1617	1529	1080	1080	769	1375	1357	1140
Density (g/cc)	1.59	1.76	1.65	1.77	1.71	1.82	1.96	1.73
m.p. (°C)	13.2	141.3	80.8	122.5	232	204	275	129.5
VOD (m/s)	7600	8400	6900	7350	8200	8750	9100	7570
Impact sensitivity (relative % to TNT)		20	100	100	200	35	35	50
Det. pressure (GPa)	-	32	18	26.5	27.3	33.8	39.3	26.2

nitramine), or heterocyclic like RDX (cyclic trimethylene trinitramine) or HMX (cyclic tetramethylene tetranitramine). Their properties are given in Table 4.4.

Their stability is between that of nitroaromatics and nitric esters, and they are very powerful. One reason for the higher power or high VOD of these explosives is the "energetic" (positive heat of formation) nature of N–NO<sub>2</sub> bonds. This explains the positive heat of the formation of RDX, HMX, and tetryl.

## 4.3.3 The Types of Explosive Trains

Today's conventional warfare cannot be imagined without the use of explosives and propellants. An explosive train is a part of any ammunition, whether it is a round fired from a pistol, large-caliber gun ammunition, hand grenade, or a guided missile. The explosive train is of two types viz.

- 1. Igniferous train (or "burning train")
- 2. Disruptive train (or "detonative train")

As mentioned earlier, in both these types of trains, the three components viz "initiator-booster-main charge" are present in the same order.

In the igniferous train, the transmission is by burning or, more correctly, deflagration, whereas in disruptive train, the transmission is by the process of detonation. In many ammunitions, both these mechanisms are operative in sequence.

Figure 4.6 schematically shows a full round of HE ammunition readily loaded in a gun for action. The full round consists of two parts. The part-1, which is shown as Explosive Train-1 (ET-1), is an igniferous train. Train ET-1 starts like this:

1. A striker pin strikes the percussion cap at the base of the cartridge and, due to high impact cum friction, the sensitive pyro composition ignites the moment the striker pin punctures the cap with force.

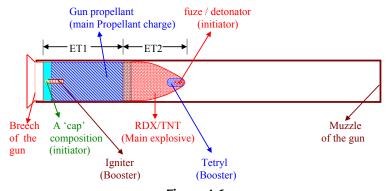


Figure 4.6

Two Types of Explosive Trains Operating in an Ammunition.

- 2. The initiated cap composition ignites gunpowder in the igniter housing, which burns, giving out hot particles, and the flame engulfs the entire bulk of large quantity of gun propellant.
- 3. The main gun propellant charge weighing a few kilograms burns in a matter of a few milliseconds, creating high pressure, high temperature gases that propel the projectile (HE shell) to a great speed.

The entire drama of the eflagration train that results in propulsion of the HE shell takes only a few milliseconds.

The second drama of "explosive train-2" (ET-2) takes place when the HE shell lands on its target (naturally, we should not have this drama enacted when it is still inside the barrel!) with the fuze getting initiated. The sequence of ET-2 will be:

- The fuse initiates the detonator on striking the target.
- 2. The shock wave of the detonator is sufficient to initiate the booster pellet
- The amplified shock wave initiates the main HE charge, wreaking havoc on the target.

# 4.4 Performance Parameters of Military Explosives

Interestingly, the destructive capabilities of military explosives are varied. The "shattering effect" of an explosive in a grenade kills or injures personnel or damages sensitive targets over a given area. The "scabbing effect" cuts out a chunk of armor plate of an enemy's tank and throws it right into their cabin. The overpressure of the "blast effect" brings down structures. The "shaped charge effect" causes deep penetration through heavy armor plates. The formulation of explosive composition and the overall ammunition design are so made that the final ammunition achieves one of these specific objectives. We will see in a little more detail as to how these effects operate.

# 4.4.1 Fragmentation

The destructive fragmentation effect of an explosive charge on its immediate vicinity is termed as "brisance." In a battle scenario, when a brisant explosive shatters a shell or a grenade, the high velocity fragments create extensive damage on the personnel or objects in its vicinity. What should be the shape, size, and weight of the fragments depends on the nature of the target. In case of an antipersonnel grenade, even small fragments will achieve the purpose of killing or incapacitating the enemy as each fragment acts like a virtual bullet. On the other hand, if an aircraft is to be destroyed or damaged, the fragments have to be bigger, each weighing at least about 5 g. The average velocity of the fragments may vary from as low as 1000 m/s in the case of HE shells to 4000 m/s in the case of large bombs. The shape, size, and velocity of fragments can be tailored by

changing the explosive composition and the ratio of explosive-to-case weight. In a prefragmented ammunition, the size of the fragments to be formed is predecided by designing the outer shell accordingly.

What decides the effectiveness or lethality or range of the fragments? The effectiveness of fragmentation depends on three factors related to the explosive composition filled, viz.:

- 1. VOD of the explosive
- 2. Its density
- 3. Its power (i.e., its specific energy)

Immediately after detonation, the shock front exerts the entire detonation pressure on the shell. The nature of resulting fragments (their number, size, and velocity) depends on the detonation pressure, which again depends on factors (1) and (2) above. Just after the formation of fragments, they are propelled at high velocities by the high pressure gases produced, and factor (3) above plays the role here.

Kast has come up with the concept of "brisance values." To achieve high brisance, high VOD explosive compositions like RDX/TNT are used in fragmenting ammunitions. Different empirical methods have been reported in literature for comparing the brisance values of explosive, taking TNT as standard. The "Sand Test" determines the proportion of standard Ottawa sand crushed by 0.4 g of an explosive using standard sieves. The "Plate Dent Test" measures the dent produced on a standard steel plate by detonating a cylindrical column of explosive of known weight. "Upsetting Tests" measure the fragmentation effect of explosives by detonating a cylindrical column of the explosive kept over a lead or copper cylinder (keeping standardized buffer plates in between) and measuring the compression of the metallic cylinder after explosion.

# 4.4.2 Scabbing

If you want to damage an armor plate of a tank, can you do it without perforating it from its front side? Sound strange? Yes, it is possible if you exploit the "scabbing" effect of an explosive (Figure 4.7). It works like this:

The mechanism of scabbing is shown in Figure 4.8. When the explosive in close contact detonates, the plane shock front travels from left to right (front to rear of the plate) as a *compression wave*. The intensity or amplitude of the wave is proportional to its height. The moment the shock front reaches the rear end, it is "shocked" to see the total difference in the medium (steel to air) and, therefore, gets *reflected back as tension wave* (i.e., "negative shock wave," which instead of compressing the medium, does the opposite process of elongating it). At a particular place of the plate, as shown in the figure, the difference between tension and compression intensifies  $(a_t-a_c)$  and exceeds the fracture

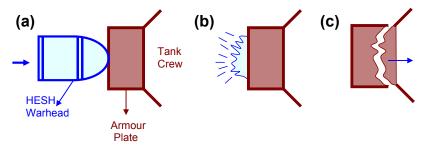
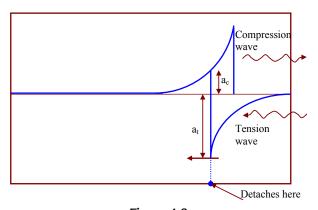


Figure 4.7

The Scabbing of an Armor Plate. (a) A High Explosive Squash Head (HESH) Ammunition Hits the Armor Plate. (b) The High Explosive inside the Warhead is "Spread" on the Plate, i.e., in Complete Contact with the Plate. It Goes Off. (c) A Large Chunk of the Armor Plate on Its *Rear Side* is Detached and Thrown Right into the Crew Cabin, Killing or Injuring the Crew and Damaging the Equipment.



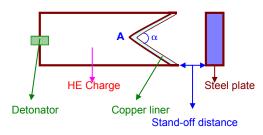
**Figure 4.8** The Mechanism of Scabbing.

strength of the plate. At this point, a large chunk gets detached and is thrown from left to right, because the effective force here is not compression but tension. Depending on the quantity and power of the explosive and nature of the armour, the velocity of the scab can vary and can go up to 130 m/s, killing the tank crew instantly.

As scabbing is purely a shock phenomenon, the HE composition used in HESH ammunition must produce a high detonation pressure. Compositions based on RDX and HMX are mostly used for this purpose.

# 4.4.3 Shaped Charge Penetration

In 1888, C. E. Munroe discovered that when a conical cavity is created in a column of explosive charge, on detonation, it could penetrate a solid object. Further research in this



**Figure 4.9** A Shaped Charge.

line established the ideal conditions for maximum penetration of hard targets like steel using such "shaped charges" or 'hollow charges.' The ideal conditions would be:

- 1. Introduce a concentric conical cavity at the end of a cylindrical column of an explosive charge.
- 2. Line the cavity with a malleable, metal-like copper
- 3. Keep a certain minimum "stand-off" distance between the base of the conical cavity and the steel plate (or target) as shown in Figure 4.9:

Once the detonation occurs, the entire explosive energy is concentrated to collapse the metallic liner, which is transformed into a high velocity jet. About 20% of the metal liner gets transformed into a jet, which has a velocity gradient from its tip (up to 9000 m/s) to tail (about 1000 m/s). A shaped charge, if properly designed, can penetrate steel plates eight times as thick as the diameter of the charge.

The mechanism of jet formation and penetration is interesting:

- 1. When the HE charge detonates, the shock wave passes over the liner, and the liner is accelerated at some small angle to the interface between the explosive and liner.
- 2. Since the liner velocity has been found to be directly proportional to the C/M (C: Charge weight of explosive over the liner, M = Weight of the metallic liner at a given point), it is observed that at the apex of the cone ("A" in Figure 4.9), the liner velocity is the highest. The liner velocity goes on decreasing as we go down the cone toward its base.
- 3. We, therefore, see that the jet comes out first from the apex and the rest of the liner is "squeezed out" following the "apex jet," but at lower and lower speeds. The remaining material, which is the bulk of the liner, forms a heavy slug that follows the jet at a much lower velocity, as shown below (Figure 4.10). In fact, after some point it becomes a discontinuous jet.

However, why do we need a stand-off distance? The stand-off distance (usually expressed as charge diameters) is essential for the proper development of a metallic jet until the tip

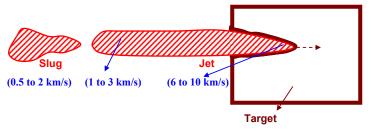


Figure 4.10
Jet and Slug Formation from a Shaped Charge.

achieves tremendous kinetic energy. The stand-off distance has to be optimal. If it is too short, we are not giving enough time and distance for the formation of high velocity jet. If it is too long, the jet breaks up and each particle hits further and further away from the center of the target. Maximum penetration has been found when the stand-off is about five times the cone diameter, with the cone angle around 42°. Optimum liner thickness is about 3% of the cone diameter for copper.

The penetration capacity of the liner is directly proportional to the kinetic energy of the jet and inversely proportional to the area of cross-section of penetration. As regards the explosive filled in a shaped charge, its VOD and density have a bearing on its performance. This is because of the fact that the main driving force behind the penetration is the detonation pressure ( $P_d$ ), which is equal to  $\rho D^2/4$ ,  $\rho$ , and D being the density and VOD of the explosive, respectively. Most of the shaped charges use RDX-based compositions. In exceptional cases, where still higher performance is needed, the much costlier  $\beta$ -HMX is used, as it has higher density and VOD than RDX.

The main applications of the "shaped charge effect" are their use in High Explosive Anti-Tank (HEAT) shells for the penetration of tank armor, in "cutting charges" used for the demolition of concrete and steel structures like bridges, and in a flexible, linear-shaped charge that consists of a flexible lead alloy with a  $\Lambda$ -shaped cross section that contains desensitized explosive composition for versatile applications.

#### 4.4.4 Blast

Blast is defined as a phenomenon caused by rapid expansion of high temperature, high pressure gases as a result of an explosion. World War II operations proved that much greater damage can be done to installations by blast effect from bombs than the fragmentation effect. In fragmentation, the flying fragments damage only the points of impact, whereas a blast wave acts like a severe earthquake covering a circular area,

damaging walls, throwing roofs and equipment, and also killing people if they are in the lethal overpressure region.

When an HE composition in a shell or a bomb undergoes detonation under confinement, the detonation pressure developed is in the order of a few  $10^5$  atm, with the temperature in the range of  $3000{-}4000^{\circ}\text{C}$ . The shell material gives way under such drastic conditions and about half of the explosive energy is used for this shattering and propelling of the fragments. The rest of the energy (due to high pressure and high temperature gases) is used for compressing the air around to form the shock wave with a steep plane front (See Chapter 3). The shock wave spreads spherically outward from the point of detonation and is followed by the gaseous products behind it. However, after a few milliseconds, the pressure falls to ambient pressure due to the inertia of moving gases (See Figure 4.11) at point A.

This is followed by a negative pressure (subatmospheric) phase from point A to point B. The major damage of the targets experiencing this blast wave (which consists of both the positive and negative pressure phases) is caused by (1) the peak pressure (represented by the height of the shock front OP), and (2) the area under the positive pressure phase (enclosed between OPA). This area is also known as the *impulse* of the blast wave, which is the (pressure X time) parameter, or the work done by the overpressure in "pushing" and damaging the object. In the second phase of negative pressure (area covered between A and B below X-axis), the gases go in the reverse direction, i.e., toward the point of detonation. At this time, the target experiences a "pulling" force rather than a push. This explains the fact that when a detonation occurs at a certain distance outside the window of

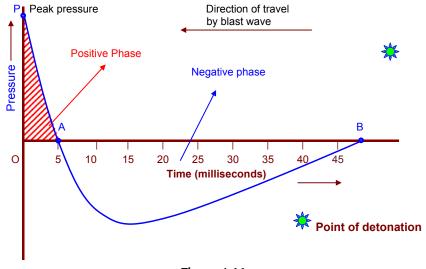


Figure 4.11
Two Phases of a Blast Wave.

a house, the window panes are shattered and the debris is found outside the house rather than inside.

Although both the peak pressure (OP) and the impulse (area POA) are destructive, their damage potential depends on the type of the target. If the target is a light and strong material (e.g., a window glass pane) a higher peak pressure is needed to break it. If it is a heavy but weak structure (e.g., a brick wall) a low peak pressure will do, but the impulse should be relatively higher. While an overpressure of 0.07–0.7 kg/cm<sup>2</sup> is enough to break a window pane, an overpressure of about 6 kg/cm<sup>2</sup> is needed to kill a man by fatally compressing his vital organs.

The blast effects depend on the medium and also the surroundings. While the blast wave attenuates quickly in an open space (its spherical area increasing in terms of  $4\pi r^2$ ), it gets reinforced in confined spaces like a closed room due to its multiple reflection. While the blast effect is enhanced in a dense medium (e.g., underwater blast), it is severely reduced in a rarified atmosphere. For this reason, large quantities of HE composition are needed for efficient blast effect from the warheads used in anti-aircraft missiles at high altitudes.

## 4.4.4.1 Aluminized HE Compositions and Blast

Most of the HE compositions used for creating blast contain a certain percentage of fine aluminium powder, e.g., Torpex (41% RDX, 41% TNT, 18% Al), Tritonal (80% to 60% TNT, 20–40% Al), and Minol (40% NH<sub>4</sub>NO<sub>3</sub>, 40% TNT, 20% Al). Aluminium plays a key role in extending the blast effect for a longer duration so that the impulse of the explosive increases. The addition of aluminium powder produces a longer, flatter P-t curve in the positive pressure phase of the blast wave as shown in Figure 4.12.

It was found that aluminium does not participate in the initial detonation reaction, but it adds a large amount of heat to the entire system by subsequently reacting with the products of detonation, viz. water and carbon dioxide exothermically.

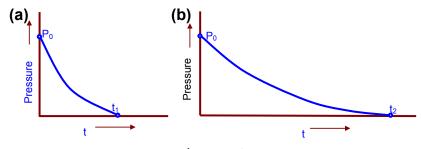


Figure 4.12

P-t Blast Profile of (a) Non-Aluminized Composition and (b) Aluminized Composition.

$$2Al_{(s)} + 3H_2O_{(v)} \rightarrow Al_2O_{3(s)} + 3H_2 + 207 \text{ k.cal}$$
  
 $2Al_{(S)} + 3CO_2 \rightarrow Al_2O_{3(S)} + 3CO + 177 \text{ k.cal}$ 

The above reactions do not alter the total number of moles of gas in the system (Al and Al<sub>2</sub>O<sub>3</sub> being solids), but at the same time, significantly increase the flame temperature due to the evolution of large quantities of the heat. This increased temperature increases the pressure of the gaseous products so that the positive pressure region gets further extended and the overall impulse (i.e., the area under the P-t curve) is enhanced.

However, increasing aluminium beyond a certain percentage is not preferable due to two reasons:

1. Firstly, excess aluminium may further react with CO to form carbon, thereby decreasing the total number of moles of gaseous products, resulting in the lowering of nRT values.

$$2Al_{(S)} + 3CO \rightarrow Al_2O_{3(S)} + 3C_{(S)}$$

Subsequent mixing of the unreacted or partly reacted gases with atmospheric oxygen
may produce a delayed secondary explosion.
 The percentage of aluminium in an HE composition should therefore be optimized.

The percentage of aluminium in an HE composition should, therefore, be optimized accordingly.

# 4.5 Industrial Explosives

#### 4.5.1 Introduction

For more than 350 years, explosives have been employed to mine ores and minerals. World annual consumption of industrial explosives is at least  $5 \times 10^6$  tons, a major part of which is ammonium nitrate—fuel oil (ANFO).

During the first 250 years of this period, only black powder was known and used, but fundamental changes occurred in the 1860s (the invention of dynamite and blasting cap by Alfred Nobel), 1950s (ANFO), and 1980s (emulsions). The search continues for less expensive products and safer techniques for production and field-use in mines, quarries, roads, tunnels, and dam construction. At the same time, the introduction of new products is restrained by the cost of existing investments and by safety and environmental regulations.

"Industrial Explosives" is too big a field to be discussed in detail in this section. The intention of the author is to sketch out only the salient concepts concerning them with respect to their chemistry vis-à-vis their application.

Gunpowder was, perhaps, the first civil explosive used. As far back as 1627, it was used for mining in Slovakia. Then came a less messy explosive in the form of dynamite



**Figure 4.13**Alfred B. Nobel.

containing 75% NG, invented by Alfred Nobel (Figure 4.13). Other developments that followed included low-freezing NG explosives, Permitted Explosives (usable in gassy coal mines), detonators, and detonating cords. A new development took place in 1930s with the development of much safer, less sensitive and more cost-effective "blasting agents," mostly based on ammonium nitrate (AN). Blasting agents include "AN-Fuel Oil (ANFO)," non-cap sensitive "slurry explosives," and "emulsion explosives," which are of fairly recent origin.

The industrial explosives have played a great role in the development of the economy of many countries. The most common applications include mining, civil engineering, agriculture, petroleum engineering (seismic prospecting and perforation of oil wells), etc.

# 4.5.2 Requirements of Industrial Explosives

The sharp differences between the requirements of industrial explosives and that of military explosives have been mentioned in Chapter 1. The major requirements of industrial explosives can be summarized as under:

- 1. Safety of processing, handling, transport, and storage
- 2. Safety during their performance (for example, when used in gassy coal mines, they should not ignite marsh gas, resulting in a disaster).
- 3. Cost-effectiveness that calls for inexpensive starting materials.

- 4. Adequate strength
- 5. Tailorability of power
- 6. Good fume characteristics: no toxic gases should be evolved
- 7. Reasonable storage life
- 8. Good water resistance

The explosives chemist who has to formulate the composition for an industrial explosive for a specific use has a rather complex task ahead of him. He will have to choose a composition that will be the best compromise of the above requirements. He will have to use a variety of ingredients for this purpose. For example, he may have to use:

- an antacid like chalk to ensure better storage life of explosives based on NG, which undergoes acid-catalyzed decomposition during storage.
- Freezing point depressants like nitroglycol (NG freezes at 13°C and the solid NG is dangerously sensitive to impact and friction) to be added to NG-based explosives.
- Gelatinizers like NC to avoid exudation of NG.
- Flame temperature depressants like sodium chloride so that they can be safely used in gassy coal mines. Methane present in coal mines easily forms a dangerous explosive mixture with air. If the mining explosive results in a flame having a high temperature, longer duration, and higher length, it will ignite this explosive mixture, causing a disaster. NaCl ensures that a part of the explosive energy of the mining explosive is spent to dissociate it, thereby decreasing the temperature and duration of the flame and avoiding such a disaster.
- Fine powder of metals, particularly aluminium (but not in gassy coal mines where a methane—air mixture can be set off by the high temperature Al<sub>2</sub>O<sub>3</sub> particles formed during the explosion) as a fuel-sensitizer.

Simultaneously, he has to ensure that all these ingredients are compatible with each other. He has to take care that the OB of the composition is almost zero. Highly positive OB and highly negative OB compositions will result in the evolution of toxic gases viz. oxides of nitrogen and carbon monoxide, respectively, and this will not be acceptable. Lastly, there should be no compromise in safety, storage stability, and the cost.

# 4.5.3 Industrial High Explosives

Today the industrial explosives can be broadly classified as "High Explosives" and "Blasting Agents." While the main ingredient in the former category is NG, the blasting agents mainly use AN in different types of formulations. NG-based explosives are quite powerful and more water-resistant than blasting agents, but the problem of their sensitivity, cost, and the limited extent of their tailorability have made them a thing of the past, paving the way for safer, cheaper, and more easily tailorable blasting agents.

The NG-based industrial explosives can be categorized as below:

- 1. "Straight dynamites" based on NG and kieselguhr. They are hardly used nowadays because of their high cost, sensitivity to shock and friction, and poor fuming characteristics (i.e., evolution of toxic gases during explosion).
- 2. "Ammonia dynamites" based on the introduction of less sensitive AN in dynamite composition. This results in lowered VOD and less objectionable shock sensitivity and fuming characteristics.
- 3. "Gelatine/Semigelatine explosives": A small amount of NC is introduced to keep the explosive in gel/semigel form along with a variety of ingredients. A typical composition may include NG (base explosive), NC (gelatinizer cum explosive), AN (oxidizer cum explosive), saw dust (carbonaceous fuel), NaCl (flame temperature depressant), and chalk (antacid). These types of explosives can be used as "Permitted Explosives" (a term that is meant for explosives that can be safely used in gassy coal mines).

## 4.5.4 Blasting Agents

As the requirement of industrial explosives increased by leaps and bounds all over the world, there arose a necessity to look for NG-free explosives and substitute the NG-based explosives by AN-containing ones, as AN is the cheapest and safest source of readily deliverable oxygen for explosives. The concept of blasting agents originated from the United States. They are mainly AN-based, often free from high explosives like NG and TNT. They are cap-insensitive (a composition is said to be cap-sensitive if it would go off when initiated by a No. 8 detonator, which in terms of power, is equivalent to a 2 g mixture of mercury fulminate and potassium chlorate in the weight proportion of 80:20, respectively). Being insensitive, the safety regulations for their transport and storage are much less severe than other explosives in many countries. Some of the popular and widely used blasting agents are given below:

1. Ammonium Nitrate-Fuel Oil (ANFO)

In 1956, Prof. Cook showed that a 94/6 mixture of AN and a fuel oil based on saturated hydrocarbons represented an oxygen-balanced composition.

$$3NH_4NO_3 + CH_2 \longrightarrow 7H_2O + CO_2 + 3N_2 + heat$$

This stoichiometric reaction yields maximum energy (1.025 k cal per gram of the explosive).

AN exists in five crystalline forms at different temperatures. At ambient temperatures, the transformation of one form to another changes the crystalline structure and unit cell volume. It is very hygroscopic and deliquesces at more than 60% relative humidity. This

leads to caking of AN into virtually unmanageable "rocks of AN." This problem has been solved to a great extent by adding anticaking agents that are coated on AN crystals. Nowadays, AN is commercially produced as porous "prills" that are free-flowing and can absorb fuel oil uniformly. ANFO has replaced conventional explosives in open-pit mining. They can be mixed on-site simply by adding oil to a bag of AN prills. ANFOs, being capinsensitive, are usually initiated with an HE booster such as pentolite (PETN/TNT:50/50). If needed, the sensitivity and energy of ANFO can be increased by the addition of explosives or powders of aluminium or ferrosilicon.

The principal disadvantage of an ANFO is that it cannot be used under wet conditions. This led to the development of "slurry explosives."

## 2. Slurry Explosives

Also referred as "watergel explosives" or simply "slurries," this class of explosives consists of:

- 1. A saturated aqueous solution of AN. This solution has a suspension of the following materials:
- 2. Undissolved nitrates like methyl ammonium nitrate.
- 3. Metallic fuels like aluminium
- 4. Organic fuels like glycols
- 5. "Sensitizers" like TNT or PETN in small amounts
- 6. A "thickener" like guar gum to impart cohesion or thickness to the entire composite mixture (like thickener added to soups).
- 7. Cross-linking agents like borax (which cross-links the —OH groups of guar gum, which is a polysaccharide. While guar gum swells due to the "unwinding" of its polymeric structure, cross-linking imparts rigidity to the watergel explosive).
- 8. Slurries are made sensitive to cap initiation by beating fine air bubbles into them. However, these have a tendency to coalesce on storage. Sometimes, "microballoons" (glass or polymeric bubbles with an average diameter of about 40 μm) are added to solve this problem. The air bubbles or microballoons increase the sensitivity of slurries to initiation due to the adiabatic compression of entrapped air in them that results in high temperatures and "hot spots."

Some of the advantages of slurries are:

- a. They can be tailor-formulated to suit the energy and sensitivity requirements.
- b. Very safe to process, handle and transport
- Water-compatible (the swelling of guar gun provides an impervious sheath that offers water resistance to the explosive)
- d. Good fuming characteristics
- e. Wide choice of densities



Figure 4.14

An Avalanche being Triggered by an Explosion. Photo Courtesy by Andrew Longstreth, Olympia Fire Dept., Bonney Lake, USA.

- f. Directly loadable by priming straight into boreholes.
- 3. Emulsion Explosives (or "emulsions")

Emulsions are fairly recent and have superior properties in comparison to ANFO and slurries. They are based on a "water-in-oil emulsion" system in which small droplets of saturated AN solution in water are dispersed in a mineral oil phase. This emulsion is stabilized by the use of surfactants. The advantages of emulsion explosives are:

- 1. As the fine droplets of oxidizer are in intimate contact with fuel, the explosive reaction is complete and it confers the advantages of low post-detonation toxic fumes, high VOD, and being highly waterproof.
- 2. High density
- 3. Higher oxygen balance
- 4. All these factors impart better blasting efficiency to emulsions. Emulsions can be made pumpable in large boreholes. They can be made in the form of cartridges also to replace the conventional NG-based explosives.

Apart from mining and quarrying, explosives have many other uses such as avalanche control, as shown in Figure 4.14.

# **Explosives in Avalanche Control**

Loss of human life and property takes place every year due to snow avalanches. Artificial Triggering by firing the slopes is an economical and practical method of avalanche control and is used in various countries. Natural avalanches are triggered when the bonds that hold the snowpack together break from additional stresses created by factors such as rain, wind, rising temperatures, and the weight of new snow. It is difficult to predict exactly when or where an avalanche will occur. The most common way that avalanches are artificially triggered is

through the use of explosives. The objective of avalanche control is to reduce or eliminate the hazard from potentially destructive avalanches. Avalanches may be initiated by detonating high explosives either in or above the snowpack. When such artificial triggers produce avalanches, impressions about snow stability can be ascertained, and options for avoiding the consequent hazards can be formulated. Explosives can be thrown by hand onto target zones or shot from mortar/artillery guns for more remote delivery of explosive charges.

# 4.6 Processing of the Compositions

Let us briefly see the principles based on which the explosives are processed. Firstly, explosives in pure form are hardly used for any application; rather, "HE compositions" containing one or more explosives and other ingredients are only used. The finished composition for military applications requires certain mechanical properties like machineability, and the pure explosives do not possess them. To get an explosive material of required mechanical property, thermal, and sensitivity characteristics, and also output, a composition of explosives containing certain ingredients is resorted to. Once this composition is decided, the technique of processing the composition is decided based on the physical properties of the ingredients. Three major methods of processing techniques are mentioned below:

## 4.6.1 Melt-Casting

TNT is the main explosive base in this technique. The major advantage of TNT is that its melting point is quite low (~81 °C), whereas its ignition temperature is much higher (240 °C). Other major explosives do not enjoy this advantage. For example, the melting point and ignition temperatures of RDX are 204 and 213 °C, respectively, and they are dangerously close. Unlike TNT, we cannot take the risk of melting RDX for making an RDX-based composition. Because of such a low melting point, the melting of TNT can be achieved by steam. High melting explosives like RDX or HMX can be incorporated in the molten TNT and cast in shells or bombs.

TNT has a very low OB (-74%). It is, therefore, mixed with explosives of higher OB like RDX (OB = -22%), which also adds to the VOD of the final composition, and with oxidizers like AN. Apart from the above, in some compositions, Al (to enhance the blast) and wax (to "phlegmatize," i.e., to desensitize) are also added. Some typical castables are given in Table 4.5.

Most of the castable explosives are machineable. Although the melt-casting process is simple and cheap, the final charges are sometimes prone to cracking, become sensitive, and cause settling of "heavy" ingredients during solidification, resulting in inhomogeneity in the composition.

Explosive	Composition	Density (g/cm <sup>3</sup> )
Amatol	TNT:60, AN:40	1.56
Composition B	TNT:39, RDX:60, wax: 1	1.713
Comp B2	40% TNT, 60% RDX	1.65
Torpex	TNT:40.5, Al:18, RDX:40.5, wax: 1	1.81
Octol	23.7% TNT, 76.3%HMX	1.809
Cyclotol	23% TNT, 77%RDX	1.743
Tritonal	80%TNT, 20%Al	1.72

Table 4.5: Composition and density of typical castable mixtures.

## 4.6.2 Pressing

The crystalline forms of most of the explosives are such that they cannot be pressed as such. The pressed pellets may not have the desired cohesion or the crystals may be sensitive to friction or static electricity development during processing. A lubricant or phlegmatizer like wax is added to the composition before pressing. The pressing can be of different types: direct pressing (with or without vacuum), incremental pressing, or isostatic pressing. During the pressing, the pressure may be in the order of a few tons per square inch. The temperature and duration of pressing may also vary. It is possible in some cases to achieve a density of the final pellet almost close (about 99%) to the crystal density or sometimes called TMD.

# 4.6.3 Plastic Bonded Explosives (PBX)

PBXs are explosive compositions containing crystalline explosives like RDX or HMX to which polymeric binders have been added. The procedure of making a PBX is as follows:

- 1. The binder polymer is dissolved in a volatile solvent.
- 2. The explosive crystals/powder are added and mixed to form a slurry.
- 3. The solvent is evaporated, leaving a coating of the polymeric binder on the explosive particles.
- 4. These coated particles are die-pressed or isostatically pressed at high temperatures (~120°C) and pressures (1–20 kpsi) to get PBX pellets with densities very close to TMD.

Very high "solid loading" (percentage of solids like RDX in the overall composition) can be achieved, sometimes as high as about 97% in PBX compositions. A large variety of polymeric binders can be used like polyurethanes (Estane 5702-F1), polystyrene, fluoropolymers/copolymers (Viton A, Kel-F-800), nitroacetals/formals (BDNPA-F), etc. The major requirements of a binder for PBX are: thermal stability, low toxicity,

Name of PBX	Empirical Formula	Composition	Density (g/cm³)
PBX-9010	$C_{3.42}H_6N_6O_6F_{0.6354}CI_{0.212}$	90% RDX, 10% Kel-F	1.781
PBX-9011	$C_{4.406}H_{7.5768}N_6O_{6.049}$	92% RDX, 6% polystyrene, 2% DOP	1.69
PBX-9205	$C_{4.406}H_{7.5768}N_6O_{6.049}$	92% RDX, 6% polystyrene, 2% DOP	1.69
PBX-9501	$C_{4.575}H_{8.8678}N_{8.112}O_{8.39}$	95% HMX, 2.5% estane, 2.5%	1.841
		BDNPF	
PBX-9404	$C_{4.42}H_{8.659}N_{8.075}O_{8.47}CI_{00993}P_{0.033}$	94% HMX, 3% NC, 3% tris-	1.844
		β-chloroethyl phosphate	
PBX-9407	$C_{3.32}H_{6.238}N_6O_6F_{0.2377}CI_{0.158}$	94% RDX, 6% exon	1.61
PBX-9408	$C_{4.49}H_{8.76}N_{8.111}O_{8.44}CI_{0.0795}P_{0.026}$	94% HMX, 3.6% DNPA, 2.4% CEF	1.842
PBX-9502	$C_{6.27}H_{6.085}N_6O_6F_{0.3662}CI_{0.123}$	95% TATB, 5% kel-F	1.894

Table 4.6: Composition and density of a few plastic-bonded explosives.

compatibility with explosive ingredients, ease of processing, safe and fast curing characteristics, and low glass transition temperature.

The main advantages of PBXs are their good mechanical properties, thermal stability, and safety in processing and handling. Some of the PBXs with their composition and density are listed in Table 4.6.

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# **Questions**

- 1. What decides the spontaneity of a reaction?
- 2. Coal gives more heat than TNT. But TNT detonates but not a piece of coal. Why?
- 3. How does the bond polarity of a functional group in an explosive molecule affect its sensitivity?
- 4. What are the two major parts of explosive energy?
- 5. Which major factors affect the VOD of an explosive?
- 6. What is meant by "Critical diameter" of an explosive? How is it explained?
- 7. The detonation temperature of PETN is 3400 K. Calculate its specific energy in J/g. (Ans: 984 J/g).
- 8. Why is lead styphnate added to lead azide in detonators?
- 9. Why are nitroaromatic explosives more stable than the nitric ester explosives?
- 10. What is the difference between an "igniferous train" and a "disruptive train"?
- 11. How can you increase the fragmenting power of an explosive?
- 12. What is the mechanism of scabbing action?
- 13. How does a conical liner collapse into a jet in an SC?
- 14. Why is the "stand-off" distance essential in an SC?
- 15. How does the addition of aluminium increase the blast effect?
- 16. What are the major requirements of an industrial explosive?
- 17. What are "Permitted Explosives"? Why is sodium chloride added in Permitted Explosives?
- 18. Why is the ratio of AN and fuel oil 94:6 by weight in ANFO explosives?
- 19. What is the role of (a) guar gum (b) microballoons in slurries?
- 20. Why are emulsions superior to slurries?
- 21. What are the three main types of processing explosive compositions?
- 22. What are the advantages of PBXs?
- 23. Give two examples for high melting point explosives.
- 24. What is the relationship between VOD, density and detonation temperature?
- 25. Define power index of an explosive.
- 26. Give some examples for "explosophores" and "auoxoploses."
- 27. Why is a high VOD explosive dangerous for coal mining application?
- 28. Who invented the dynamite and blasting cap?
- 29. Give some examples for castable explosives.