

CHAPTER 12

GUN PROPELLANTS

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12 GUN PROPELLANTS

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12.1 AWARENESS SUMMARY

Gun propellants consist of a polymer (normally nitrocellulose (see 12.2.2.1)) plus additional explosives and additives, carefully formulated to burn smoothly without detonating to produce hot gases to propel a projectile. Gun propellants are sometimes called smokeless powders, a term which originated in the nineteenth century to distinguish the newly developed nitrocellulose (NC) propellants from the traditional corned gunpowder ones. They are indeed largely smokeless on firing, certainly so when compared with gunpowder, which gives more than 50 % of its weight as solid products.

They are not, however, 'powders' in the ordinary sense of the word. They are produced in characteristic shapes such as flakes, ribbons, spheres, cylinders or tubes. The charge in a gun consists of an aggregate of such shapes, which are called grains, or if greatly elongated, sticks, even in small arms cartridges the individual grains are large enough for their characteristic shape to be discernible to the naked eye.

In addition to the wide spectrum of size and shape, the many possible combinations of ingredients multiply the variety of gun propellants. All conventional propellants contain NC in the form of a gel, together with at least one non-explosive additive. NC, being a nitrated natural polymer, gives the mechanical strength and resilience necessary to prevent breaking up of the grains during handling and firing which would otherwise alter the ballistic performance of the charge. Furthermore, NC gives a degree of choice as to the amount of chemical energy available, since it can be of different degrees of nitration and hence of different energy content.

In addition to NC, there are two other major ingredients of conventional gun propellants, which are explosive in character, nitroglycerine (NG) and nitroguanidine (NQ). Most conventional gun propellants comprise three basic types of composition, called respectively single-, double- and triple-base depending on how many of the above ingredients they contain.

The Force constant of a propellant, F also known as Specific Energy or propellant impetus (in the USA), is one of the energy features of a propellant. It is an important ballistic character of the propellant that can be used to compare propellant performance. Its value is calculated as shown in Equation (12-1).

$$F = nRT_o = \frac{RT_o}{\overline{M}} \quad (12-1)$$

Where n is the number of moles of gas produced by 1 g of propellant, $\overline{M}$ is the mean molar mass of the gas produced (g mol^{-1}), R is the gas constant ($\text{J K}^{-1} \text{mol}^{-1}$), and T_o is the adiabatic flame temperature (K).

A propellant in which NC is the only explosive ingredient is called a single-base type. These are employed in all kinds of guns from pistols to artillery weapons. Their Specific Energy (or F value) is generally in the range 920-1075 J g⁻¹.

Double-base propellants contain nitroglycerine (NG) or a similar liquid nitrate ester in addition to NC. They are more energetic than single base propellants, having F values 1075-1175 J g⁻¹ depending on the proportion of NG present. The percentage of NG is much lower than when double base propellants were first introduced in the late nineteenth century, due to the erosive effect of 'hot' propellants.

Triple-base propellants contain, as well as NC and a limited amount of NG, a large proportion of nitroguanidine (NQ), up to about 55 % w/w. NQ, which has the pseudonym picrite, is a white crystalline solid, and it is finely ground before being mixed with the NC/NG gel to form a particulate suspension. The triple-base propellants have F values intermediate between those of the other two types, ranging from 1000-1100 J g⁻¹. Their use is restricted to the larger types of guns because of their difficult ignition characteristics and because their chief virtue, the production of minimal gun-flash, is of most value in that field.

Single- and double-base propellants have existed for a century or more. The triple-base ones date back only half that time, having been developed between the world wars with the object of reducing flash and making gun positions less easy for the enemy to locate during night firing.

Despite the large number of compositions that have been manufactured and tested over the years, no single formulation comes near to fulfilling all user requirements. This is not surprising when considering the list below, particularly bearing in mind that each separate requirement covers a range of problems and in some cases mutually exclusive solutions. Briefly an ideal propellant should possess the following properties:

1. An acceptably high energy/bulk ratio
2. A predictable burning rate over a wide range of pressures
3. An acceptably low flame temperature
4. Capability of being easily and rapidly ignited
5. An acceptably low sensitiveness (see 20.2.1) to all other possible causes of initiation
6. Capability of cheap, easy and rapid manufacture and blending
7. Long shelf life under all environmental conditions
8. Minimum tendency to produce flash or smoke
9. Minimum tendency to produce toxic fumes

Because the search for more efficient weaponry is never-ending, and because the propellant is an essential part of a gun system, research aimed at superior propellants goes on continuously in various parts of the world. One successful line is to incorporate a cyclic nitramine such as RDX (see Figure 4-4), into traditional propellant mixes, which increases performance without unduly compromising safety. Other compositions, which have superficial attractions, have to be disregarded for various reasons. For instance, the 'composite' type

of rocket propellants, which are based on ammonium perchlorate suspended in a fuel matrix, have high-energy values but give toxic and corrosive combustion products and much smoke making them unsuitable for use in guns. Attempts to develop completely revolutionary types of propellant are being made in several countries, but for the moment the conventional types of propellant continue to give good service and they provide a wide choice to the designers of gun systems.

Table 12-1 Some Conventional Gun Propellant Compositions

Type	Name (Country)	Nitrocellulose (NC)		NG (% w/w)	NQ (% w/w)	Other Ingredients (% w/w)
		(% w/w)	% N (w/w)			
SB	FNH (USA)	84.0	13.15	-	-	DNT 10.0, DBP 5.0, DPA 1.0 + Solvent
	AR2206 (Aus)	92.0	13.15	-	-	DNT 7.0, DPA 1.0 + K ₂ SO ₄ , Graphite, Solvent
	IMR (USA)	89.0	13.15	-	-	DNT 7.0, DPA 0.5, K ₂ SO ₄ 1.0 + Solvent
	Snia GM3 (Italy)	96.0	13.1	-	-	DPA 1.0, MC 1.0, DBP 2.0
	Neonite (UK)	95.0	13.1	-	-	DPA 1.0, MC 2.0, DBP 2.0
DB	Nitro Neonite (UK)	90.0	13.2	8.0	-	EC 2.0 + Graphite
	M9 (USA)	57.5	13.25	40.0	-	EC 1.0, KNO ₃ 1.5 + Solvent
	HSC (UK)	49.5	12.2	47.0	-	EC 3.0, Chalk, 0.5
	[Mark 1 Cordite (UK)	37.0	13.1	58.0	-	Mineral jelly 5.0
TB	M30 (USA)	22.0	13.15	21.5	54.7	EC 1.5, Cryolite 0.3 + Solvent
	NQ (UK)	20.8	13.1	20.6	54.7	EC 3.6, Cryolite 0.3 + Solvent
	Cordite-N (USA)	18.5	13.15	18.5	55.0	EC 7.0, K ₂ SO ₄ 1.0 + Solvent
	MNLF2P (UK)	16.25	12.30	16.25	54.0	EC 7.5, K ₂ SO ₄ 2.0, DBP 4.0 + Solvent

12.2 TYPES OF PROPELLANT CHARGES

12.2.1 Introduction

In this chapter the term gun propellants includes small arms propellants unless otherwise indicated, but where both types are included in the same table care has been taken to distinguish small arms propellants from artillery types. As far as the formulation and thermochemistry of the traditional propellants are concerned, there is little difference between the two types. The in-bore pressures and temperatures developed, and the associated muzzle velocities acquired by the projectiles, are of the same order of magnitude, although the rate of acceleration of small arms and cannon projectiles is generally much greater than that of a large calibre gun projectile and the whole ballistic cycle considerably shorter. In the future there may arise wide differences of composition and physical form between artillery, cannon and small arms propellants, because modern developments aimed at the final elimination of the traditional metallic cartridge case are proceeding in different directions, as will be seen later in this chapter. At the present time, however, British service ammunition for both guns and small arms contains the familiar solid, colloidal propellants in granular form, which in essence have changed little over the last fifty years.

In addition to NC, there are two other major ingredients of conventional gun propellants that are explosive in character, nitroglycerine (NG) and nitroguanidine (NQ). They are compared in the table shown below.

Table 12-2 Comparison of Key Ingredients in NC Propellants

Energetic compound	Q* (w.g) J g⁻¹	V* at STP cm³ g⁻¹	Flame temp. K
NC - Nitrocellulose (C ₆ H ₇ N ₃ O ₁₁) _n (13.1 % N)	3745	880	3290
NG - Nitroglycerine C ₃ H ₅ N ₃ O ₉	6275	740	4900
NQ - Nitroguanidine CH ₄ N ₄ O ₂	2680	1077	2100

* Q = Heat of explosion (see 4.4.2), ** V = Gas volume (see 4.4.3)

In theory, many stable explosive compounds of low volatility that do not very readily burn to detonation are candidate ingredients of gun propellants. For instance, in World War II the Germans made extensive use of di-ethylene glycol dinitrate (DEGDN) as a replacement for NG, thus avoiding the diversion of raw material needed for the manufacture of foodstuffs. Meanwhile the Americans tried tetramethylolcyclopentanone tetranitrate (fivonite) and also di-(2-nitroxyethyl)-nitramine (DINA), similarly to replace NG, and from the latter they developed in 1945 the 'flashless' propellant 'albanite' for large naval guns.

In more recent times some countries have replaced NG in propellants by ethylene glycol dinitrate (EGDN), which is more energetic but more volatile

having a higher vapour pressure. In practice, conventional gun propellants comprise three basic types of composition, called respectively single-base, double base and triple-base depending on how many of the ingredients NC, NG and nitroguanidine they contain.

12.2.2 Conventional (Nitrocellulose) Propellants

The first part of this chapter is concerned with these 'conventional' propellants, this term being used to include the new high energy, colloidal propellants containing RDX. A note is included on the intended next step forward, the use of an insensitive synthetic binder to replace the traditional NC/NG gel for RDX propellants.

Table 12-3 Summary of the Different Types of NC Propellants

Designation	Energetic Compounds	Comments*
Single-base propellant	NC	Low F 900 - 1000 J g ⁻¹
Double-base propellant	NC + NG	High F and T _o 1100 - 1200 J g ⁻¹
Triple-base propellant	NC + NG + Nitroguanidine (NQ)	Intermediate F and T _o Lower flash 1000-1100 J g ⁻¹
Multibase, High Energy or Nitramine propellant	NC + NG + NQ + RDX	Very high F and T _o 1100-1250 J g ⁻¹

* F = Force constant and T_o = Flame temperature

12.2.2.1 Nitrocellulose (NC)

NC, being a nitrated natural polymer, gives the mechanical strength and resilience necessary to prevent breaking up of the grains during handling and firing, which would otherwise alter the ballistic performance of the charge. Furthermore, NC gives a degree of choice as to the amount of chemical energy required, by varying the degree of nitration.

NC is a vital ingredient not only of all conventional gun propellants and many rocket propellants but also of numerous commercial blasting explosives. The compound is correctly named cellulose nitrate, and not nitrocellulose, which is a misnomer, since it contains the characteristic nitrate ester grouping -C-O-NO₂. NC is no longer manufactured in the UK and is procured from overseas. It is manufactured by the action of mixed nitric and sulphuric acids on cellulose in the form of cotton linters and also from paper originating from wood. Cellulose is a natural polymer consisting of anhydroglucose repeating units.

The effect of nitration is to replace some of the -OH groups in the molecule by nitrate groups -ONO₂. Figure 12-1 shows fully nitrated cellulose, however,

complete nitration cannot be achieved in practice; the extent to which it occurs in a given sample depends on the reaction conditions selected, particularly the composition of the acid and the time and temperature of nitration. NC is therefore an ill-defined substance consisting of a random mixture of cellulose mono-, di- and trinitrates.

The customary way to define its composition is to express the nitrogen content as a percentage by weight. If the product were entirely dinitrate $[C_6H_7O_2.OH.(ONO_2)_2]_n$ the nitrogen content would be 11.1 % w/w, however, if it were entirely trinitrate $(C_6H_7O_2.(ONO_2)_3)_n$ it would be 14.14 % w/w. In practice NC types used in various propellant applications vary from 12.2 - 13.5 % N (w/w).

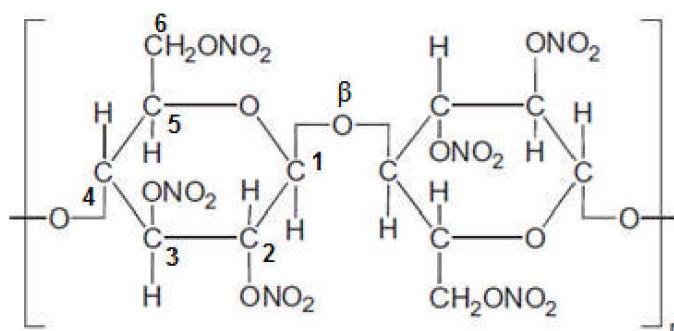


Figure 12-1 Structure of (tri)nitrocellulose

Because two additional oxygen atoms accompany each nitrogen atom, which is introduced on nitration, the percentage of oxygen is linked to that of nitrogen. In any explosive of the CHNO type, the relationship between the percentage of oxygen and that of the fuel elements, carbon and hydrogen, is known as the oxygen balance (see 4.3.1). The nearer the composition approaches to an oxygen balance of zero, the more heat is evolved per unit mass of explosive upon combustion. All grades of NC have a negative oxygen balance, but the higher their percentage of nitrogen and oxygen the higher is the Force constant (F) or (Specific Energy), their heat of explosion (Q) (see 4.4.2) and the temperature achieved by their combustion.

US MIL-DTL-244C amendment 1 (2014) defines the grades and nitrogen contents of NC and the test methods. STANAG 4178 (edn. 2) has recently been updated and the NC test methods are now aligned with the MIL-DTL.

All NC types originating from cotton and wood are pulped white solids, which do not melt but ignite in the region of 180 °C. When dry they are very sensitive to initiation by percussion, friction and flame, but these hazards can be avoided by keeping the sample wet as NC is insoluble in water. In all grades the chemical stability depends on the removal of all traces of acid in the manufacturing process amongst other things.

Whereas cellulose is insoluble in most organic solvents, NC dissolves in such solvents to some extent, forming a gel. Strictly solubility is not the correct term

to use since NC is a large molecule and is suspended in the liquids to give colloids. However, the term will continue to be used here as a shorthand. The gel retains the physical strength derived from the polymeric structure, and is an essential feature of conventional gun propellants, double-base rocket propellants and gelatine and semi-gelatine commercial blasting explosives. The important candidate solvents for the manufacture of these products are acetone, ethanol, ether/ethanol mixture and nitroglycerine. All grades of NC above 10 % N are soluble in acetone but the solubility in other solvents tends to vary with the nitrogen content. NC of up to 11.2 % N (approx.) is soluble in ethanol, but this grade of NC is not sufficiently energetic for use in explosives compositions. NC of up to 12.6 % N (approx.) is soluble in 2:1 ether/ethanol mixture, the solubility peaking at 11.5 % N. This solvent is used in the manufacture of single-base gun propellants. The solubility of NC in nitroglycerine peaks between 12.0 and 12.2 % N. and NC of this grade known as 'blasting soluble nitro-cellulose' is used in the manufacture of commercial blasting explosives. For the higher proportion of NC required in double-base gun propellants either an acetone/water mixture is used as a solvent, or alternatively a 'solventless' process is used. In the latter process a water-wet mixture of NC and NG is gelatinised by passing it between heated rollers. Triple-base gun propellants are made by a combination of the 'solvent' and 'solventless' processes, called the 'semi-solventless' process. Table 12-4 shows the application of NC for differing levels on nitrogen content.

Table 12-4 Application of NC as Function of % Nitrogen

% Nitrogen in NC	Uses
10.2-11.0	Celluloid containers for mortar bomb augmenting charges. Celluloid is NC/camphor (75/25 % w/w)
11.2-12.2	Formerly used in photographic film and currently used in paints and lacquers
12.2 (known as "Type A")	Propellant SC. Extruded double-base rocket propellants
12.5	Neonites NRN*
12.6	Cast double-base (CDB) rocket propellants
12.65	Ballistite
12.9-13.1 (known as "Type B")	Propellant WM. Triple-base propellants N and NQ
13.15	Propellants NH, FNH
13.2	NNN
13.4	Neonites (NRN)*, NPP
14.14	Theoretical percentage for complete nitration

* Neonites contain mixtures of NCs having N = 12.5 % and N = 13.4 %

Some single and double-base propellants for small arms are manufactured by a technique known as the Ball-Powder process. The first steps in this process is the formation of a “lacquer” of partially gelatinised stabilised-NC (usually 13.1 % N) using a solvent, which is immiscible with water, for example, ethyl acetate. The lacquer is then tipped into water in a stirred pan and breaks up into globules. A solution of NG in the solvent may be added at this stage if a double – base propellant is required, the NG being absorbed by the globules. Raising the temperature drives off the solvent and the globules of lacquer harden to solid spheres, their consistent size and quality being maintained by careful control of conditions such as stirrer speed and heating rate.

12.2.2.2 Single-base propellants

A propellant in which NC is the only explosive ingredient is called a single-base type. These are employed in all kinds of guns from pistols to artillery weapons. Their heat of explosion (Q) (see 4.4.2) is generally between 3100 J g^{-1} and 3700 J g^{-1} . It should be noted that energy values of propellants are quoted on the conventional assumption that the water formed on combustion is in the liquid phase, unlike the case of high explosives. The water is in fact gaseous, and the difference in the calculated value of Q is of the order of 10 % higher for water gaseous (w.g) than for water liquid (w.l).

12.2.2.3 Double-base propellants

Double-base propellants contain NG or a similar liquid nitrate ester in addition to NC. They are more energetic than single-base propellants, having Q values between 4300 J g^{-1} and 5200 J g^{-1} depending on the proportion of NG present. The percentage of NG is much lower than when double-base propellants were first introduced in the late nineteenth century, due to the erosive effect of 'hot' propellants.

12.2.2.4 Triple-base propellants

Triple-base propellants were developed between the World Wars to render gun positions less easy to locate during night firing. These contain NC and NG, as well as, up to about 55 % w/w, NQ. NQ, which has the pseudonym Picrite, is a white, finely divided crystalline solid, and was mixed with the NC/NG gel to form a particulate suspension. The old triple-base propellants have Q values similar to single-base, ranging from 3200 J g^{-1} to 3700 J g^{-1} . The use of triple-base propellants has traditionally been restricted to the larger types of gun, where the production of minimal gun-flash, is of most value.

12.2.2.5 High energy gun propellants

The ideal properties required of a propellant have been enumerated previously in this chapter. Since World War II, when RDX was successfully used as a high explosive, much research has been conducted into the incorporation of this compound in gun propellants, to make them approximate more closely to the ideals. Like NQ, which had been incorporated in gun propellants before World War II, RDX is a nitramine explosive (see 4.2.2), but its thermochemical

properties are considerably different and, from certain points of view, better for propellant use. Table 12-5 shows these properties for the four main explosive constituents of solid gun propellants.

Table 12-5 Thermochemical Properties of Explosive Constituents Used in Conventional (Nitrocellulose) Propellants

	NC (13.1% N)	NG	NQ	RDX
Oxygen balance Ω (%)	-31.2	+3.5	-30.8	-21.6
Temperature of detonation T_d (K)	3278	4900	2418	4255
Gas production n (mol g ⁻¹)	0.394	0.32	0.048	0.04
Force constant F (J g ⁻¹)	1074	1568	965	1415

12.2.3 Low Vulnerability Ammunition (LOVA) Propellants

NC has remained the essential ingredient of virtually all gun propellants for over a hundred years despite numerous attempts to find a suitable alternative. Although this material has a number of advantages, one of its major disadvantages is that it is not elastomeric, and therefore a plasticiser is necessary to provide acceptable mechanical properties in NC based propellants. In double-base and triple-base propellants the plasticiser has traditionally been a liquid nitrate ester such as NG. However, experience has shown that propellants containing NC and NG are rather vulnerable to the effects of enemy attack, or to accidental stimuli.

In general, propellants containing NC have relatively low ignition temperatures of about 170 °C. If ignition is caused by an external stimulus (e.g. a high velocity fragment penetrating a cartridge case) the burning rate at atmospheric pressure is sufficiently high to ensure that the propellant charge is rapidly and completely consumed, with highly incendiary effect.

In recent years there have been moves to develop new types of propellant for large calibre guns, which contain no NC or NG. These would be less sensitive to initiation by fragment attack and would moreover have a lower burning rate at atmospheric pressure. Major programmes on these lines are now under way in the UK and the USA with the acronym LOVA (Low Vulnerability Ammunition) and in other countries. These programmes are part of a general policy towards Insensitive Munitions (IM) (see 2.12). In the United States LOVA programme the initial aim was to replace the traditional propellants by different compositions of similar force constant. This can be achieved by incorporating RDX, say 75 % (w/w), in an inert polymeric binder, such as cellulose acetate butyrates with a similarly inert plasticiser. To produce possible second generation LOVA propellants of higher force constant of around 1170 J g⁻¹, it will be necessary to use an energetic plasticiser, with examples given in Table 12-6.

These programmes were part of a general trend towards IM but this is now a basic requirement for all energetic materials and so terms such as LOVA tend not to be so widely used now. There are also other important drivers, in addition to IM, for the development of new propellants such as environmental and hazardous chemical legislation and raw material export limitations.

The ultimate high-energy, low-vulnerability advanced gun propellant, which may have a force constant of about 1300 J g^{-1} , will need to contain both an energetic plasticiser and an energetic binder to support the energetic filler. A number of candidate energetic binders have been considered; including nitrated hydroxyl-terminated polybutadiene (NHTPB) and nitro polyurethanes. The most promising binder materials appear to be polyoxetanes with nitrate-substituents, for example poly-3-nitratomethyl-3-methyloxetane (poly-NIMMO) and polymers such as glycidyl-azide-polymer (GAP), which contain energetic azido-groups. Some of the new propellants with improved performance and IM properties still retain NC as companies that manufacture NC will wish to have continuing use of this material as a major gun propellant component.

Table 12-6 Definition of LOVA Gun Propellant Generations (Comparison Between Eurenco and MSIAC)

Generation	EURENCO	MSIAC*
1 st	RDX Inert binder (CAB) Inert or energetic plasticiser NC (small amount)	Nitramine (RDX) Inert binder (CAB) Inert plasticiser
2 nd	FOX-12 or FOX-7 NC binder Energetic plasticiser	Nitramine (RDX) Inert binder (CAB) Energetic plasticiser
3 rd	FOX-7 Energetic binder (e.g. GAP) Energetic plasticiser (e.g. NENA)	Nitramine (RDX) TPE or cellulose inert binder Energetic plasticiser
4 th	—	Nitramine (RDX) ETPE (energetic) binder Energetic plasticiser

*Munitions Safety Information Analysis Centre (NATO)

Advanced gun propellant research in the UK has focused mainly on the investigation of RDX and HMX-based compositions containing an energetic binder (~15 % w/w of the composition) and an energetic plasticiser (~10 % w/w of composition). The most widely investigated binder has been poly-NIMMO but a wide range of plasticisers has been used, including GAP Azide (a GAP oligomer), Bis-dinitropropylacetal/formal (BDNPA/F), BTTN/TMETN (less shock sensitive nitrate esters) and various NENAs (nitrateoethylnitramines) such as n-

butyl-NENA, methyl-NENA and ethyl-NENA. A plasticiser has a major effect on the glass transition temperature of the propellant: in a typical poly-NIMMO composition this can range from $-15\text{ }^{\circ}\text{C}$ when there is no plasticiser to $-63\text{ }^{\circ}\text{C}$ when the plasticiser is an ethyl-NENA/methyl-NENA mixture. This in turn affects the mechanical properties of the propellant, particularly at low temperatures, and can therefore influence the vulnerability characteristics. In general it has been found that poly-NIMMO-based LOVA compositions can be formulated with specific energies of around 1300 J g^{-1} and low responses to small scale shaped charge attack. The vulnerability is influenced by the web size of the grain, with lower responses being found at smaller web sizes. Interestingly HMX-filled compositions have been found to be less vulnerable than those containing RDX. One further advantage of these propellants is that they have lower flame temperatures than conventional nitrate ester propellants of comparable energy. This can be as much as 400 K and therefore leads to significantly lower barrel erosion in the gun. Figure 12-2 shows the expected performance and combustion temperature of future LOVA gun propellants compared with the existing single- double- and triple-base propellants.

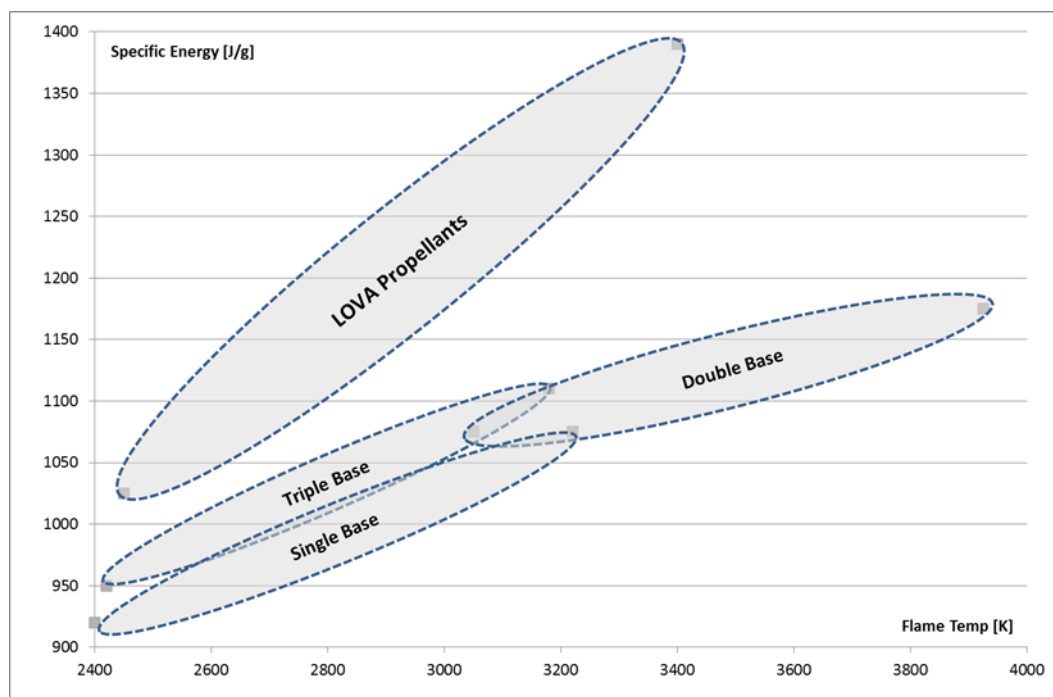


Figure 12-2 Comparative performance of existing gun propellant types and LOVA propellants

In recent years new fillers for gun propellants have been investigated that show superior properties to RDX and HMX. Two of particular note are N-guanyurea dinitramide (GUDN or FOX12) and 2-nitrimino-5-nitro-hexahydro-1,3,5-triazine (NNHT). One of the characteristics of these energetic fillers is their high nitrogen and low carbon contents, which means that on combustion the propellants produce more N_2 and H_2 (and less CO_2 and H_2O) than conventional propellants, leading to lower flame temperatures but higher specific energies.

The fillers are also less sensitive to impact than RDX. New fillers with similar features are likely to be developed in the future.

12.2.4 Propellant Additives

Each type of propellant contains one or more additives, which can be classified according to their function as follows:

1. Stabilisers
2. Plasticisers and coolants
3. Surface moderants
4. Surface lubricants
5. Flash inhibitors
6. Decoppering agents
7. Anti-wear additives

Some additives fulfil more than one of the functions listed above, and this is convenient means of simplifying the manufacture of propellants where possible.

There are three distinct ways in which an additive may be brought into contact with the parent composition:

- The additive can be incorporated in the propellant mix during manufacture and thus be evenly dispersed throughout the finished product. This is the sole method applicable in the case of stabilisers, plasticisers and coolants.
- The additive can be applied to the grains after they have been formed and can then exist either as an absorbed coating (surface moderants) or a surface glaze (lubricant).
- In cartridges for larger guns it is possible to insert the additive as a separate component in the cartridge, so that it decomposes or disintegrates under the influence of heat when the round is fired. This is an option in the case of flash inhibitors, decoppering agents and anti-wear additives.

12.2.4.1 Chemical stabilisers

NC in all types of conventional gun propellant undergoes slow degradation at normal propellant storage temperatures as a result of the loss of nitrate ester groups. Such reactions lead ultimately to stabiliser depletion (see below) and hence to autocatalytic decomposition and potential auto ignition of the propellant. The onset of autocatalysis therefore defines the "chemical safe life" of the propellant but before this is reached the NC will have degraded to a point where both the ballistic and the mechanical performance of the propellant are severely compromised. The shelf life is therefore more usually determined not by stabiliser depletion but by the deterioration of physico-mechanical properties or ballistic performance which can render the propellant unsafe to handle or unreliable in use. "Physico-mechanical life" is strongly influenced by the degradation of NC, the reduction in its average molecular weight causing increased grain brittleness. The "ballistic life" of a propellant is also affected by

the reduction in NC molecular weight with age but other factors such as surface moderant migration and changes in volatile content are often more important in this case.

The one additive common to all conventional gun propellants is the stabiliser. NC and NG are nitrate esters (see 4.2.2) and decompose slowly at normal temperatures to form oxides of nitrogen, mainly nitrogen dioxide, NO_2 . If these oxides are not chemically removed from the system as they are formed they catalyse further decomposition, eventually leading to the shortening of storage life of the propellant and in extremis to auto ignition. The natural decomposition process is shown in Figure 12-3 as NO_2 and then the acidic HNO_2 are formed. If there was no stabiliser present the HNO_2 would react with NC causing further decomposition leading to more acid and a more rapid decomposition (autocatalytic process). The stabiliser reacts with the HNO_2 as it forms and prevents further reaction with the NC. Therefore during the life of the propellant the stabiliser content will decrease and finally to a level where autocatalytic reaction will occur

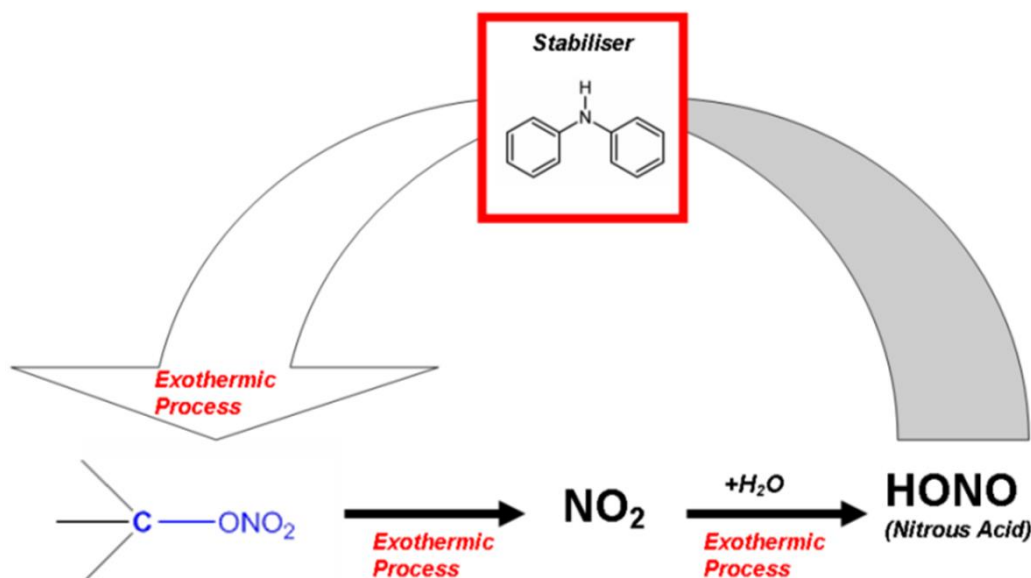


Figure 12-3 Schematic of NC decomposition – detailing the role of chemical stabilisers in preventing an autocatalytic decomposition reaction

All conventional gun propellants therefore contain an additive to react with the products of decomposition. The desirable properties of such a stabiliser are as follows:

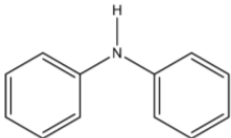
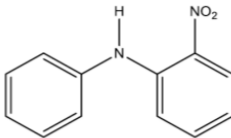
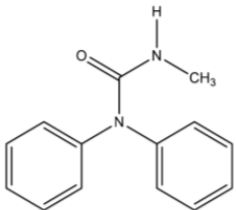
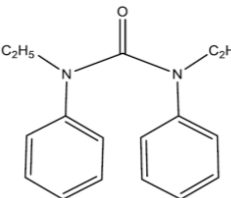
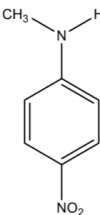
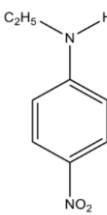
- Capacity to absorb oxides of nitrogen
- Ability to neutralise acids
- Ability to dissolve in the propellant matrix
- Inertness to NC or NG before and after reaction with the decomposition products

Recent investigations have suggested that an important additional role of some stabilisers (e.g. DPA) is to act as an anti-oxidant that blocks the oxidation

reactions of aldehydes (thereby reducing initial gas production) and terminates radical reactions within the propellant.

Stabilisers used in NC propellants are often aniline-urea compounds or their derivatives like alkyl-aryl amines, diaryl amines or aromatic urea derivatives, which are capable of reacting by chemically binding with the radical $\cdot\text{NOx}$ (generic nitrogen oxides) produced from the degradation of the C-NO_x bonds. Examples of aromatic urea derivatives (where N is substituted with a diaryl group is N-methyl-N',N'-diphenyl urea (Arkadite II). Other aromatic urea derivatives where N is substituted with alkyl aryl groups are N',N',-diethyl-N'-N'diphenylurea (ethyl centralite) and N',N'-dimethyl-N',N'diphenylurea (carbamate II). Table 12-7 is a list of common stabilisers used in nitrate ester propellants. The reaction of stabilisers with NO_x is effectively a combination of nitration and nitrosation reactions, which can lead to the formation of stabiliser derivatives or daughter products.

Table 12-7 Common Stabilisers for Nitrate Ester Propellants

Stabiliser	Structure	Stabiliser	Structure
Diphenylamine (DPA)		2- nitro diphenylamine (2 NDPA)	
N-methyl- N',N'- diphenylurea (Arkadite II)		1,3-diethyl-1,3- diphenyl urea (ethyl centralite)	
N-methyl-4- nitroaniline (pNMA)		p-nitro-N- ethylaniline	

Mineral jelly (Vaseline) was one of the earliest stabilisers, and was employed in Mark I cordite (1893), originally in the hope that it would be deposited in the bore by each round fired and would thus provide lubrication for the next projectile. Had this idea been successful in the way intended, mineral jelly would have been classed as what we now call an anti-wear additive. In fact no lubricating effect was found, but it was discovered that mineral jelly, which is a mixture of the higher alkanes from petroleum, contained small amounts of alkenes, which absorbed nitrogen dioxide from the propellant and thus acted as

a stabiliser. Mineral jelly was therefore retained in this role for several decades and was included to the extent of 5-6 % (w/w) in the early cordites. Mineral jelly does not neutralise the acids, which are also products of propellant decomposition. In the early cordites this was done by calcium carbonate, which was deposited in the mass of NC by the process of boiling in hard water during its manufacture. In some UK propellants this uncertain amount of calcium carbonate was supplemented by a fixed proportion of chalk (< 1 % w/w) incorporated in the mix.

Diphenylamine (DPA) has been used in single-base propellants from their early years to the present time. It is a white, crystalline solid, which melts at 53 °C. Chemically it behaves as a base and reacts with the initial decomposition products of NC, initially to form N-nitrosodiphenylamine, which is then converted into various nitro-derivatives of diphenylamine. Diphenylamine is used in the single-base Neonite propellant for modern 7.62-mm ammunition and also in the artillery propellants NH and FNH. It is too basic for use with NG and is therefore not used in double- or triple-base propellants. One disadvantage of diphenylamine is the difficulty of dispersing it evenly through the mix. Its derivative 2-nitrodiphenylamine is less basic and is often used in double-base propellants. In recent years the production of toxic N-nitrosamines by stabilisers such as DPA has become an increasing concern. Indeed many of these stabilisers or their daughter products are toxic in nature, and new stabilisers are being investigated that do not produce such toxic daughter products. Derivatives of α -ionone for example have shown promising stabilisation potentials and a friendly toxicity profile.

The successor of mineral jelly in double-base propellants, later used in triple-base compositions, was carbamate. This name is a pseudonym originally coined for security reasons: the chemical name is diphenyl diethyl urea, known outside the UK as ethyl centralite (EC). It forms as white crystals which, when pure, melt at 72.5 °C.

Ethyl centralite chemically acts as a weak base and reacts with the NC decomposition products to form nitro- and nitroso-derivatives. In addition to its stabilising property it acts as a plasticiser and a coolant. It is used in double-base small arms propellants and also in the triple-base artillery propellant NQ (there may be some confusion in that NQ here is a triple-base composition (see 12.9) but as seen earlier NQ is also used to denote nitroguanidine, which is present in NQ propellant). Methyl centralite is the methyl analogue of carbamate, i.e., it is diphenyl dimethyl urea. It has a melting point of 121 °C. It is a good stabiliser and serves alternatively, but not simultaneously, as a surface moderant.

NQ (nitroguanidine) has a mild stabilising effect, accounting for the extraordinary service life of triple-base propellants.

12.2.4.2 Plasticisers and coolants

In order to convert NC from its natural fibrous state into a gel it must be treated with a solvent, which may be either a volatile one (later removed by evaporation) or the NG that is part of the propellant composition. In either case the process may require the assistance of a plasticiser. The versatile substance carbamate fulfils this role well. Other plasticisers are liquid esters of viscous nature and high boiling points. They have traditionally included dibutyl phthalate (DBP) that was used in the single-base artillery propellants NH and FNH. However the use of dibutyl phthalate was restricted in 2015 under REACH (see 1.3.2.4.6). Therefore dibutyl phthalate has been replaced with liquid plasticisers such as dioctyl adipate (DOA), dioctyl sebacate (DOS), or glycerol triacetate (Triacetin), which also act as coolants.

12.2.4.3 Surface Moderants and Lubricants

Some small arms propellants have their mass burning rates reduced during the early part of the combustion process in order to slow the rise of chamber pressure. This is done by coating the surface of the grain with a substance that absorbs heat when it decomposes. Surface moderation reduces the mechanical shock imparted to the gun on firing and also increases the muzzle velocity of a projectile by allowing it to move significantly before the maximum gas generation rate is reached. This latter property can be enhanced by compacting the propellant grains to give increased loading densities.

The 'moderating' substance is allowed to penetrate the outer layer to the required depth. The volume of the grain thus moderated (or 'deterred' in US terminology) can be up to 40 % of its total volume. Thus the distinction between 'coolant' additives and 'surface moderants' lies not in their chemical identity but in the way in which they are incorporated in the grain: a coolant is dispersed evenly through the grain whilst a surface moderant is present only in the outer layer. Surface moderants can be either solid or liquid. Solids such as dinitrotoluene or methyl centralite must be dissolved in a suitable solvent in order to penetrate the grain, whilst liquids such as dibutyl phthalate can be applied in their natural state. Modern British small arms propellants, e.g. NRN (for 7.62 mm ammunition) and NNN (for 5.56 mm ammunition) employ methyl centralite as the surface moderant. Carbamate can be used as a surface moderant but in practice it is more commonly employed in its stabiliser/plasticiser/coolant role.

A glaze of graphite on the grains has been traditionally used in the case of gunpowder and in recent times has been applied to more modern propellants, including ballistite and NRN. The purpose of this is three-fold: it lubricates the surface to allow easy filling into cartridges, it renders the surface more resistant to moisture and it forms an electrical conductor to dissipate electrostatic charges that may otherwise accumulate.

12.2.4.4 Decoppering Agents

In a large gun the driving band of the shell becomes partially molten during its passage along the bore and leaves a deposit of copper there. If this deposit is allowed to accumulate it eventually affects the ballistic performance of the gun. To counter this a decoppering agent is used with the propellant. This can be done in one of two ways. Firstly, the propellant composition can contain compounds of lead or tin, or secondly a piece of lead or tin foil can be juxtaposed to the propellant in the cartridge. In either case the metallic element combines with the copper deposit and forms a brittle alloy, which is removed by friction when the next projectile is fired.

Table 12-8 summarises some possible functions of the additives mentioned thus far. Notice that some can function in more than one role.

Table 12-8 Possible Function(s) of Some Propellant Additives

<i>Function</i> <i>Additive</i>	Stabiliser	Plasticiser	Coolant	Surface Moderant	Typical % w/w
Chalk	✓	-	-	-	0.4
Diphenylamine	✓	-	-	-	1
Carbamite	✓	✓	✓	✓	1-9
Methyl Centralite	✓	✓	✓	✓	4
Dibutyl Phthalate	-	✓	✓	✓	2
Dinitrotoluene	-	-	✓	✓	10

12.3 CAUSES AND REDUCTION OF MUZZLE FLASH

The flash from a gun can be regarded as comprising two portions:

1. **Muzzle glow** - red in colour and probably due to incandescent particles in the hot gases from the propellant.
2. **Secondary flash** - a much larger flame, usually of considerable light intensity, occurring for some distance in front of the muzzle. This is due to the burning of the gases hydrogen and carbon monoxide after admixture with oxygen from the air.



Secondary flash from large guns is undesirable because at night it can disclose the position of the gun to the enemy and it can also temporarily impair the vision

of the crew. Accordingly, for many decades attempts have been made to overcome the problem, via both gun design and propellant chemistry. What might seem to be the obvious remedy, i.e. increasing the oxygen content of the propellant so that complete combustion occurs within the gun, cannot be applied, because the extra heat liberated by the reactions will increase bore erosion and heat transfer to an unacceptable extent.

There are, however, some practical methods by which flash can be reduced, though not eliminated. Flash can be reduced by the addition of metallic salts, especially by those of potassium, such as potassium sulphate or nitrate, and potassium cryolite. Sodium cryolite can also be used. The predominant mechanism of the reaction is probably the breaking of one of the chain reactions that occur in the oxidation of hydrogen, by radical removal processes. This theory is supported by the fact that potassium hydroxide, which is formed from the original potassium salt additive under the influence of the high in bore temperature, has been found to be a more effective flash-inhibiting additive than any potassium salt. Another mechanism for the reduction of muzzle flash by potassium salts is the inhibition of the water-gas shift reaction ($\text{CO} + \text{H}_2\text{O} \leftrightarrow \text{CO}_2 + \text{H}_2$) that normally occurs as the propellant gases cool producing flammable hydrogen. However, the addition of such salts may increase the amount of smoke.

Another method is to decrease the calorimetric value of the propellant by the addition of coolants such as dinitrotoluene. Experiments have shown that the gases from the 'cooler' propellants contain more methane than those from the 'hotter' propellants, and methane is less easily flammable than hydrogen. This may explain why the comparatively 'cool' single-base propellants (NH and FNH) give relatively little flash although the calculated compositions of their muzzle gases show a greater proportion of $\text{CO} + \text{H}_2$ than for the 'hotter' double-base propellants.

The most effective method is to add to a double-base composition an additional constituent which liberates a large quantity of nitrogen in its combustion and which may also act as a coolant. The best candidate substance is nitroguanidine (NQ), which has the structural formula:

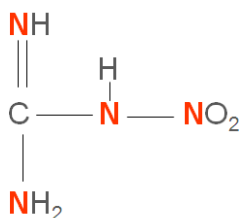


Figure 12-4 Structure of nitroguanidine

Nitroguanidine contains 53.9 % w/w of nitrogen and it is necessary for NQ to be present in a large proportion of the propellant to be effective producing the triple base class of propellants. Table 12-9 shows that the muzzle gases produced by triple-base propellants contain a much lower ratio of flammable gases to

nitrogen than do either single-base or double-base types. The three methods of flash reduction can be combined; propellants N and NQ contain not only nitroguanidine but also sodium cryolite and carbamate as additives.

An interesting property of certain flash inhibitors, particularly potassium bicarbonate and ammonium bicarbonate, is that these additives are also useful in reducing gun bore erosion. The mechanism of the latter affect is not known but it is thought that the decomposition products of the additives bring about changes in the processes of heat transfer to the bore. Ammonium bicarbonate has the further advantage, when incorporated in gun propellants, of not increasing the production of smoke.

Table 12-9 Composition of Muzzle Gases for Different Propellants

Propellant	Gas Volume at STP (cm ³ g ⁻¹)	Molar composition of muzzle gases	
		% CO + H ₂ ,	Ratio %CO + H ₂ to %N ₂
Single-base			
NRN*	924	57.1	5.2
NH	980	67.6	6.4
FNH	1030	71.2	7.0
Double-base			
NPP*	870	44.7	3.5
NNN*	920	56.9	4.9
Triple-base			
N	1060	53.8	2.0
NQ	1000	44.5	1.5

* Small arms propellants

12.4 ELIMINATION OF THE CARTRIDGE CASE

The main purposes of the small arms cartridge case is to grip the bullet to allow an initial pressure rise in the cartridge case before the bullet is ejected, to contain the percussion cap and the discrete quantity of propellant and to provide rearward obturation. Other functions include protection of the propellant from moisture and other environmental contamination, providing a fixed initial free volume for the propellant gases and removing some of the unwanted heat from the gun upon ejection. Thus the cartridge case opened the way for revolutionary improvements in firearms and became regarded as an indispensable component of small arms ammunition.

Although the shotgun cartridge can be cheaply made from paper or polythene, the more exacting requirements of rifled weapons can be met only by metal cases, with the preferred material being 70/30 brass, although aluminium and steel are also used. This alloy is favoured because of its elasticity, hardness range, ductility and corrosion resistance. The brass cartridge case has now been in use for over a century, but in recent decades concerns regarding its use have arisen. The cost of brass, like other metals and alloys, has increased as mineral reserves become depleted, and the cost of the approximately ten energy consuming operations needed to shape it into a case has also risen. The high cost of brass encourages efforts to salvage spent cases, but this is a time consuming and, therefore, expensive exercise in itself. Furthermore brass is a fairly dense material, accounting for some 50 % of the total weight of the cartridge, and because the increased firepower of modern armed forces demands the transportation of increasingly large amounts of ammunition, the total weight of brass, which has to be carried by vehicles and soldier, has increased greatly.

Three separate solutions to the foregoing problems, as they apply to small arms ammunition, have been pursued in recent decades. One is the small calibre concept, which advocates scaling down the size of the cartridge with consequent reduction of range and barrel life. The second is the complete elimination of the metal case. The third is the replacement of the metal case by a combustible one. This latter method has been successful in large calibre ammunition, particularly for tank guns, but has proved unsatisfactory when applied to small arms ammunition. The two on-going solutions are not mutually exclusive; the caseless concept can be, and nowadays is, allied to that of the small calibre.

12.4.1 The Design of the Caseless Small Arms Round

If the cartridge case is eliminated from the weapon system it follows that the vital functions hitherto performed by the case must be transferred either to the gun or to the remaining components of the ammunition. Expanding on the foregoing paragraphs, the main functions of the case are:

1. To hold the bullet and present it accurately to the bore
2. To contain the percussion cap and provide an anvil for it
3. To contain the propellant
4. To protect the propellant from environmental contamination and accidental ignition
5. To provide rearward obturation of the gun
6. To provide a free volume for the combustion gases
7. To remove waste heat from the gun

Of these functions only (1) and to some extent (6) and (7) can be taken over by the gun. In compensation for these added requirements of gun design, there is no spent case to be extracted so the mechanical action can be simpler and faster. All the other functions have to be provided by the ammunition, which

comprises, essentially, only a bullet, propellant and ignition system. Since the bullet cannot be radically modified from its evolved shape and size, the propellant is required to fulfil functions (1) to (4) in addition to its basic one of providing the hot gases for propulsion. Clearly the propellant has to be changed from its traditional form of an aggregate of loose grains into a block of strong materials to grip the bullet and to provide a firm, sheltered recess for the percussion cap. It must also withstand the high stresses imposed by automatic handling at high rates of fire.

Although the propellant must exist as a firm, cohesive body up to the moment of firing, no known propellant has a sufficiently fast mass-burning rate in that condition to set up the required pressure time cycle in the gun. It must be broken up to achieve an adequate specific surface in order to increase its mass-burning rate. Hence the ignition system is in two parts. The percussion cap is situated at the rear of the round in the conventional way. Between it and the bullet is a booster explosive, part of which is in the form of a heavily compressed pellet which acts as an anvil for the cap, and which contains fire holes. When the cap is struck it ignites the booster explosive, which burns to a detonation. This provides a carefully optimised brisant effect that shatters the propellant in a consistent way. It also pushes the bullet further into the bore, providing forward obturation. The fragments of the propellant then burn in the free volume thus produced, as would a conventional granular propellant. The manufacturer claimed that there was no more than the normal round to round variation in peak chamber pressure. This was quoted as 380 MPa at 21 °C imparting a muzzle velocity of 930 m s⁻¹ to the 3.4 g bullet. The weight of propellant was 1.6 g. Since the round is not required to supply the rearward obturation of the gun there is no need for the propellant block or the chamber to retain the traditional circular cross-section. The original cartridge section for the first production caseless small arms round, the Heckler and Koch G11 was rectangular. This was later modified to a bevelled shape for storage in boxes or for fitting the magazine of the rifle. A complete round showing these various features, in diagrammatic form, is illustrated in Figure 12-5. The propellant block was made in separate lateral halves, formed under pressure. The bullet and booster charge were placed between them and the halves were joined with adhesive. The block was then lacquered and when dry the surplus lacquer was machined off. The cap composition was inserted as a wet mix and was covered with a disc of the propellant material. The whole block was then given a final coat of lacquer, which completed its short-term resistance to contaminants such as moisture and oil.

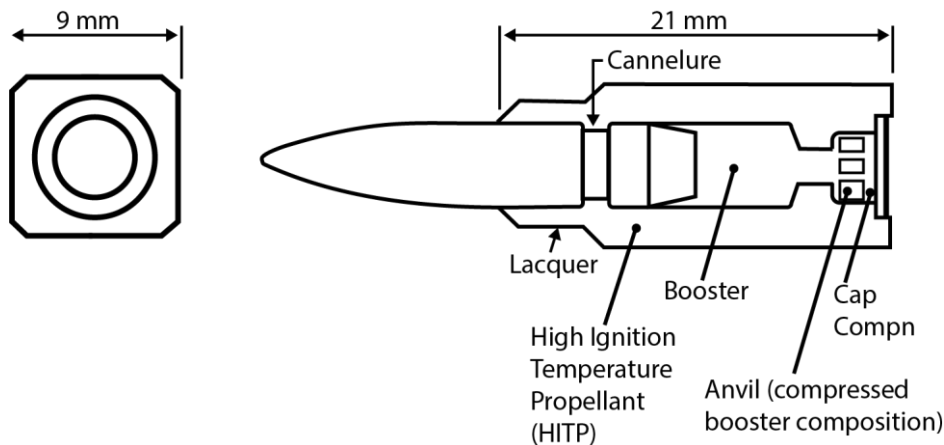


Figure 12-5 Caseless 4.7 mm round for an automatic rifle (diagrammatic)

The propellant for the G11 was originally a granular NC (single-base) type in a combustible plastic matrix, but, this was particularly prone to premature ignition due to conducted and radiated heat known as 'cook-off' when the cartridge was left in a hot chamber, since NC propellant ignites in the region of 170 °C. The US researchers encountered the same problem when attempting to develop caseless rounds in the late 1960s. They then sought a propellant composition which would not self ignite in a chamber below 300 °C. Such a composition was designated 'high ignition temperature propellant' (HITP), but this was considered not sufficient: it was required also to be resistant to accidental ignition outside the chamber, e.g. from flash or sparks, and this was described as 'self extinguishing at ambient pressures' (SEAP). A number of ideas were tried, including a resistant outer covering around an NC core, an HMX/polyurethane propellant and combinations of HMX, TAGN (triaminoguanidine nitrate) and plastic matrix. Some of these experimental compositions achieved the heat resistance requirements but failed on internal ballistic properties and residue free combustion. It was this failure to develop a completely satisfactory HITP/SEAP on which the US development programs for caseless small arms ammunition foundered at that time.

Furthermore, it appears that even the resistance of a caseless round to cook off at 300 °C may not be adequate, as experiments showed that the chamber temperature of a light support weapon may reach 400 °C in battle conditions. It is doubtful whether any viable propellant could reach this degree of insensitiveness to heat (see 5.1.1.1) while still remaining susceptible to ignition by the normal process, and retaining its ability, once ignited, to burn rapidly and completely.

12.4.2 Combustible Charge Containers (CCC)

It has been shown that the increasingly serious disadvantages of the metal cartridge case constitute a major reason for the persistent attempts to develop the caseless small arms round. For weapons of larger calibre, there are similar arguments in favour of eliminating the metal case but the possible solutions are different. It is difficult to imagine, for example, a block of propellant, 10 cm or

more in diameter, being broken up by a booster charge into ballistically consistent pieces. Ordnance varies greatly in size and purpose and, therefore, employs many different cartridge systems. The very largest guns, such as those formally installed in capital ships and coastal batteries, were never loaded with metal cartridge cases. Instead, the propellant was loaded in combustible bags. This system is referred to as the BL system, which originally signified 'breech loading' but which nowadays implies that obturation is chiefly a function of the gun rather than of the ammunition. The BL system still applies to medium calibre equipment (120 mm to 175 mm), both tank guns and indirect fire weapons. There are two other basic cartridge systems. That known as the QF system, employs a metal case which serves to obturate the breech, whilst the RCL (recoilless) system also uses a metal case, but one which is modified to vent at a fixed chamber pressure. It is, however, in the BL system that a significant step forward has been taken with the introduction of the combustible charge containers (CCC). The propellant is loaded into a rigid container manufactured from a mixture of NC, paper pulp and resin. Such containers are lacquered for waterproofing and replace (or in some instances complement) the fabric charge bags, over which they have the following advantages:

1. They are more easily handled than bagged charges.
2. They give better protection to the propellant in storage and transportation.
3. They contain an energetic material (NC) which contributes to the internal ballistic performance of the round.
4. They form, on firing, a boundary layer of comparatively cool gases that helps to preserve the internal surface of the chamber and bore against erosion.

When carried in an Armoured Fighting Vehicle, CCCs are kept in bins that are surrounded by a pressurised water jacket. They are thus protected against an outbreak of fire in the fighting compartment. If an enemy projectile penetrates the jacketed bins the water immediately floods the CCC and propellant in case they are ignited by the impact. The CCC shares its main disadvantage with the caseless small arms round; it is susceptible to accidental causes of ignition, including cook off in hot guns and such random hazards as lighted cigarettes. The CCC is not seen as a straight substitute for a metal cartridge case but rather as an improvement on the bag charge for the BL system.

12.5 Performance Parameters

A gun, regardless of its size, is a device for converting the chemical energy of the propellant to kinetic energy in the projectile. The propellant must be carefully matched to the ballistic requirements, to its limitations of mechanical strength and to its resistance to corrosion and erosion, so as not to compromise its safety, degrade its performance or shorten its useful life.

The propellant is loaded into the gun at the required charge weight in a cartridge case or other container. When the gun is actuated the charge is

ignited by means of a primer, a device designed to produce an explosive burst of flame. This ignites the propellant, effectively within a few milliseconds, and the flame rapidly burns over the entire surface of the charge. Hot gases are generated from the burning surface of each grain, and the pressure in the chamber, already raised by the functioning of the primer, continues to rise rapidly. Most projectiles offer considerable resistance to propulsion, because some part of their periphery has to be engraved by the rifling of the bore to impart rotation. This is not the case for smooth-bore guns. For fixed rounds, considerable extra force is necessary to affect projectile pull, i.e. to separate the projectile from its case. Because of this resistance the chamber pressure becomes quite high, say 20 MPa to 80 MPa, before shot-start occurs. The burning rate of the propellant is dependent on chamber pressure, so although the available volume increases as the projectile moves along the bore, the rate of gas production is so rapid that the pressure continues to increase until the projectile has moved approximately 10 % of the bore length. The peak pressure reached can be as high as 600 MPa. The pressure then drops and by the time the projectile has reached the half-way point of the bore in most gun types, the propellant has been entirely consumed. The pressure continues to fall, but the fall is less rapid because the acceleration of the projectile is now less pronounced. At the instant the projectile leaves the muzzle, the pressure has dropped to about 20 % of its peak value and the acceleration is insignificant due to continuing friction which has had to be overcome. From the foregoing, it will be understood that the pressure/time curve (Figure 12-6) gives the impulse, which is exerted by the hot gases on the base of the projectile. The work done on the projectile, and hence the muzzle velocity, is determined by this impulse.

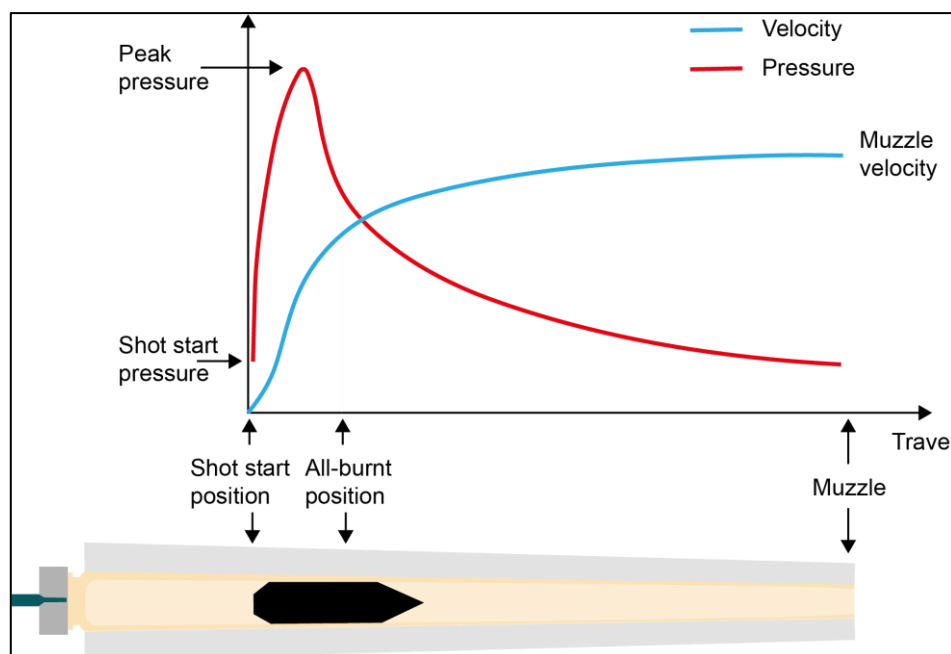


Figure 12-6 In-bore pressure versus distance travelled by the projectile

12.6 GUN PROPELLANT THERMODYNAMICS

12.6.1 Specific Energy F

The work capacity of a propellant is called the specific energy or force constant ('impetus' in the USA) and is designated F. Its value is calculated from Equation **Error! Reference source not found..**

where n is the number of moles of gas produced by 1 g of propellant, $\bar{M}$ is the mean molar mass of the gas produced (g mol^{-1}), R is the gas constant ($\text{J K}^{-1} \text{mol}^{-1}$), and T_0 is the adiabatic flame temperature (K).

The force energy is not measured in units of force but in units of energy per unit mass, or 'specific energy'. These are the same units (J g^{-1}), which are used to quantify Q, the heat of explosion, but the value of F for a given propellant is much smaller than Q. The work capacity depends on the quantity of the essential working fluid produced (in this case a mixture of gases) as well as on the heat available. However carefully the respective output of heat and gas is optimised for a given application, the resulting internal energy of the gas cannot be entirely converted into the work done on the projectile and hence into kinetic energy. Nevertheless, the thermal efficiency of a modern gun, when expressed as energy absorbed in to kinetic energy of the projectile (32 %) compares well with that of an internal combustion engine (20 %), as illustrated in Table 12-10.

Table 12-10 Energy Conversion Values for a Typical Medium Calibre Gun

Energy Conversion	Energy Absorbed %
Translation of projectile	32.00
Rotation of projectile	0.14
Frictional losses	2.17
Total work done on projectile	34.31
Translation of recoiling parts	0.12
Translation of propelling gases	3.14
Heat loss to gun and projectile	20.17
Sensible and latent heat losses in the propelling gases	42.26
Total	100.00

The chemical energy of the propellant gives an approximate indication of the resulting velocity imparted to the projectile. If the efficiency of the gun is expressed in a simplistic way as η then:

$$WQ\eta = \frac{mv^2}{2} \quad (12-2)$$

where Q is the total chemical energy of the propellant, in J kg^{-1} , W is the propellant mass in kg, m is the projectile mass in kg, v is the muzzle velocity of the projectile in m s^{-1} .

Rearranging this equation gives:

$$v = \frac{2WQ\eta}{m} \quad (12-3)$$

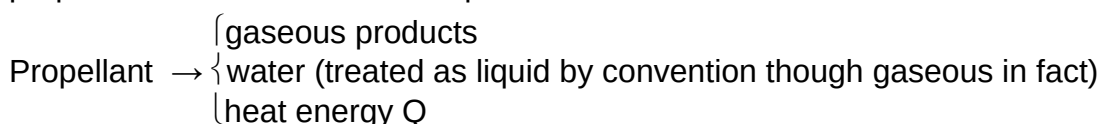
The range of velocities required for different kinds of weapon is from about 300-1500 m s^{-1} . The value of Q for various propellants differs by a factor of no more than 1.5 and the same is true of η , for rifled weapons. It follows that the ratio of propellant mass to projectile mass must widely vary. In fact it ranges from 1:50 in pistol cartridges to nearly 1:1 in high velocity tank gun rounds.

12.6.2 Calorimetric Value and Flame Temperature

The parameter Q of a propellant, hitherto referred to as the heat of explosion (see 4.4.2), can be calculated in the same way as that of a single high explosive, as shown in Chapter 4. The symbol Q denotes a modulus value of the net heat lost to the surroundings by the explosion process, or in other words it is the heat of combustion ΔH with the sign removed. Thus:

$$Q = |\Delta H| = \Sigma \Delta H_f (\text{products}) - \Sigma \Delta H_f (\text{propellant ingredients}) \quad (12-4)$$

where $\Sigma \Delta H_f$ refers to the sum of the standard heats of formation of the compounds involved. Strictly, the value of Q should be called the 'heat of explosion' if calculated or 'calorimetric value' if measured experimentally. The latter term will be used for simplicity. From thermochemistry, the process of propellant combustion can be represented thus:



It can be seen that the force (F) of a propellant is proportional to the product of the pressure of the gas mixture and the volume which it occupies, i.e. $F = PV$.

In turn, the value of PV is given by the basic equation of state for an ideal gas at up to moderately high temperatures.

$$PV = nRT \quad (12-5)$$

where n is the amount of gas (moles) produced by unit mass of propellant, R is the molar gas constant, T is temperature (K).

In order to conform to usage in internal ballistics, the symbol T becomes T_0 . It represents another important parameter of a propellant, the adiabatic flame temperature (again expressed in Kelvin). This is defined as the maximum

thermodynamic standard state temperature ideally achievable under adiabatic conditions.

The value of T_o for a given propellant composition is related to the chemical energy Q by the equation:

$$T_o = \left(\frac{Q}{\Sigma \bar{C}_v} \right) + 298 \quad (12-6)$$

where $\Sigma \bar{C}_v$ is the sum of the mean molar heat capacities of the combustion products (at constant volume). For conventional propellants the value of the expression $\Sigma \bar{C}_v$ does not vary greatly, so T_o is approximately proportional to Q . The value of T_o is of considerable importance to the ballisticians as a factor in the calculation of the force constant. Moreover, to the gun systems designer it is of importance in itself because it plays a large part in determining the characteristic performance of the gun in relation to heat transfer, bore erosion and muzzle flash. Therefore, since T_o depends on Q it is necessary to understand the way in which this is controlled by the combustion chemistry.

12.6.2.1 Oxygen Balance

All the major ingredients of propellants are essentially organic in nature, and are composed of carbon, hydrogen, nitrogen and oxygen. Thus the atomic composition of the propellant can, like that of its constituents, be represented by the general formula $C_aH_bN_cO_d$.

This implies that 'd' moles of oxygen atoms are available to oxidise the fuel elements present, namely 'a' moles of carbon atoms and 'b' moles of hydrogen atoms, more or less completely to oxides of carbon and to water respectively.

The dominant term in the thermochemistry Equation (12-4) is $\Sigma \Delta H_f$ (products). In fact, if small quantities of methane, ammonia, nitrogen dioxide etc. are ignored, this term comprises:

$$p\Delta H_f(\text{CO}) + q\Delta H_f(\text{CO}_2) + r\Delta H_f(\text{H}_2) + s\Delta H_f(\text{H}_2\text{O}(\text{liq})) + t\Delta H_f(\text{N}_2) \quad (12-7)$$

where p, q, r, s and t are the numbers of moles of CO , CO_2 , H_2 , H_2O and N_2 that make up the composition of the products.

The ratios p:q and r:s vary with propellant composition and are chiefly dependent on the oxygen balance (see 4.3.1). If the oxygen balance is high, these ratios will be smaller, and vice versa. The heats of formation of CO_2 and H_2O are considerably higher than those of CO and H_2 respectively. Hence a high oxygen content increases the value of Q , as shown in Figure 12-7.

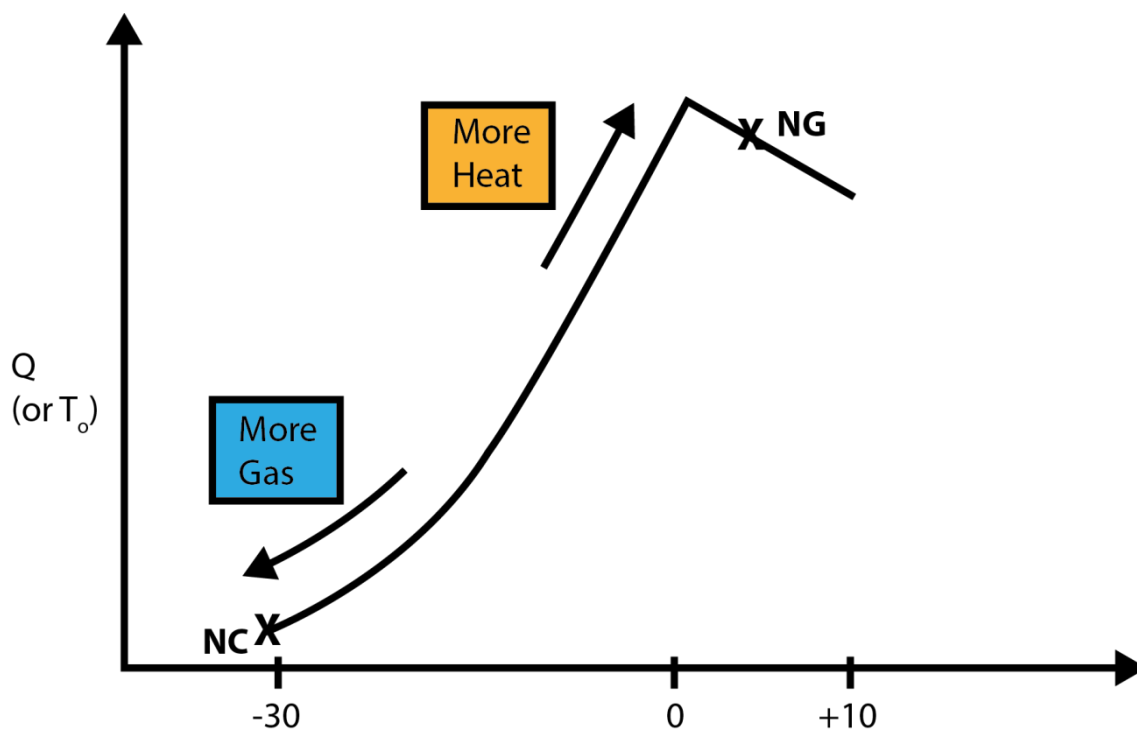


Figure 12-7 Comparison between oxygen balance and Heat of Explosion Q

It follows that single-base propellants derived from NC with 13.3 % N will be correspondingly richer in oxygen, and more energetic, than propellants derived from NC of lower N content. In some compositions a compromise requirement is achieved by blending two different grades of nitrocellulose.

In fact, all gun propellants are formulated to be deficient in oxygen and normally have oxygen balance values within the range -20 to -40 %. The reason for this is to ensure that the flame temperature is not too high, as it would be if the propellant had a zero oxygen balance, and that not too much hydrogen gas is produced, thereby increasing both flash and barrel erosion.

Of the three traditional basic ingredients of gun propellants, NC and NQ are heavily oxygen-deficient but NG has a slightly positive oxygen balance. The oxygen balance of double- and triple-base propellants is therefore very sensitive to the percentage of NG present and the adjustment of this percentage provides a second way of obtaining the required oxygen balance. An example of this can be seen with propellant types cordite-N and NQ. A difference of 2 % in the NG content causes a difference of 15 % in the respective calorimetric values.

A third way to adjust the calorimetric value (Q) of a propellant is by the use of an appropriate additive. Such additives are called coolants. A coolant, in this connection is a substance that absorbs heat when it decomposes during combustion. The original stabiliser, mineral jelly, doubled in this role and so does carbamate. Dinitrotoluene represents 10 % by mass of the artillery propellants NH and FNH and this accounts for the conveniently low flame temperatures of these compositions. Dinitrotoluene also imparts a moisture-repellent quality to propellants. The liquid plasticisers such as dibutyl

phthalate, diethyl phthalate and glycerol triacetate double as coolants and are sometimes referred to as coolant-plasticisers.

To summarise the calorimetric value of a gun propellant composition can be adjusted by:

1. Varying the nitrogen content, and hence the oxygen content of the universal ingredient NC
2. Varying the proportion (if any) of NG
3. Including small amounts of non-explosive additives called coolants

12.7 Burning Characteristics

12.7.1 Propellant Ignition

The Ignition of solid propellant charges in guns is achieved by the direct impingement of hot gas as a flame on the surface of the propellant. The ignition process is essentially a thermal phenomenon, in which the propellant surface is heated from its initial temperature, T_p , to the ignition temperature, T_i , which is typically in the range 160 -175 °C. At this point explosive burning develops, with the rapid liberation of heat and gas. The initial heating is the result of conductive and radiative heat transfer from the primer flame to the hot surface of the propellant, aided by the contact of hot particles with the surface.

When propellant charges are ignited there are additional considerations, the main one being the ability of the flame front to move through the bed of propellant in a cartridge case or charge bag. For small charges such as found in small arms ammunition this poses little problem and the flash of flame from the percussion cap can reliably ignite the propellant in a controlled manner.

When large charges are considered such as in 105 and 155 mm ammunition a method must be found to assist in the flame front moving through the propellant bed in a controlled and consistent manner. This has led to two methods being employed, the first is to use a primer tube that is situated within a cartridge case and allows flame to be introduced throughout the propellant bed through holes along its length. An example of this arrangement is shown in Figure 12-8. This is particularly suited to propellant beds that are made from granular propellant where there will be a complex pathway between the packed grains. Ignition from one end, for example with a base pad igniter, can cause impinging flame fronts moving around the grains to produce localised pressure increase that affect the burning rate in an uncontrolled manner.

The second method allows a base pad igniter to be employed by having a bed of stick propellant with a structure of uncooked spaghetti. The flame can easily flow through the propellant following the channels between the grains. This is known as stick propellant.

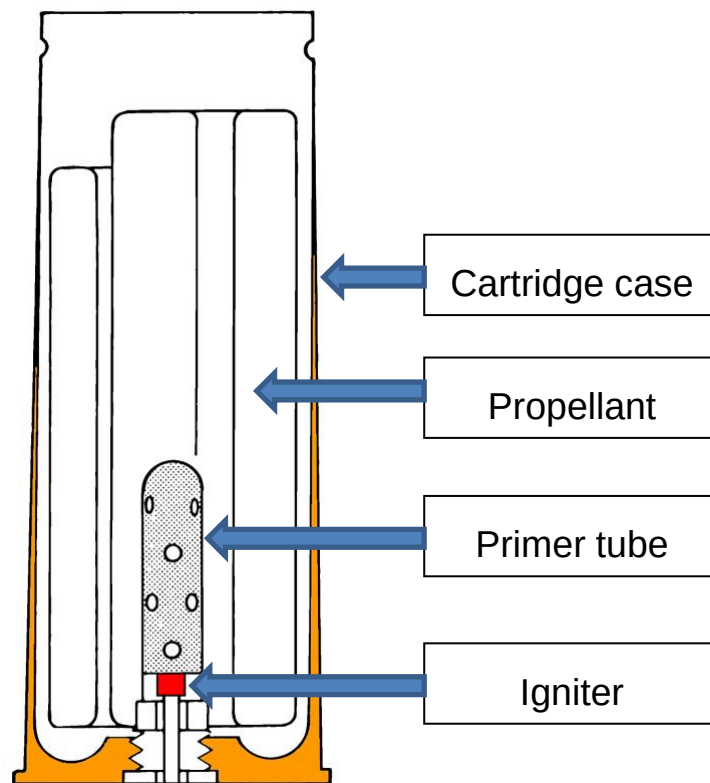


Figure 12-8 Cartridge case with primer tube

12.7.2 The Rate of Burning

The burning process for explosives, which includes gun propellants, is introduced in Chapter 7 for non-porous grains (see 7.2.4.1). The majority of propellants are non-porous in order to provide the utmost ballistic regularity. Certain types of small arms propellant, however, are manufactured by processes designed to produce porosity in the grains. When such a propellant is ignited, the flame penetrates the pores of the grains and so the rate of burning increases rapidly. This property is necessary in short-barrelled weapons such as pistols, and also in blank cartridges, which offer little resistance to the escape of gas and so cannot produce the pressure rises in the chamber necessary for fast burning.

As noted in Chapter 7, Vieille's Law can be described by equation:

$$r = a P_c^n \quad (12-8)$$

where a is the pressure index. If Vieille's equation is written in the form:

$$\log r = \log a + n \log P_c \quad (12-9)$$

and values of $\log r$ are plotted against the corresponding values of $\log P_c$, then the pressure index, a , is given by the gradient of the resulting straight line and n is the antilog of the intercept. In order to obtain the values of burning rate (r) and pressure (P) to construct such a graph, an experimental method is required to measure the burning rate of a given propellant at various pressures. Clearly a compact grain, such as a sphere, is unsuitable for this purpose. If, however, the propellant is produced in the form of a 'cord', or 'strand', e.g. by extrusion, it can be burned from one end under controlled conditions. Suitable sensing devices will provide the time (t) taken by the burning surface to recede by a distance L so that the burning rate is given by: $r = L/t$.

In practice the 'strand' of propellant is inhibited by coating its surface with a flame-resistant film, leaving only the end exposed. Burning rate measurements are made in a strand burner. This consists of a closed, isobaric bomb, filled with an inert gas, such as argon, at a predetermined pressure and provided with electrical ignition and a means of measuring the time taken for the flame to travel down the strand. The propellant should be conditioned to a standard temperature (298 K) before use, because the rate of burning has a small but significant temperature dependence.

It should be noted that the parameter r is sometimes called the 'linear burning rate' to distinguish it from the 'mass burning rate', in the sense of units. However, unless the value of the pressure index, a , is exactly unity, the relationship of r to P_c is clearly not linear in the mathematical sense. In fact the value of a is not exactly 1 for most conventional propellants, as shown in Table 12-11, so the use of the prefix 'linear' can be misleading and is perhaps best avoided in this context. A more accurate interpretation of the word 'linear' in this context is that it represents the speed at which the flame front of an ignited surface travels in to the bulk of the propellant.

Table 12-11 Values of pressure index α for some propellants

Propellant	Pressure index α
WM	1.05
SC	1.04
N	0.93
NQ	0.89
NH	0.99
FNH	1.02

Given the burning rate, r , for a particular pressure it is possible to calculate the rate at which a grain of a particular shape and dimension will be consumed under (hypothetical) isobaric conditions, assuming also that ignition occurs instantaneously over the entire surface. The critical dimension, in the case of common shapes other than multi-tubular, is the 'ballistic size' (designated D), which is defined as the least thickness to be burnt through for complete combustion of the grain. For propellant in the form of ribbon and flake, D is the thickness. For cord, D is the diameter. For tube and slotted tube, D is the annular thickness. In all these cases the time taken by the combustion process is that in which the burning surface recedes by a distance of $D/2$, i.e. $t = D/2r$. However, recognised values of the burning rate coefficient (n) are based on the fact that the grain is burning all over and that its thickness is therefore decreasing at twice the rate of regression of a single area of surface. Therefore the 2 disappears from the denominator of the fraction, and $t = D/B$.

The French ballistician H. Muraour, prominent during the inter-war period, made several important contributions to the study of burning rates. One was that the burning rate equation $r = a P_c^n$ could be replaced, for the high-pressure conditions obtaining in guns, by the linear relationship:

$$r = X + YP \quad (12-10)$$

where X and Y are constants for a particular propellant. In practice, Vieille's equation is frequently changed to linear law for a maximum pressure of 340 MPa, and the value of the burning rate coefficient (β) calculated for this purpose is denoted by β_1 where r is the total rate (mm s⁻¹) of reduction of thickness during burning.

Then:

$$r = \beta_1 P \quad (12-11)$$

Table 12-12 Typical Values of β and β_1 for Some Propellants

Propellant	Non-linear burning rate coefficient, β	Coefficient in the linear law, β_1
	(r/P^2)	(r/P)
WM	1.81	2.02
SC	1.60	1.76
N	1.32	1.11
NQ	1.72	1.32
NH	1.37	1.34
FNH/P	1.20	1.25
AX	-	0.95

In Chapter 7 the mass rate of burning (see 7.2.2) was shown to be given by:

$$m^* = A_t \cdot r \cdot \rho \quad (12-12)$$

where A_t is the burning surface area at time t .

Vieille's equation can now be adapted to the mass-burning rate to give:

$$m^* = kP^\alpha \quad (12-13)$$

where k is a constant that takes into account the values of β_1 , A_t and ρ .

When the parameter m^* is applied to the gun, the isobaric condition under which the fundamental parameter r was measured no longer exists. By the time the propellant is ignited the pressure has already been raised by the explosion of the primer, and it continues to rise rapidly as the propellant releases heat and gas, until relieved by shot travel and completion of burning. The value of m^* will therefore also change with time, but its rate of change will be related to the original parameter r .

For a given propellant burning at a defined pressure P , the values of r and ρ are constant. Therefore, it follows that:

$$m^* \propto A_t \quad (12-14)$$

It can be shown mathematically that by subdividing the volume of a given solid shape into a number of smaller shapes of the same proportions, a considerable increase in the total surface area is obtained. The effect of this increasing surface area by sub-division of grains is conveniently measured by the 'specific surface' of the charge.

$$\text{Specific surface} = \text{Total surface area of the grains}/v_0 \quad (12-15)$$

where v_0 is the initial net propellant volume, i.e. mass of propellant/density.

For surface area in cm^2 and v_0 in cm^3 , specific surface is expressed in cm^{-1} . As the degree of sub-division of the charge increases, as measured by the number of grains per unit mass, the specific surface also increases, for a given grain geometry. In turn, this will increase the initial mass rate of burning. Thus finely divided charges burn more rapidly than coarsely divided ones, and their rate of gas output is correspondingly higher.

The foregoing treatment of burning rates applies to an idealised condition known as 'non-erosive burning'. This simplifying assumption is not strictly true. In practice the turbulent flow of hot gases over the burning surface can erode it faster than the normal rate of regression and at the same time the enhancement of heat conduction and radiation at the edges causes them to be rounded off as burning proceeds. These local accelerations in the burning rate are called 'erosive burning', but in proceeding to discuss grain geometry it is necessary to ignore this phenomenon and to maintain the original assumption.

12.7.3 Effect of Propellant Temperature on Burning Rate

The burning rate equation is more correctly written as:

$$[r]T_p = \beta P^\alpha \quad (12-16)$$

since the value of r is dependent on the initial temperature T_p of the propellant as well as on the chamber pressure. (This important discovery was made by Muraour). As the flame front travels into the propellant, each successive layer ahead of it is heated by radiation, conduction and the heat of its own decomposition until the ignition temperature is reached. The higher the initial temperature, the less heat is required to raise unit mass of propellant to its ignition temperatures so the values of r and m^* will increase.

To determine the temperature dependence of the burning rate, r , an empirical equation is used:

$$r = \beta P^\alpha f(T_p) \quad (12-17)$$

where $f(T_p)$ is an increasing function of T_p .

This function is approximately linear over the range -40°C to $+60^\circ\text{C}$. Then:

$$f(T_p) = 1 + c(T_p - x) \quad (12-18)$$

where T_p is in Kelvin, c is the temperature coefficient of the particular propellant composition, x depends on the reference temperature applying to β . Values of c are of the order of 0.002 per $^\circ\text{C}$ at 300 MPa.

The effect of charge temperature on burning rate is small in relation to the pressure dependence, but it is large enough to cause an appreciable difference in gun chamber pressures, and hence in muzzle velocities, at extremes of charge temperatures. For an indirect fire weapon of, say, 105 mm calibre, there

would be a difference of several hundred metres at extreme range. In the field, efforts are made to protect artillery cartridges against extremes of ambient temperature and the actual temperature of the charges is monitored and used in the computation of trajectories.

12.7.4 Grain Geometry and Surface Effects

The precise geometric form of the individual propellant grain in its unburned state is of great importance to the internal ballistics of the gun. The grain geometry governs the following factors:

1. Mass burning rate (m^*)
2. Loading density (Δ)
3. Ignition efficiency

The dependence of mass burning rate on grain geometry is considered in the following sub-paragraphs.

- Solid forms. It is evident that solid propellant grains in the form of spheres, flakes or cord will undergo a decrease in surface area during burning. This behaviour is termed 'degressive burning' (sometimes called 'regressive burning'), and it results in a decrease of m^* with time at a theoretical constant pressure.
- Single-perforated forms. A tubular grain of propellant burns with maintenance of approximately constant burning area, because the surface of the perforation is increasing at approximately the same rate as that at which the outer surface of the grain is decreasing. This form of grain geometry is said to have a 'neutral burning' characteristic, resulting in a constant value of m^* at a (theoretical) constant pressure. Tubular propellant is unsuitable for use in the form of long grains (sticks) because of the initial slowness of the inner surface to ignite, the erosive burning which occurs when it finally does so and the fact that it chatters due to pressure in its bore during burning.
- Slotted tube. The disadvantages of tubular grains can be overcome by slotting the tube during the extrusion process of manufacture. There is then no problem in using the propellant in the form of long sticks, which is common UK practice. However, the neutral burning characteristic is lost because the onset of burning widens the slot and decreases both the outer and inner burning surfaces. Slotted tube therefore behaves like a curled ribbon shape and burns degressively.
- Multitubular grains. The single perforation can be replaced by a larger number of holes, usually seven. In all multitubular grains, when the burning reaches the stage at which the perforations meet, the grain disintegrates into a number of longitudinal slivers. This is known as sliver-point, and the type of burning then changes from progressive to degressive. Like single-perforated (tubular) grains, multitubular ones are limited in their ratio of length to diameter because of ignition and erosion problems. The usual limiting ratio is 2.25:1.

12.7.4.1 The form function

The way in which the surface area, and hence the mass burning rate, of a particular shape of grain changes with time during burning can be calculated. The mathematic function that describes the process is called the 'geometrical form function'. Its standard expression is:

$$z = (1 - f) (1 + \theta f) \quad (12-19)$$

where z is the fraction of grain mass burnt at a given instant, f is the fraction remaining, at the same instant, of the least original thickness, θ is the 'form coefficient' relating to the particular shape of the grain.

The numerical value of θ is positive for a degressive grain, zero for a neutral grain and negative for a progressive grain. Examples are +1 for long cord, zero for long tube and -0.172 for multitubular. Values of θ for other common shapes including slotted tube, ribbon and square flake, depend on the magnitude of their dimensions. Using these standard or calculated values of θ , the values of z for particular shapes of propellant can be calculated. This enables the ballistician to estimate the rate of gas production for any instant during combustion, and hence to predict the shape of the pressure/time curve for the propellant/gun combination. If the values of z are then plotted against the value of the changing surface area, A_t , at the corresponding instant (expressed as a fraction of the original area A_0) the characteristic burning behaviour of the various shapes is clearly seen (Figure 12-9). The curve for multitubular propellant does not show the change to degressive burning on slivering because it is based on a theoretical value of θ determined only up to sliver-point.

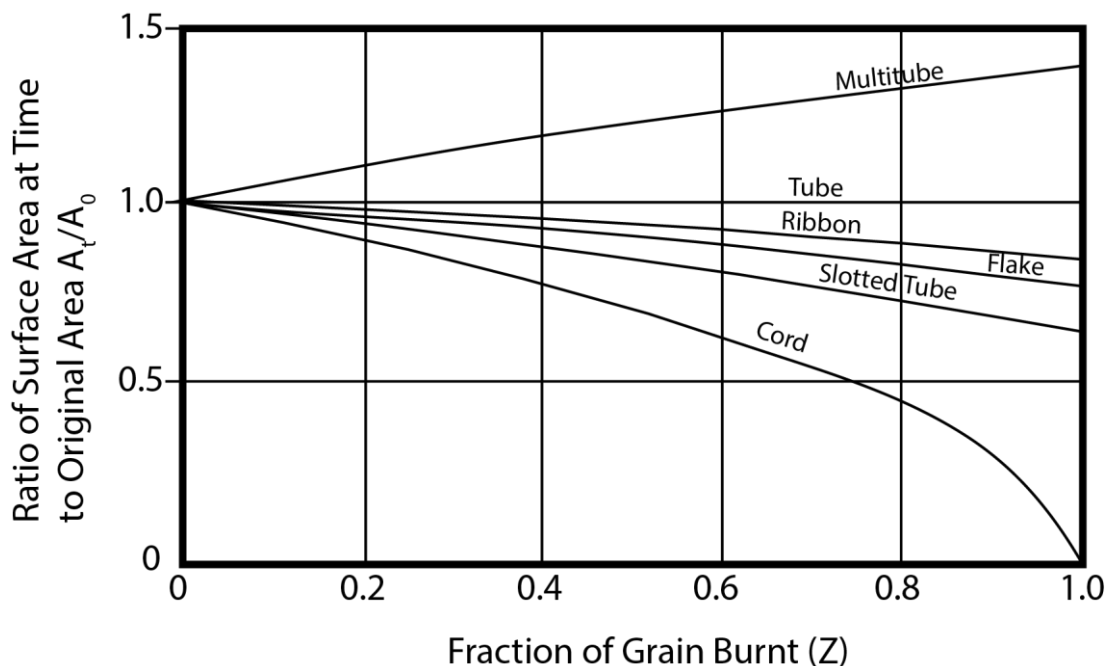


Figure 12-9 Variation of A_t/A_0 with fraction of grain burnt

12.7.4.2 The choice of grain geometry

From the range of available shapes the ballisticians select one which, combined with the thermochemical and burning rate parameters of the composition, will give the required pressure/time curve in the gun. There are further considerations in making a choice between certain shapes. For small arms cartridges, small, compact grains make for easier and more compact loading than sticks, so SAA propellants are manufactured in the form of spheres, flakes or short, single-perforated grains. For larger calibres there is a choice between sticks and compact grains of the single- or multi-perforated type. Compact grains give a higher loading density, which is necessary for a gun designed to work at high pressure but there is a penalty of slower ignition because the flow of hot gas and particles from the much larger igniting device are impeded. Stick propellant is preferred in the UK for bagged charges because it imparts a rigid shape to the bag, thus assisting handling, and requires a smaller ignition device. For large calibre charges the diameter and cross-sections of the sticks can be mixed as an additional means of obtaining the optimum pressure/time curve in the gun.

12.8 CLOSED VESSEL TESTING

12.8.1 Determination of Force Constant

Although the force constant and other parameters are ultimately required for use in the design of guns and propellant charges, the gun itself is not a suitable apparatus to use in determining transient high pressures and their rate of change with time because of the rapid forward movement of the projectile, gas and burning propellant. A constant volume condition is required, and the apparatus that provides this is the 'closed vessel'. The current standard UK vessel consists of a thick steel cylinder, threaded and plugged at both ends and having a lined interior volume of some 700 cm³ (Figure 12-10). A sample of propellant, usually up to about 140 g, is filled into the cavity, which also contains an electrical initiating device. A piezo-electric transducer that is connected to an oscilloscope gives a record of pressure vs. time, from which the maximum pressure $P_{\max}$ can also be read (Figure 12-11).

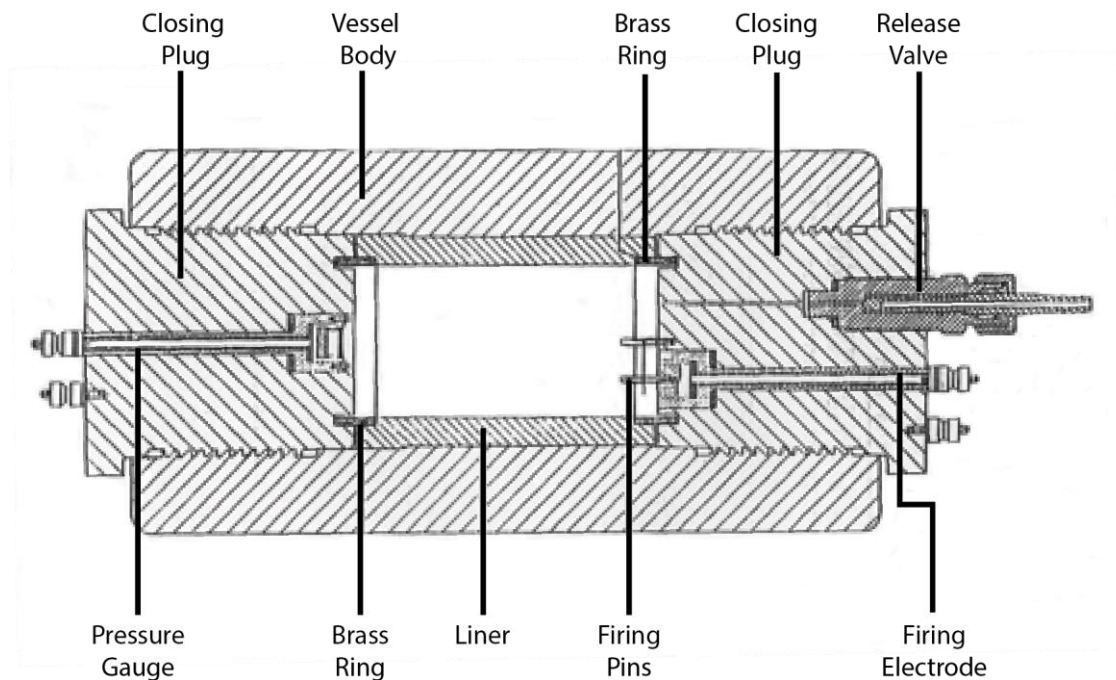


Figure 12-10 Diagram of Closed Vessel (UK Standard CV21)

More recently, smaller capacity closed vessels (100 cm^3) have been constructed with a modified internal geometry to improve signal output quality.

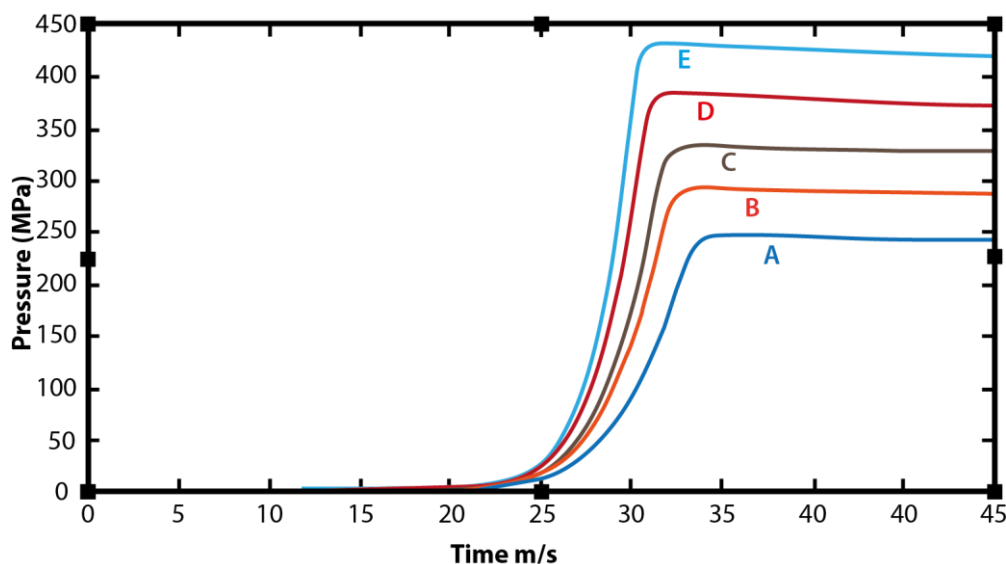


Figure 12-11 Example Pressure time curves at different loading densities⁽¹⁾.

The force constant F for a particular propellant can be calculated using the ideal gas law, Equation (12-5). However, the simple gas law is not a suitable Equation of State (EOS) for conditions found in a gun or closed vessel. At high pressures it is necessary to take into account the volume of the gas molecules

themselves. A suitable EOS for closed vessel purposes is the Nobel-Abel equation:

$$P(V - b) = nRT \quad (12-20)$$

Where b is the co-volume (volume of gas molecule per gram). Substituting in the Force constant the equation becomes:

$$F = P_{max}(V - b) \quad (12-21)$$

where P_{max} is the maximum pressure produced by burning an accurately weighed sample of propellant in a confined space. Then V is the specific volume, i.e. the volume of the interior per unit mass of propellant, normally expressed in $\text{cm}^3 \text{g}^{-1}$.

The Noble-Abel equation of state shown above has to be modified by a correction term for the heat lost to the vessel during propellant combustion:

$$F = \left(1 + \frac{k}{100}\right) P_{max}(V - b) \quad (12-22)$$

where k is the percentage of heat lost to the vessel at P_{max} .

A typical value of P_{max} in closed vessel work would be 240 MPa, so if $(V - b)$ is equal to, say, 4.1, then F is in the region of 1000 J g^{-1} .

The closed vessel (CV) is used routinely for the quality control of 'lots' of propellant during manufacture. The force constant is markedly affected by small variations of moisture content and residual solvent. In order to check whether the effect of such variations has been nullified by adequate blending, samples of the propellant are tested in the CV and parallel tests are done on a standard sample.

In order to obtain an absolute value for the force constant of a propellant the modified Noble-Abel equation is first rearranged to give:

$$\left[P_{max} \left(1 + \frac{k}{100} \right) \right] \cdot \frac{1}{\Delta} = b \cdot P_{max} \left(1 + \frac{k}{100} \right) + F \quad (12-23)$$

This expression is of the form $y = mx + c$ and therefore a plot of:

$$\left\{ \left[P_{max} \left(1 + \frac{k}{100} \right) \right] \cdot \frac{1}{\Delta} \right\} \text{ against } \left\{ P_{max} \left(1 + \frac{k}{100} \right) \right\} \quad (12-24)$$

at different loading densities will produce a straight line with an intercept of F on the y-axis. The co-volume (b) of the propellant can also be determined from this plot since this will be the gradient of the line.

12.8.2 Determination of Vivacity and Quickness

The function of gun propellants is to impart kinetic energy efficiently to the projectile. The amount of kinetic energy thus acquired by the projectile determines its muzzle velocity. A plot of pressure vs. time for a particular combination of gun and propellant gives an indication of two of the parameters of the propellant, which are of importance to the ballisticians and gun systems designer.

The magnitude of the impulse integral, as we have seen, gives a measure of the work capacity, or force constant, of the propellant.

The shape of the curve is determined by the way in which the mass rate of burning of the propellant varies under the changing conditions of pressure, temperature, grain size and grain shape which occur in the gun during the time between ignition and the 'all-burnt' point. This behavior, which depends in a complex way on several factors, is called the 'vivacity' of the propellant. It is not amenable to direct calculation and must be determined experimentally.

The shape of pressure-time curve, which is sought by the gun systems designer, represents a compromise between conflicting ballistic requirements. On the one hand a high ratio of energy/bulk in the propellant is necessary for compactness of the ammunition, and this entails a high force constant and the associated large impulse integral. On the other hand, the maximum permitted pressure is limited throughout the length of the gun by the need of mobility, which places a constraint on weight and hence on strength. Furthermore it is necessary to keep the all-burnt point well back in the bore to avoid the round-to-round variation of muzzle velocity that would result from a high pressure at the muzzle. In order that the curve shall conform to these constraints, careful optimisation of the force constant and vivacity is necessary, followed by rigorous quality control of the manufactured propellant. As already stated, vivacity depends on several factors, and one of these, grain geometry, has already been discussed. The form function Equation (12-19) relates only to the geometrical shape of the grains and not generally to their size. However, the grain size as well as the grain shape determines the initial burning area of a charge, which is described by the specific surface of the propellant. In general a finely divided charge burns more rapidly than a coarsely divided charge of the same composition. The ballistic size D must therefore be taken into account.

A further factor is the composition of the propellant. This determines the kinetics of propellant combustion as a function of temperature and pressure. The rate constants for thermal decomposition, which apply to the main propellant constituents, and their heats of explosion, are the determining factors. Broadly, in the absence of reliable kinetic data in the burning phase, we can predict that high vivacity will be found in more energetic propellants.

In the expression of the burning rate law of Vieille, Equation (12-8), the index n is approximately 0.9 for conventional gun propellants, but for the present purpose it is taken to be 1.0 and the coefficient is changed to β_1 to denote the

change to linear law. Then at a selected pressure P_s (the action pressure), which is less than $P_{\max}$:

$$\beta_1 P_s = -D \left(\frac{df}{dt} \right) \quad (12-25)$$

Therefore:

$$\frac{\beta_1 P_s}{D} = - \left(\frac{df}{dt} \right) \quad (12-26)$$

The term df/dt is related, as seen earlier, to the form function z and β_1/D is the vivacity of the propellant sample. Rearranging the form function equation [$z = (1-f)(1+\theta f)$] and solving the quadratic for f gives:

$$f = -\frac{1}{2\theta} + \frac{1}{2} \pm \frac{\sqrt{(1+\theta)^2 - 4\theta z}}{2\theta} \quad (12-27)$$

Differentiating with respect to time t then gives:

$$\frac{df}{dt} = \frac{-dz}{dt} \cdot \frac{1}{\sqrt{(1+\theta)^2 - 4\theta z}} \quad (12-28)$$

From a consideration of the pressure in a closed vessel as a function of the fraction of propellant consumed, it can be shown that:

$$z = \frac{(1+x)P}{(P_{\max} + xP)} \quad (12-29)$$

$$\text{where } x = \frac{b-1/\rho}{1/\Delta-b}$$

Most propellants have co-volumes (b) of approximately $1 \text{ cm}^3 \text{ g}^{-1}$ and densities (ρ) of about 1.5 g cm^{-3} . Therefore, for typical Closed Vessel loading densities (Δ) x is very much less than 1, and hence:

$$z = P/P_{\max} \quad (12-30)$$

Therefore, at a pressure P_s :

$$\frac{dz}{dt} = \left[\frac{dP}{dt} \right]_{P_s} \cdot \frac{1}{P_{\max}} \quad (12-31)$$

and

$$\frac{df}{dt} = - \left[\frac{dP}{dt} \right]_{P_s} \frac{1}{P_{\max}} \frac{1}{\sqrt{(1+\theta)^2 - 4\theta P_s / P_{\max}}} \quad (12-32)$$

Therefore Vivacity is expressed as:

$$\frac{\beta_1}{D} = \left[\frac{dP}{dt} \right]_{P_s} \cdot \frac{.1.}{P_s P_{max}} \cdot \frac{1}{\sqrt{(1+\theta)^2 - 4\theta P_s / P_{max}}} \quad (12-33)$$

The expression $[dP/dt]_{P_s}$ is deduced from closed vessel results, as follows. The closed vessel gives a curve of pressure vs. time as shown in Figure 12-11. The differential of this curve, dP/dt , is then plotted against P , giving a new curve $\frac{dP/dt}{P}$ as shown in Figure 12-12.

At pressure P_s , (the action pressure) which is selected with regard to the particular gun/propellant combination concerned, the value of $[dP/dt]_{P_s}$ is obtained as shown in Figure 12-12. The value of P_s , P_{max} , $[dP/dt]_{P_s}$ and θ can then be substituted into the above equation to give the vivacity. In fact for most propellant grain shapes of interest $\theta = 0$, and the expression for what is termed the 'dynamic vivacity' then simplifies to:

$$\text{Dynamic Vivacity} = \left[\frac{dP}{dt} \right]_{P_s} \cdot \frac{1}{P_s P_{max}} \quad (12-34)$$

(units of $\text{Pa}^{-1} \text{s}^{-1}$)

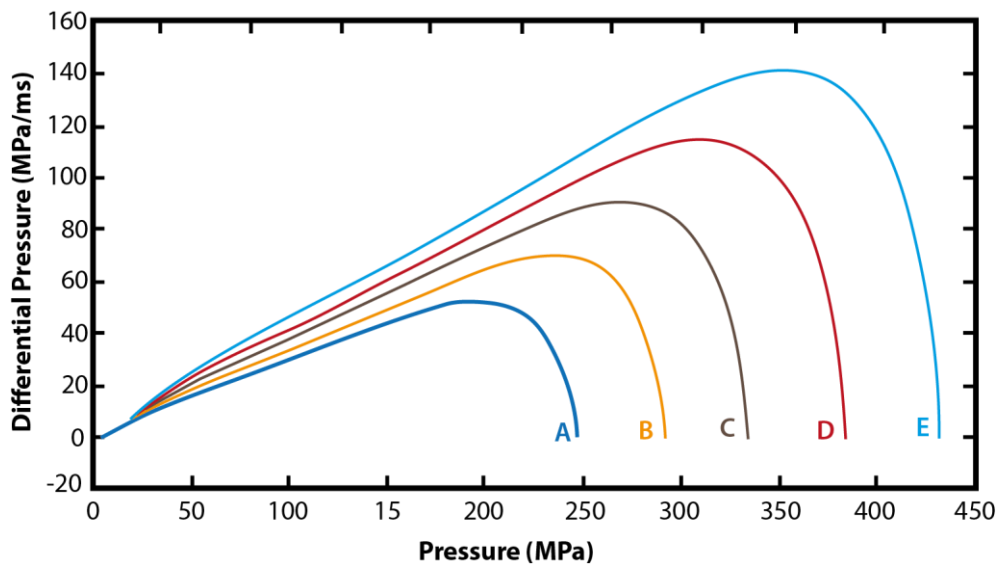


Figure 12-12 Example plot of differential pressure versus pressure curves at different loading densities⁽¹⁾.

A more general vivacity that is easy to determine using a closed vessel can be defined thus:

$$Vivacity = \left[\frac{dP}{dt} \right]_{mean} \cdot \frac{1}{P_{max}} \quad (12-35)$$

(units of s⁻¹)

where the mean value of the differential is measured over a defined pressure range below P_{max} (usually 0.25 P_{max} to 0.55 P_{max}).

When the closed vessel is used routinely for comparing the vivacity of a propellant lot with that of a standard sample, a 'relative vivacity' is determined. This is usually expressed as a percentage, in the following way:

$$Relative Vivacity = \frac{vivacity\ of\ propellant \times 100}{vivacity\ of\ standard\ propellant} \quad (12-36)$$

A further propellant parameter sometimes required is called 'quickness'. This word is sometimes used, erroneously, as being synonymous with vivacity. In fact, quickness is the product of the two parameters already described, i.e. force constant and vivacity.

$$Quickness = \frac{F \times \beta_1}{D} \quad (12-37)$$

When closed vessel expressions for relative force constant and vivacity are multiplied together, the P_{max} term disappears. Therefore CV testing thus can establish the relative quickness of two propellants:

$$\frac{Quickness\ of\ propellant\ X}{Quickness\ of\ propellant\ Y} = \frac{[dP/dt](X)}{[dP/dt](Y)} \quad (12-38)$$

A closed vessel can also be used to determine burning rate (r) at high pressures by measuring P_{max}, P and dP/dt and substituting the values in an expression for r derived from the fact that:

$$r = -D \cdot \frac{df}{dt} \quad (12-39)$$

12.9 PROPELLANT NOMENCLATURE

The examples of propellant compositions in this chapter are limited to British or imported types, but the nomenclature of even this small number is a complicated subject. In dealing with British propellants a clear distinction must be made between small arms types and artillery types. In small arms types the

frequently recurring letter N has a separate set of meanings. Thus NRN is Nobel Rifle Neonite, NNN is Nobel Nitro-Neonite and NPP is Nobel Parabellum Powder.

In the designations of post-1941 British artillery propellants the letter N is again commonly found, but has a different and unambiguous meaning. It signifies that the composition contains nitroguanidine (picrite), generally to the extent of 55%, and is therefore classed as 'flashless'. Hence it may be helpful to remember N as being an abbreviation of 'nolite', which is its origin. Various letters prefixed or suffixed to N by Land Service or Naval Service users have specific meanings as follows:

Prefix:

M 'modified' and as applied to N-type propellants in Naval Service this means that the propellant is made by the semi-solvent process.

Suffixes:

F	containing nitrocellulose made from wood
/K	containing potassium cryolite
L	lower calorimetric value than the standard N composition
/P	containing 1 % potassium sulphate
/2P	containing 2 % potassium sulphate, and so on
Q	higher calorimetric value than the standard N composition
B	blended nitrocellulose

Propellants N and NQ both contain 55 % (w/w) nitroguanidine, NQ having the higher calorimetric value. As another example, the naval propellant MNF/2P has the following composition, some of which is deducible from the designation.

Parts by weight:

16.5	nitrocellulose, made from wood and contains 12.2 % nitrogen
21.0	nitroglycerine
55.0	nitroguanidine
7.5	carbamite
2.0	potassium sulphate

It should be noted that the original American propellants NH and FNH, although having been given British suffixes such as P or 3P, were not designated in accordance with the basic British system and do not, in fact, contain nitroguanidine. Propellants NH (Non-Hygroscopic) and FNH (Flashless NH) were manufactured in the United Kingdom by Nobel's Explosive Company Limited under the more modern designations M6 and M2 respectively, for use in US-manufactured guns, some of which are British army equipment.

The latest British Gun propellants, the X series, mostly contain RDX and the basic designations are in both alphabetical and chronological order, followed by the letter X, e.g. AX, BX etc. The whole series are sometimes called Rowanites, a name derived from the initials of Royal Ordnance Waltham, Abbey.

In both the N series and X series a second suffix is separated from the composition designation by an oblique stroke, and denotes the geometrical shape of the grain, except in the case of cord, which has no such suffix. The meanings of the second suffixes are as follows:

/MT or

M multitubular. A number may be added, e.g. MT7 or MT19, to denote the number of holes in the grain

/R ribbon

/S slotted tube

/T tubular, i.e. single-hole

/Z scroll, which is paper-thin sheet of double-base propellant, usually SC.

To give an indication of the most ballistically important dimension of the grain, i.e. the thickness that must be burned through for complete combustion, some digits are added after the grain geometry suffix. Until a few years ago grain size was generally indicated in thousandths of an inch. Thus cord was expressed as the diameter (e.g. WM 029), tube and slotted tube by the external and internal dimensions (e.g. N/S 164-048), multitubular by the space between the holes, i.e. 'web size' (e.g. N/2P/M 055), ribbon by the width and thickness (e.g. MNQF/R 032 x 160) and scroll by the thickness of the sheet. Certain double-base small arms propellants were expressed in hundredths of an inch (e.g. CDT 5-2). Because ammunition is stored for many years in peacetime, much of it will continue to carry such markings long into the future.

More recently, however, propellant sizes have been metricized by the use of a two-digit centimetre system prefixed 'M' to distinguish it from the three-digit inch system. In both systems the existence of a decimal point before the digits is assumed. An example of the metric systems is N M04, i.e. propellant N of cord diameter 0.04 cm. Some examples of inch sizes and their metric equivalents are shown in Table 12-13.

Table 12-13 Comparison of Imperial Vs. Metric Propellant Nomenclature

Propellant	Size	
	Imperial	Metric
MNF/2P/S	164-048	M43-12
MNLF/2P/M	032	M08
NQ/S	207-047	M53-12
NQ/M	047	M12
NQ/M	044	M12
N	017	M04
SC/Z	008	M02
HX MT19	-	M05

12.10 REFERENCES

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