CHAPTER 5

The Propulsive Facet of HEMs: I (Gun Propellants)

5.1 Introduction

Until the nineteenth century, gunpowder was widely used in most types of firearms. The invention of various smokeless powders led to the ultimate replacement of gunpowder as a propellant in rifles and guns. It was seen in the first chapter that a breakthrough was made by Alfred Nobel in the second half of nineteenth century by the invention of "Smokeless powder," by gelatinizing NC with NG. It was called "powder" as it was to replace the messy and inefficient "gunpowder" as a propelling charge. In fact, the propellants for small arms, mortars, and guns are in the form of "grains" of various shapes (solid cylinders, monotubular or multitubular or slotted-tubular cylinders, flakes, etc.) and sizes (as low as 1 mm in length and as high as a few centimeters) depending on the ammunition in which they are used. We will see shortly why we have to go in for such different shapes and sizes. As the propellant is meant to convert the chemical energy packed in it into mechanical/kinetic energy of the projectile, over the years, efforts were concentrated to develop propellants with higher and higher energy to propel projectiles of higher and higher masses to longer and longer ranges. At the same time, care was to be taken to control the flame temperature of the propellant and barrel pressure up to certain levels to avoid the erosion and bursting of the costly gun barrel, respectively. More than a century after the invention by Nobel, we have come a long way in the development of solid gun propellants for small arms, mortars, and guns of various calibers. The development of a gun propellant for a given ammunition for a given weapon is a joint exercise by the gun ballistician and the propellant chemist. While the former takes care of the physics of the drama inside the barrel during the propellant burning and projectile movement, the latter takes care of the chemistry, particularly the thermochemistry of the propellant ingredients.

5.2 Gun: the Heat Engine

Figure 5.1 gives a schematic representation of gun propulsion. "*W*" grams of the propellant inside the cartridge case (to which the projectile is crimped) would burn in a matter of a few milliseconds and the high pressure, high temperature gases would propel the projectile (a shot or a shell) weighing "*M*" grams, through the muzzle of the barrel.

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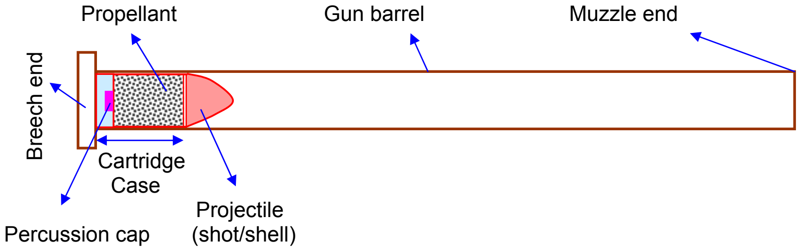


Figure 5.1
Schematic Diagram of Gun Propulsion.

The basic question is: how much of the chemical energy evolved (due to propellant burning) is converted into the kinetic energy of the projectile?

In thermodynamics, we call a system as a "heat engine" if it receives some heat from a "source," does some work out of it, and gives the balance to the "sink." If "Q" is the heat received, and W is the work done, then $(Q - W)$ is "wasted out" to the sink.

The efficiency of the heat engine is defined as the ratio of the useful work done (W) to the total quantity of heat it originally received from the source. When we apply this to a gun, we can realize that it behaves like a heat engine. The "source" is a propellant that gives total heat "Q" (which is the total heat produced by burning = Cal val × weight of the propellant) and the work is the movement of the projectile (or its kinetic energy). The wasted out energy $(Q - W)$ appears in terms of unutilized hot gases, heat transmitted to barrel walls, etc.

We can, therefore, write that:

$$\text{Efficiency of the gun} = \mathrm{e} = \frac{W}{Q} = \frac{1}{2} \cdot \frac{Mv^2}{Q}$$

where v is the velocity of the projectile.

As we know the value of Q and can measure the projectile velocity, v, we can calculate the value of "e" of a gun. The efficiency of a gun is found to be in the range of 30–45%. (There is no need to feel disappointed about this. This is a much better efficiency as compared to our automobiles, whose efficiency is never more than 20–25%).

A rough break-up of the distribution of the evolved energy is given below:

Mechanical energy	1.	For projectile motion = 42%
	2.	Friction = 3%
Thermal energy	1.	To hot gases = 29%
	2.	To barrel wall = 25%
Chemical energy	:	In unburnt propellant = 1%

(The above figures are reproduced from Ref. [11] given at the end. Although the efficiency figure of 42% quoted appears to be rather high, these figures give a rough idea about the propellant energy distribution.)

The Second Law of Thermodynamics states that heat can never be totally converted to work. This applies to the heat engine (gun) too. However, let us see which factors reduce the gun efficiency.

1. *Heat losses to barrel*: Proper design of the gun can minimize it but never eliminate it.
2. *Expansion ratio*: If V_1 and V_2 are the volumes of the product gases before and after expansion (i.e., the total volume of the barrel), respectively, assuming adiabatic conditions (although, strictly speaking it is not true, due to the heating up of walls), the efficiency of conversion of chemical energy to mechanical energy, "e" will be:

$$e = \left[1 - \left(\frac{V_1}{V_2}\right)^{\gamma-1}\right]$$

where γ is the ratio of specific heat of the gases evolved.

The more the gases expand, the better is the above conversion. If we need 100% efficiency, V_2 has to be infinity or we should have a barrel of infinite length.

3. *Pressure gradient*: There exists a pressure gradient in the barrel during the projectile movement. The pressure of the gases near the breech end (P_1) is far more than that is at the muzzle end (P_2). They are related as:

$$\frac{P_2}{P_1} = 1 - \frac{CZ}{2M}$$

where "C" is the propellant charge mass, Z is the fraction of the propellant burnt, and M is the mass of the projectile. The pressure gradient, which increases as the propellant burns and the projectile moves (causing the reduced efficiency as a higher pressure near the breech end), is not fully available to the projectile.

Worked Example 5.1

A gun has been designed for 35% efficiency. The ammunition of the gun contains 6.0 kg of a propellant of cal val 1050 cal g^{-1}. What muzzle velocity is expected of a projectile that weights 5.5 kg?

$$\text{The efficiency} = 35\% = 0.35 = \frac{1}{2}\cdot\frac{Mv^2}{Q}$$

[$M = 5.5$ kg, $Q = 1050$ cal $g^{-1} = (1050 \times 4.18 \times 1000)$ J $kg^{-1} \times (6$ kg$)$]

[Note: $\mathrm{J} = \mathrm{kg\ m^2\ s^{-2}}$, $\mathrm{J} = 4.18\ \mathrm{cal\ g^{-1}}$]

$$0.35 = \frac{5.5\,\mathrm{kg} \times v^2}{2 \times (1050 \times 4.18 \times 1000)\,\mathrm{J\ kg^{-1}} \times 6\,\mathrm{kg}}$$

$$v^2 = \frac{(0.35 \times 2 \times 1050 \times 4.18 \times 1000 \times 6)}{5.5}\mathrm{m^2 s^{-2}} = 3351600\ \mathrm{m^2 s^{-2}}$$

Therefore, $v = 1831\ \mathrm{ms^{-1}}$ is the expected muzzle velocity.

5.3 Unfolding Drama inside the Barrel

Figure 5.2 and the description below might help the reader to understand the sequence of events concerning gun propulsion. Gun barrel is the theater of this vivacious drama, which lasts for a few milliseconds. The first scene is the ignition of the propellant and the last scene is the exit of the projectile from the muzzle end. Figure 5.2 describes the change in the barrel pressure as well as projectile (or shot) velocity against shot travel.

1. The percussion cap at the base of the cartridge case is punctured by the striker pin. The forces of impact and friction ignite the pyrotechnic composition of the cap. This, in turn, ignites the propellant. It is assumed that all the grains of the propellant are simultaneously ignited, although it may not be exactly so.
2. The deflagration of the propellant results in the evolution of large amounts of high pressure gases within the cartridge. However, the projectile has certain inertia and also is crimped to the cartridge case. Only after the development of certain threshold pressure

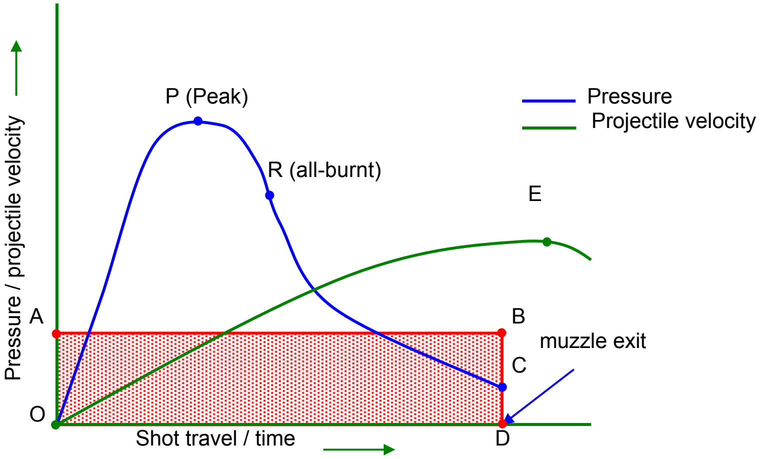


Figure 5.2
Pressure/Velocity—Time Profile inside a Gun Barrel.

(called Shot-start pressure), the projectile detaches itself from the cartridge case and starts moving along the barrel from point O.

3. We should understand that there are two types of pressure-time variation in the entire event. Firstly, it is the positive build-up of pressure in the barrel due to the continuous burning of propellant and evolution of gases, say, $+\left(\frac{dp}{dt}\right)_x$.

Secondly, as the shot moves, the gases have to expand, resulting in the reduction of pressure with the time, say $-\left(\frac{dp}{dt}\right)_y$. The main feature of the in-barrel drama is the competition between these two types of pressure variations. The net pressure-time, i.e., $\left(\frac{dp}{dt}\right)$ variation in the barrel, depends on which one of these is more dominating.

Initially, from point O to point P, there is a steep pressure rise due to the fact $\left(\frac{dp}{dt}\right)_x > \left(\frac{-dp}{dt}\right)_y$

It is because, right from the word "go," the propellant starts burning promptly, whereas the projectile, due to its inertia, starts its acceleration process rather slowly.

4. At peak pressure, viz point P, they are equally competitive. At this stage, neither the propellant is fully consumed nor the projectile is out of the barrel.
5. From point P onwards, it is now the turn of the accelerating shot to outshadow the burning of the propellant so that:

$$\left(\frac{-dp}{dt}\right)_y > \left(\frac{dp}{dt}\right)_x$$

6. At point R, the entire propellant is burnt (called "all burnt" position) and the projectile has traveled only about one-third of its journey through the barrel.
7. At point C, the shot ultimately escapes from the muzzle but still gets further accelerated even beyond the muzzle up to point E (see the velocity curve) because of the muzzle pressure. Muzzle pressure is an important parameter in the design of the gun system because it gives that "extra kick" to the shot just when it is shunted out of the barrel! Similarly, the muzzle velocity is a vital parameter in gun ballistics.

The entire area under OPRCD represents the total work done by the gases to eject the projectile out. This area can be equated to the area of the rectangle OABD where OD is the time for the shot travel inside the barrel. OA is referred as the mean pressure of the barrel.

5.4 Energetics of Gun Propellant

It was said in Chapter 3 that the “mass burning rate,” or sometimes called mass flow rate during burning denoted by “$\dot{m}$”, is a very important parameter.

$$\dot{m} = rA\rho$$

Two parameters decide the value of $\dot{m}$ (apart from density ρ). Firstly, it is the ENERGETICS factor, i.e., the heat output (cal val) of the composition that decides value of “r”. For example, if we take two identical strands of NG-based (high cal val) propellant and picrite-based (low cal val) propellant at a given pressure and temperature, the linear burning rate “r” of former will be much higher than that of the latter. The second factor is the CONFIGURATION. For a given composition (having a given value of “r”), if we make two grains of equal weight (same composition), one with larger surface area for burning (A) than the second, the former gets consumed much faster than the latter. If one measures the rate of rise of pressure of gases due to the burning of these two grains, (dp/dt) of the first will be higher than that of the second.

Let us take an interesting example. Picrite-based propellants (sometimes called “cool” propellants) are known to burn more slowly than NG-based propellants (“hot” propellants) as mentioned above. However, if we take two cartridge cases, the first containing 1 g of picrite propellant in the form of 1000 small cylindrical grains and the second containing 1 g of NG propellant in the form of 100 big cylindrical grains, on simultaneous ignition the former will burn out much earlier than the latter because of the larger surface area available for burning in case of picrite propellant, although it happens to be a cooler propellant.

We have seen in Chapter 2 that when a propellant burns, only a part of the evolved energy is diverted for the useful work of gas expansion $P\Delta V$, and the rest goes only to increase the internal energy of the gases (ΔE), i.e.,

$$Q = \Delta E + P\Delta V$$

In fact, $P\Delta V$ should be substituted by PV because in ΔV ($\Delta V = V_{\text{products}} - V_{\text{reactants}}$) the volume of the gaseous products is far higher than that of the reactant, i.e., the solid propellants (about 1 g of the propellant occupying a volume of less than 1 cc evolves about 1000 cc of the gaseous products). Secondly, at such high pressures as we deal with in gun propulsion, the gases are no longer ideal in behavior and therefore, we have to correct the volume occupied by the gases with the co-volume factor “b” because of the significant value of the volume of molecules themselves at high pressures. The effective volume occupied by the gases will be $(V - b)$ in place of V. During the deflagration of the propellant inside a gun barrel, these parameters are related as:

$P(V - b) = nRT_0$. (where T_0 is the flame temperature of the propellant)

If we substitute this in the above equation:

$$Q = \Delta E + nRT_0.$$

The following points need to be remembered with regard to the energetics of the gun propellants:

1. nRT_0 is the index of useful energy of a gun propellant. It shows how many joules of energy can be tapped from a burning propellant *exclusively* to propel a projectile. So, it has the units of J/g and is called the IMPETUS or FORCE CONSTANT of the propellant. For a given projectile weight and propellant charge mass, *the higher the value of* nRT_0, *the higher will be the muzzle velocity as well as the range of the projectile*. The maximum value of nRT_0 achieved in solid gun propellants today is of the order of 1300 J g^{-1}.
2. As T_0 is directly proportional to Q, *a higher cal val propellant achieves higher impetus.*
3. Similarly, if the propellant is based on a compound whose decomposition results in large values of "n" (number of moles of gaseous products per gram of the propellant) (low average mol.wt. of the product gases), the nRT_0 value goes up.
4. It is quite possible that propellant A has a lower cal val than that of B but has a higher force constant. The cal val. of NG and RDX are 1750 cal g^{-1} and 1360 cal g^{-1}, respectively. However, their impetus values are 1318 J g^{-1} and 1354 J g^{-1}, respectively. This is because 1 mole of NG evolves 7.25 moles of gaseous products, whereas 1 mole of RDX evolves 9 moles of the same. The increase in "n" value in case of RDX in comparison to NG has more than offset its lower cal val figure.
5. Beyond certain flame temperature, the gases start eroding the internal walls of the costly gun barrel. A limit for T_0 is, therefore, a must. Hence, the attempt of a propellant chemist is to formulate propellant compositions which have higher and higher values of "n" for an *optimized value of* T_0. Going by the above example, RDX-enriched propellants are preferred to the hot NG-based propellants.
6. The ratio of specific heats γ ($= C_p/C_v$) of the product gases influences the performance of the gun. We have seen in Section 5.2 that the efficiency of conversion of chemical energy to mechanical energy "e" is related as:

$$e = \left[1 - \left(\frac{V_1}{V_2}\right)^{\gamma-1}\right]$$

For a given expansion ratio, viz. (V_2/V_1) the efficiency increases as the value of γ increases.

For example, if we compare NG and RDX, the molar mean values of γ of their respective products of deflagration can be calculated (using standard values of γ available for CO, CO_2, H_2O, N_2, and O_2) as 1.3350 and 1.3773, respectively. If we substitute these values in the above equation, say, for an expansion ratio of 20 (i.e., $V_1/V_2 = 1/20$), it can be calculated that the values of "e" (efficiency) are 63.3 and 67.7% for NG and RDX, respectively. Thus, apart from the point of view of "nRT_0", RDX scores over NG in terms of "reduced inefficiency" due to expansion of gases inside the barrel.

The three parameters of energetics that matter for a gun propellant are, therefore.

1. T_0 = flame temperature (with an upper limit).
2. n = the no. of moles of the products per gram of the propellant.
3. γ = the ratio of specific heats of the product gases.

Worked Example 5.2

The impetus of picrite ($CH_4N_4O_2$, mol.wt. = 104.1) is 964 J g^{-1}. Calculate its adiabatic, isochoric flame temperature, T_0 ($R = 8.314$ J dg^{-1} $mole^{-1}$)

The deflagration of picrite is given as below:

$$\underset{(104.1\ g)}{CH_4N_4O_2} \rightarrow \underbrace{CO + H_2O + H_2 + 2N_2}_{(5\ moles)}$$

104.1 g evolves 5 mol of gases.

Therefore, 1 g evolves 5/104.1 mol, i.e., n = 5/104.1 mol g^{-1}

i.e., n = 0.048 mole g^{-1}

Impetus (or force constant), F = 964 J g^{-1}

$F = nRT_0$, therefore, $T_0 = F/nR$.

$$T_0 = \frac{964\ J\ g^{-1}}{0.048\ mole\ g^{-1} \times 8.314\ J\ dg^{-1}\ mole^{-1}} = 2416\ K$$

(Note: This temperature is much lower than the T_0 values of many deflagrating explosives. That is why picrite-based propellants are also called "cool" propellants.)

5.5 Configuration of Propellant Grains

The pressure-time profile inside the gun chamber and the actual value of the peak pressure are very important. While the energetics of the propellant (nRT_0) matters a lot, the *rate of delivery of this energy* also matters equally. Imagine a high energy propellant in a cartridge case inside the barrel burning as slow as an incense stick for several minutes! Certainly, the projectile will never reach the end of the tunnel! The propellant grain configuration should, therefore, be optimally designed so that the required peak pressure is achieved within a matter of a few milliseconds to propel the shot promptly with the desired velocity.

If we imagine that the shot does not move, i.e., the volume available for propellant burning is a constant, for a given value of ṁ, the pressure of the gases will rise nearly linearly, i.e.,

$$\frac{dp}{dt} \propto \dot{m} \propto r\, A.\rho$$

However, let us remember that the shot is not stationary. It moves and the gases expand. Therefore, a constant value of ṁ will not ensure a fast increasing value of (dp/dt); on the other hand, the (dp/dt) value might decrease if the rate of gas expansion is faster than the rate of its production. Therefore, the grain configuration is designed in such a way that the value of ṁ increases with time. This is done by making the grain *progressively burning, i.e., with increasing surface area with time.* Mathematically:

$\dot{m} = rA\rho$ Assuming r and ρ are constants, $\frac{d\dot{m}}{dt} = (r\rho)\frac{dA}{dt}$

How do we achieve a progressive burning grain? Let us digress a little and see what is a "web" and what are the three modes of burning viz. regressive, neutral, and progressive burning.

Web is the minimum distance that can burn through as measured perpendicular to the burning surface.

A tubular grain is shown in Figure 5.3. When this grain is ignited, the burning proceeds from inside-to-outside (e.g., B → A) as well as from outside-to-inside (A → B). In this grain, the thickness AB, CD, etc. is the web of the grain as it represents the minimum distance that burns through. As the burning is two-sided in this case (viz. A to B, as well as B to A), the *effective web* will be AB/2 or CD/2. If the propellant burns at the rate of "r" mm s^{-1} and the web length (AB or CD) is "x" mm, the time taken to burn the entire grain will be $\frac{x/2}{r}$ s. Now let us see the three modes of burning:

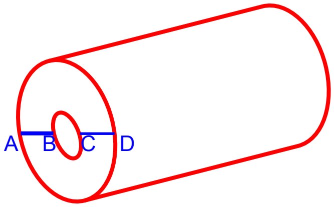


Figure 5.3
Web of a Grain.

5.5.1 Regressive Burning

If the surface area of the grain starts decreasing as the burning proceeds, it is called "regressive burning," e.g., a cord (i.e., solid cylinder). The P-t profile during such a burning is shown in Figure 5.4.

5.5.2 Neutral Burning

If the surface area of the grain remains same or nearly same during the burning, it is called "neutral burning," e.g., tubular grains. The P-t profile is shown below (Figure 5.5).

As the burning proceeds in a tubular grain, the increase in burning surface area due to inside-to-outside burning is compensated by its decrease due to outside-to-inside burning so that at any given time, the total available surface area for burning is same. Therefore, the value of does not change and the P-t profile is horizontal. Strictly speaking, although the changes in the peripheral areas of the cylinder (inside and outside) compensate each other, the areas at both the ends (shaded in the figure) decrease, thereby slightly decreasing the overall surface area of the propellant. This imparts a slight regressiveness making the burning "nearly neutral." This effect is reduced when the length-to-diameter ratio of the grain is increased. (In rocket propellants, as we will see later, the ends are "inhibited" by applying an inert polymeric coat so that they do not burn. This results in a perfectly neutral P-t profile.)

5.5.3 Progressive Burning

When we take a multiperforated grain like the heptatubular grain shown in Figure 5.6, it can be realized that the ignition starts simultaneously from all the seven holes as well as from the periphery. The rate of cumulative increase of surface area originating from seven holes far outshadows the rate of decrease of surface area due to burning from the periphery. As a result, the net surface area available for burning goes on increasing as the burning progresses as shown.

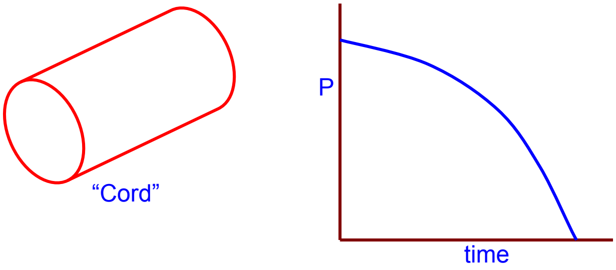


Figure 5.4
Regressive Burning of a Cord.

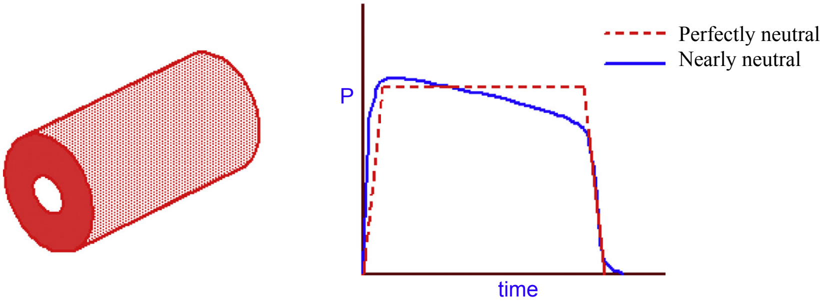


Figure 5.5
Neutral Burning of a Tubular Grain.

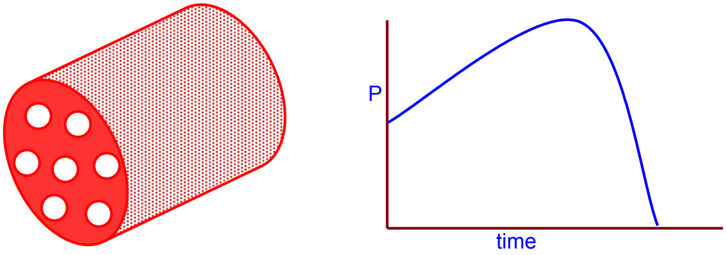


Figure 5.6
Progressive Burning of a Multitubular Grain.

Coming back to our problem of designing a progressively burning grain to achieve a high peak pressure (within the acceptable limits), we can see the reason why the multitubular geometry of the grains is common among gun propellants, especially for high performance guns such as tank guns.

One would find, particularly in small arms ammunitions, cord-type or spherical-shaped propellant grains (sometimes called "Ball Powder") that are obviously regressive burning. The reason is to be found in the fact that the barrels of these weapons are very short as compared to large caliber guns. There is just no time to "allow" the development of progressivity. The sense of urgency for the peak pressure development is much greater here. The cord or ball powder propellants have the maximum surface area right in the beginning to give the shock-kick to the projectile. However, care is taken to see that the pressure does not overshoot and burst the barrel by "moderating" the propellant grains by coating their surfaces with materials of negative cal val (e.g., phthalate esters that also act as plasticizers), and thereby keeping the burn rate under some check. It is like starting an automobile right on the fourth gear, but keeping a cautious pressure on the brake!

The foregoing two sections show that the two factors viz. energetics and grain configuration jointly decide how quickly the grain can burn, and this "quickness" is referred as the VIVACITY of the propellant.

5.6 Salient Aspects of Internal Ballistics of Guns

The term *"ballistics" means the study of the motion of a projectile.* "Internal ballistics" of gun refers to the branch of applied physics that deals with ballistic properties of propellants in relation to the motion of the projectile inside a gun barrel. Much of the theoretical work in this field started as far back as 1870s. In this section, it is not possible to give a detailed analysis of all the work done in this field, but a few salient points are mentioned.

1. The equations involved in the internal ballistics of gun establish the relation between the "gun parameters" (e.g., caliber of the gun, projectile mass, its velocity, its travel distance at any time "t", chamber volume, etc.) and "propellant parameters" (e.g., its cal val, force constant, web size and "form function" of the propellant grain, density of the grain, the pressure/temperature/ratio of specific heats/co-volume of the product gases, and the Equation of State for non-ideal behavior of the gases) by "Energy equivalence" equations, "Dynamic equations" (related to projectile movement), burning rate laws for propellants under ballistic conditions, and "form function."
2. *Burning rate law*: In 1885, Vielle established an important relation between the linear burning rate (r) of a propellant and the pressure (P) under which it burns as:

   $$r = \beta P^{\alpha}$$

   where α is the pressure exponent and β is the "burning rate coefficient" of the propellant. This law also applies to both the rocket propellants and gun propellants. The value of "α" may vary from 0.2 to 0.5 in the case of rocket propellants (actually, the symbol "n" will be used in the case of rocket propellants), and in case of gun propellants the value is in the range of 0.8–0.9. This higher exponential variation in the case of gun propellants is due to high pressures under which a gun propellant burns (about 4000–6000 kg cm^{-2}) as compared to rocket propellants, whereas P rarely exceeds 200 kg cm^{-2}.

   Higher pressures lead to:
   a. faster combustive chemical reactions.
   b. Faster heat transmission from the hot gaseous phase to the burning surface ("condensed phase").

A linear plot of "log r" against "log P" gives a straight line with "α" as slope and log β as its intercept on Y-axis.

While the value of α is almost a constant for gun propellants, *the value of* β *is quite characteristic of a propellant composition.* A higher value of β is undesirable for a given propellant composition as it may cause either uncontrolled burning or the problem of loadability. Let us consider two propellant compositions "1" and "2". Assuming their "α" values $\sim$1, their burn rate equations are as given below:

$$r_1 = \beta_1 P, \quad r_2 = \beta_2 P$$
$$\beta_1 = \left(\frac{r_1}{P}\right) \quad \beta_2 = \left(\frac{r_2}{P}\right)$$

The units of "β" are expressed as cm s^{-1} $(MPa)^{-1}$ (where 1MPa $\sim$ 10.1 kg/cm^2). If $\beta_1 >> \beta_2$, it means that propellant "1" has a much higher burning rate than propellant "2" at any given pressure. As a result, for a given grain configuration, its will be so high that the pressure generated within the barrel will exceed the safe specified limit. On the other hand, if we want to increase the web size of the propellant (thereby decreasing the total surface area per grain and hence), the available cartridge case volume may not accommodate the required charge weight of the propellant, i.e., the propellant becomes "unloadable." It should be noted that in a given volume of a cartridge case, the bigger the individual grains, the lower will be the quantity of the propellant that can be loaded in it.

Today, the value of β of many propellants lies in the range of 0.2–0.3 cm s^{-1} MPa^{-1}.

Worked Example 5.3

A gun propellant burning at a pressure of 500 MPa has the values of β and α as 0.25 cm s^{-1} MPa^{-1} and 0.92, respectively. Calculate the linear burning rate of the propellant at that pressure.

According to Vielle's Law:

$$\begin{aligned}
r &= \beta P^{\alpha} \quad \left(\beta = 0.25\,\text{cms}^{-1}\text{MPa}^{-1},\ \alpha = 0.92,\ P = 500\,\text{MPa},\ r = ?\right)\\
\log r &= \log \beta + \alpha \log P\\
&= \log(0.25) + 0.92(\log 500)\\
&= 1.8810\\
r &= A\log\left(1.8810\right) = 76.03\ \text{cm s}^{-1}
\end{aligned}$$

3. Equations of State (EOS): The well-known EOS is PV = RT (for 1 mol of an ideal gas). No gas is ideal, and the non-ideal behavior increases at higher and higher pressures when:
   a. the volume of the molecules becomes significant when compared to the volume of the vessel which they occupy, necessitating a correction for their "co-volume" (denoted by "b" so that EOS becomes P(V−b) = RT).

b. due to further closeness between molecules, their intermolecular attractive forces increase, necessitating a positive correction for the real pressure they exert on the vessel by an amount $= a/V^2$.

The van der Waals equation thus takes the form:

$$\left(P + \frac{a}{V^2}\right)(V - b) = RT$$

("a" and "b" are called van der Waals constants)

It was argued by Abel and Noble that in the range of 2000–3000 K (the deflagration temperature range of gun propellants), the effects due to intermolecular forces can be neglected so that the above equation reduces to:

$P(V - b) = RT$ or $PV = k + bP$, (k = a constant), which is known as Noble–Abel equation. A plot of PV against P should give a straight line with a slope equal to "b". Mostly, the value of "b" is in the range of 1 ml g^{-1}.

The exclusion of intermolecular forces between molecules at high pressures does not really present the correct picture. Therefore, the Noble–Abel equation could not become the exact base for ballistic calculations. Numerous non-ideal gas equations were proposed, but most of them could not be applied for the gun ballistic conditions. The "truncated Virial equation," which takes into account the intermolecular potential (based on the method proposed by Lennard–Jones), was an improvement, although it too was not exact.

4. Computer Programs

Although many computer programs are available for performing thermodynamic computations of different reactions, only a few specific programs exist for the burning of gun propellants like TRAN 72 and BLAKE, which take into account of the non-ideality of gases more quantitatively to arrive at realistic solutions. They perform thermodynamic calculations including equilibrium concentration of gaseous products at constant, as well as varying pressures and temperatures under gun ballistic conditions. For more information, the readers may see the references given at the end of the chapter.

5. Closed Vessel (CV) Test

Gun firing using large amounts of gun propellants for the purpose of initial evaluation or for quality control during production is a costly affair. A CV apparatus is used for such purposes. The principle of a CV test is to fire a propellant of known loading density (i.e., a known mass of the propellant in a fixed space available inside the CV) using an "igniter" like gun powder and measuring the change of pressure (P) as well as (dP/dt) with respect to time. CV is a rudimentary laboratory tool that may not exactly replace a gun because (1) it does not exactly simulate the condition of gas expansion due to projectile movement as it happens in a gun barrel, and (2) the gases cool immediately after the firing in CV. However, CV firing can serve as a useful precursor before the actual gun firing.

The measurement of pressure versus time, (dP/dt) versus P, etc. is normally done for a propellant with reference to a "standard propellant" for the ballistic evaluation.

A typical (dP/dt) versus P curve of a gun propellant is shown in Figure 5.7. The standard (or reference) propellant and the candidate propellant are fired at the same conditions of loading density and temperature, and they are compared for two parameters viz.

a. *Relative Force (RF)*: which is a function of maximum pressure and that tells you about the total output of mechanical energy per gram of the propellant.
b. *Relative Vivacity (RV)*: which is a function of:

$$\left(\frac{dp}{dt}\right)_{max} \times \frac{1}{P_{max}}$$

(detailed equation are not given here) tells you how quickly or "vivaciously" the propellant burns, i.e., *the rate at which the mechanical energy is delivered.* As mentioned earlier, it is jointly decided by the energetics (nRT) factor of the composition and the configuration of the propellant grains.

One of the main factors defined in the interior ballistic calculations of guns is the "FORM FUNCTION." It defines the way in which the surface area of a particular grain shape changes during the course of burning. It is given by the following equation:

$$Z = (1 - f)\,(1 + \theta f),$$

where

Z = fraction of the grain burnt at time "t".

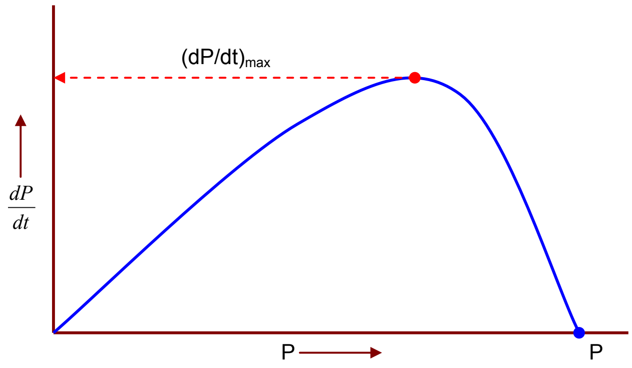


Figure 5.7
A Closed Vessel Firing Curve.

f = fraction remaining at the time of least thickness.

θ = form function.

The value of θ is zero for neutral burning geometries (e.g., Long tubes). It is positive and negative for grains that burn regressively (e.g., cords) and progressively (e.g., multitubular grains), respectively.

5.7 The Chemistry of Gun Propellant Formulations

The propellant chemist has rather a hard job on his/her hands. He/she is required to develop a propellant with suitable composition, shape, and size to meet the complex needs of an ammunition. It is not only the energy requirements he/she has to bother about. The propellant he/she develops should meet the following requirements in general:

1. *Energy delivery requirement*: In terms of cal val/nRT_0/loadability.
2. *Manufacturing characteristics*: In terms of cost and availability of raw materials/hazards of manufacture/propellant viscosity and flowability/environmental considerations, reproducibility, etc.
3. *Storage requirements*: Effect of (low and high) temperature cycling on performance, mechanical properties, moisture absorption, exudation of plasticizer, etc.
4. *Compatibility requirements*: Compatibility with the process equipments and processing personnel (mainly toxicity) and compatibility among ingredients.
5. *Mechanical properties requirements*: To have good compression strength and percentage of compression at high (gun barrel) pressures. (If the grains crack under pressure before ignition, the extra surface area exposed will boost the barrel pressure to disastrous levels.) To withstand high acceleration forces and rough handling.
6. *Reliability of performance*: To ensure lot-to-lot reproducibility characteristics in terms of burning rate, RF, and RV.
7. *System requirements*: Smokeless and flashless exhaust gases, ignition and combustion stability, absence of pressure waves, absence of deflagration-to-detonation (DDT) characteristics, minimum sensitivity to heat, high velocity fragments, and other stimuli.

Very often, the achievement of all the above requirements at the same time may be quite difficult and the propellant composition is chosen as the best compromise of all these factors.

A gun propellant consists of the following main classes of ingredients:

1. "*Energetic binder*": To 'bind" all the ingredients into a cohesive grain and also impart energy (NC is the most commonly used binder).
2. *Plasticizers*: Energetic plasticizer like NG and fuel type plasticizers like phthalate esters.

3. *Stabilizers*: e.g., Carbamite, diphenylamine, etc.
4. *Coolants*: e.g., Dinitrotoluene.
5. *Flash suppressants*: e.g., potassium salts.

Today, we can classify gun propellants into four categories:

1. *Single base propellants*: Based mainly on NC. They also generally contain plasticizer, stabilizer, and flash suppressants (used in small arms and low caliber guns). Grain shape may be of cord or tubular, depending on ballistic requirements. Made by "solvent" extrusion method.
2. *Double base propellants*: (used mainly in low caliber guns and mortars).

Based on NC + NG gel matrix (more energetic than single base) + plasticizer + stabilizer + coolant—grain shape may be of tubular or multitubular or tiny spheres called "ball powder," flakes in case of propellant used for mortars. They are made by solvent as well as solventless extrusion methods.

3. *Triple base propellants*: Based on the (NC + NG + picrite) system containing similar additives as above—"cooler" (low flame temperature) and more "gassy" due to the presence of nitrogen-rich picrite (nitroguanidine)—used in large caliber guns. They are made by the solvent extrusion method.
4. *Low vulnerability ammunition (LOVA) propellants*: Propellant compositions excluding NC have been developed to impart insensitivity to accidental initiation of the propellant by high velocity projectile impact. They are based on inert polymeric binders like cellulose acetate in the matrix in which fine, desensitized RDX is dispersed to impart more impetus to the propellant. Some typical compositions and their performance parameters are given in Table 5.1.

(Abbreviation of the names of chemicals: DNT = Dinitrotoluene, DBP = Dibutyl phthalate, DPA = Diphenyl amine, DOP = Dioctyl phthalate, NC = Nitrocellulose, NG = Nitroglycerine.)

Except "ball powders," i.e., ball-shaped propellants, most of the gun propellants are made by the extrusion technique. The major steps involved in the processing of a typical single base propellant are given below:

1. *Dehydration*: Water-wet NC is dehydrated by mixing with alcohol and squeezing out in a press (Dry NC is highly sensitive to impact and heat and is, therefore, always stored with not less than 30% water in it).
2. *Incorporation*: NC (still containing a little water and alcohol) is mixed in a "sigma blade" mixer along with other ingredients. A calculated amount of ether and alcohol mixture is added at the time of this mixing to *partly "gelatinize" NC*. During the semi-gelatinization, the fibrous nature of the NC is partly destroyed. (The fibrous

Table 5.1: Composition and energetics of some typical gun propellants.

Parameter	Single Base		Double Base		Triple Base		Nitramine Base	
Composition (%)	NC (13.15%N)	90	NC (12.2%N)	49.5	NC (13.1%N)	20.8	NC (13.15%N)	30
	DNT	7.5	NG	47.0	NG	20.6	RDX	60
	DBP	1.5	Carbamite	3.5	Picrite	55.0	DNT	5
	DPA	1.0			Carbamite	3.6	DOP	4
	(+0.5 part K_2SO_4)						Carbamite (+1 part K_2SO_4)	1
Cal val (cal g^{-1})	850		1175		880		1000	
Flame temp (K)	2850		3600		2793		3236	
Average molecular wt ($mole^{-1}$)	23.8		25.6		22.4		22.4	
Force constant (J g^{-1})	987		1168		1037		1190	
Linear burn rate coeff., β_1 (cm s^{-1} MPa^{-1})	0.10		0.25		0.13		0.15	

Note: The linear burn rate coefficient β is denoted as β_1 when it is assumed that $\alpha = 1$ in Vielle's equation.

NC burns too fast. In a finished propellant grain, this may result in the development of very high pressures and burst the gun barrel. If fully gelatinized, the burn rate will be too low to create the necessary peak pressure and P-t profile for imparting the required muzzle velocity to the shot. That is why we go in for semi-gelatinization.)

3. *Extrusion*: The mixed dough is extruded through a die-pin assembly to get long strands of required cross-section.
4. *Cutting*: The long strands are cut into grains of required length and dried well to bring down the solvent content (Volatile Matter%) as per specification.
5. *Graphiting*: The dried grains are given a fine coating of graphite with the following purposes:
    a. Graphiting ensures free flow of the grains and, therefore, better loadability in cartridge cases.
    b. Graphite, being a good conductor, helps in avoiding static electricity hazards that might accidentally initiate the propellant ignition.
    c. It helps in insulating the grain from ingress of moisture during storage.
6. *Sieving*: The grains are sieved to eliminate any odd-shaped or broken grains and fine powder.

7. *Blending*: Each batch is evaluated ballistically (e.g., by CV) and different batches are blended accordingly to realize the expected ballistics.

Three major factors that are to be taken care of during a propellant manufacture are:

a. *Quality Control*: Strict quality control needs to be exercised *right from raw material inspection to blending of finished batches.* For example, if NC has a lower "nitrogen content" (less percentage of nitrato groups in the chain), it will result in lower energy of the propellant. If its "ether-alcohol solubility" is more than specified, it might cause excessive gelatinization and reduction in burning rate of the finished propellant. Each and every process parameter is to be scrupulously respected to ensure the quality and reproducibility of performance of the finished propellant. (Sometimes, propellant making is described as an art. There is some truth in this statement, although each aspect or step of propellant processing has a scientific explanation. It is like giving the job of baking a cake to an experienced baker and a novice simultaneously. Although both of them know the finer details of the recipe and start with the same type of raw materials, the veteran baker comes out with a better cake! In the propellant processing, too, the experience plays a key role. For example, a veteran propellant processing technician knows by the look and texture of the dough whether the correct level of gelatinization has been reached or not.)

b. *Safety*: A baker can take a chance, but not a propellant technician! The latter deals with sensitive energetic materials and flammable solvents during the propellant processing. There can be no compromise with safety regulations during propellant manufacture like excellent housekeeping, flame-proof fittings, wearing of cotton clothes and conducting shoes (to dissipate any static electric charges), maintenance of the required relative humidity (min 60%), use of personnel protective equipments, strict adherence to the process schedule, etc. There have been a large number of instances when even a minor lapse in safety precautions resulted in disastrous accidents.

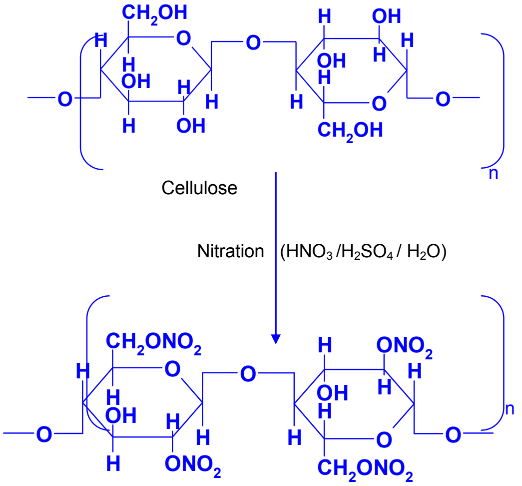
c. *Packing*: Proper packing of the propellant (both internal and external) as per the regulation not only ensures safety during transport and storage, but also ensures a long shelf-life of the propellant.

5.7.1 Role of Ingredients

The role played by some major ingredients used in gun propellants is described below:

1. Nitrocellulose (NC)

NC was synthesized more than a century back. Still, it rules the roost in many propellant compositions. That is because, its parent compound, viz. cellulose is a wonderful material. Cellulose is the natural polymer found in plants. It is a long polymeric carbohydrate chain interconnected by β-glucopyranose units. The molecular structures of cellulose and NC are shown below:



Nitrocellulose (partly $\left(\frac{2}{3}rd\right)$ nitrated)

Each glycosydyl unit of the cellulose structure has three hydroxyl groups, viz. one primary OH (i.e., CH_2OH) group and two secondary OH (i.e., −CHOH) groups. Each unit of NC can be represented by the empirical formula ($C_6H_7O_2(OH)_3$). The square bracket shown in the figure covers two such units.

The cellulose polymer is a long chain with a large number of repeating units (n) and hence has a high molecular weight. The actual molecular weight of cellulose depends on the source and type of cotton linters or wood pulp from which it is prepared. Its molecular weight may vary from a few 100 thousands to a few millions. When cellulose is purified and nitrated using $HNO_3/H_2SO_4/H_2O$ mixture (called "nitrating mixture"), we get NC as shown above. Some of the interesting points in this connection are:

a. Depending on the end use of NC, the specification of properties of NC is varied. Some of the important properties of NC are (1) Nitrogen content, (2) Molecular weight (which determines the viscosity of NC when dissolved in a solvent like acetone or when gelatinized in a mixture of solvents like ether + alcohol), (3) average fiber length. The required properties depend on the source of cellulose and the nitrating conditions such as temperature, pressure, duration, and the actual composition of the nitrating mixture, as well as further processing of nitrated cellulose. For example, for the NC required for double base rocket propellants, we need NC with lower viscosity (and therefore molecular weight) as compared to NC for gun propellants. To achieve this, NC is pressure-boiled to breakdown the molecular chain of NC to a certain level.

b. It is very difficult to nitrate all the −OH groups of cellulose to get fully nitrated NC (which theoretically corresponds to 14.14% N content).
c. *Nitrogen content (% N)*: By varying the nitrating mixture composition, the ratio of the nitrating mixture to cellulose, nitration temperature and nitration duration, NC with varying % N can be obtained. If x is the average number of nitrated groups (out of three in a unit) and y is the % N, we can show that and:

$$y = \frac{1400.8x}{162.14 + 45x} \qquad x = \frac{162.14y}{1400.8 - 45y}$$

Worked Example 5.4

Only 75% of the hydroxyl groups of cellulose could be nitrated during the manufacture of a batch of NC. Calculate the percentage nitrogen of NC obtained.

Every glycosydyl unit of cellulose contains three hydroxyl groups. The number of $-ONO_2$ groups in the final product (NC) corresponds to 75% of three OH groups, i.e., = 2.25 groups.

The above formula:

$$y = \frac{1400.8x}{162.14 + (45x)} = \frac{1400.8 \times 2.25}{162.14 + (45 \times 2.25)}$$
$$= 11.97\% \text{ is the nitrogen content}$$

An increase in % N (i.e., percentage of NO_3 groups) increases the energy (cal val) of NC. For example, the cal vals of NC samples with 12.60, 13.15, and 14.00% nitrogen contents are 3.91, 4.25, and 4.77 kJ g^{-1}, respectively. The percent N value of NC is, therefore, an important property, as that will be a decisive factor for the energetics and, to some extent, the mechanical properties of the propellants that are NC-based. The use of NC varies depending on its % N as shown below.

% N	Use
12.2−13.15	Propellants
11−12	Blasting gelatine
8−11.5	Commercial use (celluloids, lacquers, etc.)

d. *Viscosity*: Cellulose has a fibrous texture. After its nitration, NC still retains the fibrous texture although X-ray diffraction study shows a crystalline structure for NC of higher %N. The main characteristic of NC is its polymeric chain length, i.e., its molecular weight. During nitration of cellulose, the number of repeating units in the molecule gets reduced from 1000 to 3000 units (depending on the source and initial chemical treatment of cellulose) to somewhere between 400 and 700 units because of the molecular chain degradation owing to nitration conditions. The average molecular weight of NC plays an important role in propellant chemistry in terms of (a) *processibility*—for example, a high mol.wt. NC gives a highly viscous dough that cannot be extruded; and (b) *mechanical properties*: a lower molecular weight NC reduces the mechanical properties like tensile strength and compression strength of the finished propellant grain. It is, therefore, essential to have NC of optimum molecular weight.

The viscosity of standard solutions of NC (e.g., a given weight of NC dissolved in a solvent consisting a mixture of acetone and water in the ratio of 93:7 by volume, respectively) is indicative of its average molecular weight. Hence, the determination of viscosity of NC is an important quality-control aspect in a propellant manufacture. As mentioned above, the viscosity of NC can be brought down during its manufacture by "pressure-boiling" of its aqueous suspension in mild alkaline medium, and the process parameters need to be optimized and established to get NC of desired viscosity.

e. "*Blended NC*": During the manufacture of NC for small arms and gun propellants, there is a dual requirement. The NC sample to be used in propellant composition should have certain specified N% (let us say, N_x), and certain specified ether-alcohol solubility (let us say, S_x). While N_x ensures the correct energy level of the finished propellant, S_x ensures that NC will be gelatinized *to the required extent.* However, NC manufactured by nitration (called "straight cut NC") may not meet this dual need. Two different batches of straight cut NC (say having the values of N_1, S_1; and N_2, S_2, respectively) are blended in such a proportion that the blended NC meets the requirement of N_x and S_x.

2. Plasticizers/gelatinizers

The term "gelatinizer" is not to be confused with the term "plasticizer." Plasticizer facilitates the mobility of the molecules in relation to one another. Even inactive and inert compounds like Vaseline, which is a mixture of hydrocarbons, act as plasticizer. When they are added, say, during polymer processing, it increases the workability/flexibility/plasticity of the polymer apart from providing better low temperature properties like lower Glass Transition temperature to the final polymer product. *Gelatinizer*, on the other hand, interacts with the polymer by an electron donor/acceptor mechanism. Some compounds play both these roles as NG does with NC.

The fibrous texture of NC is mainly due to the interchain adhesion due to hydrogen bonding between the adjacent layers. In the case of NG, its molecules are small enough to penetrate through the interstitial space between NC layers and undo such interchain adhesion with the help of their own polar $-ONO_2$ groups. This helps in slidability of NC layers, thus effacing the fibrous texture of NC. What results is a gel matrix of NC/NG that becomes workable and safe, too. Thus, NG is a gelatinizer and also performs the function of a plasticizer.

Two major types of plasticizers are used in propellant manufacture viz. (1) energetic plasticizers (mainly NG) and (2) non-energetic/low energy plasticizers. Solvents like acetone and alcohol (containing polar groups of $C{=}O$ and $-OH$, respectively) are volatizable gelatinizers, i.e., they can be easily removed almost completely by the end of propellant processing. Phthalate esters (e.g., diethyl, diamyl phthalates) are nonvolatile plasticizers and are permanently present in the propellant composition. Phthalate esters also serve as fuels and have some stabilizing effect by absorbing any products of decomposition like oxides of nitrogen during the propellant storage.

3. Stabilizers

Being nitric esters, NC and NG have limited stability as the $RO{-}NO_2$ bond is susceptible to hydrolytic cleavage, resulting in the evolution of oxides of nitrogen over a period of time.

$$R-O-NO_2 \xrightarrow[\text{Higher storage temp.}]{H_2O(\text{moisture})} R-OH + HNO_3$$

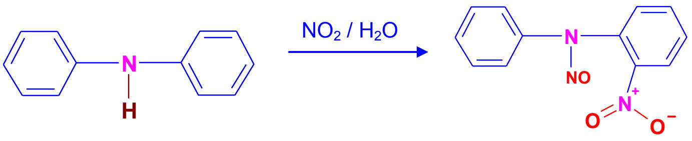
$$2HNO_3 \rightarrow 2NO_2 + H_2O + (O)$$

Although the concentration of NO_2 evolved may be very small, it is sufficient to catalyze further decomposition of NC or NG, resulting in what is called the “autocatalysis” of the propellant decomposition. This is undesirable in terms of safety as well as the ballistic shelf-life (since loss of ONO_2 groups means loss of energy).

To arrest this possibility of the autocatalysis, some stabilizing compounds are added so that they can absorb in situ such oxides of nitrogen in their molecular structure and prevent the catalyzed decomposition of NC and NG. Some well-known examples of the stabilizers used in the propellant industry are given below:

a. Diphenyl amine (DPA)

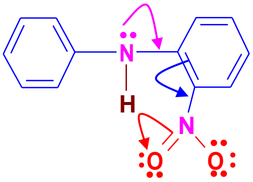
DPA is a base and it absorbs the acidic oxides of nitrogen to form the nitro/nitroso derivative, thereby protecting NC from their attack. (DPA is used only in single base propellants. *It is not used in NG-based compositions* as it is too strong a base and initiates the base-catalyzed hydrolysis of NG.)



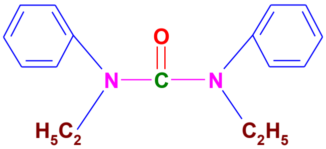
DPA N-nitroso, 2 nitro DPA

b. 2-nitro diphenyl amine (2NDPA)

As shown below, the nitro group of 2NDPA, due to its electron withdrawing tendency, reduces the basicity of DPA. NG-*containing compositions, therefore, use* 2NDPA *as stabilizer.*



c. Sym-diethyl diphenyl urea (also called carbamite or ethyl centralite)



It is an excellent stabilizer, which readily absorbs any evolved oxides of nitrogen. It also acts as a plasticizer and a moderant.

4. Antacids (e.g., chalk)

NC-containing propellants are likely to have "acidity problems" originating from the manufacture of NC, wherein strong nitrating mixture is used. Chalk ($CaCO_3$) in small quantities is added to neutralize this acidity and prevent any acid-catalyzed decomposition of NC and NG in propellant composition during storage.

5. Coolants

Compounds with low cal val are added to propellant to bring down the flame temperature of propellants in certain compositions. These compounds endothermically decompose and thereby, reduce the overall heat output during propellant deflagration. Dinitrotoluene (DNT) and phthalate esters act as coolants.

6. Flash suppressants

NC, the major ingredient in most of the gun propellants, has a negative OB. All other ingredients, with the exception of NG, have a still higher negative OB, with the result that the propellant composition, as a whole, always has a negative OB. As a result, when the propellant deflagrates within the barrel, the product gases that come out are severely underoxidized and abound in CO and to a fair extent, H_2. The deflagration of NC (with 12.75% N) can be written as:

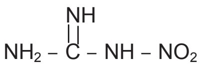
$$2C_{12}H_{15}O_{20}N_5 \rightarrow 6CO_2 + 18CO + 10H_2O + 5H_2 + 5N_2 + \text{Heat}$$

($C_{12}H_{15}O_{20}N_5$ refers to the empirical formula of one repeating unit, i.e., with two glycosydyl units in NC molecule, where five out of six hydroxyl groups of its cellulose precursor have been replaced by $-ONO_2$ groups.)

When large quantities of hot and oxygen-hungry gases of CO and H_2 rush out of the muzzle, they are greeted by the atmospheric oxygen and immediately get oxidized to CO_2 and H_2O, respectively. As these reactions are highly exothermic, the heat of their combustion appears as a big flash. (The Lower Explosive Limits of CO and H_2 in air are 12.5 and 4%, respectively).

Such a big muzzle flash in a battle scenario is undesirable as it reveals the position of the gunner to the enemy, particularly in the nights. To suppress the muzzle flash, salts of potassium such as K_2SO_4, KNO_3, and K_3AlF_6 are added in the propellant composition. Studies have revealed that at the high deflagration temperatures of the propellant, these salts decompose to form the free radicals of the potassium metal that, being highly reactive, immediately combine with oxygen and thereby inhibit the chain reactions that are responsible for the oxidation of CO and H_2. At the muzzle condition, the preference of atmospheric oxygen goes to higher reactive potassium free radicals rather than CO and H_2. One disadvantage of these inorganic salts is that, although they suppress the flash, they cause some amount of smoke.

It is relevant to make a mention about the role of nitroguanidine (picrite) in triple base propellants that, for instance, are used in the large caliber gun ammunitions. Picrite has two advantages viz. (1) it is very rich in nitrogen (53.8%) with the following structure:



$$NH_2-\overset{\overset{\displaystyle NH}{\|}}{C}-NH-NO_2$$

Large amounts of nitrogen in the product gases dilute the CO and H_2 and reduce the chances of their oxidation and generation of flash (2) It is a "cool" ingredient (cal val $= 769$ cal g^{-1}) and hence, the flame temperature of the propellant is low. This significantly reduces the barrel erosion and enhances the barrel life.

(A question might arise in the light of above description: Why then, do we not go in for a propellant composition that has zero or positive OB so that we avert the formation of CO and H_2? Firstly, such a composition will generate more of CO_2 and H_2O and increase the average molecular weight of gases, or decrease the value of "n", thereby decreasing the impetus of the propellant. Secondly, the complete oxidation being much more exothermic than in the case of production of underoxidized CO and H_2, means that the flame temperature of the products will rise to unacceptable levels and cause severe barrel erosion). (3) When the OB of the propellant moves closer to zero, there is a tendency for the propellant to undergo DDT within the barrel, and this would be disastrous.

7. Surface moderants

It was mentioned in Section 5.5 (under "regressive burning") that certain propellant grains, particularly those of regressive burning type, should be surface-coated with substances that decelerate the initial burning rate of the propellant. Substances such as DNT, phthalate esters, carbamite, etc. are useful for this role. They should have either a very low or negative cal val and should be nonvolatile. They are dissolved in ethanol and the solution is sprayed on the propellant grains in a sweetie-pan. Subsequently, the solvent is removed by heating, leaving a thin layer of the moderant on the surface of the propellant grains.

8. Wear reducers

A gun barrel is a costly material. It is a product of precision engineering and made of costly alloy. It has to withstand high pressures and high temperature gases, from round to round. Beyond certain increase in caliber, the barrel has to be abandoned as the sealing of product gases, for the generation of required pressure will cease to operate. Efforts are, therefore, directed to incorporate certain ingredients either in the propellant composition or in a "wear-reducing liner" that is inserted in the cartridge case before loading the propellant in it. Some of the anti-wear additives used are TiO_2 and talc, which are naturally occurring magnesium silicate. These compounds are "waxed" to the surface of the anti-wear liners and when the propellant deflagrates, the wax melts and a fine layer of TiO_2 or talc gets deposited on the inner walls of the barrel. TiO_2 and talc, being excellent heat insulators, are contained by a layer that protects the barrel walls from hot gases to a great extent. This layer gets removed when the next round of ammunition is fired, but then, a fresh layer is formed. This cyclic process of layer formation, thermal insulation from hot gases, layer removal, and layer reformation goes on. Eventually, it increases the barrel life.

9. Decoppering agents

Many of the gun barrels have "rifled bore," i.e., they have grooves made inside, commencing from a certain distance from the muzzle end. These grooves impart a high spin to the moving projectile because a spin-stabilized projectile has a better aerodynamic stability during its travel from the muzzle to the target. The fast spinning, high-speed projectile causes great frictional force between the barrel and the driving band of the projectile. This results in the deposit of fine copper particles from the driving band into the grooves, which is undesirable both in terms of safety and ballistics.

To solve this problem, compounds of lead and tin are added in small amounts in the propellant composition. During the propellant deflagration at high temperatures, these compounds decompose and form a low melting, high density alloy of lead and tin that flushes out the fine copper deposits from the grooves.

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Questions

1. What is the order of efficiency of a gun? Which factors affect the efficiency?
2. In an anti-tank gun ammunition, 5.1 kg of a double base propellant whose cal val is 1100 cal g^{-1} is used. If the projectile of this ammunition weighs 5.2 kg and achieves a muzzle velocity of 1440 ms^{-1}, calculate the efficiency of the gun. (Ans: 23.0%).
3. Why is muzzle pressure an important parameter?
4. What is meant by "Impetus" or "Force Constant" of a propellant?
5. The average molecular weight of gases produced during the deflagration of a propellant is 21. If the adiabatic isochoric flame temperature reached during the deflagration is 3000 K, calculate the impetus of the propellant. (Ans: 1188 J g^{-1}).
6. How do the shape and size of a propellant grain influence the rate of pressure rise inside a gun barrel?
7. The propellant grain configuration in some cases is meant for progressive burning, whereas in some others for regressive burning. Why?

8. What is Vielle's Law? Why should one be concerned about the value of the burning rate coefficient of a gun propellant?
9. A gun propellant, burning at a pressure of 400 MPa, has the values of β and α as 0.2 cm s^{-1} MPa^{-1} and 0.90, respectively. What is its linear burning rate at that pressure? (Ans: 43.95 cm s^{-1}).
10. What is the purpose of a closed vessel? What do you understand by relative force and relative vivacity?
11. What are the major requirements of a propellant?
12. Distinguish between single base, double base, triple base, and nitramine base propellants.
13. Why are certain propellant grains graphited?
14. Why is it said that the propellant making is an art?
15. Nitrogen content of a sample of NC is 13.00%. Calculate what percentage of hydroxyl groups of its precursor (cellulose) has been nitrated. (Ans: 86.13%).
16. Distinguish between a plasticizer and a gelatinizer. Why do we "semi-gelatinize" NC while processing propellants for small arms?
17. Why do we blend NC batches before the processing of gun propellants is commenced?
18. Write the possible chemical equation to explain the mechanism of how carbamite addition stabilizes a propellant composition.
19. In double base propellants, DPA cannot be used as a stabilizer. Why?
20. What is the mechanism of production of muzzle flashes and also their suppression using inorganic salts in the propellant composition?
21. What are the roles of (a) Surface moderants, (b) Wear reducers, and (c) Decoppering agents in a propellant composition?