

# CHAPTER 13

## ROCKET PROPELLANTS

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## 13 ROCKET PROPELLANTS

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### 13.1 AWARENESS SUMMARY

Solid rocket propellants consist of a polymer (either nitrocellulose or polyurethane) plus additional explosives and additives, carefully formulated to burn smoothly without detonating to produce hot gases to propel a rocket.

All present day solid rocket propellants are more energetic than the best liquid monopropellants, and are fully capable of providing the main propulsion for all kinds of rockets and missiles up to and including ICBM and satellite launch vehicles. In terms of energy the best solid propellants are almost equal to the best packageable bipropellants, though not to the cryogenic ones. For military purposes the advantages of solid propellants outweigh their disadvantages, and for that reason the vast majority of military rockets, whatever their size and purpose, utilise solid propellants. In space applications the balance is more even.

The general advantages of solid rocket propellants are as follows:

- a. They favour simple and lightweight designs of motor.
- b. They permit instant readiness of a missile system.
- c. They present little or no toxic vapour hazard and are therefore safer to store and handle than liquid propellants.
- d. They have good chemical and thermal stability, and therefore long shelf life (routine surveillance is necessary however).
- e. They are of high density, giving a good energy/bulk ratio ('volume impulse').

The general disadvantages of solid rocket propellants are as follows:

- a. They are expensive, being complex mixtures which require lengthy manufacturing processes.
- b. Once ignited, solid propellant motors cannot be shut down, and it is difficult to change the level of thrust during the burning time.
- c. Solid propellants cause extremely severe heating of the exhaust nozzle, necessitating either the use of expensive nozzle materials or the suppression of the maximum achievable combustion temperature and therefore maximum specific impulse (see 13.6.3).
- d. The rocket motor is also the propellant container; therefore the amount of propellant contained in a missile may be limited by the overall system design requirements.

As with liquid propellants, the physical and chemical characteristics of solid propellants vary considerably and each type has its own additional disadvantages.

Apart from categorisation by the method of fabrication, solid rocket propellants fall into two broad divisions according to their chemistry; Double-base (alternatively called 'homogeneous' or 'colloidal') and are nitrocellulose (NC) based, and composite propellants. Historically, the Double-base type propellant evolved from cordite gun propellants in the 1920s, and was followed by composite propellants some twenty years later. Vast amounts of research and development have been carried out on both types since then to improve their safety, reliability and performance.

Double-base propellants, in their simplest forms, are very similar to those of the same name used in ammunition for certain small arms and guns. One of the base ingredients is the nitrated natural polymer nitrocellulose (NC) and the other is an energetic plasticiser, normally nitroglycerine (NG), both of these substances being nitrate esters. Certain additives are normally required, the most essential of which is a chemical stabiliser. Nitrocellulose burns smokelessly, if formulated correctly the Double-base propellant will also burn smokelessly. This smokeless burn enables stealthily rocket systems to be manufactured. The disadvantages of Double-base propellants are: (i) they have low energy density and therefore performance; (ii) the nitrocellulose polymer has poor strain capability, particularly at low temperatures, meaning the mechanical properties of Double-base propellants can be a key failure mode for the rocket; and (iii) NC propellants have poor vulnerability characteristics in storage and use.

Composite propellants are two-phase mixtures comprising a synthetic polymeric matrix (usually a polyurethane) which serves both as a fuel and a binder, together with an oxidant, usually the inorganic salt ammonium perchlorate (AP). The advantages of composite propellants are: (i) they have a high energy density and therefore performance; (ii) the polyurethane polymer has a very good strain capability meaning composite propellants have much better mechanical properties than Double-base propellants; and (iii) composite propellants have very good vulnerability characteristics in storage and use. The disadvantage of composite propellants is that they are not stealthy. The combustion of ammonium perchlorate generates hydrogen chloride (HCl), a white smoke. An ammonium perchlorate composite propellant was used as the solid rocket boosters for the US Space Shuttle systems, and produced tonnes of white HCl during launch.

In order to achieve a high performance with reduced smoke, propellants using nitramines (RDX and HMX) have been developed. These propellants typically contain no aluminium, a low AP content ~10 % (w/w), 50-85 % (w/w) nitramines, with hydroxyl-terminated polybutadiene or polyurethane as a binder. These low smoke or reduced smoke propellants produce no primary smoke, while secondary smoke (created when water vapour is present) appears only at low ambient temperatures. The two disadvantages of reduced smoke are: (i) the burning rate of the nitramines are much lower than ammonium perchlorate, this means the range of the rocket is likely to be limited compared to a composite

propellant; and (ii) the high energy reduced smoke composites such as the nitrate ester plasticised elastomers (NEPE) have poor vulnerability characteristics.

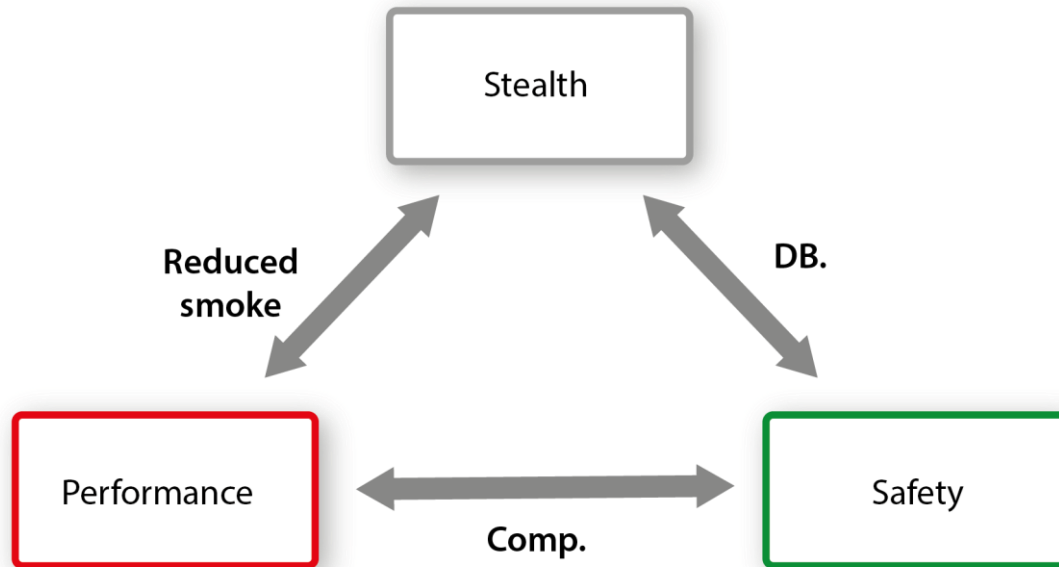


**Figure 13-1 Diagram showing the design compromises of solid rocket propellants and the roles of the three main types of solid rocket propellants**

Today the rocket propellant chemist must make a design compromise and choose any two of the three requirements stealth, performance or safety. Figure 13-1 shows that Double-base propellant are the best choice for stealth and acceptable safety; composite propellants are best for high performance and safety; and reduced smoke composites are best for high performance and stealth. No single propellant can fulfil all three requirements.

## 13.2 SOLID ROCKET PROPELLANTS

### 13.2.1 Grain Shape and Inhibition

All solid rocket propellants are mixtures formulated and manufactured in such a way that they will burn smoothly within the motor, without any tendency to detonate. Their mode of combustion is similar to that of gun propellants, but the rate of burning, in terms of both linear regression and mass burning rate (see 7.2.2), is much lower, mainly because of the lower operating pressure in a motor (~10 MPa) compared with a gun (up to 600 MPa). Like gun propellants, rocket propellants are manufactured in the form of geometrical shapes called grains, regardless of size. Almost all rocket propellant grains are basically cylindrical in shape. They may contain one or more lengthwise perforations called conduits. In a small, simple missile for use at short range the charge may consist of a bundle of tubular grains (sticks) which burn all over their surface.

The motor case is therefore exposed to the flame but in the short time of burning (<1 second) it will not be burned through.

Alternatively, the same large surface area can be provided by one suitably perforated grain of equal weight, and the larger the missile and the longer its burning time, the more likely this is to be so. A single grain is not usually intended to burn on its outer surface, but only in its conduit(s) and/or on its rear surface. In this way the head end and sides of the motor case are protected from the flame until the last fraction of a second of burning time. To achieve this the outer surface of the grain is prevented from igniting, in one of two ways:

- a. The grain can be bonded to the motor case (case bonded).
- b. It can be contained in a tight fitting, non-flammable sheath, called an 'inhibitor' which is bonded to the grain and is a sliding fit within the motor case.

The first method is preferable, because less of the valuable space inside the motor is wasted by holding a volume of non-energetic material, in this case an adhesive. There is, however, a difficulty in that the rocket may become conditioned to any ambient temperature from  $-55^{\circ}\text{C}$  to  $+70^{\circ}\text{C}$ , and the coefficient of thermal expansion of the case is very different from that of any solid propellant. Therefore case bonding is practicable only if the propellant material is sufficiently elastic or plastic to conform to the changing dimensions of the bonding surface without either itself cracking or shearing the bond. In the event of either mode of failure, the extra area of propellant surface thus allowed to burn would increase the mass burning rate to well above its designed level, the chamber pressure would exceed the relatively narrow safety margin and the motor would burst.

For all but the smallest missiles the propellant charge is likely to consist either of one case bonded or otherwise inhibited grain, or of two such grains in tandem. A single grain, or the rearmost of a pair, is required to have a high mass rate of burning so that the motor provides high thrust for the launch of the missile. It therefore has one or more conduits, perhaps of complex cross section, in order to provide adequate burning surface area in addition to the rear surface, which is not usually inhibited (Figure 13-2).

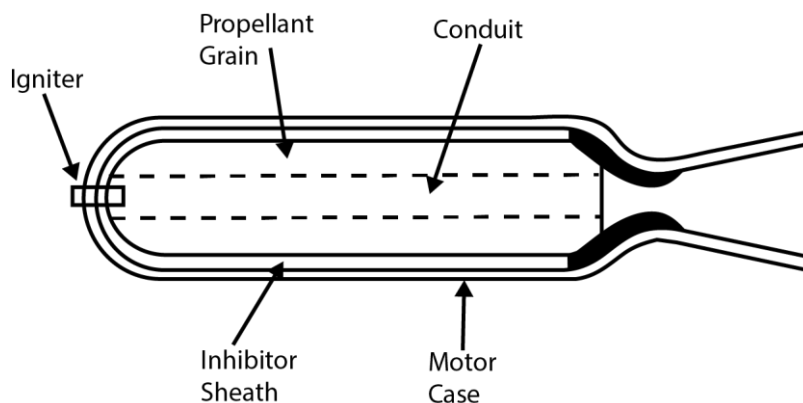


**Figure 13-2 Rocket motor containing inhibited radial burning propellant grain (diagrammatic)**

Since the burning surfaces within the conduit(s) regress in mostly radial directions, such a grain is called radial burning. If the motor contains a second grain this is likely to be for sustaining the speed of the missile over a longer period of thrust. A sustainer grain may not have any conduits, being intended instead to burn on its rear surface only. This is called 'end burning' or 'cigarette burning'. A pair of grains, boost and sustainer may consist of the same propellant composition or may be chemically quite different. They may be separately loaded into the motor, or joined together end to end. Alternatively, one grain may serve as both boost and sustainer, having a conduit and/or slits at the rear end but not in the front portion.

Not all propellant grains are cylindrical. Certain boost grains, for example as found in shoulder launched anti-tank or surface to air missiles, which burns out in tenths or hundredths of a second are made of thin layers of propellant combined together in such a way as to expose a maximum surface area to the igniter flame. This type of configuration is used if the grain is required to burn out before the missile has left its launch tube and before the sustainer grain (if any) is fully ignited. This type of grain or motor is designated ABOL (all burnt on launch).

Cylindrical grains vary greatly in their diameters, from a few centimetres to over a metre, and their weight varies accordingly by five or six orders of magnitude.

**13.2.2 Double-base Propellants****13.2.2.1 Extruded Double-base (EDB) propellants**

Double-base propellants consist of mixtures of nitrocellulose and nitroglycerine and take the form of a fairly rigid, colloidal material of density  $\sim 1.6 \text{ g cm}^{-3}$ . As used in guns, such propellants are manufactured by extrusion, and this process can be applied to rocket motor grains up to a limiting diameter of about 35 cm. Such extrusions are suitable for air-to-air missiles ( $\sim 5 \text{ cm}$ ), decoy types ( $\sim 8 \text{ cm}$ ) and Giant Viper (13 cm). Typically, an extruded Double-base propellant (Table 13-1) has a lower specific impulse (see 13.6.3) than aluminised composites (Table 13-10) and moreover has the disadvantage that it cannot be case bonded.

**Table 13-1 A Typical Extruded Double-base (EDB) Propellant (Solventless)**

| Ingredients                | % (w/w) | Specific impulse $2320 \text{ N s kg}^{-1}$<br>(for a typical expansion ratio)<br><br>$Q_p = 5110 \text{ J g}^{-1}$<br>Burning rate $15 \text{ mm s}^{-1}$ at<br>$5.9 \text{ MN m}^{-2}$ |
|----------------------------|---------|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| Nitrocellulose (13.25 % N) | 51.5    |                                                                                                                                                                                          |
| Nitro glycerine            | 43      |                                                                                                                                                                                          |
| Diethyl phthalate          | 3       |                                                                                                                                                                                          |
| 2-Nitrodiphenylamine       | 1       |                                                                                                                                                                                          |
| Potassium sulphate         | 1.25    |                                                                                                                                                                                          |

|              |      |  |
|--------------|------|--|
| Carbon black | 0.25 |  |
| Wax          | 0.05 |  |

The additives employed in EDB propellants are mostly similar to those in gun propellants. In Table 13-1 diethyl phthalate is a plasticiser to supplement the plasticising effects of the NG. 2-Nitrodiphenylamine (2-NDPA) is the stabiliser. Potassium sulphate is a flash suppressant and also promotes smooth burning at low temperatures. Carbon black is an opacifying agent which prevents the radiant heat of the combustion from penetrating deep into the grain where it might cause sub surface ignition. The wax is added to act as a die lubricant during extrusion.

### 13.2.2.2 Cast Double-base (CDB) propellants

The alternative method to extrusion for the manufacture of Double-base propellant grains is casting. Cast Double-base (CDB) propellants can be made in grain diameters from 5 cm upwards, and the maximum diameter is, in theory, unlimited, as is the length. Other advantages which they have over extruded Double-base (EDB) propellant types are a better capacity for very complex cross sections, greater precision of dimensions for longer grains, and in manufacturing processes. There are two essential components used in the process, a casting powder and a casting liquid. The casting powder is an aggregate of small, cylindrical grains of gelatinised nitrocellulose, similar to a small arms propellant. It may contain a proportion of nitroglycerine. Some of the additives required in the final composition, are incorporated in the casting powder before it is extruded and chopped into the form of granules. Table 13-2 shows the composition of a typical Single-base casting powder.

**Table 13-2 A Typical Single-base Casting Powder (Solvent Processed)**

| Ingredients                           | % (w/w) |
|---------------------------------------|---------|
| Nitrocellulose (from paper, 12.2 % N) | 88      |
| 2 Nitro-diphenylamine                 | 2       |
| Lead stearate                         | 5       |
| Di octyl phthalate                    | 5       |

In the foregoing composition the 2-nitrodiphenylamine is the stabiliser, lead stearate is the platoning agent and di octyl phthalate is the plasticiser. The composition of a typical casting liquid is given in Table 13-3.

**Table 13-3 A Typical Casting Liquid Composition**

| Ingredients                     | % (w/w) |
|---------------------------------|---------|
| Nitroglycerine                  | 72      |
| Triacetin (glyceryl triacetate) | 27      |
| 2 Nitro-diphenylamine           | 1       |

In this composition the Triacetin is a desensitiser and the 2-nitro-diphenylamine is a further increment of stabiliser. The casting process commences with the filling of the powder into a mould, in which inserts are made for any conduits required. The casting liquid is then added under vacuum and as it is absorbed into the grains of the powder, they swell and eventually coalesce into a solid mass, which is then consolidated by applied pressure. No chemical reaction takes place during this process, it is a physical one and there is virtually no mould shrinkage. The curing process normally takes a few days at a temperature of 60 °C.

Ordinary cast double-base (CDB) propellants tend to contain a relatively high percentage of non-energetic additives (Table 13-4) and therefore provide an even lower specific impulse (see 13.6.3) than the extruded type. However, they have the advantage over extruded double-base (EDB) propellant types that they can be case bonded, because they are heavily plasticised, and this to some extent counterbalances the low volume impulse. Furthermore, like EDB types they can be platonised (see 13.2.4.1.1) and they give relatively smokeless burning. The low specific impulse of unfilled CDB propellants is not a serious disadvantage in one of their main applications, which is in motors for anti-tank guided weapons (ATGW), since such missiles are not required to exceed velocities of about 200 m s<sup>-1</sup>. CDB grains for ATGW have a weight of the order of 1 kg and cost several hundred pounds each, a small fraction of the unit cost of the missile. British rocket motors containing CDB propellants included the Cadiz and Titus in the Seawolf missile and the US Javelin anti-tank missile. The motor grains are inhibited by either Hypalon or ethyl cellulose sleeves. The French SNPE Artus sustainer motor for the Milan ATGW was also a CDB propellant type and was inhibited by polyurethane.

**Table 13-4 A Typical Unfilled Cast Double-base (CDB) Propellant (Semi-Solvent Processed)**

| Ingredients               | % (w/w) | Specific impulse 2060 N s kg <sup>-1</sup><br>(for a typical expansion ratio)<br><br>Qp = 2930 J g <sup>-1</sup> |
|---------------------------|---------|------------------------------------------------------------------------------------------------------------------|
| Nitrocellulose (12.6 % N) | 59      |                                                                                                                  |
| Nitro glycerine           | 24      |                                                                                                                  |
| Triacetin                 | 9       |                                                                                                                  |
| Di-octyl phthalate        | 3       |                                                                                                                  |
| Stabiliser                | 2       |                                                                                                                  |
| Lead Stearate             | 3       |                                                                                                                  |

### 13.2.2.3 Filled cast double-base (CDB) propellants

Cast double-base propellants can be modified by filling them with RDX or HMX, analogously to high-energy gun propellants (see 12.2.2). The capacity for platonisation is retained and there is no increase in smokiness but the quality of the plateau might be impaired. CDB propellants cannot be energised by the

addition of aluminium alone, because of the low oxygen balance of the nitrocellulose content. If, however, ammonium perchlorate is introduced into the composition via the casting powder, the oxygen balance is thereby increased and aluminium can then be added with advantage. This latter type of filled CDB propellant is called 'composite modified CDB (CMCDB).

Such compositions may also contain RDX or HMX. In any case the specific impulse of CMCDB (Table 13-5) is considerably higher than that of unfilled CDB. Their density is also better than that of CMCDB, which is  $\sim 1.78 \text{ g cm}^{-3}$ . There are however, penalties incurred by the addition of ammonium perchlorate and aluminium; the capacity for platonisation is lost and the additives give rise to smoky burning. The propellant in the British boost motor for the Sea Dart missile, Chow, was a case bonded CMCDB type.

**Table 13-5 Two Typical Composite Modified Case Double-base (CMCDB) Propellants**

| Ingredients              | % (w/w) |     | (a) Specific impulse = $2630 \text{ N s kg}^{-1}$<br>(for typical expansion ratio)<br>$Q_p = 7718 \text{ J g}^{-1}$<br><br>(b) Specific impulse = $2600 \text{ N s kg}^{-1}$<br>(for typical expansion ratio)<br>$Q_p = 7438 \text{ J g}^{-1}$ |
|--------------------------|---------|-----|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
|                          | (a)     | (b) |                                                                                                                                                                                                                                                |
| Nitrocellulose (12.5% N) | 20      | 22  |                                                                                                                                                                                                                                                |
| Nitroglycerine           | 30      | 30  |                                                                                                                                                                                                                                                |
| Triacetin                | 6       | 5   |                                                                                                                                                                                                                                                |
| Ammonium perchlorate     | 11      | 20  |                                                                                                                                                                                                                                                |
| Aluminium                | 20      | 21  |                                                                                                                                                                                                                                                |
| HMX                      | 11      | -   |                                                                                                                                                                                                                                                |
| Stabiliser               | 2       | 2   |                                                                                                                                                                                                                                                |

#### 13.2.2.4 Slurry cast double-base propellants

Cast Double-base rocket propellants may also be manufactured by slurry casting. This process has the advantage of not requiring a pre-formed casting powder, the propellant grain being made in a single stage operation from granular nitrocellulose. It is therefore faster than the powder casting technique but is, in general, less flexible in terms of the size and type of grain it can produce. In the slurry casting process, the solid ingredients, which may include a nitramine or ammonium perchlorate in addition to the granular nitrocellulose (approx. 0.25 mm particle size), are simply added to a liquid plasticiser mixture (stabilised nitroglycerine plus, for example, Triacetin). The resulting slurry is stirred for some minutes, then poured into the rocket motor case and cured. The second stage motor in the Polaris SLBM contained a slurry cast CMCDB propellant (DDP 880) with the composition shown in Table 13-6.

Modifying the CDB colloidal matrix by the introduction of an elastomer, creates as elastomer modified CDB (EMCDB). Its low temperature strain capability is claimed to be comparable to the polyurethane composites, giving an extensibility of 20 % at  $-40^\circ\text{C}$  and unfilled EMCDB propellants share the

advantages of unfilled CDB propellants, such as platonisation, case bonding and long shelf life.

**Table 13-6 A Typical Slurry Cast CMCDDB Propellants**

| Ingredients           | % (w/w) |
|-----------------------|---------|
| Nitrocellulose        | 14.4    |
| Nitroglycerine        | 32.4    |
| Aluminium             | 18      |
| Ammonium perchlorate  | 5.1     |
| HMX                   | 25.9    |
| 2 nitro-diphenylamine | 1       |
| Resorcinol            | 0.7     |
| Triacetin             | 2.5     |

#### 13.2.2.5 Elastomer modified cast double-base (EMCDB) propellants

The following are performance figures for a non-aluminised EMCDB propellant:

- Burning rate  $5 \text{ mm s}^{-1}$  to  $25 \text{ mm s}^{-1}$  on plateau
- Plateau pressure range  $20/35 \text{ MPa}$  to  $90/200 \text{ MPa}$
- Density  $1.59 \text{ g cm}^{-3}$
- Specific impulse  $2300 \text{ N s kg}^{-1}$

EMCDB propellants can be filled with aluminium and ammonium perchlorate and/or nitramines without undue loss of their main advantage, i.e. the low temperature elasticity. In general, the formulation of filled CDB propellant is governed by the principle of energising with aluminium for applications where smoke creates no problem, or using a nitramine where smoke would be disadvantageous. The propellant used in the British surface to air missile, Rapier, is an RDX filled EMCDB.

#### 13.2.2.6 Advantages and disadvantages of double-base propellants

The general advantages of double-base rocket propellants, taking cast and extruded types together, are as follows:

- They have high mechanical strength.
- Complex cross sections can be produced, by casting or extrusion.
- They are relatively smokeless, provided they are not filled with ammonium perchlorate and aluminium.
- They can be platonised, provided they are not filled with ammonium perchlorate and aluminium.

- They can be filled with RDX or HMX, giving higher impulse without loss of platonisation or low smoke characteristics.

The general disadvantages of double-base rocket propellants are as follows:

- They tend to crack at low temperatures, unless elastomer modified, or highly plasticised.
- They cannot be case bonded, unless heavily plasticised as in CDB types.
- They tend to exhibit resonant and therefore unstable burning, but additives or motor design can suppress this.
- Chemical decomposition of the nitrate esters produces gas in storage which can cause 'gas cracking' in large webs during high temperature storage.
- Double-base propellants cannot be energised by aluminium, unless ammonium perchlorate is also added.

### **13.2.3 Composite Propellants**

#### **13.2.3.1 Binder requirements**

Composite propellants are subdivided into three classes; 'plastic', 'rubbery' and 'pressed'. Pressed propellant comprises ammonium nitrate as the oxidant and guanidine nitrate or wax as the fuel. This class is not widely used. The following paragraphs refer to plastic and rubbery composites.

The binder makes up only 10-15 % (w/w) of a composite propellant but determines its mechanical properties. Such properties need to be considered carefully when a motor is designed, because the problem of differential thermal expansion entails that the binder must remain elastic over a wide temperature range (-55 °C to +70 °C). From the manufacturing point of view an ideal binder should be a liquid in the prepolymer (uncured) form with a workable viscosity (1-10 N s m<sup>-2</sup> in the temperature range 20 °C to 70 °C), which can accept a high solids loading and be capable of conversion by a suitable process (cooling or curing) into an elastomeric material with high tensile and compressive strength and good elasticity.

For most applications a composite propellant binder will need to be non-hygroscopic, be compatible with other propellant ingredients and have good storage stability. For reasons of rocket motor performance, the binder, on combustion with the oxidant, should yield species having low molar mass and/or high heats of formation. In general, for a binder it is necessary to strike a balance between high propellant performance and good mechanical properties. The importance of the latter is demonstrated by the fact that most composite propellants are not formulated at the binder proportion which corresponds to maximum performance (~9 % w/w) but at a higher proportion (~12-15 % w/w), conducive to better mechanical properties and processing characteristics.

### 13.2.3.2 Oxidant requirements

The oxidant constitutes the major proportion by weight of a composite propellant and largely determines the specific impulse (see 13.6.3) and the burning rate of the propellant. From the view point of safety, manufacture and storage, an oxidant should have low sensitiveness (see 20.2.1) to initiation by impact and friction, and high thermal stability. It should be non-hygroscopic and should be chemically compatible with the propellant binder and other ingredients. To ensure good propellant performance an oxidant should ideally have a large, positive heat of formation and should produce gases of low molar mass. High density is also a desirable feature of an oxidant.

#### 13.2.3.2.1 Ammonium perchlorate

Ammonium perchlorate ( $\text{NH}_4\text{ClO}_4$ ) is currently the most widely used oxidant as it meets most of the desired requirements. It is a white, odourless, crystalline solid with a crystal density of  $1.94 \text{ g cm}^{-3}$  and has low hygroscopicity. Contact of the material with the human skin causes irritation, as does its inhalation to the mucous membranes. Ammonium perchlorate is moderately sensitive to initiation by impact ( $F$  of  $I = 95$ ) (see 20.10.2.1), shock or external heating. The unmixed salt is likely to deflagrate if initiated in these ways, but if it is mixed with any combustible substance initiation may lead to explosion or even detonation, the likelihood of which increases as the mixture approaches the stoichiometric proportions.

#### 13.2.3.3 Plastic composite propellants

Plastic composite propellants were the favoured British rocket propellants in the 1950's and 1960's and were used in, for example, the boost motors for the now obsolete Thunderbird surface to air missile, the Gosling boost motors for Bloodhound (reproved 1987) and the sounding rocket motors Raven and Stonechat. Much research was carried out in the United Kingdom up to the late 1970s to improve plastic propellants but by that time rubbery composites had been found superior, especially in their low temperature mechanical properties. Consequently, plastic propellants now have few applications in military rocketry.

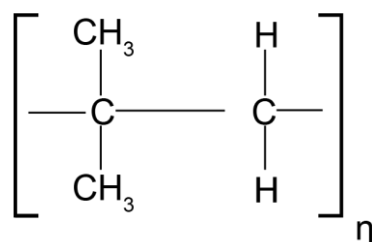


**Figure 13-3 Chemical structure of polyisobutene (PIB)**

Plastic propellant consists of a thermoplastic fuel/binder and the oxidant ammonium perchlorate. The usual fuel/binder is polyisobutene (PIB) (Figure 13-3), sometimes with the addition of ethyl oleate as a plasticiser to improve the low temperature mechanical properties. Some plastic composites have contained polyvinylchloride (PVC). To manufacture PIB and PVC plastic

composites the polymer is first dispersed in a heated plasticiser such as di-octyl-sebacate to give a mixture known as a plastisol, which is then mixed with the oxidant prior to extrusion and cooling. The plastic propellant is extruded into the motor case, leaving a small axial conduit which is then enlarged often to a star cross section, or some other fairly simple shape, by forcing an appropriately shaped mandrel through the centre and then withdrawing it. Plastic propellants have densities between  $1.65 \text{ g cm}^{-3}$  and  $1.75 \text{ g cm}^{-3}$ . The maximum practical grain size is limited by the tendency of the propellant to deform under its own weight. Grains up to 57 cm diameter and weighing one tonne have been made in the UK. At ordinary humidity levels, plastic propellants produce a moderate amount of smoke containing hydrogen chloride. Plastic propellants burn reliably at temperatures down to  $-30^\circ\text{C}$  although their performance is somewhat degraded below about  $0^\circ\text{C}$ .

An oxygen-balanced mixture of PIB and ammonium perchlorate would contain 9 % (w/w) PIB and 91 % (w/w) ammonium perchlorate by weight. The maximum obtainable specific impulse, of about  $2400 \text{ N s kg}^{-1}$  is however, given by a 10/90 mix and this may be further altered to 12/88 to improve the mechanical properties. The burning rate in this range is too high for practical purposes and most UK plastic propellants have had ammonium picrate added as a coolant and burning rate modifier. This has the disadvantage, if the picrate is present in large proportion, of reducing the specific impulse (see 13.6.3). It also increases smoke. Ammonium picrate (Ammonium 2,4,6-trinitrophenolate) is an insensitive explosive in its own right. Table 13-7 gives some typical compositions of plastic composites. Basic copper chromate and titanium dioxides are catalysts which steady the burning rate at low temperatures. Oxamide ( $\text{CONH}_2)_2$  is a fuel and a coolant which has a slightly platonising (see 13.2.4.1.1) effect on the burning rate/pressure curve but, in general, plastic composites cannot be platonised as can double-base composites. Lecithin is a surface acting agent (surfactant) but has now been almost entirely superseded by di-2-ethylhexyl sebacate. Plastic propellant grains can be case bonded because the strain on the bonding caused by unequal expansion at extreme temperatures is relieved by irreversible viscous flow of the propellant material.

**Table 13-7 Typical Plastic Propellant Compositions**

|                       | Compositions % (w/w) |      |    |    |    |    |
|-----------------------|----------------------|------|----|----|----|----|
|                       | 1                    | 2    | 3  | 4  | 5  | 6  |
| Ammonium perchlorate  | 64                   | 84.5 | 82 | 74 | 70 | 42 |
| Ammonium picrate      | 10                   | -    | 5  | -  | -  | 42 |
| PIB (plasticised)     | 11                   | 13.5 | 12 | 11 | 11 | 13 |
| Aluminium             | 15                   | -    | -  | 14 | 18 | 5  |
| Basic copper chromate | -                    | 2    | -  | 1  | -  | -  |
| Titanium dioxide      | -                    | -    | 2  | -  | 1  | -  |
| Oxamide               | -                    | -    | -  | -  | -  | 2  |

#### 13.2.3.4 Rubbery composite propellants

The advantages of plastic propellants for small rocket motors, namely their simplicity of manufacture and the fact that no potentially hazardous exothermic reaction or toxic curing agent is involved, are offset by their poor physical properties from the point of view of rocket propellant requirements. Furthermore, plastic propellant suffers from an inadequate 'solids capacity' (achievable ratio of oxidant to binder) and, therefore, has not attained the specific impulse of which it is theoretically capable, while still retaining acceptable mechanical properties.

Most composite rocket propellants in use today (2017) are of the rubbery type. These propellants were originally developed for casting into large grains, but recent advances in processing have led to the development of extruded rubbery propellants (the so called extrudable curables) so that even the smallest motor, which might previously have employed plastic propellant, can now benefit from the superior mechanical properties of rubbery composites. This sequence of development is in the reverse order to that of double-base propellants.

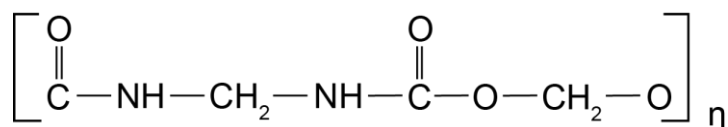
The main types of rubber which are mixed with ammonium perchlorate in present day rubbery composites are as follows:

- Polyurethane (PU)
- Polybutadiene (PB)
- Polybutadiene acrylic acid acetonitrile (PBAN)

A former elastomer, the polyalkyl sulphide or polysulphide type, is now obsolete for this purpose. The manufacture of a rubbery composite propellant, particularly when compared with that of a double-base propellant, can be a relatively simple process, and cast rubbery composites are cheaper than cast double-base (CDB) types. The crystalline oxidant, of an appropriate particle size, is mixed with the prepolymer and the curing agent. Other materials such as a burning rate catalyst and a fuel element (usually aluminium) may also be added at this stage. The mixture is heated and carefully agitated to ensure complete mixing. It is then degassed and cast or extruded into the desired grain shape. Curing takes place over several weeks at an elevated temperature (~60 °C) in the case of the cast propellant grain. Extrudable curables require a very much tighter control over viscosity during the mixing stage, but if this is achieved and extrusion is successful, curing can be carried out over a much shorter period of time (3-4 days) at the same temperature. The mechanical properties of the product are determined by the degree of polymerisation and cross-linking achieved in the final curing stage.

#### 13.2.3.5 Polyurethane (PU) composite propellants

Polyurethane composite propellants are polymerised from di-isocyanate/glycol type monomers, producing a polyurethane chain of the type shown in Figure 13-4, which has the molecular composition  $(C_6H_{10}O_4N_2)_n$ .

**Figure 13-4 Chemical structure of a polyurethane chain**

PU composite propellants originated in the early 1950's, and the cancelled British artillery missile Blue Water (1958-62) contained a PU propellant. The first stage motor of SLBM Polaris, developed in the same general period, contained a PU composite (ANP 2969). Its composition is shown in Table 13-8.

**Table 13-8 A Typical Polyurethane Composite Propellant**

| Ingredients          | % (w/w) |
|----------------------|---------|
| Ammonium perchlorate | 55.0    |
| Polyurethane         | 12.5    |
| Aluminium            | 20.0    |
| Nitro-plasticisers   | 12.5    |

### 13.2.3.6 Polybutadiene (PB) composite propellants

Polybutadiene propellants were developed in the late 1950's. Polybutadiene consists of the polymer chain (Figure 13-15) which can be either carboxyl terminated (CTPB) or hydroxyl terminated (HTPB). The two types differ in the method of cross-linking, and HTPB propellants have longer shelf lives for this reason.

**Figure 13-5 Chemical structure of polybutadiene binder**

HTPB propellants are the most widely used composites, examples of their use include: ASRAAM (Advanced Short Range Air-to-Air Missile); SEA Viper (Surface-Air ship launched missile); the Hoopoe motor for Sky Flash (air to air missile); and the motor for the LAW 80 light anti-tank weapon which burns for only 12 milliseconds. CTPB propellants have been used in the Linnet and Sparrow motors. Cast HTPB propellants have the best low temperature strain capabilities of all solid propellants. They have an extensibility of up to 40 % between +20 °C and -20 °C and this falls only to about 30 % at -60 °C, so they can be safely case bonded for any ambient temperature likely to be encountered. Typical compositions for the two PB types, with corresponding performance figures, are shown in Table 13-9, together with a PU and a PBAN type propellant.

The particular manufacture of HTPB propellants serves to illustrate the general principles of modern rubbery propellant production. The liquid prepolymer for HTPB propellants consists of a mixture of polybutadiene prepolymer molecules, each with either two, three or four hydroxyl end groups, i.e. HO-(CH<sub>2</sub>CH=CH

$\text{CH}_2)_n\text{-OH}$  etc., such that the overall functionality (number of hydroxyl groups/number of molecules) is about 2.5. The actual functionality is very important in determining the physical properties of the manufactured propellant and needs to be chosen so that the propellant is as lightly cross linked as possible but has good low temperature elasticity and can withstand the stresses arising from temperature and pressure increases when the motor is fired.

**Table 13-9 Typical Compositions and Properties of Rubbery Composite Propellants**

|                                               | <b>PU</b><br>% (w/w) | <b>PBAN</b><br>% (w/w) | <b>CTPB</b><br>% (w/w) | <b>HTPB</b><br>% (w/w) |
|-----------------------------------------------|----------------------|------------------------|------------------------|------------------------|
| Ammonium perchlorate                          | 70                   | 69                     | 63                     | 70                     |
| Fuel/binder                                   | 21                   | 11                     | 10                     | 12                     |
| Aluminium                                     | 8                    | 15                     | 17                     | 18                     |
| Di-octyl adipate                              | -                    | 4                      | -                      | -                      |
| HMX                                           |                      | -                      | 10                     |                        |
| Other                                         | 1                    | 1                      | -                      |                        |
| Specific impulse ( $\text{N s kg}^{-1}$ )     | 2400                 | 2600                   | 2600                   | 2550                   |
| Heat of explosion $Q_p$ ( $\text{J g}^{-1}$ ) | 4540                 | 5970                   | -                      | 6450                   |

The hydroxyl-terminated polybutadiene (HTPB) prepolymer is mixed with the curing agent, ammonium perchlorate (~70 % w/w), aluminium powder (~15-20 % w/w) and other minor additives in the manner described. The curing agent, normally a di-isocyanate, is added in a precise concentration so that the ratio 'isocyanate groups/hydroxyl groups' in the prepolymer mix is within very closely controlled limits. This ratio, like the prepolymer functionality, is critical in determining the mechanical properties of the final propellant. The curing reaction (Figure 13-6) which takes place between the isocyanate and hydroxyl groups, following casting or extrusion of the propellant, produces no elimination products.

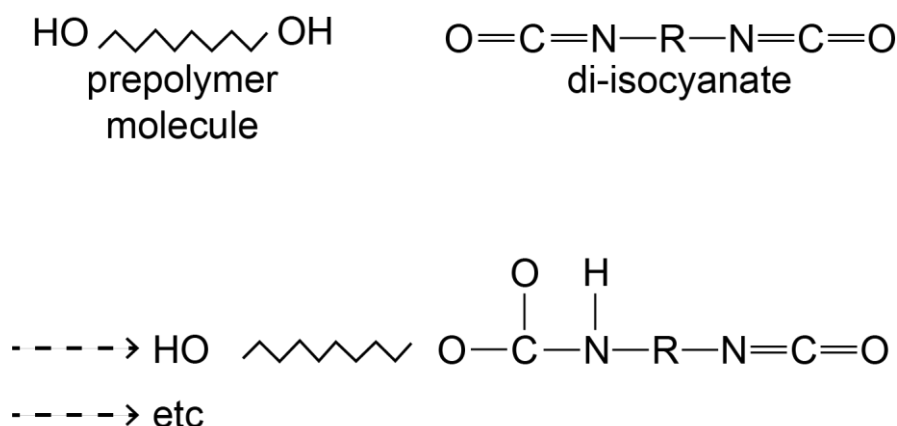


**Figure 13-6 Hydroxyl terminated polybutadiene curing reaction**

Besides the components already mentioned, a number of other materials are added to HTPB propellants. One such, an antioxidant (e.g. a hindered phenol), is important in prolonging the storage life, while others, (e.g. iron oxide and copper salts) affect the ballistic properties. Further additives may be present to attenuate electromagnetic radiation (e.g.  $\text{MoO}_3$ ) and, as pot life extenders, to reduce the curing rate (e.g. catechol). A bonding agent is also essential to improve the physical properties of the propellant.

In carboxyl terminated polybutadiene (CTPB) the prepolymers are cured by reaction with epoxides or aziridines. PBAN, which is a terpolymer of polybutadiene acrylic acid acetonitrile formed by free radical copolymerisation, is also cured by reaction of the carboxyl groups with epoxides or aziridines.

### 13.2.3.7 Reduced smoke nitramine propellants

In order to achieve a high performance with reduced smoke, propellants using nitramines (RDX and HMX) have been developed. These propellants typically contain no aluminium, a low AP content ~10 % (w/w), 50-85 % (w/w) nitramines, with hydroxyl-terminated polybutadiene or polyurethane as a binder. These low smoke or reduced smoke propellants produce no primary smoke, while secondary smoke, created when water vapour is present, appears only at low ambient temperatures. Removing the aluminium from the composite will significantly reduce the performance and density of the composition. This is offset somewhat by the replacement of AP with RDX/HMX. The Evolved Sea Sparrow (Surface to Air) Missile is an example of a reduced smoke composite propellant. An energetic plasticiser such as nitroglycerine can also be added to give a modest increase in performance. These nitrate ester plasticised elastomers (NEPE) almost match the performance of an aluminised composite propellant Table 13-10, but with the reduced smoke nature of a double-base propellant. The major design compromise with using these propellants is safety. They have poor safety and vulnerability characteristics compared to composite propellants, which means their use is normally limited to small rocket motors where the required critical diameter for detonation is less likely to be achieved. The Hellfire missile (Air-Surface missile) is an example that employs a nitrate ester plasticised elastomer (NEPE) propellant.

**Table 13-10 Comparison of Typical (a) Aluminised (Smokey) Rubbery Composite and (b) Reduced Smoke NEPE Propellant**

| Ingredients    | % (w/w) |     | (a) density x specific impulse = 4300 N s dm <sup>-3</sup><br>(for typical expansion ratio)<br><br>(b) density x specific impulse = 4110 N s dm <sup>-3</sup><br>(for typical expansion ratio) |
|----------------|---------|-----|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
|                | (a)     | (b) |                                                                                                                                                                                                |
| HTPB           | 15      | 12  |                                                                                                                                                                                                |
| Nitroglycerine | -       | 25  |                                                                                                                                                                                                |
| AP             | 70      | 10  |                                                                                                                                                                                                |
| Aluminium      | 15      | -   |                                                                                                                                                                                                |
| RDX            | -       | 53  |                                                                                                                                                                                                |

**13.2.3.8 Advantages and disadvantages of rubbery composite propellants**

The general advantages of rubbery composite propellants are as follows:

- They have good mechanical properties over a wide temperature range
- They can be satisfactorily case bonded
- They can be energised by aluminium
- They can be energised by RDX or HMX
- They burn smoothly, especially if aluminised
- They have high characteristic velocity ( $c^*$ ) (see 13.6.4) values

Their general disadvantages are as follows:

- They have a smoky exhaust
- They require careful curing
- They cause interference with Electromagnetic (EM) radiation
- They may undergo stress cracking on storage
- They cannot be platonised (see 13.2.4.1.1)

Figure 13-7 summarises the various types of solid rocket propellant.

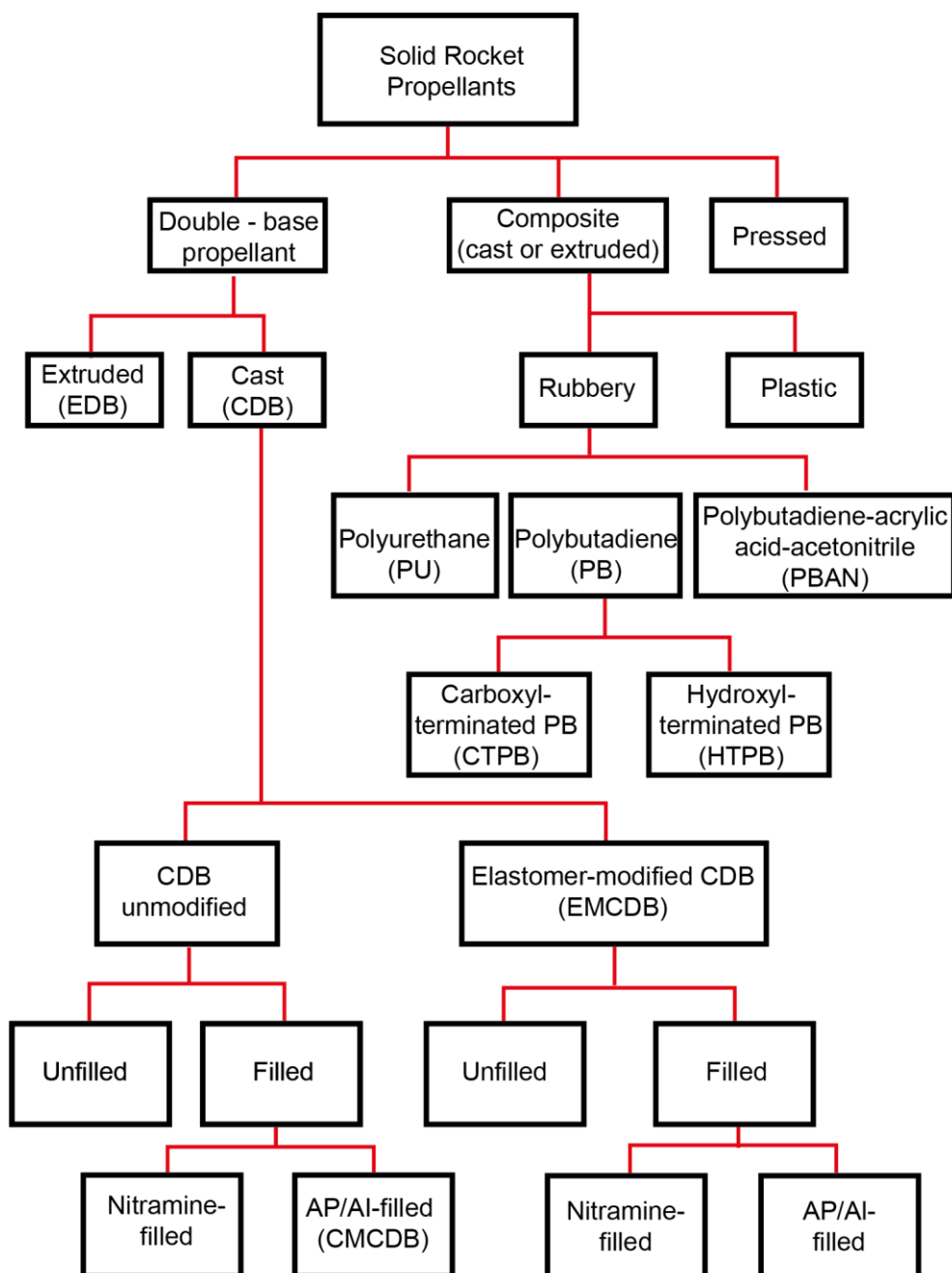


Figure 13-7 Types of solid rocket-propellant

### 13.2.4 DB Propellant Combustion

The burning surface of a double-base propellant (see 7.2.4.1) is known as the 'foam zone'. It is about 1 mm thick at rocket chamber pressures and its temperature is up to 300 °C. The chemical reaction mechanism in this zone is the breaking of the O-N bond in the R-O-NO<sub>2</sub> structure of the nitrate esters, followed by the formation of aldehydes, alcohols etc. Above the foam zone is a non-luminous gaseous reaction zone called the 'fizz zone, or 'dark zone', about

0.05 mm thick and at about 1200 °C, where the decomposition products are converted into compounds of lower molar mass including the gases CO, CO<sub>2</sub>, H<sub>2</sub>O, N<sub>2</sub> and NO<sub>2</sub>. Finally, in the 'flame zone', which is approximately 0.01 mm thick and at 1200 °C to 3000 °C, all the compounds are converted into the final gaseous species as the foregoing, but with little or no NO<sub>2</sub>.

As the pressure increases, the thickness of the 'fizz' and 'flame zones' is decreased and more of the generated heat is conducted or radiated back into the outer layers of propellant, causing them to reach the ignition temperature more quickly. Hence the rate of regression, the linear burning rate ( $r$ ) (see 7.2.2) is dependent on the chamber pressure ( $P_c$ ). The relationship is expressed in Vieille's law shown in Equation (13-1), where  $a$  is the pressure index and  $n$  is the burning rate coefficient. The value of  $n$  for double-base propellants is between 0.8 and 1.0; that for composite propellants is usually between 0.4 and 0.6. This relationship, when plotted, gives curves of the form shown in Figure 13-8 and Figure 13-9.

$$r = a P_c^n \quad (13-1)$$

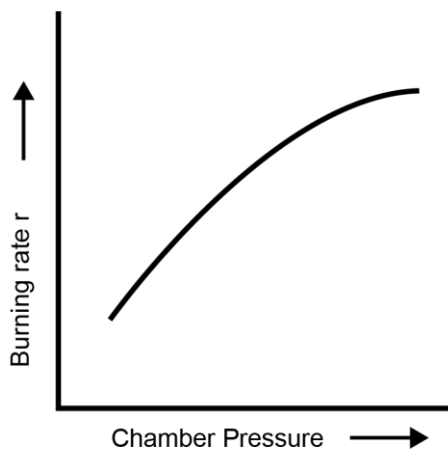


**Figure 13-8 Burning rate ( $r$ ) versus chamber pressure ( $n < 1.0$ )**

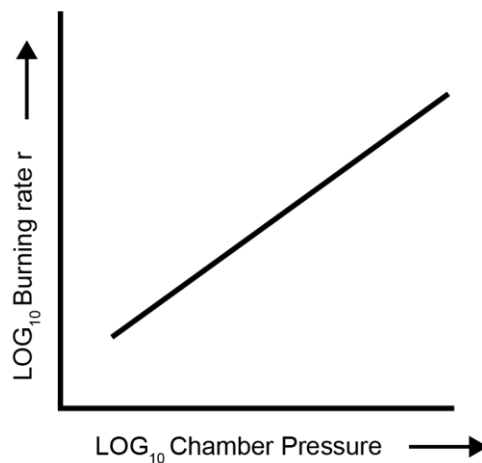


**Figure 13-9 Log10 burning rate ( $r$ ) versus Log10 chamber pressure**

An important parameter of a solid propellant is its rate of burning at chamber pressure. In order to achieve the required mass-burning rate ( $\dot{m}$ ) for a particular application it is necessary to obtain the optimum values for the expression:

$$\dot{m} = A_s \dot{x} a P_c^n \times \rho \quad (13-2)$$

where  $\rho$  is the propellant density and  $A_s$  is the burning surface area. The value of  $A$  is important to the efficient functioning of a rocket motor. The combustion chamber pressure is given by:

$$P_c = k \left( \frac{A_s}{A_t} \right)^N \quad (13-3)$$

where  $A_t$  is the nozzle throat cross-sectional area and  $k$  and  $N$  are characteristic of the propellant in use. The value of  $N$  is greater than unity and is related to  $n$  by the expression:

$$N = \frac{1}{1 - n} \quad (13-4)$$

Hence a large value of  $n$  implies excessive sensitivity of chamber pressure to variation of burning surface area. This is difficult to avoid in practice, but under no circumstances must  $n$  exceed 1.0.

One reason for the variation of burning surface area is a phenomenon known as erosive burning. Within the motor the pressure is highest at the head end, but the gas velocity is greatest at the nozzle end. Although pressure affects the burning rate, a stream of hot gas passing rapidly over the burning surface causes a greater effect. Hence the grain burns away faster at the nozzle end than calculations would predict, especially in the early stage of the combustion when the conduit is still narrow. Erosive burning can be limited by keeping the cross-sectional area of the conduit(s) adequately large in proportion to the nozzle throat area, but this imposes a limit on the impulse/total bulk ratio achievable in a radial burning grain.

#### 13.2.4.1 Platonisation and mesonisation

Values for the linear burning rate of double-base propellants range between 5 mm s<sup>-1</sup> and 20 mm s<sup>-1</sup> at commonly encountered pressures, depending largely on the percentage of nitroglycerine present. It is possible to produce an important alteration in the burning rate/pressure curve by introducing small amounts (1 – 5 % w/w) of certain lead or copper compounds into the propellant composition. This reduces the value of  $n$  to zero over a limited range of pressure, typically 7 MPa to 14 MPa, making the burning rate virtually independent of pressure within this range. The burning rate, and hence the thrust, will therefore be as constant as the grain geometry allows, provided the plateau covers the operating pressure of the motor (Figure 13-10).

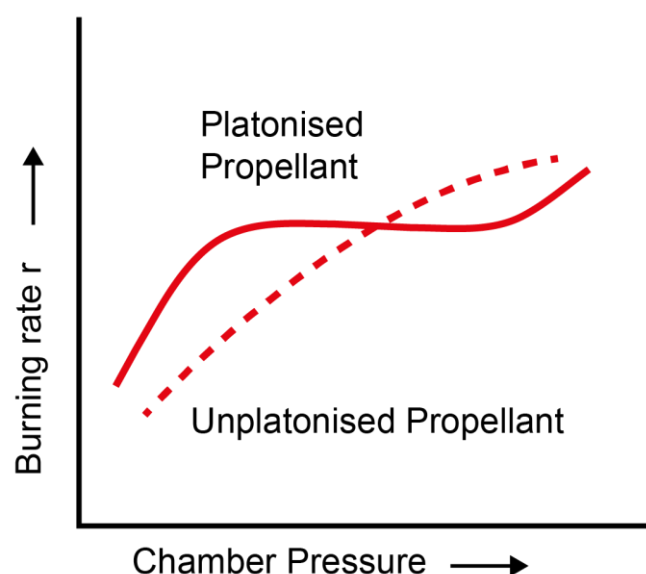


**Figure 13-10 Burning rate ( $r$ ) versus chamber pressure, for platonised and unplatonised propellants**

The platonisation effect was discovered accidentally in the US about 1950, when they used lead stearate as a component of a die lubricant and thus contaminated a sample of propellant. The mechanism of catalysis in platonisation is imperfectly understood and differing accounts are found in the literature. It is currently believed that the lead compounds act as positive catalysts of the burning process at low rocket pressures and that the effect disappears as the pressure increases, the plateau marking the limiting pressure range for the catalysis. Lead stearate, the original agent, is still among those in use, but to be effective it must be well dispersed throughout the composition. Lead acetyl salicylate and lead ethyl hexoate are more effective, since they are soluble in nitroglycerine. Lead stannate produces high plateau rates of burning at acceptable pressures. Other platonising agents include lead resorcyate, white lead (basic lead carbonate), and a few copper compounds. Lead and copper compounds are often used in combination. Lead salts also increase the rate of regression before the onset of platonisation (i.e. a super-rate at lower pressures).

Other particulate materials, including inorganic salts such as ammonium perchlorate, tend to destroy the plateau. The type of nitrocellulose used in double-base propellants has an effect on the plateau characteristics.

A variation of platonisation, called mesonisation, is sometimes encountered and is illustrated at Figure 13-11. The burning rate at the base of the hump (mesa) may be below that of the matrix.

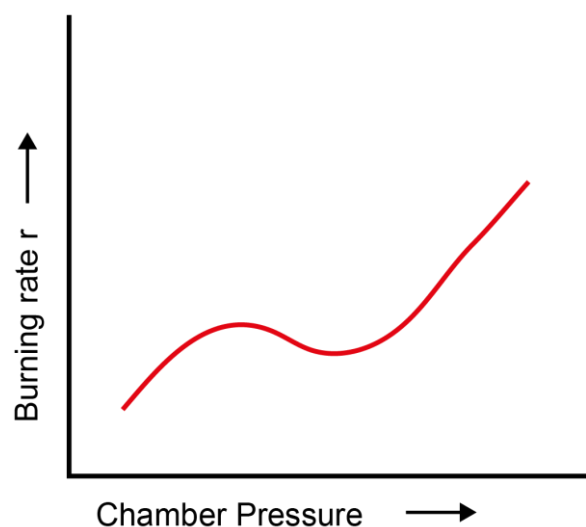


**Figure 13-11 Burning rate (r) versus chamber pressure for a mesonised propellant**

The advantages of platonising double-base rocket propellants can be summarised as follows.

- It minimises the effect of pressure fluctuations on linear burning rate.
- It enables the linear burning rate at given pressures to be increased by up to 100 %.
- It reduces the effects of manufacturing tolerances and grain geometry on the burning rate.
- It reduces the dependence of linear burning rate on conditioned grain temperature.

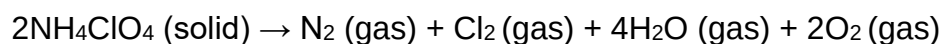
The disadvantages are as follows:

- The presence of a platonising agent, which is a non-energetic material, lowers the calorimetric value of the propellant.
- The presence of a platonising agent may increase the production of smoke.

### 13.2.5 Composite Propellant Combustion

#### 13.2.5.1 Ammonium perchlorate combustion

Combustion of ammonium perchlorate in the unmixed state causes decomposition into entirely gaseous products with considerable evolution of heat:



$$\Delta H = -193 \text{ kJ mol}^{-1}$$

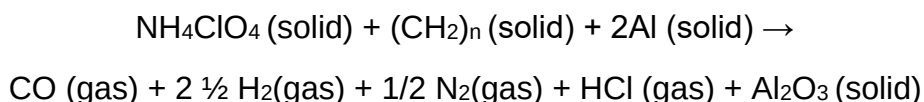
When burnt with a hydrocarbon fuel, ammonium perchlorate yields hydrogen chloride gas, which is toxic and corrosive and which forms a smoke cloud in the atmosphere if a normal amount of moisture is present.

In composite propellants the rate of burning ( $r$ ) (see 7.2.2) for a fixed  $Q_p$  (see 13.6.2) value and combustion pressure depends on the particle size of the ammonium perchlorate, as measured by its specific surface ( $S_o$ ). The value of  $r$  increases with decreasing particle size and increasing specific surface. The normal specific surface requirement for ammonium perchlorate in composite propellants is  $\sim 2000 \text{ cm}^{-1}$ . This corresponds to a rate of burning of  $\sim 18 \text{ mm s}^{-1}$  (at 6.9 MPa) for a standard plastic composite propellant containing 85 % (w/w) of ammonium perchlorate. The same propellant composition, containing ammonium perchlorate milled to a specific surface of  $8000 \text{ cm}^{-1}$  gives a rate of burning of  $38 \text{ mm s}^{-1}$  (at 6.9 MPa).

### 13.2.5.2 Combustion of aluminium

The mechanism of combustion of composite propellants differs from that of Double-base propellants. It is believed that the primary reaction zone lies almost entirely in the gas phase, which is less than 0.1 mm thick at rocket pressures. The ammonium perchlorate particles and the fuel matrix are decomposed mainly by the heat conducted from the gas phase, and pockets occur in the surface, their size being related to that of the original particles. Many composite propellants contain aluminium, incorporated primarily to increase the calorimetric value. As the surface recedes during burning the metal accumulates on the surface to form molten droplets up to 20 times the diameter of the original particles. The oxidation of these particles to  $\text{Al}_2\text{O}_3$  occurs during their passage from the surface to the nozzle throat. They tend to promote smooth burning by suppressing resonance within the chamber.

Aluminium can be added to composite propellants up to an optimum 22 % (w/w). Its inclusion reduces the number of moles of gas produced but, beneficially, it also lowers the mean molar mass  $\bar{M}$  of the gaseous products by reducing the gaseous water to hydrogen, which has a molar mass of only  $2 \text{ g mol}^{-1}$ . Aluminium also increases the value of  $T_c$  by virtue of its high heat of combustion. The overall reaction in a typical aluminised composite may be expressed as follows:



### 13.2.5.3 Combustion of nitramines

The highly energetic nitramine explosives RDX and HMX are added to some cast Double-base (CDB), extruded Double-base (EDB) and composite propellants for several reasons. In modified CDB propellants they are better gas producers than the nitroglycerine which they partly replace, but with somewhat lower heats of explosion ( $Q_p$ ). When burning in a propellant composition, RDX and HMX melt as the temperature of the propellant rises with the regression of

the burning surface. The melting process absorbs latent heat from the system, thus slowing its temperature rise and reducing the burning rate. When present in composite propellants RDX and HMX replace part of the ammonium perchlorate, thus lowering the burning rate with little reduction of the specific impulse (see 13.6.3). The capacity of the nitramines to reduce burning rates applies only at low combustion pressure; at higher pressures RDX and HMX exhibit increasing values of  $\alpha$  which may exceed unity and compositions containing them would, therefore, tend to give unstable burning.

### 13.2.6 Grain Geometry

The three types of burning (progressive, neutral, degressive) give rise to different shapes of thrust/time curve (Figures 13-12, 13-13 and 13-14). In all three cases it is an important feature of grain design to achieve an abrupt burn out, because any slivers or other remnants of propellant which burn at a greatly reduced pressure are virtually wasted.

In order that the missile follows a predictable trajectory, neutral burning is often a desirable property of a propellant grain. There are several apparent ways of achieving this. One is an uninhibited tubular grain (which could be multiplied within a single motor): this is feasible for very short-range missile, but the flame impinges directly on chamber walls, which would quickly fail. The same applies to the serrated cruciform section grain which was used in some British rockets of World War II. Most rocket-motor grains are therefore designed to burn only in the conduits and/or on the rear surface.

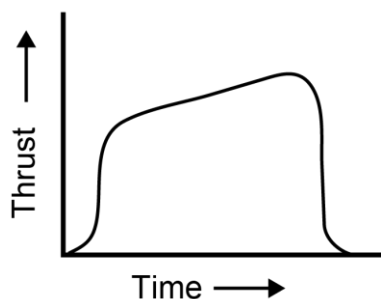


Figure 13-12 Thrust versus time for progressive burning

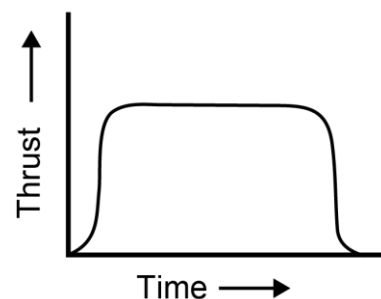


Figure 13-13 Thrust versus time for neutral burning

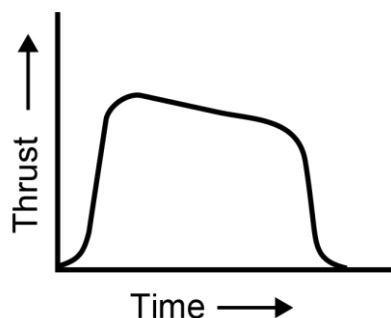


Figure 13-14 Thrust versus time for degressive burning

Neutral burning of an inhibited grain can be achieved in several ways. The simplest is the cigarette burning or end burning grain, which is inhibited at the circumference and head end, burning only at the nozzle end. A plain cylindrical grain is easy to produce, but has two disadvantages. One is that its centre of gravity (and hence that of the missile) moves forward as burning proceeds. The other is that there is insufficient burning area to give a high boost thrust. The latter disadvantage can be overcome by forming radial slots and an axial conduit at the nozzle end, thus giving large surface area for the boost phase followed by neutral and slower burning for the sustain phase. This design is called a slotted cylinder (Figure 13-15).

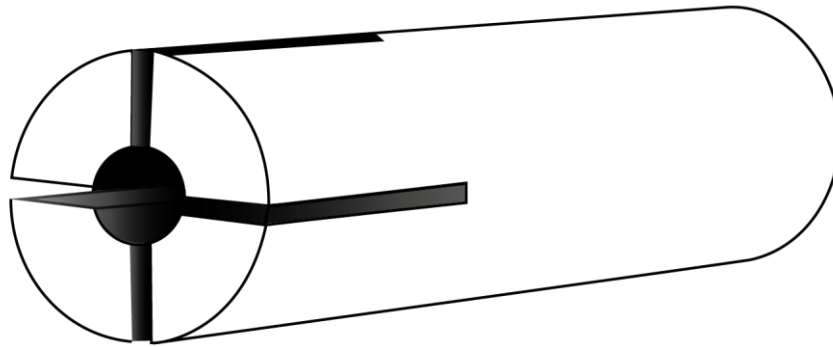


**Figure 13-15 Slotted cylinder grain**

Most boost grains are inhibited and radial burning. Their geometry is contrived so as to provide a large burning surface area while protecting the motor case from the high flame temperature. One way to achieve this is the 'tube and rod' design shown in Figure 13-16. The increasing outer surface of the conduits is balanced by the decreasing surface of the inner ones. This concept can be developed into more complex shapes such as Figure 13-17.

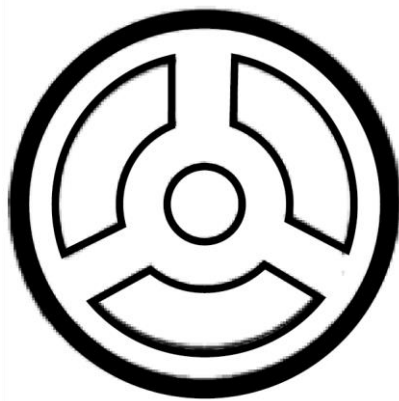


**Figure 13-16 Tube and rod grain**

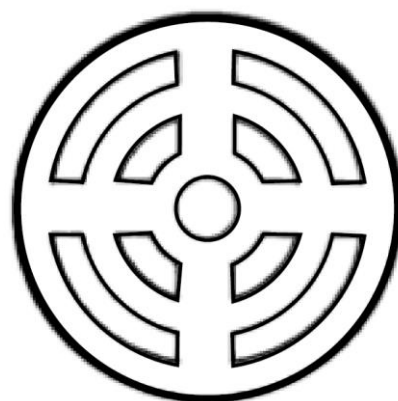


**Figure 13-17 Multiperforated grain**

The star centre grain (Figure 13-18) is the most commonly used design. There are many possible variations of the basic design, including both degressive and progressive shapes, but it is possible to obtain neutral burning combined with a high impulse and bulk ratio with minimal sliver formation. The star-section

imparts longitudinal strength to the grain but it is necessary to round or square the points of the star in order to distribute the stresses which are concentrated there.

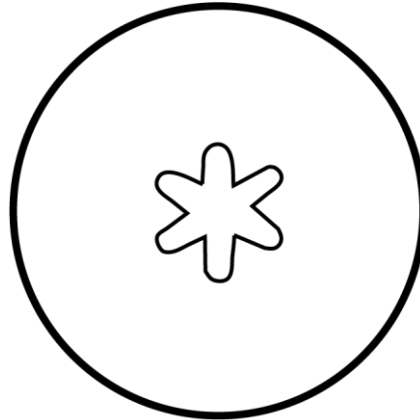


Figure 13-18 Star-centre grain

### 13.2.7 The Effect of Grain Temperature on Burning Rate

The burning rate of a solid propellant depends on the initial temperature ( $T_p$ ) of the propellant. This is normally the ambient temperature to which the grain has become conditioned. Any change in temperature ( $T_p$ ) causes a change in the rate of burning, which in turn affects the gas pressure at the burning surface and thus produces a further change in the rate of burning.

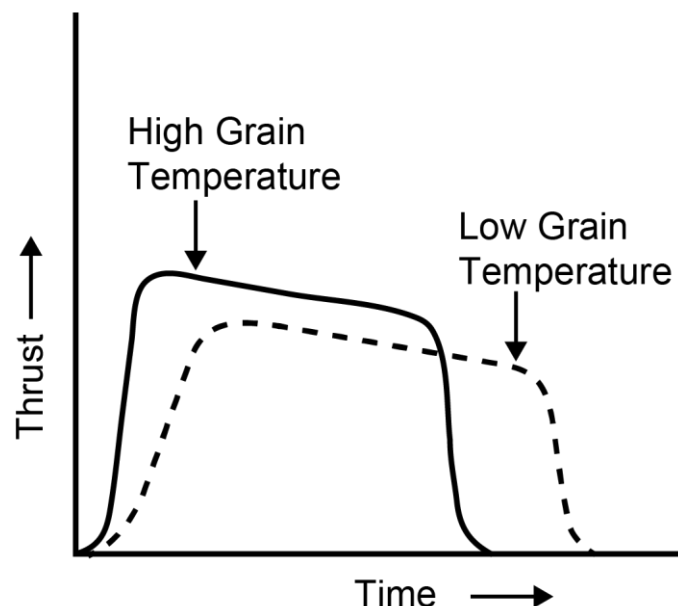


Figure 13-19 Thrust versus time for two different values of grain temperature. (degressive burning grain in both cases)

There are, therefore, two effects, the intrinsic effect of grain temperature on burning rate and the additional effect caused by the consequent increase in pressure.

Figure 13-19 shows diagrammatically the difference brought about in the thrust/time curve by different values of  $T_p$ . The ratio of the area of the burning propellant surface ( $A_s$ ) to the area of the nozzle throat ( $A_t$ ) is the area ratio and is given the symbol  $K$ . The chamber pressure in the rocket is  $P_c$ . At constant  $K$  the temperature sensitivity of pressure is measured by the parameter  $\pi_k$  which can be derived as shown in Equation (13-5).

$$\pi_k = \frac{1}{P_c} \cdot \left( \frac{dP_c}{dT_p} \right) K \quad (13-5)$$

Differentiation of the equation the yields:

$$\pi_k = \frac{1}{1 - \alpha} \cdot \frac{1}{\beta} \cdot \frac{d\beta}{dT_p} \quad (13-6)$$

The sensitivity of burning rate to grain temperature, as measured by the  $\pi_k$  value, is a very important property of a solid rocket propellant. It is a fundamental design parameter, together with the rate of burning ( $r$ ), density ( $\rho$ ) and characteristic velocity ( $c^*$ ). From the view point of motor design and reliability it is clearly desirable that a rocket propellant has a low  $\pi_k$  value. This will reduce those differences in chamber pressure which are due to grain temperature changes, and will lead to more consistent motor performance over a wide range of conditioned grain temperatures. An important factor which helps to minimise the  $\pi_k$  value is a low value of the pressure index  $n$  (see Equation (13-1)).

**Table 13-11 Typical Values for  $\pi_k$  for Different Types of Solid Rocket Propellant**

|                                | <b>Propellant</b>        | $\pi_k \cdot (\% \text{ } ^\circ\text{C}^{-1})$ |
|--------------------------------|--------------------------|-------------------------------------------------|
| <b>Platonised propellant</b>   | EDB, unfilled            | <0.15                                           |
|                                | EDB, nitramine filled    | <0.15                                           |
|                                | CDB, unfilled            | 0.1 - 0.2                                       |
|                                | CDB, nitramine filled    | 0.1 - 0.2                                       |
|                                | EMCDB, unfilled          | 0.1 - 0.25                                      |
|                                | EMCDB, nitramine filled  | 0.1 - 0.25                                      |
| <b>Unplatonised propellant</b> | CMCDB                    | 0.5                                             |
|                                | Elastomer modified CMCDB | 0.5                                             |
|                                | Plastic composite        | 0.2 - 0.4                                       |
|                                | HTPB composite           | 0.2 - 0.3 and below                             |

In platonised Double-base propellants  $n$  is zero or close to it, therefore these propellants are characterised by low values of  $\pi_k$ . This feature is one of the

advantages of platonisation. Table 13-11 shows the differences in  $\pi_k$  values between platonised and unplatonised propellants.

### 13.2.8 Smoke Emission

The production of smoke by a missile motor is undesirable as it may give away the firing position to the enemy, obscure the missile from the firer, or interfere with optical guidance. Some of the substances which comprise the smoke, such as HCl, can be toxic to personnel near the firing point and corrosive to equipment. Nevertheless, many types of missile produce smoke and its effects must be minimised and tolerated. The smoke consists of minute solid particles of free carbon, alumina and other metal oxides, or as mists of liquid droplets, e.g. HCl. Double-base propellants produce little smoke unless they contain a high proportion of additives.

Composite propellants produce considerable smoke, caused by the HCl produced from ammonium perchlorate supported combustion and, in many cases, by the inclusion in the composition of aluminium which is oxidised to alumina. Any other additives will tend to exacerbate the problem.

In addition to the propellant, other components of the motor may produce smoke. In inhibitor sheaths, the proportion of carbon to oxygen is a factor in smoke production. If this ratio can be kept down without prejudice to the numerous other requirements of inhibitor material, an advantage can be gained. Within the material itself, smoke-producing plasticisers may be identified. Smoke can be reduced by using aliphatic plasticisers such as ethyl carbonate ( $\text{C}_2\text{H}_5\text{O}-\text{CO}-\text{OC}_2\text{H}_5$ ) with a C/O ratio of 1.7 as compared to aromatic plasticisers like di-ethyl phthalate ( $\text{C}_6\text{H}_4(\text{CO}_2\text{C}_2\text{H}_5)_2$ ) with a C/O ratio of 3. The use of inorganic fillers in the inhibitor may also increase smoke production.

#### 13.2.8.1 Attenuation of Electromagnetic (EM) radiation by rocket exhaust

Electromagnetic signals for missile guidance, usually of micro wavelength, beamed from a point behind the missile have to pass through at least part of the motor exhaust flame. This flame is an ionised conducting medium and therefore interferes with the signal, attenuating it and introducing noise like amplitude and phase modulations. The flame is an envelope of reacting gases, which comprise a number of species including neutral molecules, atoms, free radicals (e.g.  $\cdot\text{OH}$ ), ions (e.g.  $\text{M}^+$  and  $\text{H}^+$ ) and free electrons ( $\text{e}^-$ ). In practice it is largely the free electrons which cause electromagnetic interference. The following are some ways in which the concentration of free electrons can be reduced, but clearly some of the remedies conflict with other requirements of propellant technology.

- a) Exclusion from the propellant composition of elements with low ionisation potentials, i.e. light metals. This conflicts with the use of aluminium to increase specific impulse. Other metals which may be present are potassium and sodium as impurities in ammonium perchlorate.
- b) Reduction of flame temperatures by flame suppressors such as cobalt stannate, molybdenum oxide or iron penta-carbonyl.

- c) Inclusion in the propellant composition of an electron absorbing species such as halocarbons. Polytetrafluoroethylene (PTFE) is a possibility.
- d) Suppression of molecule dissociation by increasing chamber pressure.

### 13.2.9 New Solid Propellant Developments

A number of new energetic compounds have been developed in recent years and some of these are being actively considered for use in solid rocket propellants. One of the main areas of interest is the development of 'minimum smoke composite propellants' for tactical missiles. These are designed to offer comparable or better performance and mechanical properties compared to existing AP/HTPB composite propellants but with minimum smoke combustion (as in DB propellants), brought about by substituting the ammonium perchlorate oxidizer with cleaner burning components. Good Insensitive Munitions (IM) characteristics (see 2.12) are also required for modern propellant systems.

There are two types of composition being considered for minimum smoke composite formulations. One involves the use of an alternative oxidizer to AP together with an energetic fuel/binder. The oxidizer that is currently most favoured is ammonium dinitramide (ADN), with the formula  $\text{NH}_4^+\text{N}(\text{NO}_2)_2^-$ , which was first made and used by the former Soviet Union in the 1970s but not announced to the rest of the world until 1980s when it was independently made in the USA.

Another oxidizer being investigated is hydrazinium nitroformate (HNF), with the formula  $\text{N}_2\text{H}_5^+\text{C}(\text{NO}_2)_3^-$ , however, this has major stability problems at elevated storage temperatures. The binder could be a cross-linked energetic polymer such as poly-3-nitratomethyl-3-methyloxetane (poly-NIMMO) or glycidylazide polymer (GAP). A plasticiser would also be required and this again could be an energetic compound, possibly GAP-azide (a GAP oligomer) or a nitratoethylnitramine (NENA) such as ethyl NENA.

**Table 13-12 Performance Comparison of Different Types of Composite Propellant**

| Oxidizer/<br>filler | Binder    | Plasticizer       | $c^*$<br>( $\text{m s}^{-1}$ ) | % increase of $c^*$<br>over AP/HTPB |
|---------------------|-----------|-------------------|--------------------------------|-------------------------------------|
| AP                  | HTPB      | di-octyl sebacate | 1511                           | -                                   |
| ADN                 | polyNIMMO | GAP azide         | 1619                           | 7.1                                 |
| CL20                | polyNIMMO | GAP azide         | 1645                           | 8.9                                 |

The other type of minimum smoke composite propellant being considered is that based on an energetic compound held in an energetic binder/plasticizer matrix. The energetic compounds of most interest for this case are RDX, HMX and hexanitrohexa-azaisowurtzitane (HNIW), which is also known as CL20 (see 10.3.3.5). This is a very high density material ( $2.04 \text{ g cm}^{-3}$ ), which is available commercially and is being actively investigated as a higher performance alternative to RDX and HMX in high explosive formulations. A comparison of

the performance of the two types of minimum smoke composite propellant with the current AP/HTPB type is presented in Table 13-12.

While existing AP/HTPB composite propellants show acceptable response in most safety tests they are less successful in meeting the requirements of the slow cook-off test that is included in IM test specifications such as STANAG 4439. This is thought to be because HTPB propellants harden during heating under slow cook-off and are unable to dissipate energy slowly during this process. For this reason, an area of interest in composite propellant technology is the development of Hydroxy Terminated Polyether (HTPE) propellants. These propellants use polyethers as binders and do not undergo the same degradation processes as polybutadiene during slow cook-off. They soften during heating under slow cook-off and their energy is released more slowly, giving a less severe response than HTPB based compositions. However, the level of technical risk and cost required to replace HTPB with HTPE is seen as too great at this time (2017); and most nations are remaining with HTPB and using engineering controls to mitigating the risk from slow cook-off.

In recent years there has been increasing pressure to reduce propellant costs and ensure the continuity of supply of propellant ingredients. The latter point is of growing concern because of International Traffic in Arms Regulations (ITAR) issues from the USA and the introduction of stricter environmental regulations such as REACH (see 1.3.2.4.6) that limit the availability of toxic chemicals. Manufacturers are now beginning to focus on producing solid propellants for tactical systems that can meet the requirements for most applications within the limits imposed by reduced budgets and materials availability. The traditional considerations remain: maintaining high performance ( $c^*$ ), minimum smoke combustion, low toxicity efflux where possible, good mechanical properties and high stability/long storage life.

### 13.3 HYBRID PROPELLANTS

The concept of a hybrid propellant system dates back to the early years of liquid propellants. A 'normal' hybrid system is one in which a solid or gelled fuel is burned in a stream of liquid oxidant, while a reverse hybrid system employs a solid oxidant and a liquid fuel. Research on hybrids has been carried out by several US agencies since about 1950, using a variety of exotic fuels and oxidants, but little useful result emerged until recently, when the American Rocket Company (Amroc) started to test its prototype motor for the Industrial Launch Vehicle. This is a large, four stage vehicle for launching satellites into low earth orbit, and its thrust is provided by 19 nearly identical hybrid motors, each of which burns 2200 kg of solid fuel in combination with 3620 kg of liquid oxidant. There is still no military system known to be using hybrid propellants, but the prospect may have been brought closer by the foregoing commercial development. The putative advantages of military hybrid rocket systems are as follows:

- a. Capability of thrust control and 'on off' functioning by control of the rate of injection of the oxidant.
- b. Capability of employing very energetic oxidant fuel combinations which are incompatible under normal conditions.
- c. Reduced hazard under fragment attack because oxidant and fuel are separated.

The disadvantages are:

- a. Greater complexity of the propulsion system.
- b. Non-uniform consumption (that is, erosion) of the fuel charge, with resulting incomplete utilisation of the charge.
- c. Low performance when operating outside conditions of stoichiometric combustion.

## **13.4 RAMJET FUELS**

### **13.4.1 Ramjet Propulsion**

The topic of hybrid propellants for pure rocket systems is allied to that of fuels for ramjet systems, since the latter can be thought of as utilising a gaseous oxidant (atmospheric oxygen) to oxidise a liquid or solid fuel.

### **13.4.2 Liquid Ramjet Fuels**

Liquid fuel ramjet engines have been in UK service, including Thor (Bloodhound) and Odin (Sea Dart) and were fuelled by kerosene, the heat of combustion of which is about  $44,300 \text{ J g}^{-1}$ . This was about five times better than a kerosene/LOX bipropellant system, because the oxygen consumed was not stored in the missile and therefore its weight does not enter into the calculation. On this basis, the effective specific impulse (see 13.6.3) of a kerosene fuelled ramjet motor is about 14500 MPa, compared with 2500 MPa for the bipropellant system. A disadvantage of kerosene is its low density of  $0.8 \text{ g cm}^{-3}$ . Because of this the Shell company developed a superior hydrocarbon fuel named Shelldyne H, which has the formula  $\text{C}_{14}\text{H}_{20}$  and consists of reduced dimers of bicycloheptadiene. The compact molecule provides a high density of about  $1.1 \text{ g cm}^{-3}$  in the liquid, which in turn permits a more compact design of missile than one fuelled by an equal weight of kerosene. Shelldyne H is, however, much more expensive.

### **13.4.3 Solid Ramjet Fuels (Propellants)**

In ramjet propulsion, as in pure rocketry, solid propellants have an obvious advantage over liquid propellants in that they allow the motor to be more simply designed, lighter and cheaper to manufacture. Solid fuels present no leakage or vapour hazard. Furthermore, they have a higher density than any liquid fuel. In order to burn in the ramjet however, they must, unlike liquid fuels, contain some

oxygen in their chemical structure, in addition to carbon and hydrogen. The minimum oxygen balance for this purpose is much lower than the near stoichiometric balance which is normal in a conventional rocket propellant. This rules out the use of double-base propellants for ramjets, because such propellants are capable of only limited adjustment to their oxygen balance. Instead, composite propellants are used, as these can provide a wide range of oxygen balance by variation of the fuel binder to oxidant ratio. The ammonium perchlorate content is reduced to about 30 % (w/w), making the oxygen balance heavily negative. As a result, the propellant yields under oxidised gases rich in flammable  $H_2$  and CO. A typical composition would consist of 30 % (w/w) ammonium perchlorate dispersed in a solid fuel matrix of polybutadiene rubber 70 % (w/w). The density of the mixture would be about  $1.2 \text{ g cm}^{-3}$ .

The energy, and hence the specific impulse, of composite propellants can be improved by the addition of a fuel element which itself has a high heat of combustion. The additive commonly employed in pure rocket propellants is aluminium. An aluminised version of the solid fuel ram rocket (SFRR) composite propellant would have the typical composition:

- |                         |            |
|-------------------------|------------|
| 1. Ammonium perchlorate | 50 % (w/w) |
| 2. Polybutadiene        | 20 % (w/w) |
| 3. Aluminium            | 30 % (w/w) |

This propellant would provide fuel rich gases at a higher temperature than the non-aluminised version, and furthermore the presence of hot solid particles would help to maintain steady combustion in the afterburner.

## 13.5 LIQUID ROCKET PROPELLANTS

### 13.5.1 The Uses of Liquid Propellants

Within a rocket system, propellants can be used in three fairly distinct roles:

- In powerful rocket motors, for the rapid forward propulsion of the entire vehicle.
- In motors which are small and of low thrust in proportion to the size and mass of the vehicle, but which are adequate, in a space environment or re-entry process, to change its course, speed or attitude (orientation). These motors are called by such names as manoeuvring systems or thrusters.
- In small units within the system, known as gas generators, power supplies or auxiliary power units, which generate hot gas under pressure as an energy source to operate mechanical and/or electrical devices, to pressurize fuel tanks or to induce spin of the moving vehicle.

In theory all three of these roles can be performed by either liquid or solid propellant, but in practical designs the choice between the two types is made on the basis of suitability.

### 13.5.2 Advantages and Disadvantages of Liquid Propellants

The inherent advantages of liquid propellants are as follows:

- a. Some have higher specific impulse (see 13.6.3) than solids;
- b. The weight or volume of the propellants carried in the vehicle, and hence the range, is not directly limited by the size of the motor, as is the case with solid propellants;
- c. The thrust can be varied by throttling, and if necessary combustion can be stopped and restarted;
- d. The combustion chamber and efflux nozzle can be cooled by the regenerative method, thus reducing dependence on expensive, highly heat-resistant materials and avoiding a constraint on combustion temperature;
- e. They give less smoke than some solid propellants;
- f. Liquid propellants are relatively cheap;
- g. Some bipropellant combinations are hypergolic (self-igniting on contact of the two liquids).

The main disadvantages are as follows:

- a. The motor is much more complicated than a solid-propellant one, usually with two storage tanks, several lengths of pipe, a pump or pressurising tank, valves etc. This adds to the weight of the motor, makes maintenance more difficult and decreases reliability. A requirement of instant readiness is more difficult to meet than with solid propellants.
- b. The liquid propellants are mostly of lower density than solid propellants.
- c. The liquid propellants are in most cases either toxic, corrosive or cryogenic.

For main propulsion motors a small size of missile favours the use of solid propellants, to provide simplicity and lightness. As the size of the vehicle increases there is more advantage to be gained from liquid propellants. The largest civil rocket vehicles, which are used for launching large satellites or space probes, employ liquid propellants for high specific impulse and for cheapness, but in such vehicles the axially-positioned liquid-propellant motor is commonly supplemented by two or more add on' or 'strap on' booster motors to assist the launch. These parallel mounted motors have traditionally been of the solid propellant type in both medium size military systems (e.g. Bloodhound and Seaslug) and in large civil ones (e.g. the NASA/DOD space shuttle and ESA Ariane 5). In the 1980-90s there was a trend towards liquid propellants for the add on motors in the large civil systems, e.g. Arians 44L, the Soviet Energia and the Chinese Long March 2-8L.

The main propulsion of Inter-Continental Ballistic Missiles (ICBM) changed in the 1960's from the liquid bipropellants founded on the German technology of World War II towards solid propellants. This change arose from the increased need for instant readiness of ballistic missiles and was facilitated by the improvement of solid propellant technology.

Thruster motors mostly burn liquid propellants, because these provide an on off capability which solid propellants do not. Large numbers of satellites have liquid propellant thrusters, and in the same general category were the re-entry motors of the British Chevaline system for the Polaris missile and the post boost propulsion system (PBPS) of the American Minuteman III missile. For gas generators the tendency is the same as for main propulsion motors, that is, solid propellants in small rockets and liquid ones in large rockets.

### **13.5.3 Liquid Monopropellants**

Liquid propellants are sub-divided into monopropellants and bipropellants. Monopropellants are liquids, which burn, or otherwise decompose, in the absence of external oxygen. They have comparatively low calorimetric values and provide only low specific impulse, and for this reason they are not used in the main propulsion motors of rocket vehicles, except that some monopropellants double as energetic fuels in bipropellant combinations. Instead, they are used in thrusters and gas generators. Monopropellant motors need only one propellant tank, and this permits a simpler, lighter and more reliable system than bipropellant motors. Monopropellants have to be decomposed, either on a catalyst or by heat, to provide gas at a high mass flow rate. A catalyst provides the simpler of these two systems, but care has to be taken to ensure that the catalyst does not become poisoned if the motor is required to operate intermittently over a period of months or years in a space application. Since monopropellants are reactive substances, it is also necessary to ensure that their containers are made of compatible materials. Table 13-13 shows some monopropellants, of which hydrazine is currently the most widely used.

#### **13.5.3.1 Hydrazine**

The Americans first used hydrazine as a monopropellant in the 1950's. Later it found application in the propulsion units of lunar and deep space probes, for example the U.S. Ranger. When the Shell 405 spontaneous catalyst was introduced, hydrazine replaced hydrogen peroxide in satellite thruster motors, and this use continues. It is also used in auxiliary power units and gas generators for large rockets and its use is likely to continue for some years. Anhydrous hydrazine ( $N_2H_4$ ) is a colourless, mobile liquid (see

Table 13-14). It fumes in air, has a pungent, ammonia smell and is very toxic (Long Term Exposure Limit = 0.02 ppm, Short Term Exposure Limit = 0.1 ppm) (see 18.1.2.2). Its vapour damages the eyes and mucous membranes, liver and blood.

**Table 13-13 Properties of Some Monopropellants**

| Propellant         | Boiling Point (°C) | Freeze Point (°C) | $\bar{M}$ (g mol <sup>-1</sup> ) | Combustion Temp (K) | Is* (N s kg <sup>-1</sup> ) | Density at 25 °C (g cm <sup>-3</sup> ) |
|--------------------|--------------------|-------------------|----------------------------------|---------------------|-----------------------------|----------------------------------------|
| Hydrazine          | 114                | 2.0               | 10.3                             | 966                 | 1951                        | 1.011                                  |
| Hydrogen peroxide  | 150                | -0.4              | 22.7                             | 1278                | 1618                        | 1.412                                  |
| Nitromethane       | 101                | -28.5             | 20.3                             | 2190                | 2500                        | 1.137                                  |
| Iso-propyl nitrate | 102                | -29.0             | 17.5                             | 1252                | 1630                        | 1.04                                   |
| Ethylene oxide     | 10.7               | -113.3            | 22.0                             | -                   | 1717                        | 0.87                                   |

\* All values refer to  $P_c = 7$  MPa and an ideal expansion to  $P_e = 0.1$  MPa,  $P_e/P_c = 0.014$ .

Although in the future hydrazine might be used as a bipropellant fuel in the manoeuvring motors of satellites, it is currently used almost entirely as a monopropellant. It has a number of advantages in the monopropellant role:

- It can be readily decomposed on a catalyst when required.
- It has a high calorimetric value ( $Q_p$ ) compared with some other monopropellants, the exact value depending on the particular mode in which it decomposes.
- It can be stored, given suitable conditions, for extended periods of time without undue decomposition.
- It is compatible with many (though by no means all) engineering materials.
- It is readily and fairly cheaply available, being used also in the plastics and other industries.
- It has a relatively low vapour pressure.

It has however, the following disadvantages:

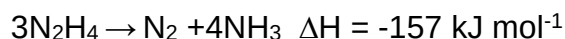
- a. High toxicity
- b. Comparatively high freezing point.
- c. High hygroscopicity.
- d. Susceptibility to catalysed decomposition on various surfaces, e.g. stainless steels and many elastomers, which is increased by the presence of acidic impurities in the liquid, such as carbon dioxide.
- e. Lower specific impulse than some other monopropellants.
- f. Slight susceptibility to dieseling, i.e. accidental ignition by the rapid, adiabatic compression of entrained bubbles.

**Table 13-14 Physical Properties of Anhydrous Hydrazine and Water**

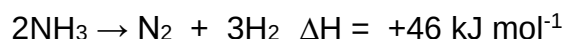
|                                                            | <b>Hydrazine</b> | <b>Water</b> |
|------------------------------------------------------------|------------------|--------------|
| Freezing point (°C)                                        | 2.0              | 0.0          |
| Boiling point (°C)                                         | 114.0            | 100.0        |
| Density (g cm <sup>-3</sup> )*                             | 1.004            | 0.997        |
| Viscosity (centipoise (cP))*                               | 0.91             | 0.89         |
| Vapour pressure (kN m <sup>-2</sup> )*                     | 1.89             | 3.16         |
| Heat capacity (J g <sup>-1</sup> K <sup>-1</sup> )*        | 3.08             | 4.18         |
| Thermal conductivity (W m <sup>-1</sup> K <sup>-1</sup> )* | 0.54             | 0.58         |

\* At 25 °C

In a propulsion unit hydrazine is normally stored in a titanium alloy or stainless steel tank and is utilised by decomposition on a spontaneous (cold-start) catalyst, the most effective of which is Shell 405 containing 30 % (w/w) iridium on high-surface-area alumina. The decomposition reaction is usually considered as taking place in two steps. The initial reaction, which is exothermic, produces mainly nitrogen and ammonia and causes the catalyst to heat up:



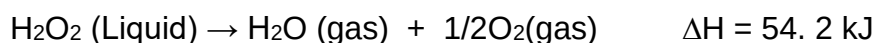
Once the catalyst is at a high temperature (1500 °C) some of the ammonia is dissociated into hydrogen and nitrogen. This reaction is endothermic:



### 13.5.3.2 Hydrogen peroxide

Until the mid-1960s, when the Shell 405 catalyst was developed for hydrazine, hydrogen peroxide was the most widely-used liquid monopropellant, as well as an oxidant in bipropellant systems. Anhydrous hydrogen peroxide is a colourless, mobile liquid with a bitter taste and an acidic smell; physical properties are given in Table 13-13. The pure substance is unstable and is readily decomposed by various impurities or reagents. Hydrogen peroxide is not as toxic as hydrazine, but its vapour causes irritation of the eyes and mucous membranes while the liquid, if it comes in contact with the skin, causes temporary discoloration and irritation. In rocketry applications an 80-90 % (v/v) solution of hydrogen peroxide in water is used, called 'high test peroxide' (HTP). At 25 °C, 90 % (v/v) HTP has a density of 1.387 g cm<sup>-3</sup>, 80 % (v/v) HTP has a density of 1.334 g cm<sup>-3</sup>. HTP is compatible with aluminium, most stainless steels and some polymers. It is incompatible with iron, carbon steel, copper, lead, some polymers and elastomers, cork and wood.

Under the influence of a catalyst hydrogen peroxide decomposes into steam and oxygen:



The decomposition of 85 % (v/v) HTP on metal gauze at a chamber pressure of 3 MPa gives a combustion temperature of about 1000 K and a specific impulse of about 1180 N.s.kg<sup>-1</sup>. The main disadvantage of hydrogen peroxide and its solutions as monopropellants is their lack of stability in storage. They decompose relatively quickly into water and oxygen. Also, the specific impulse of hydrogen peroxide as a monopropellant is inferior to that of hydrazine, and at present the compound is little used in rocket systems.

### 13.5.3.3 Nitromethane

Nitromethane (CH<sub>3</sub>NO<sub>2</sub>) was the first successful monopropellant, its use as such having been originated by the Italian L. Crocco in about 1934. It is a colourless, mobile liquid with properties shown in Table 13-13. It is slightly miscible with water. Its vapour pressure is 81 kPa (108 mm Hg) at 10 °C. The vapour is highly toxic, being capable of damaging the nervous system, liver and kidneys. Nitro-methane can be stored in mild-steel containers coated internally with plastic. Impurities in nitro-methane may render it detonable by explosive shock; also, it will detonate regardless of its purity, if heated to 260 °C while heavily confined. Like hydrazine and HTP, nitro-methane can be used either as a monopropellant or as a bipropellant, but in the monopropellant role it cannot be decomposed by any known catalyst and has to be decomposed thermally. It is difficult to ignite, but once ignited it has a high flame temperature of 2190 K and a specific impulse of 2500 N s kg<sup>-1</sup>. Despite its long history, nitromethane has not found widespread use as a monopropellant.

### 13.5.3.4 Isopropyl nitrate (IPN)

This substance, more correctly called 2-propyl nitrate with the formula (CH<sub>3</sub>)<sub>2</sub>CHONO<sub>2</sub>, is a colourless, mobile liquid with properties given in Table 13-13. It is not highly toxic, and it can be stored in stainless steel or aluminium containers but is not compatible with copper or nickel. It can be detonated by an explosive shock. Like nitromethane, it cannot be decomposed catalytically, but it ignites more readily than nitromethane. It is very susceptible to detonation by dieseling, more so than hydrazine. IPN has a calculated flame temperature of 1252 K and at a chamber pressure of 2 MPa it gives a calculated specific impulse of 1630 N s kg<sup>-1</sup>. An alternative to IPN is the isomer 1-propyl nitrate. IPN has found use in British Service under the acronym AVPIN, in starter capsules for gas turbine aero-engines.

### 13.5.3.5 Oxirane

Oxirane (C<sub>2</sub>H<sub>4</sub>O) a cyclic epoxide often called ethylene oxide, is a colourless, mobile liquid and has an inconveniently low boiling point for most monopropellant applications with properties given in Table 13-13. Ethylene oxide vapour has a pleasant smell but is very toxic. At low concentrations it causes nausea and loss of the sense of smell. Higher concentrations it causes irritation of the eyes and mucous membranes together with oedema of the

lungs, while very high concentrations can prove fatal within minutes. The liquid can be stored in steel, stainless steel or aluminium containers. It is readily polymerised, sometimes with explosion, by chloride or alkaline contaminants. It is insensitive to explosive shock but is easily ignited. It decomposes to carbon monoxide and methane, giving a flame temperature of 1450 K and a specific impulse of about  $1600 \text{ N s kg}^{-1}$ . It has a potential use in gas generators.

### 13.5.4 Liquid Bipropellants

Since liquid monopropellants do not provide sufficient specific impulse for the main propulsion of large rockets, the choice of propellants for the first stage, or two stages, of such vehicles is between liquid bipropellants, solid propellants, or a combination of both types of motor. Large rocket systems which contain liquid bipropellant main motors include the NASA/DOD space shuttle, ESA Ariane, the American Atlas, the Titan and Delta series and a number of Soviet and Chinese space launch vehicles. Liquid bipropellant systems comprise a pair of propellants, one serving as the fuel and the other as the oxidant. They are contained in separate tanks and are mixed by injection into the combustion chamber, where they either ignite spontaneously on mixing (hypergolically) or are ignited by a pyrotechnic charge. Bipropellant fuels are to some extent interchangeable, but what originally appeared to be a large number of possible fuel-oxidant combinations in the 1950's has dwindled in the course of much subsequent research, most of it carried out in the USA. The current world total of liquid-bipropellant motors now employs a very limited number of combinations.

Liquid bipropellants as a whole are divided not only by their chemical functions, but also separately by their storage characteristics. They are classed either as cryogenic ('space-storable') or packageable ('earth-storable'). A cryogenic propellant is one which must be kept at low temperatures to keep it liquid throughout the feed system. The most common examples are liquid oxygen (LOX), which has a critical temperature of  $-118.6^\circ\text{C}$  at 50.5 bar pressure, and liquid hydrogen with a critical temperature of  $-240^\circ\text{C}$  at 13 bar pressure. Non-cryogenic bipropellants are those which can be stored as liquids at normal ambient temperatures and under a pressure no greater than their own vapour pressure. If, in addition, they are chemically stable over long periods, they are classed as packageable (earth-storable). The criterion of chemical stability excludes hydrogen peroxide and its solutions from the packageable category. Hydrazine, although usually classed as packageable, is not a good example because of its high freezing point. Better examples are its derivatives, monomethyl hydrazine and unsymmetrical dimethyl hydrazine. Other packageable components include the fuel kerosene and the oxidants fuming nitric acid and dinitrogen tetroxide. The small number of substances mentioned in this paragraph comprise virtually the entire range from which present-day bipropellant combinations are selected.

A fuel-oxidant pair of bipropellants can be either of the same storability type or of different types. For example, the common oxidant LOX can be paired with the

similarly cryogenic fuel liquid hydrogen, or alternatively with kerosene, which is packageable. Cryogenic liquids are difficult and wasteful to store and handle, and are used only because they provide the high specific impulses necessary to accelerate space vehicles to their required orbital or escape velocity. The only cryogenic liquids now used in rocketry are LOX and liquid hydrogen and these are not used in ballistic missiles, because of the requirement of short-notice readiness. Liquid ammonia, formerly used with LOX by the Americans in the Bell X-15 aircraft, is now obsolete. Liquid fluorine, which boils at  $-188\text{ }^{\circ}\text{C}$  though attractive on thermochemical grounds, is too reactive for practical storage purposes and liquid ozone is dangerously explosive.

The main requirements of bipropellants for a packaged military missile system are:

- a. Wide operational temperature range ( $-54\text{ }^{\circ}\text{C}$  to  $+71\text{ }^{\circ}\text{C}$ ), implying a low freezing point
- b. Maximum vapour pressure of less than 3500 kPa at the upper temperature limit of  $71\text{ }^{\circ}\text{C}$
- c. Shelf life of at least two years
- d. Hypergolic ignition
- e. Low or zero shock sensitiveness (see 20.2.1)
- f. High density

#### **13.5.4.1 Liquid-bipropellant oxidants**

The storable liquid oxidants which are used for modern bipropellant systems are few in number, and are related to each other. One is inhibited red fuming nitric acid (IRFNA) and the others are dinitrogen tetroxide (DNTO) and mixtures based on it, called mixed oxides of nitrogen (MON). The bipropellant oxidant hydrogen peroxide (HTP) which was used in British rockets of the past, including Blue Steel (1957), Black Knight (1958) and Black Arrow (1969), can now be considered obsolete for this purpose.

##### ***13.5.4.1.1 Inhibited red fuming nitric acid (IRFNA)***

Nitric acid  $\text{HNO}_3$  has been used in three forms in rocketry:

- a. Anhydrous nitric acid, containing 99.0 % (w/w) of  $\text{HNO}_3$
- b. White fuming nitric acid (WFNA), containing 97.5 % (w/w) of  $\text{HNO}_3$  and 2 % (w/w) water
- c. Red fuming nitric acid (RFNA), consisting of between 82-85 % (w/w) of  $\text{HNO}_3$ , 13.15 % (w/w) dinitrogen tetroxide (DNTO) and between 2-3% (w/w) water

The most commonly used form in rocketry is RFNA, which was introduced for this purpose by the Austrian, F. W. Sander in 1931. German work on bipropellant chemistry in the fertile period of 1940-1945 was divided between three oxidants: LOX, hydrogen peroxide and RFNA, and in 1940 H. Mueller and H. Von Zborowski discovered that RFNA was hypergolic (self-igniting) with aniline, which is an aromatic amine. Later it was discovered that the tertiary amine triethylamine was also satisfactorily hypergolic with RFNA. The German

amine fuels were called Tonkas, and another class of hypergolic fuels were vinyl ethers, known as Visols. After the war Tonka and Visol development was abandoned, but the Americans persevered with the ethylaniline/furfuryl alcohol/nitric acid system for some years until mixtures of hydrazine and its derivatives replaced it.

RFNA is a brown (not red), mobile liquid with a very unpleasant odour. It is highly toxic. The vapour pressure depends heavily on the DNTO content: a typical value is 17.9 kPa, (135 mm Hg) at 25 °C. RFNA has a density of about 1.5 g cm<sup>-3</sup>, the exact value depending on the composition. It freezes at between -53 °C and -61 °C. Ordinary RFNA is highly corrosive to most container materials, but it was discovered by chance in about 1950 that when at least 0.4 % (w/w) of hydrofluoric acid (HF) is added it can be safely kept for long periods of time in containers made of certain aluminium alloys or of stainless steel. The present day inhibited form of the oxidant, IRFNA, contains 0.7 % (w/w) HF. IRFNA is a dangerous material to handle: the briefest contact with the skin causes yellow staining, and longer contact causes serious burns. Hydrogen fluoride vapour is an acute poison that may immediately and permanently damage lungs and the corneas of the eyes. Aqueous hydrofluoric acid is a contact-poison with the potential for deep, initially painless burns and ensuing tissue death. By interfering with body calcium metabolism, the concentrated acid may also cause systemic toxicity and eventual cardiac arrest and fatality.

#### **13.5.4.1.2 Dinitrogen tetroxide (DNTO) and MON**

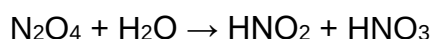
Like IRFNA, which contains DNTO, straight DNTO (N<sub>2</sub>O<sub>4</sub>) is not a new oxidant for bipropellant systems: it was first used as such by the Italian L. Crocco in 1930, but it was not adopted by the Germans in World War II, or by the Americans until some years after the war. At room temperature DNTO is a yellow, mobile liquid with a very unpleasant smell. It has a vapour pressure of 96.5 kN m<sup>-2</sup> (724 mm Hg) at 20 °C, and 151 kN m<sup>-2</sup> (1134 mm Hg) at 30 °C. It is very toxic, with an OEL of 3 ppm. It freezes at -11.2 °C to a colourless solid and boils at 21.1 °C to a red-brown gas. The density of the liquid at 20 °C is 1.45 g cm<sup>-3</sup>.

DNTO poses problems of storage because when containing more than 0.2 % (w/w) moisture, it is unacceptably corrosive towards steel containers, and also the presence of dissolved oxygen in DNTO induces stress corrosion in titanium alloys, which are commonly used for rocket propellant tanks. Because of the latter problem DNTO is more often employed as the major constituent of the bipropellant oxidant called 'mixed oxides of nitrogen' (MON), which is DNTO containing a small amount of nitric oxide (NO). Nitric oxide reacts with dissolved oxygen in DNTO to give nitrogen dioxide and hence reduces the problem of stress corrosion. A particular MON mixture is identified by the weight percentage of nitric oxide which it contains, e.g. MON 3 is DNTO containing 3 % (w/w) of NO.

Although DNTO containing less than 0.6 % (w/w) NO is a yellow liquid at room temperature it is referred to as 'red brown DNTO' to distinguish it from MON,

which takes on a green colour when containing more than about 0.6 % (w/w) NO due to the formation of dinitrogen trioxide  $\text{N}_2\text{O}_3$ . MON propellants thus contain four different oxides of nitrogen in equilibrium with one another.

The corrosive effect of DNTO towards metals is not too severe provided the water content of the propellant is kept below 0.2 % (w/w), the (1987) accepted specification limit in most grades of the propellant. At water levels above this value the increase in the corrosion rate of stainless steel and titanium alloys is very steep and arises from the formation of nitric and nitrous acids in the propellant:



Increased iron contamination in the propellant also causes problems since the metal precipitates from DNTO at extremely low levels (0.5 ppm) as a gelatinous nitrate complex which blocks valves and other components, giving rise to a phenomenon known as 'flow decay'. In order to minimise its effect, the iron content of MON must be kept as low as possible. The (1987) specification limit for iron in MON 3 is 1 ppm (US National Aerospace Standard NAS 3620, August 1983).

Because of its strong oxidising effect, very few non-metallic materials are compatible with DNTO; of elastomers, only perfluoro-derivatives are suitable for extended periods of contact. The same arguments apply to IRFNA and in this case even glass is incompatible, owing to the presence of hydrogen fluoride (HF) in the composition.

#### **13.5.4.2 Liquid bipropellant fuels**

The number of possible bipropellant rocket fuels has always exceeded the number of possible oxidants, and in former decades even single classes of fuels, like the German Tonkas and Visols already mentioned, contained numerous member compositions. Following the rationalisation of bipropellant chemistry in recent years however, the number to be considered is very small. The best cryogenic fuel on performance grounds is liquid hydrogen, which is used with LOX in the main motors of the American space shuttle and in the upper stages of a few other space launch vehicles, but its density of  $0.07 \text{ g cm}^{-3}$  is so low that when used in large quantities this fuel adds greatly to the bulk of the system, e.g. as seen in the external tank of the US space shuttle. Added to this disadvantage its cryogenic nature renders liquid hydrogen unsuitable for military rockets. With the elimination of liquid hydrogen for this purpose the remaining current candidates are classed as packageable. These are used both in space launch vehicles and military missiles.

##### **13.5.4.2.1 Packageable bipropellant fuels requirements**

These fuels are used both in space launch vehicles and military missiles. An ideal fuel should satisfy the following requirements:

- a. The fuel must give an adequate specific impulse when burned with the selected oxidant.

- b. It should have a high density, to minimise its bulk and therefore that of the missile.
- c. It should be of low viscosity for ease of pumping, especially at low temperature.
- d. The freezing and boiling points must be compatible with the operating environment.
- e. It should be capable of being stored for extended periods of time without significant decomposition.
- f. It must be rapidly hypergolic with the oxidant if the design requires it.
- g. It should preferably not be toxic or corrosive.
- h. It should not be detonable.

In more than ninety years of liquid rocket propellant technology, no fuel has been discovered which complies with all these requirements. One example out of the many problem areas is hypergolicity. If a fuel/oxidant combination is not infallibly self-igniting within a few milliseconds of the first contact the delayed ignition may cause an explosion within the chamber of the motor. The modern candidate fuels described in the following sub-paragraphs are all descended from the German and American types of the 1930's and 1940's.

#### **13.5.4.2.2 Kerosene**

Kerosene is a mixture of alkanes, alkenes and aromatics from petroleum, its properties approximating to those of decane ( $C_{10}H_{22}$ ). It is a colourless, mobile liquid which freezes at  $-40\text{ }^{\circ}\text{C}$  and boils over a wide range, typically  $150\text{ }^{\circ}\text{C}$  to  $290\text{ }^{\circ}\text{C}$  and has a density of about  $0.8\text{ g cm}^{-3}$ . It presents no serious toxic hazard. Kerosene has been used in rocket motors in combination with, variously, LOX, nitric acid and hydrogen peroxide. It can be seen as the logical successor to the ethanol/water mixture oxidised by LOX, as first used by the Germans Riedel and Ley in 1932, then by Von Braun in the V.2 in 1944 and later by the Americans, e.g. in the Viking (1949) and the Redstone (1953) rockets. The ethanol/water/LOX system was relatively cheap and clean burning but, like petrol/LOX and kerosene/LOX, it could not be made hypergolic despite all attempts to do so. All these fuels give very similar specific impulses with LOX, so the cheapest of them, kerosene, is now the definitive one. It was used with LOX in the American Jupiter (1954), Thor (1956) and Atlas (1957), also in the British ICBM Blue Streak (1960), and it is still used in the first-stage motors of some space launch vehicles, e.g. the US Delta and the Soyuz-2.

#### **13.5.4.2.3 Hydrazine**

The physical characteristics of hydrazine ( $N_2H_4$ ) have been mentioned (13.5.3.1). Anhydrous hydrazine, unmixed with substituted hydrazines, has not, until very recently, been used as a bipropellant fuel with DNTO, partly because the reaction is extremely violent. Hydrazine has other disadvantages: its freezing point,  $+2\text{ }^{\circ}\text{C}$  is far above the maximum  $-54\text{ }^{\circ}\text{C}$  required of a military propellant for use in all climatic conditions. Also, hydrazine and mixtures rich in it, are apt to detonate when used in regenerative cooling systems. For these reasons, the Americans developed mixtures of anhydrous hydrazine with

substituted hydrazines, notably unsymmetrical dimethylhydrazine (UDMH) and monomethylhydrazine (MMH), as bipropellant fuels. These mixtures were named Mixed Hydrazine Fuels (MHF).

#### 13.5.4.2.4 UDMH and Aerozine-50

The unsymmetrical dimethyl derivative of hydrazine (UDMH), is a colourless, mobile liquid with a strong, unpleasant odour and has the structure shown in Figure 13-20. It has a much lower freezing point than hydrazine,  $-57^{\circ}\text{C}$ , as compared with  $+2^{\circ}\text{C}$  and in this respect, it is also much better than symmetrical dimethyl hydrazine with a freezing point of  $-9^{\circ}\text{C}$ . A compromise has to be made with regard to its boiling point of  $62^{\circ}\text{C}$ , which is below the lower limit of  $71^{\circ}\text{C}$  preferred for defence use. UDMH has a relatively high vapour pressure of 22.3 kPa (167 mm Hg) at  $25^{\circ}\text{C}$  compared to the vapour pressure of hydrazine of 1.89 kPa, and it is highly toxic with a Threshold Limit Value (US Long Term Exposure Limit (see 18.1.2.2)) of 0.5 ppm. UDMH has a rather low density of  $0.786\text{ g cm}^{-3}$ .

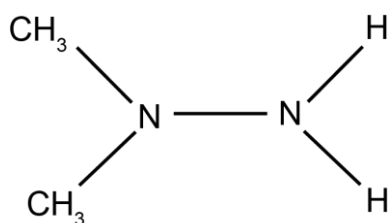


**Figure 13-20 Chemical structure of UDMH**

Despite its disadvantages UDMH was adopted by the Americans in the 1950's and was first used in admixture with hydrazine in the bipropellant fuel Aerozine-50, which consists of equal parts by weight of hydrazine and UDMH. In addition to having a lower freezing point (about  $-7^{\circ}\text{C}$ ) than hydrazine, the mixture is safe to use as a regenerative coolant. Aerozine-50 was used in the first two stages of the Titan series of space launcher/ICBM and in the second stage of the Delta launchers, with DNTO as oxidant in both cases. UDMH, after its first employment as a constituent of Aerozine-50, became a bipropellant fuel in its own right. It was used in the second stage of the earliest Delta space launchers, in Agena and in Vanguard, oxidised by IRFNA in all cases. The Russians have used UDMH, oxidised by LOX, in at least two of their space launchers and it is currently (2017) used in the first two stages of the Soyuz-FG launcher. The Lance tactical missile, which was employed by the British Army used UDMH and IRFNA bipropellant. The Lance propellant system was fully packaged, the two propellant components being storable for several years in the sealed, aluminium tanks contained in the missile. The propellants and the tanks underwent only negligible deterioration and were proof against extreme conditions of environment and handling. The Lance missile held 170 kg of UDMH and 502 kg of IRFNA, representing together about 45 % of its launch weight. The motor gave two different levels of thrust and was able to deliver a pulsed thrust in flight, a capability not shared by solid propellant motors.

**13.5.4.2.5 Mixed Amine Fuel (MAF)**

In the 1960s, the Americans developed a series of rocket propellant fuels called Mixed Amine Fuels (MAF), based on UDMH and diethylenetriamine (DETA). DETA is included in the mixture to increase its density, and in some cases acetonitrile ( $\text{CH}_3\text{CN}$ ) was also included, to reduce the viscosity. The composition of three of the MAF types is shown in Table 13-15.

**Table 13-15 Composition of MAF Fuels**

|                      | MAF 1 | MAF 3 | MAF 4 |
|----------------------|-------|-------|-------|
| UDMH (% w/w)         | 40    | 20    | 60    |
| DETA (% w/w)         | 50    | 80    | 40    |
| Acetonitrile (% w/w) | 10    | -     | -     |

These fuels are used in hypergolic combination with IRFNA. MAF 1 was used notably in the American Bullpup family of air-to-surface missiles (circa 1960-80), one type of which was used by the Royal Navy to arm Buccaneer aircraft.

**13.5.4.2.6 Monomethylhydrazine (MMH)**

Another hydrazine derivative used for rocket propulsion is monomethylhydrazine (MMH), which has the formula  $\text{N}_2\text{H}_3\cdot\text{CH}_3$ . It is a colourless, mobile liquid with a density of  $0.87 \text{ g cm}^{-3}$  at  $25^\circ\text{C}$ . It freezes at  $-52^\circ\text{C}$  and boils at  $+88^\circ\text{C}$ . Its vapour pressure is 6.6 kPa (49 mm Hg) at  $25^\circ\text{C}$  and its toxicity is intermediate between that of hydrazine and UDMH, with a Long Term Exposure Limit of 0.2 ppm.

MMH is miscible with water and forms a hydrate  $\text{N}_2\text{H}_3\cdot\text{CH}_3\cdot\text{H}_2\text{O}$  which freezes at  $-60^\circ\text{C}$ . The density of MMH,  $0.87 \text{ g cm}^{-3}$ , is better than that of UDMH. Like UDMH, MMH has been used in mixtures with hydrazine as a propellant. The most frequently used mixture is 14 % (w/w) hydrazine with 86 % (w/w) MMH, which freezes at  $-54^\circ\text{C}$ . Also, like UDMH, MMH has been used extensively in its own right as a bipropellant fuel, with DNTO or MON as a hypergolic oxidant. The second stage of the Ariane 5 launcher uses monomethylhydrazine (MMH) as a fuel oxidised by dinitrogen tetroxide ( $\text{N}_2\text{O}_4$ ).

Historic applications include the orbital manoeuvring system (OMS) of the American space shuttle, the post-boost propulsion system (PBPS) of the Minuteman III missile and the attitude control thrusters of many existing satellites. The MM/DNTO system provides a specific impulse of  $2717 \text{ N s kg}^{-1}$ , which is much better than a hydrazine monopropellant system at  $1951 \text{ N s kg}^{-1}$  and is therefore a competitor with it for certain space applications. However, MMH has some disadvantages, one of which is that if incomplete combustion of the mixture upon shutdown of the motor occurs, it leaves an explosive residue in the chamber which is apt to detonate at the next start-up. Table 13-16 gives the chief physical properties of hydrazine, MMH and UDMH.

**Table 13-16 Physical Properties of Hydrazine, MMH and UDMH**

|           | Molar mass<br>(g mol <sup>-1</sup> ) | Density at 25 °C<br>(g cm <sup>-3</sup> ) | Freeze Point<br>(°C) | Boil Point<br>(°C) | Vapour pressure at 25°C |         | TLV (ppm) |
|-----------|--------------------------------------|-------------------------------------------|----------------------|--------------------|-------------------------|---------|-----------|
|           |                                      |                                           |                      |                    | (kPa)                   | (mm Hg) |           |
| Hydrazine | 32.05                                | 1.004                                     | +2                   | 114                | 1.89                    | 14      | 0.1       |
| MMH       | 46.07                                | 0.870                                     | -52                  | 88                 | 6.6                     | 49      | 0.2       |
| UDMH      | 60.10                                | 0.786                                     | -57                  | 62                 | 22.3                    | 167     | 0.5       |

**13.5.4.2.7 Fuel tank materials for hydrazine propellants**

Hydrazine and substituted hydrazine propellants are normally stored in titanium alloy or stainless-steel tanks. The incompatibility problems of these propellants with other metals relate principally to the effect of the metal in increasing the decomposition rate of the hydrazine, rather than to any gross corrosiveness of the propellant. Slow decomposition during storage is a particular problem with hydrazine whatever the nature of the storage vessel, the reaction being catalysed by trace metals and dissolved acids such as carbon dioxide. The problem is less marked with MMH and UDMH. A number of elastomeric and other non-metallic materials are not suitable for use with hydrazines because of their effect on propellant decomposition rates. However, ethylene-propylene rubber has been used successfully as a bladder material in the expulsion of hydrazine from propellant tanks in satellites.

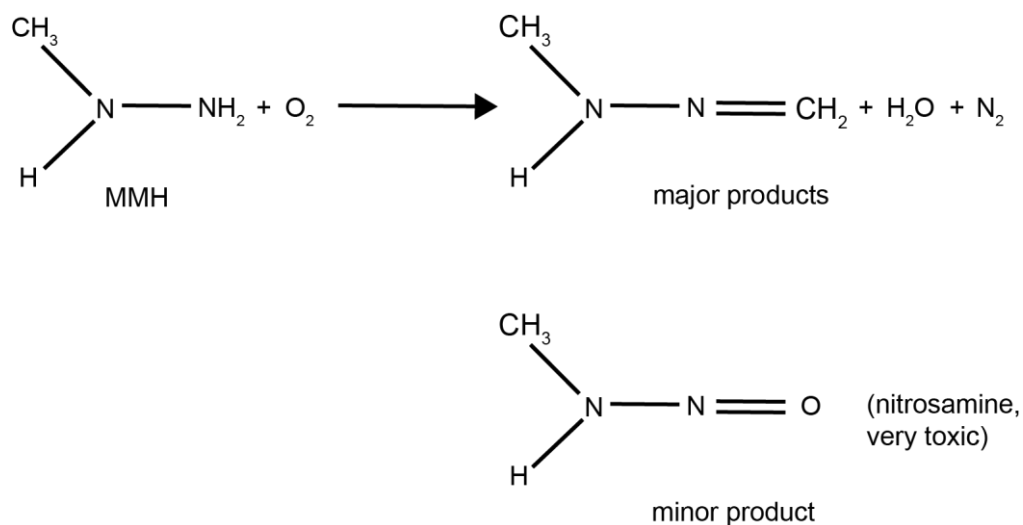
**Figure 13-21 Reaction products of air and hydrazine****13.5.4.3 Liquid bipropellant performance**

Table 13-17 provides details of some bipropellant performance parameters, which when compared to those of typical monopropellants given in Table 13-3 shows the far superior performance of the bipropellants.

**Table 13-17 Performance of Some Bipropellant Combinations**

| Fuel                             | Oxidant  | Ratio | $\bar{M}$<br>g mol <sup>-1</sup> | Combustion<br>Temp. (K) | $I_{sp}^*$<br>(N s kg <sup>-1</sup> ) | Density<br>(g cm <sup>-3</sup> ) |
|----------------------------------|----------|-------|----------------------------------|-------------------------|---------------------------------------|----------------------------------|
| Hydrogen                         | Oxygen   | 4.00  | 10.0                             | 2980                    | 3824                                  | 0.280                            |
|                                  | Fluorine | 8.00  | 12.8                             | 4117                    | 4020                                  | 0.460                            |
| Kerosene                         | IRFNA    | 4.80  | 25.7                             | 3156                    | 2628                                  | 1.355                            |
| Hydrazine                        | Fluorine | 2.18  | 19.4                             | 4687                    | 3569                                  | 1.310                            |
| (N <sub>2</sub> H <sub>4</sub> ) | DNTO     | 1.30  | 20.7                             | 3255                    | 2854                                  | 1.225                            |
| UDMH                             | IRFNA    | 3.00  | 23.7                             | 3222                    | 2706                                  | 1.220                            |
|                                  | DNTO     | 1.30  | 23.5                             | 3436                    | 2805                                  | 1.185                            |
| MMH                              | IRFNA    | 2.60  | -                                | 3091                    | 2659                                  | 1.230                            |
|                                  | DNTO     | -     | -                                | 3255                    | 2717                                  | -                                |
| Aerozine - 50                    | IRFNA    | -     | -                                | 2997                    | 2668                                  | -                                |
| Aerozine - 50                    | DNTO     | -     | -                                | 3230                    | 2727                                  | -                                |

\* All values refer to  $P_c = 7 \text{ MPa}$  and an ideal expansion to  $P_e$  of  $0.1 \text{ MPa}$ ,  $P_e/P_c = 0.014$

### 13.5.5 Summary of Liquid Rocket-Propellants

The roles of the various propellants discussed in this chapter are summarised in **Figure 13-22** in the form of a 'family tree'.

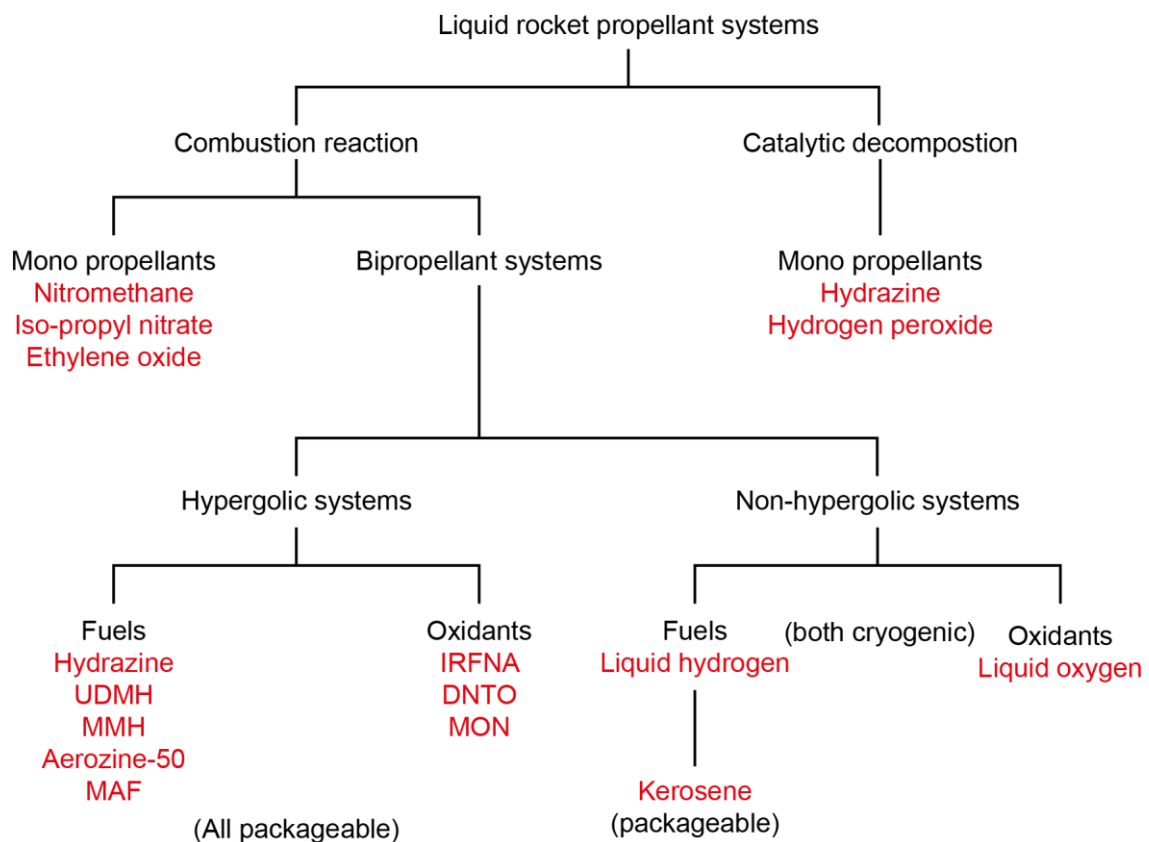


**Figure 13-22** Types of liquid rocket propellant

## 13.6 PERFORMANCE PARAMETERS

### 13.6.1 Rocket Propulsion

Rocket propulsion is produced by the reaction of the missile to the thrust created by burning propellant in a combustion chamber or tube. As in the case of gun propellants, only a portion of the heat released by the combustion of the propellant can be converted into useful work, in this instance the acceleration of

the rocket and the overcoming of gravity and drag. The remainder of the heat is lost in sensible heat transfer to the hardware, in the residual heat and kinetic energy of the exhaust plume and in the emission of light and sound. The thermal efficiency of the motor is the ratio of useful work output to the chemical energy (heat of combustion,  $Q$ ), of the propellant(s), and is in the region of 20 % for rockets generally. This percentage increases with the exit velocity of the gases, but is still less than the corresponding figure of >30 % for a typical gun.

### 13.6.2 Calorimetric Value and Gas Production

The total chemical energy of a rocket propellant, or of a bipropellant combination, is called its heat of combustion (see 4.4.2) or, as for a gun propellant, its calorimetric value. (Strictly, the latter is an experimentally determined value). It is designated  $Q_p$ , the p denoting that the value is measured under conditions of constant pressure as distinct from the (theoretically) constant volume conditions of a gun. Like its gun propellant counterpart  $Q_v$ , the parameter  $Q_p$  is measured in  $\text{kJ kg}^{-1}$ .

On combustion of the propellant its whole mass is converted (ideally) into a mixture of gases, each of which has its own characteristic molar mass (or, in older terminology, molecular weight), expressed in grams per mole. For some purposes of thermochemistry, as will be seen later, a 'mean molar mass' value, designated  $\bar{M}$ , for a gas mixture is used. This is simply the mass of mixture in grams divided by the number of moles of gas present.  $\bar{M}$  is the inverse of the  $n$  value more commonly used in connection with gun propellants.

### 13.6.3 Thrust and Specific Impulse

One of the internal forces ( $F_1$ ) in a motor is that acting over the nozzle exit plane ( $A_e$ ) which is subject to a pressure  $P_e$ , from inside the motor (**Error! Reference source not found.**).

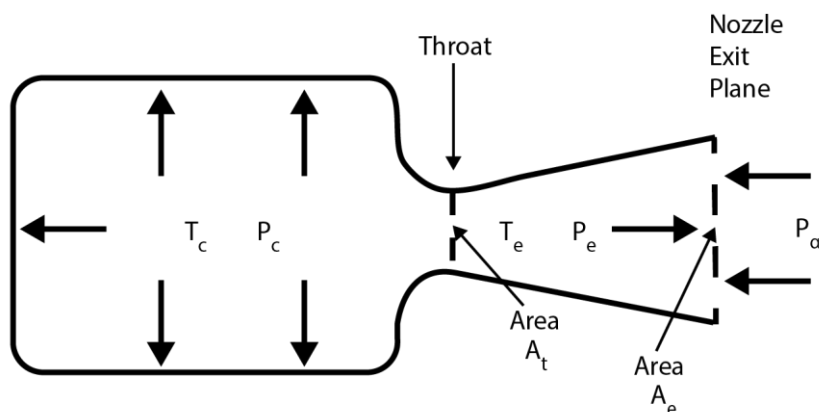


Figure 13-23 Diagram of a rocket motor

Since force = pressure  $\times$  area, therefore,

$$F_1 = P_e A_e \quad (13-7)$$

In addition there is a significant internal force ( $F_2$ ) resulting from the change in momentum of the combustion products as they pass through the nozzle exit plane at a velocity  $v_e$  which is assumed to be constant. If the mass of the combustion gases passing through in the time interval ( $d_t$ ) is  $\dot{m}$ , then this momentum change is given by:

$$F_2 = \frac{d(mv_e)}{d_t} = \dot{m}v_e \quad (13-8)$$

where  $\dot{m}$  is mass flow rate of the combustion products through the nozzle exit, which is also the mass rate of burning for either solid or liquid propellants.

There is also an external force ( $F_3$ ) which acts over the nozzle exit area ( $A_e$ ) from outside the rocket where the pressure is the ambient pressure ( $P_a$ ). This force is opposed to the internal forces, therefore,

$$F_3 = -P_a A_e \quad (13-9)$$

It is the reaction to the sum of these three principal forces which provides the propulsion of a rocket. The total force ( $F_T$ ), called the thrust of the rocket motor, is therefore given by:

$$F_T = \dot{m}v_e + A_e(P_e - P_a) \quad (13-10)$$

The thrust of a rocket motor can be controlled in various ways, but the total impulse (thrust  $\times$  time) provided by unit mass of propellant in a given motor has a finite value, known as the specific impulse ( $I_s$ ). This parameter is used to assess the performance of a rocket motor, and it is defined as the thrust per unit mass flow rate through the nozzle:

$$I_s = \frac{F_T}{\dot{m}} \quad (13-11)$$

The SI units corresponding directly with this definition are  $\text{N/kg s}^{-1}$  which can be alternatively written as  $\text{N s kg}^{-1}$ . By taking the expression for  $F_T$  in (13-10) and dividing throughout by  $\dot{m}$ , it is seen that:

$$I_s = v_e + \frac{A_e (P_e - P_a)}{\dot{m}} \quad (13-12)$$

In general the second term is small compared with  $v_e$  so the specific impulse is often taken as the velocity of the combustion products at the nozzle exit. It is easy to verify that the units are consistent, as follows.

$$\text{Units of } I_s = \frac{N}{kg \text{ s}^{-1}} = \frac{kg \text{ m s}^{-2}}{kg \text{ s}^{-1}} = m \text{ s}^{-1} \quad (13-13)$$

In order to obtain an expression for specific impulse it is necessary to make a number of assumptions about the properties of a rocket motor:

- i. The gas mixture produced by combustion of the propellant is of constant composition and behaves as a perfect gas.
- ii. The chemical reaction within the combustion chamber takes place at constant pressure.
- iii. The expansion through the nozzle is steady, is one-dimensional along the axis of the nozzle and does not involve a change in entropy.
- iv. The expansion through the nozzle is adiabatic, and factors such as friction and gas viscosity can be neglected.

By making these assumptions and by using the approximate expression for specific impulse already given, it is possible to equate the kinetic energy of the gas at the nozzle exit to the enthalpy ( $\Delta H$ ) released in a reversible adiabatic expansion of the gas from the chamber pressure ( $P_c$ ) to the nozzle exit pressure ( $P_e$ ). Since this process is a conversion of enthalpy into kinetic energy it entails a fall in the temperature of the gas from  $T_c$  to  $T_e$ , where  $T_c$  is the adiabatic flame temperature of the propellant in the constant pressure condition of the chamber and  $T_e$ , is the nozzle exit temperature.

Now by definition:

$$\Delta H = \bar{C}_p(T_c - T_e) \quad (13-14)$$

Where  $\bar{C}_p$  = mean heat capacity of the gas mixture at constant pressure, in  $J \text{ kg}^{-1} \text{ K}^{-1}$ .

Therefore, for unit mass of the gas,

$$\frac{I_s^2}{2} = \bar{C}_p(T_c - T_e) \quad (13-15)$$

For an adiabatic expansion it can be shown that:

$$\frac{T_e}{T_c} = \left( \frac{P_e}{P_c} \right)^{\frac{\gamma-1}{\gamma}} \quad (13-16)$$

Where  $\gamma$  = ratio of heat capacity of the gas at constant pressure to that at constant volume, i.e.  $\bar{C}_p/\bar{C}_v$ . For the majority of rocket propellants this value is in the range 1.2 – 1.3.

Substitution in (13-15) gives:

$$I_s^2 = 2C_p T_c \left[ 1 - \left( \frac{P_e}{P_c} \right)^{\frac{\gamma-1}{\gamma}} \right] \quad (13-17)$$

For an ideal gas  $C_p - C_v = R/\bar{M}$ . Where  $R$  = the universal gas constant (8.31 J mol<sup>-1</sup> K<sup>-1</sup>) and  $\bar{m}$  = the mean molar mass of the gas (kg mol<sup>-1</sup>). Approximately, therefore, in the present case;

$\bar{C}_p = \frac{\gamma R}{(\gamma-1)\bar{m}}$  and substitution in Equation (13-17) gives:

$$I_s = \left\{ \frac{2\gamma R T_c}{(\gamma-1)\bar{m}} \left[ 1 - \left( \frac{P_e}{P_c} \right)^{\frac{\gamma-1}{\gamma}} \right] \right\}^{1/2} \quad (13-18)$$

Alternatively, use can be made of the propellant force constant  $F$ , which is equal to  $nRT_o$  and therefore to  $\frac{\gamma R T_c}{\bar{m}}$ ;

$$\text{Thus } I_s = \left\{ \frac{2F}{\gamma-1} \left[ 1 - \left( \frac{P_e}{P_c} \right)^{\frac{\gamma-1}{\gamma}} \right] \right\}^{1/2} \quad (13-19)$$

### 13.6.4 Characteristic Velocity and the Thrust Coefficient

The specific impulse of a rocket depends both on the combustion chamber conditions, which are determined by the propellant, and the expansion ratio, which is determined by the nozzle geometry. For this reason two further parameters are defined which enable each of these components of performance to be described separately. The characteristic velocity,  $c^*$  ('c star'), is defined as:

$$c^* = \frac{P_c A_t}{\dot{m}} \quad (13-20)$$

where  $A_t$  = rocket nozzle throat area in m<sup>2</sup>. It can be shown that, for an ideal rocket;

$$c^* = \left[ \left( \frac{\gamma+1}{2} \right)^{\frac{\gamma+1}{\gamma-1}} \left( \frac{R T_c}{\gamma \bar{M}} \right) \right]^{1/2} \quad (13-21)$$

and as this expression depends only on the properties of the propellant, it is more useful than specific impulse when comparing the performance of propellants in rocket motors.

A complementary parameter to  $c^*$  is the thrust coefficient  $C_F$ , defined as:

$$C_F = \frac{F_T}{P_c A_T} \quad (13-22)$$

It can be shown that the thrust coefficient for an ideal rocket motor is largely a function of nozzle geometry. The specific impulse of a motor is then given by:

$$I_s = c^* C_F \quad (13-23)$$

### 13.6.5 Expansion Ratio

The expansion ratios ( $P_e/P_c$ ) for many dissimilar rocket motors lie within a rather narrow range. This is equivalent to stating that  $C_F$  values do not vary greatly from one motor to another, and in fact such values are mostly between 1.3 and 1.5. This is partly because the exit pressure is invariably close to the ambient pressure, but also because it is not practicable to increase  $P_c$  greatly as this would entail adding strength, and therefore weight, to the motor. Thus it is common practice to use specific impulse as a parameter for comparing the performance of different propellants, but when this is done the relative expansion ratio strictly should be quoted.

### 13.6.6 Factors Affecting Rocket Propellant Performance

From the expression for  $c^*$  and that for specific impulse,  $I_s$ , it is apparent that rocket propellant performance is proportioned to  $(T_c/\bar{M})^{1/2}$ . Therefore a high value for the flame temperature ( $T_c$ ) of a propellant increases  $c^*$ . The highest temperature which can be produced by chemical propellants is about 5000 K, but the normal combustion temperature for rocket motors is about 3000 K. The need for constraint arises from the damaging effect of extremely high temperature on the motor components, particularly the nozzle, and the difficulty of designing cooling systems for solid propellant motors. Nozzles for liquid propellant motors, however, can be cooled by the regenerative method, in which the flowing propellant passes through the thickness of the nozzle and absorbs the transferred heat.

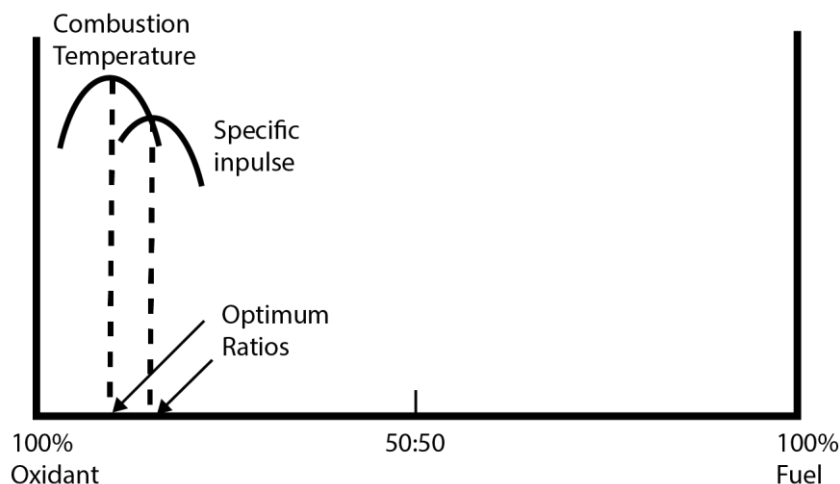


**Figure 13-24 Specific impulse and combustion temperature versus fuel/oxidant ratio (diagrammatic).**

From the expression in the foregoing paragraph, it can also be seen that the value of  $\bar{M}$ , the mean molar mass of the gas mixture, should be kept as low as possible for high  $c^*$ . This implies that no solid products should result from the combustion process, but this requirement is often compromised by other factors, as will be seen in the section on solid rocket propellant where aluminium additive is considered (see 13.2.2.3).

It is found that, for a given CHNO propellant system, the oxygen balance (see 4.3.1) figure ( $\Omega$ ) which produces the highest value of  $c^*$  is slightly on the fuel-rich side of stoichiometric as shown in Figure 13-24, that is, slightly negative. This is because the resulting products are slightly lower mean molar mass, e.g.:

**Table 13-18 Elements in the First 3 Rows of the Periodic Table**

| Group | I  | II | III | IV | V | VI | VII |
|-------|----|----|-----|----|---|----|-----|
|       | H  |    |     |    |   |    |     |
|       | Li | Be | B   | C  | N | O  | F   |
|       | Na | Mg | Al  | Si | P | S  | Cl  |

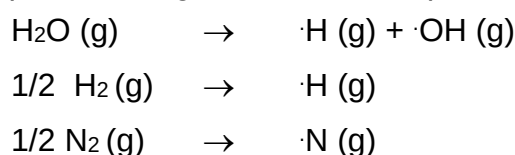
At the temperature of the exhaust gas the equilibrium tends to the formation of CO. The divergence from a zero oxygen balance should be very limited, otherwise the heat of combustion ( $Q_p$ ) falls off rapidly. The requirement to optimise the  $\bar{M}$  value of the gases also entails that propellants should contain only 'light' elements, that is, elements of low relative atomic mass ('atomic weight'), which on combustion give molecular and atomic species of low molar mass. In fact, all the chemical elements used in rocket propellants, except in a few special additives, are to be found in the first three rows of the periodic table, which are shown in Table 13-18.

The oxidising element is normally oxygen (Group VI) but fluorine (Group VII) is also a candidate. The oxygen can be in elemental form as a cryogenic liquid, but more often it is in the form of an acid, salt, nitrate ester, oxide or peroxide. The fuel elements hydrogen (Group I) and carbon (Group IV) are the most common, both of them giving gaseous products. Hydrogen provides a low heat of combustion with a value  $-240.6 \text{ kJmole}^{-1}$  compared to  $-393.5 \text{ kJmole}^{-1}$  for carbon when fully oxidised to  $\text{CO}_2$ .

Hydrogen, however, provides the gaseous product water with a very low molar mass of only  $18 \text{ g mol}^{-1}$  compared with  $44 \text{ g mol}^{-1}$  and  $28 \text{ g mol}^{-1}$  for carbon dioxide and carbon monoxide respectively. The two elements in Group III, boron and aluminium, are used in some rocket propellants even though they yield solid instead of gaseous products, on account of the high heats of combustion of these elements. From these various elements, or suitable compounds of them, together with nitrogen it is possible to synthesise or formulate propellants which provide the high combustion temperatures and low molar mass products required.

#### 13.6.6.1 Dissociation products

Under the conditions of high temperature and pressure in a rocket motor dissociation takes place among the combustion products, including:



These reactions are endothermic, so they occur more readily at higher temperatures, in general above 3000 K. The products formed are of lower molar mass than the reactants, a fact which tends to increase characteristic velocity. At the same time, however, the reactions absorb heat from the system and the temperature is thereby lowered, in turn lowering  $c^*$ . The net result depends on the value of  $T_c/M$  for the combustion process with dissociation, compared with the value in the absence of dissociation.

#### 13.6.6.2 The effect of specific impulse on missile performance

The performance of a rocket missile in terms of its velocity and range depends upon two factors, the specific impulse  $I_s$  of the missile's rocket motor and the mass ratio,  $\gamma$ , which is the ratio of the mass at launch to that at the all-burnt point. The importance of specific impulse is shown in the following generalised equations.

$$\text{Velocity at all burnt} = I_s \log_e I_s \quad (13-24)$$

Range, for an ideal ballistic trajectory,

$$= \frac{I_s^2 (\log_e \gamma)^2}{g} \quad (13-25)$$

where  $g$  is the acceleration due to gravity.

Range, for an airborne trajectory,

$$= \frac{V I_s \log_e \gamma}{g} \frac{L}{D} \quad (13-26)$$

where  $L/D$  is the lift/drag ratio for the missile and  $V$  is the post-boost velocity.

### 13.7 BIBLIOGRAPHY

- 1) G. P. Sutton and O. Biblarz, Rocket Propulsion Elements (8th Edition), John Wiley, 2010
- 2) A. Davenas, Solid Rocket Propulsion Technology, Pergamon, 1993