

Propellants (Lecture 2)

[Ancient Chinese and Korean rocket technology - history lesson](#)

Rocket propellants

[Ancient Chinese rockets - ahead of their time!](#)



- Required to produce gas at high temperatures
 - same as for gun propellants
- Rocket motor performance assessed by specific impulse (I_{sp})
 - $I_{sp} \propto F^{1/2}$ (F is specific energy)

Rocket Motors - UK history – post war push!



British Electric
Thunderbird Guided
Missile (1957)

THE BLOODHOUND -
1958

Avro Blue steel Missile

Rocket propulsion is produced by the reaction to the force exerted on gas molecules to accelerate them through a convergent-divergent nozzle.

In a conventional rocket motor both the gases which constitute the working fluid and the heat energy which is partly converted into the kinetic energy of those gases are produced by the burning of a propellant in a combustion chamber

Rocket propellants burn at an approximately constant pressure which is considerably lower than the peak pressure observed in guns

The thrust of a rocket motor can be controlled in various ways but the total impulse (thrust x time) provided by unit mass of propellant in a given motor has a definite value, known as the Specific Impulse, I_s :

$$\text{Specific impulse, } I_s = \frac{\text{Thrust of motor}}{\text{Mass flow rate through nozzle}}$$

[China Tested
Largest and
Most Powerful
Solid Fuel
motor](#)

[China - Second
Biggest Aircraft
Carrier Fleet in
the World](#)

ROCKET MOTOR PERFORMANCE – SPECIFIC IMPULSE (I_{sp})

- Thrust per unit mass flow rate of combustion products through nozzle
- Depends on propellant and on motor hardware:

$$I_{sp} = [2R \cdot \gamma \cdot T_c / \bar{M} \cdot (\gamma - 1)]^{1/2} \times \text{expansion efficiency term}$$

$$= [2F/(\gamma - 1)]^{1/2} \times \text{expansion efficiency term}$$

where R = universal gas constant ($8.314 \text{ J K}^{-1} \text{ mol}^{-1}$)
 γ = ratio of heat capacities of combustion gases (C_p/C_v)
 T_c = chamber temperature at constant pressure (K)
 F = specific energy of propellant (J g^{-1})
 $\bar{M}$ = mean molar mass of combustion products (g mol^{-1})

PROPELLANT PERFORMANCE – CHARACTERISTIC VELOCITY (c^*)

- Measure of propellant performance within the motor:

$$c^* = p_c \cdot A_t / \dot{m} \quad (\text{m s}^{-1})$$

where p_c = chamber pressure (Pa) 

A_t = nozzle cross sectional throat area (m^2) 

$\dot{m}$ = mass flow rate through nozzle (kg s^{-1}) 

- Note that: $I_{sp} = c^* \cdot C_F$

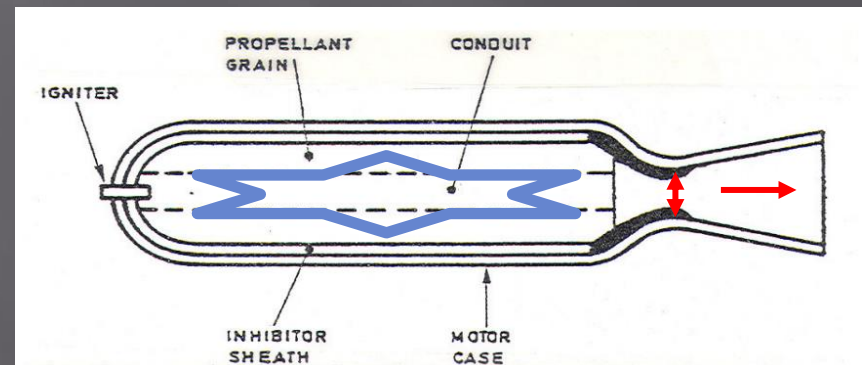
where C_F = thrust co-efficient (depends mainly on motor hardware)

C_F does not vary greatly and I_{sp} is often used to compare propellants

Nitrate de
potassium Sucre

Ammonium
Perchlorate
Rocket
Propellant

Rocket Motor -
Ammonium Nitrate
Composite
Propellant



ROCKET MOTOR THRUST

- Thrust $= I_{sp} \times \dot{m}$
 $= c^* \times C_F \times A_S \times r \times \rho$
- To increase by changing propellant:
 - Increase c^* and/or density, ρ
 - Increase burning rate, r
 - Increase burning surface area, A_S (i.e. build bigger rocket!)



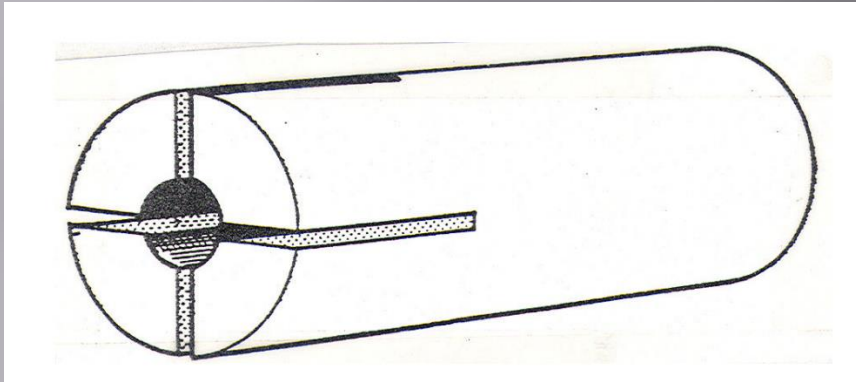
Measure of propellant performance within the motor:

$$c^* = \frac{p_c \cdot A_t \cdot \dot{m}}{\dot{m}} \quad (\text{m s}^{-1})$$

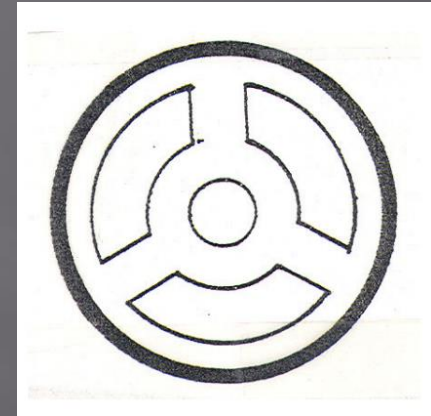
Note that: $I_{sp} = c^* \cdot C_F$

where C_F = thrust co-efficient (depends mainly on motor hardware)

Slotted cylinder grain



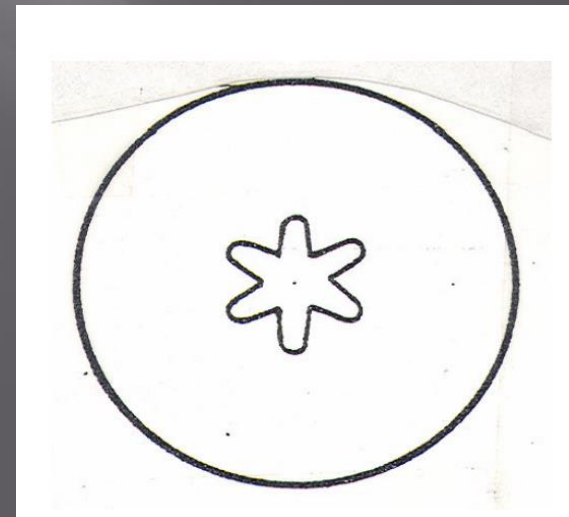
Tube-and-rod grain



Multiperforated grain



Star-centre grain



PROPELLANT BURNING RATE LAWS

■ Piobert's Law

Burning surface of a propellant grain recedes in a direction normal to the burning surface at every point

■ Vieille's Law

Rate of regression of burning surface, r , depends on pressure:

$$r = \beta p^{\alpha} \quad (\text{usually quoted in mm s}^{-1})$$

Where

p	=	pressure
β	=	the burning rate coefficient
α	=	the pressure index (typically ~ 0.9)

ROCKET AND GUN PROPELLANT COMPARISONS

- Rocket propellants are burnt at much lower pressures (7-10 MPa compared to over 500 MPa for gun propellants)
- RP grains have a much larger web size than GP grains
- RP combustion products are immediately ejected from the motor but GP products are initially confined to the combustion chamber
- Barrel wear is not an issue in rocket motors

MAIN TYPES OF SOLID ROCKET PROPELLANT

Double Base (Homogeneous)

- Nitrocellulose and nitroglycerine mixtures
- Minimum smoke combustion but poor mechanical properties

Composite (Heterogeneous)

- Crystalline oxidiser in a CH-based polymeric fuel/binder
- Good mechanical properties but smoky combustion

Composite Modified Double Base

- Double base composition with added oxidiser and metallic fuel
- Better performance than double base but smoky combustion

KEY PROPERTIES OF SOLID ROCKET PROPELLANTS

- Characteristic velocity (c^*) or specific impulse (I_{sp})
- Burning rate (r) and its pressure and temperature dependence
- Density
- Physical and mechanical properties (extensibility)
- Storage properties
- Combustion signature, especially smokiness and toxicity
- Vulnerability and safety in handling (IM-ness)
- Environmental impact
- Through Life Costs

DOUBLE BASE ROCKET PROPELLANT TYPES

Extruded (EDB)

- Preformed NC/NG mixtures extruded horizontally through a die

Cast (CDB)

- NG-based casting liquid added to an NC-based casting powder

General characteristics

The general advantages of solid rocket propellants are as follows:

1. They favour simple and lightweight designs of motor.
2. They permit instant readiness of a missile system.
3. They present little or no toxic vapour hazard and are therefore safe to store and handle.
4. They have good chemical and thermal stability, and therefore long shelf-life.
5. They are of high density, giving a good energy/bulk ratio.

General characteristics

The general disadvantages of solid rocket propellants are as follows:

1. They are expensive, being complex mixtures which require lengthy manufacturing processes.
2. Once ignited, solid-propellant motors cannot be shut down, and the level of thrust cannot be changed at random during the burning time.
3. 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.
4. The motor is also the propellant container, therefore the amount of propellant contained in a missile may be limited by the overall system design requirements.

CAST DOUBLE BASE (CDB) PROPELLANTS

Casting powder (NC based) + Casting liquid (NG based)



Unfilled

Minimum smoke
Plateau burning
Lower density and c^*

Nitramine filled

Minimum smoke
Plateau burning
Higher density and c^*

- Elastomer modified variants (EMCDB) of both types can also be made, giving improved low temperature mechanical properties

Cast double-base (CDB) propellants can be made in grain diameters from 50 mm upwards, and the maximum diameter is, in theory, unlimited, as is the length. Other advantages which they have over EDB types are a better capacity for very complex cross-sections, greater precision of dimensions, greater safety in manufacture and, compared with solvent EDBs a saving of drying time

Filled CDB propellants

CDB propellants can be modified by filling them with RDX or HMX, analogously to high energy gun propellants. The nitramines are better gas producers than the NG which they partly replace, but have somewhat lower heats of explosion (Q_p). The capacity for platonisation is retained and there is no increase in smokiness

ENERGETIC FILLERS FOR DOUBLE BASE PROPELLANTS

- Crystalline energetic compounds added to increase c^*
- RDX is most widely used. Also HMX and hexanitroisowurzitane (HNIW or CL20) but these are more expensive
- Nitramine addition might increase the UN hazard classification of a propellant, from 1.3 to 1.1
 - Not normally acceptable

COMPARISON OF EDB AND CDB PROPELLANTS

■ Extruded DB

- Higher c^* and burning rates (more energetic components)
- Grains can have smaller web thicknesses - faster burning
- Cannot be case-bonded

■ Cast DB

- Superior mechanical properties (more non-energetic plasticiser)
- Single grain can be made with boost and sustain sections
- Can be case-bonded

DB rocket propellants - taking cast and extruded types together, are as follows:

Advantages

1. They have high mechanical strength.
2. Complex cross-sections can be produced, by casting or extrusion.
3. They are relatively smokeless ("minimum smoke"), provided they are not filled with ammonium perchlorate and aluminium.
4. They can be platonised, again provided they are not filled with ammonium perchlorate and aluminium.
5. They can be filled with RDX or HMX, giving higher impulse without loss of platonisation or low-smoke characteristics.

Disadvantages

1. They tend to crack at low temperatures, unless elastomer-modified.
2. They cannot be case-bonded, unless heavily plasticised.
3. They tend to exhibit unstable and resonant burning, but this can be suppressed by additives.
4. Chemical decomposition of the nitrate esters produces gas in storage.
5. Double-base propellants cannot be energized by aluminium, unless ammonium perchlorate is also added.

MAJOR ADDITIVES IN DOUBLE BASE PROPELLANTS

Stabilisers (e.g. 2-nitrodiphenylamine)

- Increase propellant storage life by delaying onset of autocatalytic decomposition of NC and NG

Ballistic Modifiers (BMs, e.g. lead stearate)

- Increase propellant burning rate and bring about 'plateau burning', where rate is independent of pressure

Non-energetic Plasticisers (e.g. triacetin)

- Improve propellant mechanical properties at low temperatures

....and as with gun propellants (but higher risk!)

STABILISERS IN DOUBLE BASE PROPELLANTS

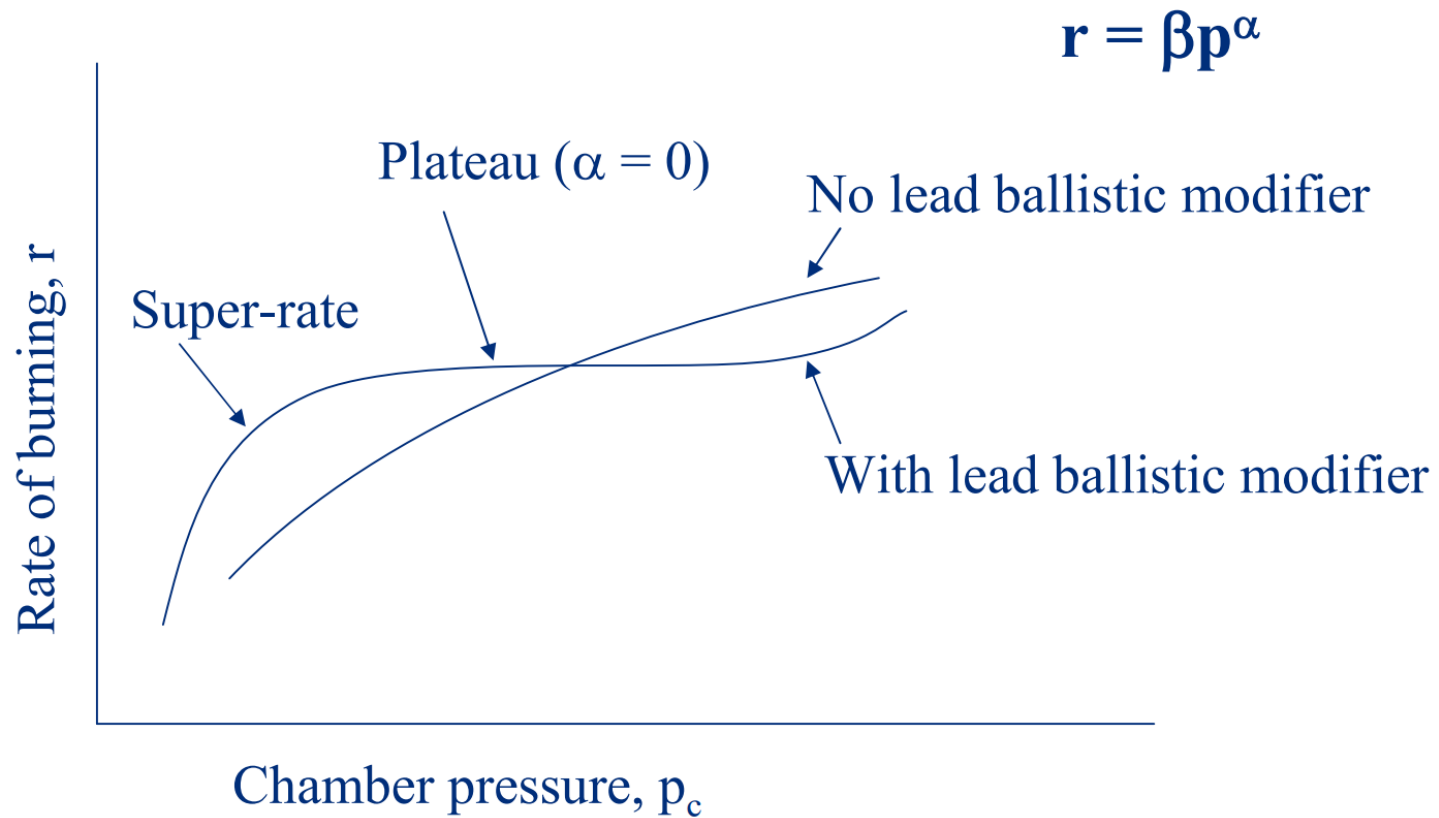
- NC, NG undergo slow decomposition at storage temperatures:



NO_2 catalyses further decomposition, resulting in exothermic 'autocatalytic' reaction and propellant auto-ignition.

- An added stabiliser (~1%) reacts rapidly with the NO_2 to give safe products, thereby allowing extended propellant storage.

PLATEAU BURNING (PLATONISATION)



FEATURES OF PLATEAU BURNING

- Minimises changes in propellant burning rate resulting from fluctuations in combustion chamber pressure
- Increases the propellant burning rate (r) by up to 100%
- Reduces the temperature coefficient of the propellant (π_K)
- Ballistic modifiers lower propellant energy and generate smoke

Platonising – Pros & Cons

The advantages of platonising double-base rocket propellants

1. It minimises the effect of pressure fluctuations on burning rate.
2. It enables the burning rate at given pressures to be increased by up to 100% (see fig.IV-4).
3. It reduces the effects of manufacturing tolerances and grain geometry on the burning rate.
4. It reduces the dependence of burning rate on conditioned grain temperature.

The disadvantages are

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

KEY PROPERTIES OF DOUBLE BASE PROPELLANTS

- 'Minimum smoke' combustion (AA under STANAG 6016)
- Super-rate and plateau burning - with added lead BMs
- Relatively poor mechanical properties
 - CDB improved by incorporating an elastomer to give EMCDB
- Relatively low energies
 - increased by addition of a high energy nitramine (e.g. RDX)

COMPOSITE ROCKET PROPELLANTS



MLRS

COMPOSITE ROCKET PROPELLANT TYPES

Plastic

- Extruded mixtures of Ammonium Perchlorate (AP), Aluminium (Al) and a preformed plastic binder (e.g. polyisobutene, PIB)

Rubbery

- AP and Al in a cross-linked elastomeric binder/fuel formed by reacting a liquid pre-polymer (e.g. HTPB) with a curing agent.

Note – plastic no longer popular due to poor mechanical properties

CURRENT OXIDISERS FOR RUBBERY COMPOSITE PROPELLANTS

■ Ammonium perchlorate (AP)



- high density, low shock sensitiveness and high burning rate
- HCl production on combustion is a drawback in some systems

■ Phased-stabilised ammonium nitrate (PSAN)



- unmodified AN undergoes a phase change at $\sim 32^\circ\text{C}$
- major disadvantage of PSAN is its low burning rate

NEW 'CLEAN' OXIDISERS FOR RUBBERY COMPOSITE PROPELLANTS

■ Ammonium dinitramide (ADN)



- Light sensitive
- Low melting point (93°C)
- High impact and friction sensitiveness
- Incompatible with many curing agents

■ Hydrazinium nitroformate (HNF)



- Poor thermal stability
- Incompatible with many curing agents

ADDITIONAL FUELS FOR RUBBERY COMPOSITE PROPELLANTS

- Powdered metals that burn by reacting with oxygen (from the oxidiser), thereby increasing T_c (and hence I_{sp})
- Aluminium (5 – 40 μm particle diameter) is most common
- More energetic possibilities than Al have drawbacks
 - Be is very toxic, Mg is difficult to handle, B burns inefficiently
- Also function as unstable burning rate suppressants

MAJOR ADDITIVES IN RUBBERY COMPOSITE PROPELLANTS

- **Antioxidants** (e.g. A-2246, a phenol)
 - extend HTPB grain life by suppressing reaction between oxygen and polymeric binder, which degrades mechanical properties

- **Bonding Agents** (e.g. MAPO)
 - improve mechanical properties by enhancing adhesion between binder and filler, thus preventing void formation

- **Burning Rate Catalysts** (e.g. ferrocene and its derivatives)
 - increase the burning rate of the propellant

KEY PROPERTIES OF RUBBERY COMPOSITE PROPELLANTS

- Good mechanical properties, even at low temperatures (-40°C)
- High energy, particularly when aluminised
- High densities and intrinsically low temperature coefficients (π_K)
- Wide range of burning rates, controlled by AP surface area
- Smoky combustion signature, due to HCl and Al_2O_3 production

AGEING OF RUBBERY COMPOSITE PROPELLANTS

Three main ageing processes affect propellant performance:

- Moisture hardening due to agglomeration of AP crystals
- Migration of additives, e.g. plasticisers
- Oxidative cross-linking of HTPB binder, leading to 'age hardening'
 - caused by reaction of C=C bonds with O₂ in air
 - mitigated by incorporating an antioxidant or by storing motor in inert atmosphere

The general advantages of rubbery composite propellants are as follows:

1. They have good mechanical properties over a wide temperature range.
2. They can be satisfactorily case-bonded.
3. They can be energised by aluminium.
4. They can be energised by RDX or HMX.
5. They burn smoothly, especially if aluminised.

Their general disadvantages are as follows:

1. They require careful curing.
2. They exhibit smoky burning.
3. They cause interference with EM radiation.
4. They may undergo stress cracking on storage.
5. They cannot be platonised.

REDUCED SMOKE COMPOSITE PROPELLANTS

- Propellants with a high RDX content, low AP content and no Al
 - Lower $\rho \cdot I_{sp}$ than aluminised composites but less smoky
 - ~10% AP needed to oxidise binder and maintain burning rate

Typical aluminised (smoky) rubbery composite:

15% HTPB/70% AP/15% Al

$$\rho \cdot I_{sp} = 4300 \text{ N s dm}^{-3}$$

Typical reduced smoke rubbery composite:

12% HTPB/10% AP/53% RDX/25% NG

$$\rho \cdot I_{sp} = 4110 \text{ N s dm}^{-3}$$

MINIMUM SMOKE COMPOSITE PROPELLANTS

- Combine good mechanical properties **and** minimum smoke
- Two main types under development:
 - 'Clean' oxidiser and energetic fuel/binder formulations
e.g. HNF + polyNIMMO
 - High energy nitramine and energetic binder formulations
e.g. CL20 + GAP

SOLID PROPELLANT COMPARISONS



TYPICAL SOLID PROPELLANT BURNING RATES

- **EDB on plateau (7-10 MPa)**
 - Unfilled 2.5 – 50 mm s⁻¹
- **CDB on plateau (7-10 MPa)**
 - Unfilled 2.5 – 45 mm s⁻¹
 - RDX-filled 3 – 35 mm s⁻¹
- **EMCDB on plateau (7-10 MPa)**
 - Unfilled 5 – 35 mm s⁻¹
 - RDX-filled 5 – 25 mm s⁻¹
- **Composite at 7 MPa**
 - Plastic 3 – 45 mm s⁻¹
 - Rubbery 20 – 50 mm s⁻¹

FAILURE MODES OF SOLID PROPELLANT GRAINS

■ Cracking

- Thermal expansion differences between propellant and motor case during cool-down
- Gas accumulation in DB grains during storage (gas cracking)
- Rapid pressurisation on motor firing

■ Slumping

- Gravitational stresses during storage (plastic composite)
- Set-back during motor acceleration

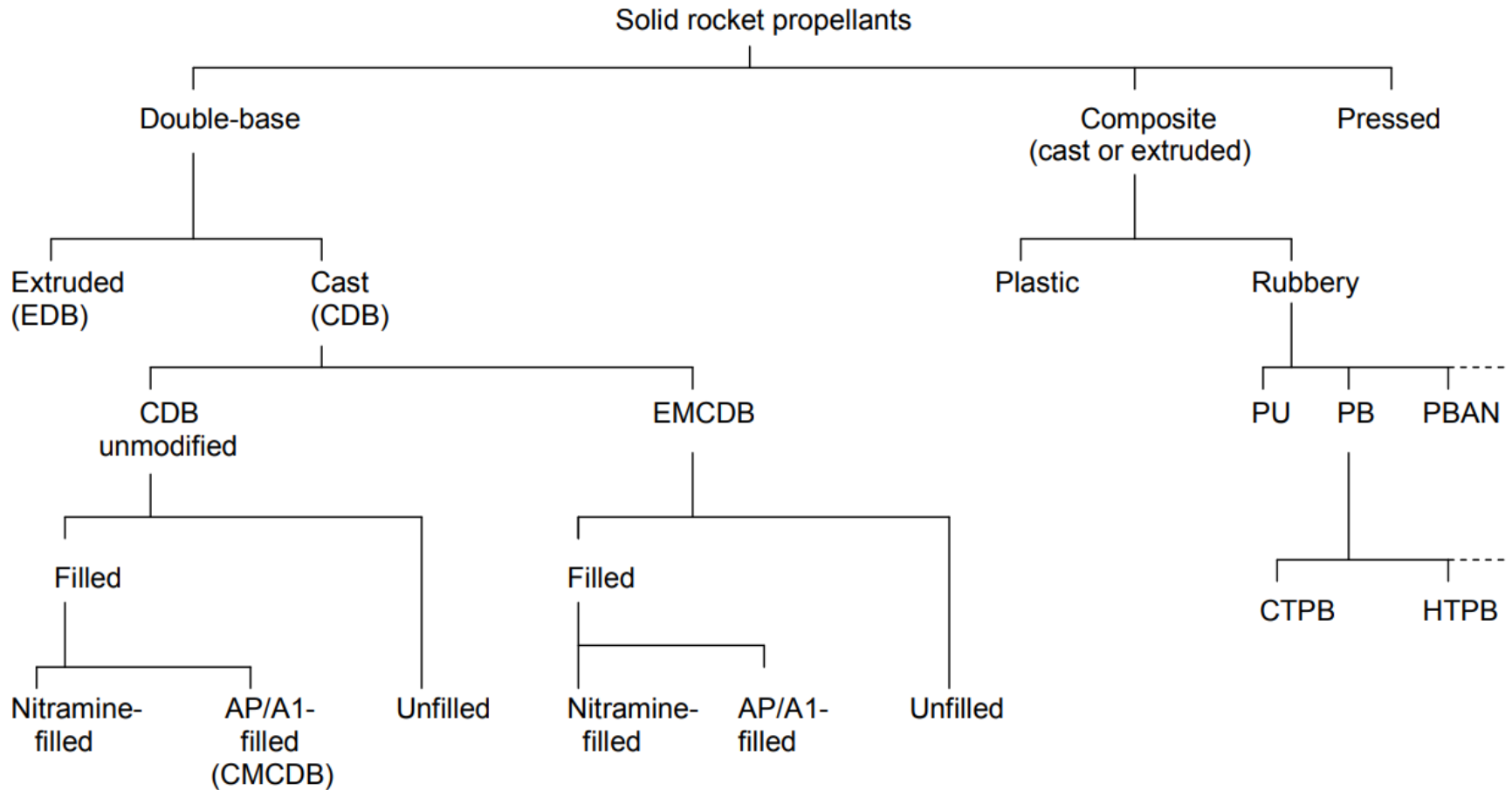
■ Debonding

- Stresses between case-bonded propellant and motor case
- Incompatibility between propellant and liner material

SOLID ROCKET PROPELLANTS IN UK MISSILES

Propellant Type	Missile	Motor
Extruded Double Base	Blowpipe Seawolf	Crake Blackcap
Cast Double Base	Swingfire Seacat	Pointer Sealyham
Composite Modified Cast Double Base	Sea Dart	Chow
Plastic composite (PIB)	Bloodhound	Gosling
Extruded rubbery composite (HTPB)	LAW 80	
Cast rubbery composite (HTPB)	Skyflash	Hoopoe

Summary of Solid Rocket Propellants



LIQUID ROCKET PROPELLANTS

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

1. In powerful rocket motors, for the rapid forward propulsion of the vehicle.
2. 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.
3. 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 propellants, but in practice the choice is made on the basis of suitability.

How do Liquid Rocket Engines work?

Solid and liquid Propellant - comparison

LIQUID ROCKET PROPELLANTS

Set against these advantages are the following main disadvantages:

1. The motor is much more complicated than a solid-propellant one, with (usually) two propellant tanks, several lengths of pipe, a pump or pressurizing 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 solids.
2. The propellants are mostly of lower density than solid propellants.
3. The propellants are often toxic, corrosive or cryogenic.

Liquid Monopropellants

Liquid propellants are subdivided 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 fuels in bipropellant combinations). Instead, they are used in thrusters, gas generators etc. Monopropellant motors need only one propellant tank, and this permits a simpler, lighter and more reliable system than bipropellant motors.

Properties of some monopropellants

Propellant	Mean molar mass of products (g mol ⁻¹)	Combustion temperature (K)	Specific impulse* (N s kg ⁻¹)	Density at 25°C (g cm ⁻³)
Hydrazine	10.3	966	1951	1.01
Hydrogen peroxide	22.7	1278	1618	1.41
Nitromethane	20.3	2190	2500	1.13
Iso-propyl nitrate	15	1251	1630	1.04

Hydrazine

It has a number of advantages in the monopropellant role:

1. It can be readily decomposed on a catalyst when required,
2. 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.
3. It can be stored, given suitable conditions, for extended periods of time without undue decomposition.
4. It is compatible with many (though by no means all) engineering materials.
5. it is readily and fairly cheaply available, being used also in the plastics and other industries.
6. It has a relatively low vapour pressure.

Hydrazine

However, hydrazine has the following disadvantages:

1. Comparatively high freezing point.
2. High hygroscopicity .
3. Susceptibility to catalysed decomposition on various surfaces, eg stainless steels and many elastomers. This is increased by the presence of acidic impurities in the liquid, such as carbon dioxide.
4. Lower specific impulse than some other monopropellants.
5. Slight susceptibility to dieseling, ie accidental ignition by the rapid, adiabatic compression of entrained bubbles.
6. High toxicity, as already noted

Other monopropellants

Hydrogen peroxide

Nitromethane.

Iso-propyl Nitrate (IPN)

Liquid Bipropellants

- ▣ Liquid propellant 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 (hypergolically) or are ignited by a pyrotechnic charge.
- ▣ 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*.
- ▣ They are classed either as cryogenic ('space-storable') or non-cryogenic ('earth-storable').

*Large rocket systems which contain liquid bipropellant main motors include the NASA/DoD space shuttle, ESA Ariane, the American Atlas and the Titan and Delta series and a number of Russian and Chinese space launch vehicles.

Liquid Bipropellant Oxidants

Inhibited red fuming nitric acid (IRFNA) – *now obsolete. RFNA is a brown (not red), mobile liquid with a very unpleasant odour. It is highly toxic*

Dinitrogen tetroxide (DNTO) - *DNTO poses problems of storage because when containing more than 0.2% moisture it is unacceptably corrosive towards steel containers.*

Liquid bipropellant fuels

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.

Other options

Hydrazine

UDMH and Aerozine-30

Mixed amine fuel (MAF)

Monomethylhydrazine (MMH)

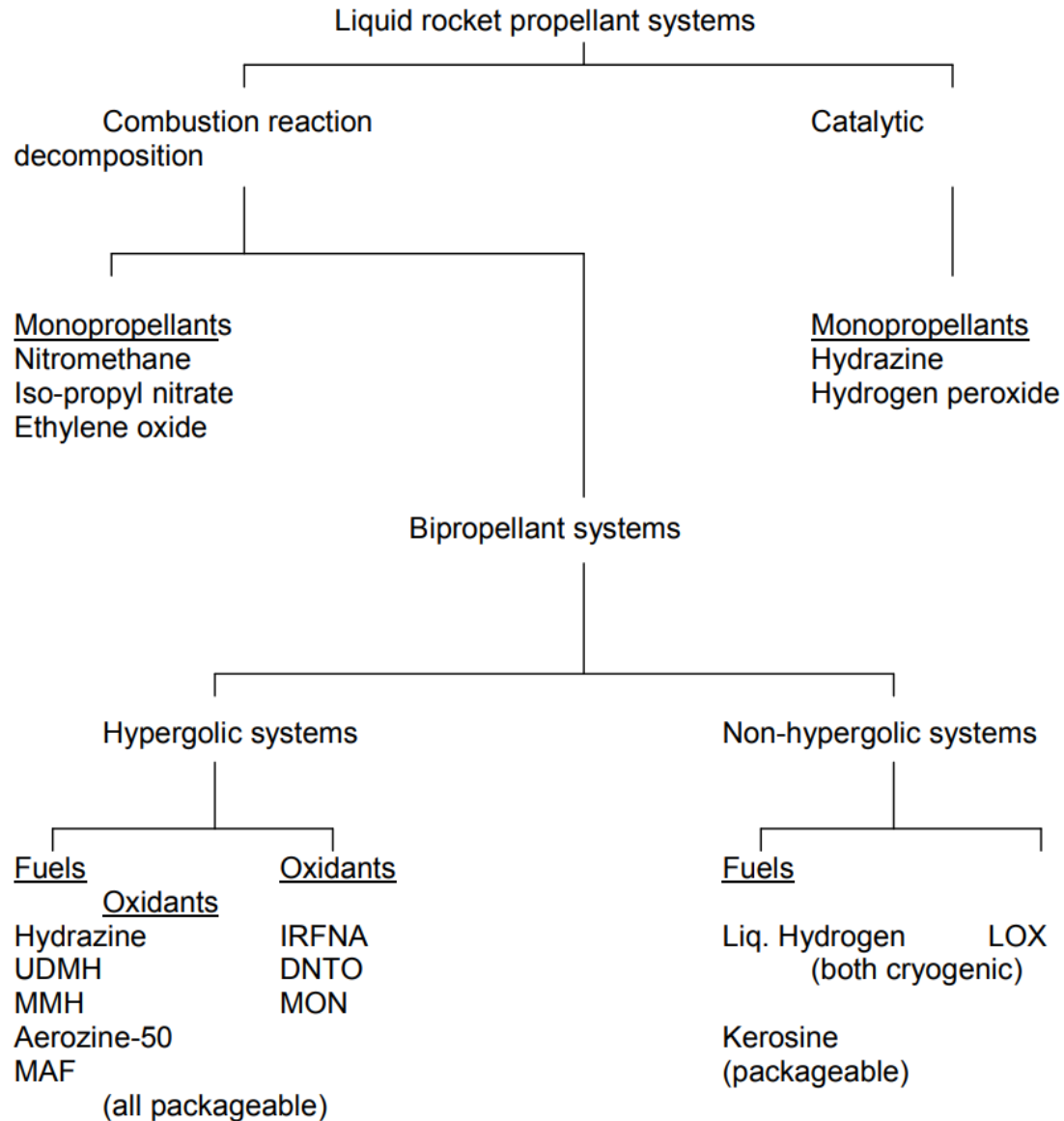
LIQUID ROCKET PROPELLANTS

Advantages and disadvantages of liquid propellants

The inherent advantages of liquid propellants are as follows:

1. Some have higher specific impulse than solids.
2. 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.
3. The thrust can be varied by throttling, and if necessary combustion can be stopped and restarted.
4. 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.
5. Liquid propellants produce less smoke than do some solid propellants.
6. Liquid propellants are relatively cheap.
7. Some bipropellant combinations are hypergolic (self-igniting on contact of the two liquids).

Summary of liquid rocket propellants



Hypergolic - igniting spontaneous mixing with another substance. The two propellant components usually consists of a fuel and an oxidizer.

Non-hypergolic - require one or both propellant to cryogenically liquefied in order to fit in an economically sized tank (bipropellants which require external ignition)

Questions & discussion

