WASC 2135

History of Propellant Development

# FROPELLANTS

History of Propellant Development

Development of modern gun propellants and the solid and liquid propellant systems used in space rockets and guided missiles owes much to the stimulus provided by two World Wars, but the principle of propulsion has a much longer history. As early as the 9th century Marcus Graecus in his "Book of Fires for Burning the Enemy" describes the "flying-fire" of the Greeks, a combustible mixture of pitch, sulphur, charcoal and turpentine, ingredients which only required the addition of potassium nitrate as oxidiser - an improvement attributed to the Chinese - to produce the first solid propellant. The Chinese appear to have used such compositions to propel their "fire arrows" at the battle of Kai-fung-fu in 1232, and soon afterwards the knowledge of this rudimentary form of blackpowder spread to the Middle East and across Europe.

In the middle of the 13th century Roger Bacon gave a detailed description of the manufacture of blackpowder, but the synonymous term "gunpowder" could not properly be applied to this product until early in the following century when the monk Berthold Schwarz is said to have invented the gun and used blackpowder to propel stones from it. This is a notable milestone since hitherto use of the mixture had been limited to pyrotechnic, incendiary and demolition effects only.

For a period of 500 years blackpowder served as priming composition, fuse mixture and propellant charge - providing the complete explosive train which led to expulsion of the projectile from the barrel of the gun after ignition by flint or torch at the bore-hole. Technical improvements came in 1425 when granulation was introduced, and in 1525 with the control of a size by screening, and blackpowce continued to be used as an important explosive .... owards the end of the 19th century.

Propellant and explosives technology moved into the modern era in the 19th century with the discovery of nitrocellulose and nitroglycerine. The former was first prepared by nitrating paper (Pelouze, 1838), and Schönbein and Böttger independently discovered its explosive properties in 1846. Sobrero made nitroclycerine in the sume year, but this extremely sensitive compound remained little more than a chemical curiosity for 20 years. The problem of excessive hazard was solved in 1867 when Nobel succeeded in de-sensitising nitroglycerine by adsorption on kieselguhr to produce dynamite. He also invented the mercury fulminate blasting cap, and assured the commercial success of this new explosive.

WASC ZI35

LS 64051 5E

Within a few years Nobel (1875) discovered the advantages of gelatinizing nitrocellulose by admixture with nitroglycerine. These mixtures, known as blasting gelatin and gelatin dynamite, are relatively safe to transport and handle compared with the individual ingredients.

Development of propellant compositions lagged behind these advances in blasting explosives, but in 1884 Vieille invented Poudre B, a smokeless gun propellant based on nitrocellulose. This was made by treating nitrocellulose with ether-ethanol solvent to form a gel, which was kneaded and rolled into sheets, then cut into squares and dried. Four years later, in 1888, Nobel introduced ballistite, the first double-base propellant powder. It consisted of soluble nitrocellulose (12.6% nitrogen content) and nitroglycerine blended with the aid of a volatile solvent such as benzene. Using insoluble nitrocellulose (that is, with nitrogen content greater than 12.9%), nitroglycerine, petroleum jelly and acetone, Kellner and Abel, in 1889, manufactured the well-known British propellant-cordite. The colloidal mixture was extruded through dies to form cords, then solvent was removed by evaporation. It turned out that petroleum jelly acted as a stabilizer in these early cordites, but in the years preceding World War I this was superseded by aromatic amines including diphenylamine and N,N'-diethyl-N,N'-diphenyl urea (carbamite or ethyl centralite). Further improvements included the development of flashless propellants in the United States and of low-erosion, diethyleneglycol dinitrate compositions in Germany and Italy.

Gun design and manufacture also underwent significant advances during the 19th century, and there were considerable improvements in the range and accuracy of conventional artillery. Indeed, although war rockets had become an important adjunct to guns, by 1900 they were completely eclipsed, and rocketry lay dormant until after World War I. However, the availability of more powerful propellants such as cordite, and an improved understanding of the principles of rocket flight led to a revival of interest. Three men are associated with this work: the American, R. Goddard; the German, H. Oberth; and the Russian, K.E. Ziolkowski. Working independently, they analyzed the problem of rocket propulsion and recognized that the most efficient way of producing forward thrust is by continuous nearward ejection of a high velocity stream of gas.

At the beginning of World War II there were military requirements for generating heavy fire power without having to deploy a large number of guns, and rockets provided the solution. Developments included cordite-propellant antia "raft rockets, anti-tank weapons such as the American "Bazooka", and the Russiar "Latusha"

- 2 -

bombardment rocket. Pre-war work on liquid-propelled rockets culminated in the German V-2, and this was the fore-runner of the large multi-stage rockets used to launch earth satellites and space vehicles.

## Classification of Propellants

The function of a propellant is to produce expanding gases at a controlled rate so that they may be used to do mechanical work in a gun, rocket, engine starter, or similar device. Explosives also produce expanding gases, but at a very high rate and the process is violent and destructive. A propellant which undergoes controlled burning is said to "deflagrate", whereas an explosive "detonates".

Propellants are conveniently divided into solid and liquid types with further sub-divisions which depend on composition or application.



Gun propellants may be of three types. The single-base variety contain plasticised nitrocellulose as the sole oxidiser; with nitroglycerine present as a second oxidiser the composition is termed double-base. A third type, known as triple-base, contains substantial amounts of an organic compound such as nitroguanidine (picrite) added to moderate the ballistic characteristics of the propellant, and in particular to reduce muzzle flash.

There are two main classes of solid rocket propellant termed double-base and composite. In double-base propellants the chemical system is mainly nitrocellulose gelatinised with nitroglycerine, and the oxidising component of the system, namely the organic nitrate group, is chemically bound into the matrix. The other main type - composite propellant - uses as oxidiser a solid crystalline material such as ammonium perchlorate supported in a rubben binder or a thermoplastic polymer which

- 3 -

acts as fuel. A wide range of rubbery binders have found application including polyurethanes, polysulphides and polybutadienes, and aluminium is often added to increase the energy of the composition. When the binder is a polymerisable rubber or resin the propellant is made by a cast-and-cure procedure. However, in the UK composition known as plastic propellant the fuel component is simply a viscous liquid, for instance, polyisobutylene. Plastic propellant is a puttylike material which can be extruded or compression moulded, but no chemical reactions are involved in the processing.

Although it is convenient to recognise these two broad groups of rocket propellants the distinction is not entirely rigid. Advanced double-base propellants may contain solid oxidising salts - these compositions are called composite-modified double-base - and conversely, nitroglycerine and other organic nitrates may be used as energetic plasticisers in composite propellants.

Liquid propellants are used only in rocket applications although attempts. have been made to devise liquid propulsion systems for guns. Their classification is generally into two types, namely monopropellants and bipropellants. The former, exemplified by hydrazine, hydrogen peroxide and isopropyl nitrate, consist of single compounds or stable mixtures of oxidising-reducing agents containing all the elements.necessary for complete combustion, whereas in a bipropellant system oxidiser and fuel are stored in separate tanks until they undergo reaction in the combustion chamber of the rocket. Monopropellants are often used as gas generators to provide auxiliary power in missiles and to drive turbines to pump prepellants oxidiser and fuel components of bipropellant combinations. are most widely used to propel large, multistage rockets for satellite launching More energetic compounds can be used than is possible and space exploration. with the relatively low energy monopropellants, and the use of liquid oxidisers and fuels enables the rocket motor designer to control thrust by throttling or, if Thrust control is particularly necessary, by extinguishment and re-ignition. important for launching manned - or highly instrumented space vehicles to avoid exposing the payload to a high gravity environment. Solid propellants are generally favoured for military purposes in view of their relative safety and simplicity, although their performance is inferior to that of liquid systems. Furthermore there are obvious tactical and strategic advantages to be gained from the immediate readiness of weapons based on solids.

Fuels for liquid bipropellant combinations are generally compounds with carbon-hydrogen bonds (e.g. keros@ne and ethyl alcohol) or nitrogen-hydrogen bonds (e.g. aniline, ammonia, hydrazine and hyurazine derivatives). Common oxidisers

- 4 -

include nitric acid, dinitrogen tetroxide, and liquid oxygen; the last compound is an example of a cryogenic oxidiser since it must be stored under refrigeration. One of the most energetic oxidisers, liquid fluorine, is used only for experimental purposes in view of its extreme reactivity. The liquid ignites spontaneously on contact with fuels, and such liquids are described as hypergolic.

In recent years there has been much interest in exploring the feasibility of a hybrid propulsion system in which a liquid fuel is used in conjunction with a solid oxidiser, or vice versa. This approach extends the range of compounds and compositions available to engine designers, but its practical implementation is complicated by additional engineering and combustion problems.

Performance of Propellants

During combustion the chemical energy of a propellant is converted into thermal and kinetic energy, and the efficiency of this process determines propellant Two functional laws, still generally applicable to the combustion performance. of propellant charges, were established from burning studies on gunpowder. In the early days it was found that the ballistic regularity or reliability of gunpowder was improved by careful control of the size and geometrical form of pellets which had been well compressed so that they were not porous to the penetration of hot Such penetration caused a progressive increase in the rate of burning gases. with consequent loss of control. This observation led to Piobert's law of burning by parallel layers (1839): if a propellant is prevented from burning on all but one plane surface that surface will regress regularly, as it were layer The law leads to the following expression for the mass rate of by layer. burning:

 $m = \rho Sr$ 

where m = mass rate of burning of propellant

 $\rho$  = propellant density

S = area of burning surface

r = linear rate of surface regression

The second fundamental law, due to de Saint Robert (1862) connects the linear rate of burning, r, with the ambient pressure, p:

 $r = ap^{\frac{2}{3}}$ 

where "a" is a constant. As a result of his work on the burning of single-base colloidal propellants, Vieille (1893) generalised this equation in the form:

 $r = ap^n$  or logr = loga + nlogp

where 'a' is known as the "burning rate coefficient" and 'n' as the "pressure index" of the propellant. The parameters 'r' and 'p' are measurable, and a logr/logp plot will have a slope 'n' and an intercept (log a) characteristic of the propellant. Thus the important characteristics 'a' and 'n' may be determined experimentally, and it is important to note that as 'n' approaches unity there will be an increasing tendency for combustion to proceed explosively; this is particularly undesirable in propellants for rocket motors.

The burning rate of a propellant depends upon its degree of confinement. Guns operate at pressures of up to 25 tons in  $^{-2}$  (400 MN m<sup>-2</sup>), whereas rocket chamber pressures may be as low as 300 lbs in  $^{-2}$  (2 MN m<sup>-2</sup>). Corresponding burning rates range from 100 to 1 mm.s<sup>-1</sup>, and total burning time is determined by the size and geometrical shape of the grain, by inhibiting or moderating exposed propellant surfaces, or by introducing porosity. Catalysts are often incorporated to enhance the burning rate of rocket propellants, and certain lead compounds are particularly useful as ingredients of double-base compositions to give burning rates which are substantially unaffected by changes in operating pressure. Such propellants are described as "platonised".

One of the variables used to control the burning rate of propellants is grain geometry or charge shape. In cord or stick form the exposed surface decreases as burning proceeds and the rate of gas evolution falls off. This is called 'regressive' burning. A tube shape gives almost "neutral" burning because the total surface area remains constant apart from slightly irregular and slower burning on the inner surface, but multi-tubular propellant burns "progressively". The latter typically has seven tubular holes, and is employed in 'grains' having a length about two-and-a-half times their external diameter. Strip or ribbon form is also employed - this is slightly regressive - and there is a "quick" form in the shape of square flakes. Progressive burning is favoured for gun propellants so that a pressure-time curve is obtained which 'peaks' near the gun breech and then decreases as the projectile travels down the barrel and the gases expand. Regressive burning geometries are usually used in small arms ammunition, but rocket propulsion requires a uniform rate of gas evolution and neutral burning grains are customary.

The initial temperature of a propellant charge also has a significant effect on its rate of burning. Decrease in initial temperature causes a marked decrease in burning rate and in the maximum pressure obtained. The effect on performance is much more pronounced in rocket propellants because these function at relatively low, essentially constant pressures. A typical value for the temperature coefficient of burning rate at constant pressure is 0.2% °C<sup>-1</sup>. Vieille's equation deals with the burning characteristics of the propellant; the other important variable is its energy content. It is possible to calculate this using readily available thermochemical data and making various simplifying assumptions about the combustion process, but a more practical approach is to determine the propellant's 'calorimetric value'. This is defined as the heat evolved when the propellant is burnt in a sealed pressure vessel (a bomb calorimeter) without added oxygen. The term should not be confused with the expression 'calorific value' used to characterise fuels such as coal, burnt in oxygen. Calorimetric values range from a few hundred calories per gramme for "cool" propellants used in power cartridges to over 2000 (9.0 MJ kg<sup>-1</sup>) for highenergy rocket compositions. Gun propellants generally fall in the range 800 to 1200 cal.g<sup>-1</sup>.

# Assessment of Gun Propellants

Ballistic properties of gun propellants are usually assessed by experimental firings in a "closed vessel". This is of very robust construction with a working volume of 700 cc and a working maximum pressure of 18 ton in<sup>-2</sup> (288 MN m<sup>-2</sup>). The vessel is fitted with firing electrodes, a value for the release of pressure, and a tourmaline crystal piezo-electric pressure gauge. A water jacket is fitted to control the initial temperature of the vessel and its contents - usually a standard charge of 140 g. of propellant. On firing, the signal from the pressure gauge is recorded as a plot of <sup>dp</sup>/dt against p, whence  $p_{max}$ . can be obtained.

Combustion in a closed vessel is a reasonable approximation to the high pressure system in which a gun propellant functions, and such tests are used with experimental compositions and to assist with proof tests of gun propellants. To compare two lots of a similar propellant the relative values of  $p_{max}$  are taken as the relative "force", and the relative values of  $(dp/dt)/p_{max}$  give the relative "vivacity". In this way it is possible to compare experimental with standard propellants and to judge the effectiveness of blending in a propellant lot, thus saving the expense of extensive gun firings.

Thus the major techniques available for evaluation and quality control of gun propellants are the bomb calorimeter (to measure calorimetric value) and the closed vessel (to obtain relative force and vivacity). In addition the composition of the propellant must be carefully checked, since this determines ballistic reproducibility, and the density, shape and dimensions of propellant grains are measured.

Stability and sensitivity tests are performed during the development stages of propellant formulation, and to a large extent these resemble the tests applied to explosives. Various accelerated ageing tests are used, in conjunction with chemical tests and long-term storage trials, to assess chemical stability. Of particular importance is the Abel heat test, in which the propellant is heated at 160 or  $180^{\circ}F$  until the liberated oxides of nitrogen produce a standard tint on a starch-potassium iodide paper. Stabiliser consumption trials at elevated temperatures (about  $65^{\circ}C$ ) are also important for predicting safe-life under normal storage conditions. For propellants stabilised with carbamite this is taken to be the length of time required for the stabiliser content to fall to 50% of its original level.

# Assessment of Rocket Propellants

Although the colloidal propellants which are used in both rockets and guns may be essentially similar in composition, the conditions under which combustion occurs are quite different. The combustion chamber of a rocket is not a high pressure chamber and operating pressures are usually restricted to the range 500 to 2000 lbs in<sup>-2</sup> ( $3.5 - 14 \text{ MN m}^{-2}$ ). On ignition the pressure in the rocket chamber rises after 0.005 to 0.05 sec. to a maximum value determined by the burning rate of the propellant and the diameter of the nozzle orifice. The charge then burns at a steady rate for a total burning time which may be a fraction of a second or several minutes.

In liquid-propelled rockets the question of control of burning rate and operating pressure depends to a large extent on engineering design. However, with solid propellants the control is achieved by changes in the propellant composition, burning surface area, and ratio of nozzle area to burning surface area. As with gun propellants, the shape and size of the charge or rocket propellant grain is an The grains, which are very much important design parameter for solid systems/ larger than those used in gun propellants, are usually cylindrical with one or more internal conduits designed so that the area of exposed propellant remains constant as burning progresses. Common designs for the axial conduit include a six-pointed star, a clover leaf, and a cylindrical hole with three radial slots. For some applications a solid cylinder of propellant is employed, and this is known as an Burning on the outer surface of the cylinder is inhibited "end-burning" grain. This is relatively straightforward by bonding the propellant to the motor case. for composite propellants, but colloidal propellants are usually protected with a suitable inhibitor.

Several methods are available for measuring the burning rate of solid rocket propellants. In the "strand burner" thin cords of propellant, inhibited on their long surface by dipping in a lacquer, are burnt in a pressurised vessel to obtain the linear rate of burning. There is also the "interrupted burning" technique which depends upon combustion of a cylinder of propellant under pressure for a given time, after which it is extinguished by suddenly releasing the pressure; the length consumed is then measured. Finally, the required rates may be determined by firing small experimental rocket motors, a technique used primarily for the direct measurement of propellant thrust.

Generally double-base propellants burn at rates between 0.3 and 1 in.s<sup>-1</sup> (8 - 25 mm.s<sup>-1</sup>) at 1000 lb in<sup>-2</sup> (6.895 MN m<sup>-2</sup>), and the range may be extended at the lower end, to 0.1 in.s<sup>-1</sup> (2.5 mm.s<sup>-1</sup>), with composite propellants containing ammonium perchlorate. Formulation variables which affect the burning rate include variation in the ratio of fuel to oxidiser, variation in the particle size of the oxidiser (in the case of composite propellants), and addition of catalysts. Mention has already been made of the special use of lead salts in colloidal propellants to achieve a "plateau" in the hgr/logp curve such that burning rate is independent of pressure over a range of several hundred lbs in<sup>-2</sup>.

The performance of a rocket propellant is usually described in terms of "specific impulse" or  $I_{sp}$ . This is the product of the thrust and time of burning divided by the total propellant mass burnt, that is lbfs.  $H_0^{-1}$  (N.s.kg<sup>-1</sup>). When Isp data are quoted they should be accompanied by rocket chamber pressure and external pressure since both have an effect on specific impulse. Standard Isp is obtained under the following operating conditions: propellant initially at 20°C is burnt at a combustion chamber pressure of 1000 lb in<sup>-2</sup> (6.895 MN m<sup>-2</sup>) absolute and expanded to one standard atmosphere 14.7 lb in<sup>-2</sup> (0.101 MN m<sup>-2</sup>) absolute with parallel flow into an atmosphere of the same pressure.

The specific impulse of rocket propellants (and the force of gun propellants) can be calculated from basic thermodynamic data provided certain properties are known, as for example the energy evolved, the volume of gas produced, and its flame temperature and heat capacity. A knowledge of the calorific value gives some indication of the burning rate and flame temperature of the propellant.

Specific impulse is calculated from the following equation:

$$I_{sp} = \left[\frac{2YR To}{(Y-1)W} \left\{1 - \left(\frac{Pa}{Po}\right)\frac{Y-1}{Y}\right\}\right]^{2}$$

where

specific heat of gas at constant pressure specific heat of gas at constant volume

- 9 -

R = universal gas constant

 $\Psi_{0}$  = stagnation temperature in the combustless chamber

W = mean molecular weight of gas

p<sub>a</sub> = external (atmospheric) pressure

 $p_o = stagnation pressure$ 

This shows that for a high specific impulse, the chamber temperature must be high, the molecular weight of the exhaust gases must be low, and p should be zero, that is the rocket motor should work into a vacuum.

Flame temperature is given by the equation:

 $T_{o} = 2500^{o}K + \frac{E_{2500}}{C_{v}}$ 

where Eggod = energy released at 2500°K (g.cal.g<sup>-1</sup>)

Cv = mean specific heat of gas at constant volume in the range  $2,000 - 3,000^{\circ}K$ 

Tables have been prepared for the many possible constituents of propellants giving  $E_{2500}$  and Cv. Hence  $E_{2500}$  and Cv may be calculated for any given composition by adding the contributions of the separate constituents. That is:

$$E_{2500} = \sum_{a} E_{2500a}$$

$$Cv = \sum_{a} Cv_{a}$$
where x is the weight fraction of ingredient a.

The tables also give individual values for n, the number of moles of gas formed per gram of ingredient. Those data may be added in a similar manner to derive the value of n for the propellant, and this in turn may be used to calculate y from the expression:

$$\gamma = 1 + \frac{nR}{Cv}$$

Measured specific impulse of rocket propellants is usually 90 to 95 per cent of the calculated value. Operational propellants exhibit I values from  $250 \ lb_f \ s.lb^{-1} \ (2450 \ N \ s \ kg^{-1})$  for solids, and up to 400  $lb_f \ s.lb^{-1} \ (3920 \ N \ s \ kg^{-1})$ for cryogenic liquids, with storable liquids in the range 270 to 290  $lb_f \ s.lb^{-1}$ .  $(2650 - 2850 \ N \ s \ kg^{-1})$ . Flame temperatures may be as low as  $1000^{\circ}$ K for liquid monopropellants, but more energetic compositions have flame temperatures in the region of  $3500^{\circ}$ K. Thus assessment of rocket propellants is seen to depend on the application of computational techniques in conjunction with experimental methods such as the strand burner (to measure burning rate) and static proof-testing of small rocket motors (to assess thrust). Several motor sizes are made and fired in the approach to the final motor, and some are subjected to flight-proof firings to test possible solutions to design problems affecting propellant charge or hardware.

Development studies also involve extensive stability and compatibility trials to establish the storage characteristics of the motor, and appropriate hazard appraisal tests are done to assess its safety. This is particularly important for military applications where extremes of climate may be encountered and rough handling, vibration or electrostatic hazards may arise. Mechanical property assessment is also an important feature of solid rocket propellant development, and this is done over a range of temperatures and under various conditions to ensure that no unacceptable physical changes are likely to occur during storage.

## Combustion Processes

Controlled burning of gun and rocket propellants is critically dependent upon maintaining operating pressures (of the order of 1000 lb in<sup>-2</sup> for rockets and 60,000 lb in<sup>-2</sup> for guns) which are relatively low compared with the several million lb in<sup>-2</sup> associated with detonation pressures. Whether nitroglycerine - nitrocellulose compositions are used as propellants (cordite) or high explosives (gelignite) the energy which is released results from the same kind of chemical reactions, but the rate at which the energy is made available is quite different. It is this which distinguishes deflagration from detonation.

The chemical and physical processes which occur during combustion of a solid propellant are very complex but research has led to a qualitative understanding of the mechanisms involved and helped to explain many experimental observations. A great deal of work has been done on nitroglycerine-nitrocellulose systems since these compounds are the basic ingredients of all gun propellants and many rocket propellants.

The initial stages of colloidal propellant combustion involve thermal decomposition of the organic nitrates to form nitrogen dioxide and low molecular weight organic compounds including alcohols and aldehydes. With an increase in temperature exothermic, oxidation-reduction reactions occur between nitrogen dioxide and organic substances to yield nitric oxide, carbon monoxide, carbon dioxide and water. The final phase of this oxidation leads to a burnt gas containing nitrogen, carbon monoxide, carbon dioxide, water and hydrogen in proportions determined by the operational temperature and pressure of the system.

- 11 -

A model which illustrates the physical situation at the surface of burning propellant is shown in Figure  $\frac{3}{4}$ .

Insert Figure # Model illustrating combustion process in a double-base propellant

The temperature profile in Figure 1 gives an indication of the contribution of each reaction zone to the release of energy which results in a final flame temperature of about  $3000^{\circ}$ K. Propellant just below (<u>ca</u>. 0.1 mm) the solid surface is at ambient temperature due to its low thermal conductivity, but molecular decomposition in the "foam" reaction zone increases the temperature to ~  $600^{\circ}$ K. This increases markedly in the "fizz" zone, to  $1500^{\circ}$ K, where about half the total heat evolved by the propellant is liberated. Reaction is completed in the "explosion" zone and the flame equilibrium conditions are established.

The explosion zone is an important feature of the model. This zone moves towards the propellant surface with the same speed (the flame velocity) as the gases move away from it, and the distance between the explosion zone and the propellant surface remains constant. Displacement of the explosion zone towards the surface increases the gasification rate, because more heat is conducted towards the propellant, and the consequent change in flow velocity forces the explosion zone away from the propellant surface.

This model explains the predominant influence of pressure on the burning rate. Increase in pressure decreases the thickness of the flame and fizz zones and the distance between these zones and the propellant surface. Heat transfer to the propellant surface increases as does the rate of the oxidation reactions in the gas phase. Higher initial temperatures also favour higher reaction rates (Figure  $\frac{4}{3}$ ).

Insert Figure &

Relation of burning rate to pressure and temperature for typical propellants

Insert Figure \$

Relation of burning rate and flame temperature to calorimetric value

The effect of composition on burning rate is less straightforward. Clearly, burning rate would be expected to increase with calorimetric value (Figure 3), and any factor which influences heat transfer between the gaseous phase to solid propellant will affect burning. It is this kind of mechanism which may explain the function of lead salts in double-base propellants in producing a "plateau" (burning rate independent of pressure) or a "mera" (burning rate decreases with pressure).

Combustion of composite propellants which consist of a heterogeneous mixture of inorganic oxidiser and organic binder is considerably more complicated. Energy release depends ultimately upon the overall reaction between oxidiser and fuel, but many intermediate steps are involved and the thermal stability of the oxidiser is an important factor. Decrease in oxidiser particle size or the presence of catalysts such as copper chromite enhance the burning rate of composite propellants, and they respond in the same manner as colloidal propellants to changes in temperature and pressure.

## Properties of Propellants Affecting Their Applications

## Gun Propellants

Large quantities of small grains of propellant are required to produce the high mass rate of burning necessary for gun applications. The compositions should be capable of rapid and easy manufacture and the processes should be safe. Safety considerations also extend to the product itself: it should be insensitive to impact, friction and electrostatic spark, and possess reasonable chemical stability. These factors are particularly important in handling, transportation Unfortunately nitrocellulose powders and cordites are adversely and storage. affected by heat and sunlight which promote chemical, and consequently, physical The chemical changes are accelerated by moisture and since cordites degradation. tend to be somewhat hygroscopic, they should be adequately sealed. At low extremes of temperature propellants may become embrittled with adverse effects on gun ballistics; exudation of nitroglycerine on to the surface of the grain may result in "sweating" or "weeping".

With regard to functioning, it is desirable that gun propellants should be ignited readily by the gunpowder priming compositions which are in general use, and that combustion should be regular, with the time to "all-burnt" readily controllable. Combustion products should ideally be free from toxic fumes, although most propellants produce carbon monoxide, and there should be no solid residues which increase gun barrel erosion. The ideal gun propellant would be smokeless and flashless; unfortunately most flash-reducing substances tend to . increase the smoke.

## Solid Rocket Propellants

The large solid propellant grain used to propel a rocket is usually developed for a specific application, and the propellant composition and geometry are "tailored" to meet certain performance requirements. A high release of energy on ignition is often the most obvious requirement and the greater the amount of chemical energy available, the higher will be the combustion temperature and specific impulse. Performance is maximised by producing exhaust gases of low mean molecular weight.

When the propellant undergoes combustion it should burn at an appropriate rate at the chosen operating pressure, and if possible without being affected by temperature. High flame temperatures are desirable, provided they can be tolerated by the hardware. Ease of ignition, relatively low thermal conductivity, and high specific heat all contribute to improved functioning by controlling heat transfer to the grain. In some military applications absence of smoke and flame from the exhaust is desirable, and for guided weapons there should be minimal interference with microwave signals by the exhaust plume.

Physical properties of solid propellants intended for rocket applications are of critical importance. Structural failure of the propellant in a rocket motor will cause serious ballistic malfunction and may even lead to burn-through or pressure bursting of the rocket motor case. The charge must be sufficiently strong (or rubber-like) to withstand changes in temperature due to climatic variations during storage, and to tolerate forces arising from ignition and, pressurisation, and acceleration in flight. Clearly, rocket grains must be free of cracks and voids which might encourage anomalous burning, and the composition should be chemically stable. Polymers chosen as binders for composite propellants should have good low temperature properties, maintaining their rubbery state during low-temperature storage and showing no tendency to "crystallise" with consequent decrease in elongation.

High density is advantageous in rocket changes because it permits a smaller (and lighter) case to be used for the same weight of propellant. For the same reason, that is to save hardware weight, the charge must occupy as much as possible of the motor volume. Case-bonded charges were developed to meet this requirement, but this approach is successful only if the case-bonded propellant is capable of withstanding the forces arising from the difference in the coefficients of expansion of propellant and motor case. If the bond between the propellant and case fails or if the propellant cracks, fresh burning surfaces will be exposed and a pressure burst may occur. Often the motor case is fitted with a rubber-based . "liner" and the propellant should bond well to this.

In the early stages of composite propellant manufacture the ingredients - oxidiser, pre-polymer, curing agent and other constituents - should give a

"processable" mix, that is to say the viscosity of the mixture before cure should be sufficiently low, and its "pot-life" sufficiently long, to ensure that the composition may be thoroughly mixed and cast into the motor whilst still in a liquid state. Reproducibility of propellant properties is assisted if the composition is relatively insensitive to trace impurities or to changes in the supply of raw materials.

Rocket propellants share the same safety requirements as gun propellants with regard to impact, friction and electric spark, but there is an additional feature, namely the risk of self-heating associated with large masses of propellants. Compositions with high autoignition temperatures are safer in this respect, and the incorporation of "stabilisers" into colloidal propellants reduces the likelihood of autocatalytic, exothermic decomposition in these nitrate-ester based mixtures.

## Liquid Propellants

In liquid bipropellant systems it is generally desirable to achieve ignition with minimal time-lag after mixing. Hypergolic systems ignite spontaneously in less than 50 msec, but the components of such systems are often highly reactive chemicals which present severe handling and storage problems. Stability and compatibility trials must be done to select the best materials for construction of tanks, pipes and other structural items, and provision must be made for venting decomposition gas formed during storage. Another factor to be considered is the toxicity of the fuel, oxidiser or exhaust products; personnel may require protective equipment if toxic hazards cannot be avoided. Explosive hazard appraisal is also important, and appropriate drop-weight and card-gap tests are in use for this purpose.

Physical properties such as viscosity, freezing point and melting point all need to be taken into account in selecting liquids for propellant applications. Clearly, low boiling-point liquids require pressurisation and relatively heavyweight tanks. Such weight penalties are minimised by choosing high density liquids whenever possible thus reducing the size of storage containers.

For most practical purposes one of the most significant factors which determines the selection of both solid and liquid rocket propellants is that of cost. Plant-scale manufacture of general-purpose propellants or large rocket motors demands that the ingredients should be readily available and relatively cheap. In practice, compounds which are difficult or expensive to make are rarely used unless they offer significant improvements in performance without prejudicing stability or safety.

- 15 -

#### Solid Propellants

## Colloidal Propellants

The term colloidal propellant is usually applied to compositions based on gelatinised nitrocellulose. In single-base types, or nitrocellulose powders the nitrocellulose is gelatinised with volatile solvents such as ether and alcohol. Gelatinisation of double-base compositions (containing nitroglycerine) or cordites may also be achieved by the action of solvents - acetone or ether-alcohol - or by the action of heat in the presence of a gelatiniser, for instance, carbamite.

It is a characteristic property of all colloidal propellants that the nitrate ester constituents, particularly nitroglycerine, undergo slow, but autocatalytic decomposition even at ambient temperatures. The decomposition products - nitrogen dioxide, nitrous and nitric acids - are absorbed by incorporating stabilising compounds, typically aromatic amines such as carbamite, diphenylamine and 2-nitrodiphenylamine, in the formulation, but the rate at which the stabilisng compound is consumed sets an effective shelf-life on the propellant charge. This is usually predicted on the basis of accelerated ageing tests in which the rate of stabiliser consumption is monitored by periodic analysis employing chromatographic and spectrophotometric techniques.

## Single-base Propellants

Invention of the first smokeless powder is credited to Captain Schultze of the Prussian Artillery in 1864 and his process led to the EC powders produced by the Explosives Company in England in 1882. The advantages of completely gelatinising nitrocellulose were first appreciated by Vieille (1884), and his Poudre B was quickly adopted by the French army for rifle ammunition. Following work by Monroe (1891) and Berdanou (1897), NCT powder, containing 0.5% diphenylamine as stabiliser, was introduced into the American Service during World War I. The propellant, gelatinised with ether-alcohol, was extruded as cord then chopped and dried. It was smokeless but the grains contained residual solvent, were hygroscopic and gave considerable Developments in the US after the war included addition of dibutylmuzzle flash. phthalate and dinitrotoluene to reduce hygroscopicity (NH- or "non-hygroscopic" powders) and of potassium sulphate to reduce muzzle flash (FNH/P- or "flashless, nonhygroscopic" powders). These powders were used extensively in World War II, although it was still necessary to add a supplementary charge of potassium sulphate The compositions have to be made in granular to reduce muzzle flash in big guns. form because they are too brittle to use as cords; however this is often advantageous for filling certain cartridge cases. It is necessary to ensure that the powders are well sealed; this reduces evaporation of solvent trapped in the grains from the manufacturing process and helps to maintain regularity of ballistics.

Single-base powders are less powerful than cordites and burn with a cooler, less erosive flame. Surface moderants such as methyl centralite (dimethyl diphenyl urea) and dibutylphthalate may be introduced to encourage progressive burning - as in the Nobel's Rifle Neonites (NRN) made by Messrs ICI Ltd - and these are particularly useful in ammunition for machine guns where long barrel life and maintained accuracy are essential. Tin (metallic, or as an organic compound) may be incorporated to reduce fouling of the gun barrel, and grains are usually graphited to make them freeflowing (for filling), and to reduce "static" hazard.

More energetic compositions known as Nobel's Nitro-Neonite (NNN) contain up to 8% nitroglycerine, with carbamite as stabiliser in place of diphenylamine. Faster burning powders are obtained by making the grains porous. This is done by incorporating potassium nitrate in the nitrocellulose "dough" then leaching out the salt by soaking or "steeping" the grains in warm water. Alternatively, fast-burning, fibrous powders suitable for shot-guns and small-arms may be made by gelatinising only the surface of the grain.

Single-base powders are manufactured by mixing alcohol-wet nitrocellulose and other ingredients with ether-alcohol solvent in an incorporator. The resulting stiff dough, which varies in colour from yellow to brown, is block-pressed  $(3,000 \text{ lb in}^{-2}, 21 \text{ MN m}^{-2})$  to remove air, then the blocks are placed in press cylinders and

- 16 -

extruded through water-cooled dies at 2,000 - 4,500 lb in<sup>-2</sup> (14 - 31 MN m<sup>-2</sup>) to form solid- or perforated cord of the required diameter. After chopping the strands to grain length, the propellant is dried in warm air, final traces of solvent being removed by steeping in warm water followed by further hot air drying.

A method of manufacture known as the Ball Powder process was developed by the Western Cartridge Company during World War II. Gun-cotton (13.1% nitrogen) is gelatinised with a water-immiscible solvent, then the resulting lacquer is added to water in a stirred pan. When the mixture is warmed to evaporate solvent the globules of lacquer harden and form spheres of nitrocellulose. Gum arabic is added to the water to improve the shape of the spheres of aitrocellulose. Gum arabic is added to the water to improve the shape of the spheres (0.25 to 1 mm diameter), and occlusion of water is minimised by adding sodium sulphate. Nitroglycerine may be incorporated into ball powder at the lacquer stage or subsequently by agitating the "base grain" with nitroglycerine in water at 60°C. Moderants such as dibutylphthalate, carbamite or dinitrotoluene may also be applied to the surface of the base grain to modify its ballistic properties.

## Table I

	Cómposition		% N	Ignition	Temperature	Cal. Val.
Name	% NC	% NC Stabiliser etc.		Temperature	°K	(water liquid)
NCT	99.5	0.5 Diphenylamine	12.6	178%	3014°%	865
NH	86	1 Diphenylamine 3 Dibutylphthalate 10 Dinitrotoluene	13.15	170	2681	770
FNH	84	1 Diphenylamine 5 Dibutylphthalate 10 Dinitrotoluene	13.15	165	2511	750
FNH/P	83	1 Diphenylamine 5 Dibutylphthalate 10 Dinitrotoluene 1 Potassium sulphate	13.15			

Single-base Propellant Compositions

- 17 -

#### Combustible Cartridge Cases

In recent years there has been an interest in making cartridge cases which burn completely before the projectile leaves the muzzle of the gun. Such cases would be lighter and cheaper than conventional brass cases, and there would be no empty case disposal problem. Success has been achieved using a resin-impregnated nitrocellulose kraft paper mixture (2:1), and large cases may be made by a felting and forming technique. These cases have not yet found wide application because there are usage problems connected with maintaining an adequate pressure seal in the breech of the gun. However, they have to some extent replaced "bag" charges for firing "separated" ammunition.

## Double-base Propellants

Early double-base colloidal propellants, for example Mk I cordite were made by mixing dry gun-cotton (13% nitrogen) with nitroglycerine using acetone as gelatinising solvent, with a small proportion of mineral jelly. The latter was added in the belief that it would lubricate the the terms of the gwn, although it was soon found that its chief benefit was to function as a stabiliser, absorbing the acidic decomposition products of the organic nitrates. British Mk I cordite was replaced by cordite MD (modified) (Table II) when it was realized that the high nitroglycerine content (58%) of the former caused 'hot', erosive burning, then, in 1935, Cordite W was introduced to take advantage of the stabilising and gelatinising properties of carbamite. Use of mineral jelly was discontinued.

Another significant development between the two World Wars was the discovery that nitroguanidine or 'picrite' markedly reduced muzzle flash, provided a sufficient amount (~50%) was present in the composition. Such propellants (N and NQ) have a low calorific value (~800 cal g.<sup>-1</sup>), and give combustion gases with a high nitrogen content, both factors contributing to reduced flash. A small amount (0.3%) of potassium cryolite also helps in this respect.

Dry guncotton is a very dangerous material, and nowadays it is handled as an aqueous slurry; this is treated with nitroglycerine, then the mixture is filtered on cloth to give a nitrocellulose-nitroglycerine pulp which is spread out on aluminium trays and dried in hot air. The resulting dough is placed in an incorporator, gelatinised with acetone-water (90:10), then treated with the additional ingredients such as stabiliser. After 4 to 6 hours incorporation the 'paste' is transferred to a press house to be pressed through steel dies at 600 - 1500 lb in<sup>-2</sup> (4 - 11 MN m<sup>-1</sup> forming cords which are cut to length and dried for several weeks at  $40^{\circ}$ C. Residual volatile matter is of the order of one per cent.

- 18 -

Manufacturing time is greatly reduced in the process for making "solventless" cordite (SC and HSC) and the product is not contaminated with solvents. Hot-rolling at  $55^{\circ}$ C replaces solvent gelatinisation, and the disappearance of the fibrous structure of the nitrocellulose is assisted by the presence of carbamite; candelilla wax is also added to aid extrusion. The gelatinised sheets are loaded into presses as discs or "carpet rolls" and extruded at  $70^{\circ}$ C and 7,000 lb in<sup>-2</sup> (48 MN m<sup>-2</sup>) to give gun cordites or large rocket charges (up to 35 cm diameter).

The solventless cordite process is attended by some fire risk during rolling and pressing, and it is customary for the plant to be fitted with drenching devices, and to be operated by remote control. However, use of dry nitrocellulose is avoided, and, since no solvent is used, the final cords require no stoving, and the grains are not subject to shrinkage. Relatively large diameter grains suitable for rocket. applications may be made by this process because no problems of solvent removal arise. The limit on diameter is set by the size of the extrusion presses which are available.

# Table II

Double-base Propellant Compositions

Name		######################################	C	Composition	% N	Ignition	Temperature	Cal.
		NG %	NC %	Stabiliser, etc.	in NC	Temperature . <sup>O</sup> C	or Expression	(water liquid)
Cordite	Mk I	58	37	5 Mineral jelly	13.1	160	3676	1225
11	MD	30	65	5 Mineral jelly	13.1	160	3217	1025
11	N	18.7	19	7.3 Carbamite	13.1	165	2426	755
				54.7 Picrite 0.3 Cryolite 0.2 Chalk		з.		
58	NQ	20	21.5	3.5 Carbamite 54.7 Picrite 0.3 Cryolite 0.15 Chalk	13.1	165	2797	880
88	SC	41.5	49.5	9 Carbamite 0.15	12.2	154	3090	970
5 P	HSC	47	49.5	3.5 Carbamite 0.15 Chalk	12.2	164	3625	1175
Ballist	ite A	39.5	60.5	<b>eo</b>	12.65	. 165	3782	1250
88	E	38	60	0.5 Carbamite 1.5 Potassium nitrate 0.6 Graphite	12.65	-	<b>G</b> 2	

Cast Double-base Propellants

Extrusion pressing of solventless cordite is satisfactory for the manufacture of certain rockets, particularly the 5, 7.5 and 12.5 cm charges used during World War II. However, very massive presses are required to make larger charges, and it is impracticable to exceed a grain diameter of about 35 cm. It was to overcome this limitation that the cast double-base process was developed in the years following the war. In essence this involves filling a mould with pre-gelatinised nitrocellulose powder which is "cured" with nitroglycerine at an elevated temperature (60 - 70°C) for a number of days.

Using this process in conjunction with suitable formers it is possible to mould complex internal grain geometries, and to cast the motor directly into a "beaker" of inhibitor material (for example, cellulose acetate). Inhibition of extruded, often involves solventless cordite is come by pasting on thin layers of inhibitor, a slow and tedious process. A further advantage of the casting technique is that the rocket motor case -

- 20 -

suitably coated internally - can itself be used as the mould in which the charge is cast.

Cast double-base charges are made from a casting powder and a casting liquid. The preparation of the former, which contains 60 - 90% nitrocellulose (12.6% nitrogen), 0 - 30% nitroglycerine, and 10% of other ingredients (stabilisers, ballistic modifier, etc), resembles the manufacture of small, cylindrical grains (~1 mm) of solvent extruded gun propellant. Alternatively the casting powder may be in the form of small spheres, made by the ball powder process. Casting liquid consists of nitroglycerine (65 - 75%) desensitised with a non-explosive plasticiser such as triacetin or diethylphthalate.

The casting powder is first loaded into the mould and evacuated overnight. Casting liquid, also de-gassed in vacuum, is admitted, usually by air pressure, and fill the interstices between the casting powder grains. These swell and coalesce as casting liquid is absorbed, forming a single large grain within the mould. Individual grain boundaries are still visible but in mechanical property tests the final grain behaves as a homogeneous mass. When the curing operation which takes about 3 days at 60°C, is complete, the mould is disassembled, and the grain is finished by sawing to length and machining any features not produced by the mould.

Composite-modified cast double-base propellant is made in a similar way, but higher propellant performance is achieved by incorporating ammonium perchlorate and aluminium into the casting powder.

### Composite Propellants

Composite propellants have three basic components - oxidiser, fuel and binder. Most of them rely on ammonium nitrate or ammonium perchlorate as oxidiser, with aluminium as the preferred fuel if additional thrust is required. A wide variety of organic elastomers and resins have been used to bind the solid ingredients together (Table III) and the binder also serves as a gas-producing fuel. Table III

Types of Propellant Binder and Their Gure Systems

Prepolymer	Curing Agent
Vinyl polyester	Hydroperoxides
Hydroxy-terminated polyesters and polyethers	Isocyanates
Carboxy-terminated polybutadiene	Aziridines, epoxides
Polysulphides	Metal oxide and epoxides
Styrene-butadiene rubbers	Sulphur, and other cure systems
Asphalt ) . Polyisobutylene )	Require no curing

One of the most important properties of composite propellants is their rubbery nature. Expansion and contraction of the charge under changing climatic conditions can be tolerated without cracking, and without separation of the case-bond between propellant and motor case. Moreover, the rubbery nature of the charge enables it to withstand the squeezing action of the rocket case in hot environments - when it undergoes only a relatively small expansion compared with the propellant.

Composite propellants are made by pressing techniques and by cast-and-cure processes. Pressed charges, manufactured by consolidating the ingredients under a pressure of 5 tons in<sup>-2</sup> (80 MN m<sup>-2</sup>) often consist of ammonium nitrate (10 - 35%), guanidine nitrate (60 - 85%) and a rubbery binder, for example epoxy-cured polybuta-diene acrylic acid (PBAA). Their size is limited by the availability of large presses, and the grains are hard and rigid, but rather brittle and temperature-sensitive. They find application in cool, slow-burning power cartridges, and share with double-base compositions the advantage of a clean exhaust.

A thermoplastic binder, usually polyisobutylene, is used in plastic propellant, and no chemical reactions are involved in the processing. Ammonium perchlorate (~85%), milled to a dry powder, is mixed to a dough with polyisobutylene (viscosity  $10^5$  poise) and a small amount of wetting agent. Other ingredients such as ammonium picrate (to moderate the burning rate), or aluminium and combustion catalysts are then incorporated. The propellant is transferred to the cylinder of a hydraulic press and extruded directly into the motor case which has first been coated with an adhesive or bonded to an inert liner. Plastic propellant is cheap and easy to manufacture, and has a very satisfactory burning rate range and storage stability. There is a limit to the size of motors for which it is suitable since plastic flow may occur especially at high storage temperatures.

Propellant compositions based on polymerisable binders are made by mixing the ingredients in a stirred vessel under vacuum. For example, hydroxy- or carboxy-terminated polyester is treated with the appropriate amount of ammonium perchlorate (65 - 75% of the final mix), followed by burning rate catalyst, and aluminium powder (up to 15%), then the mixture is warmed and de-gassed. After adding curing agent (for example, tolylene diisocyanate) to the cooled mix, it is vacuum-cast into the prepared motor case, and converted into a rubbery charge by heating in a curing stove. Removal of the silicohe-coated former from the propellant gives a case-bonded grain with the required burning surface geometry.

# Solid Propellant Performance

Considerable effort has been expended to seek improved oxidisers, fuels and binders for composite propellants. The stoichiometry of balanced combustion is such that the oxygen-carrying component of the system must comprise 70 to 80 per cent of the total weight, and research effort has been primarily directed towards attempts to improve this ingredient.

Calculations of the theoretical specific impulses obtainable from hypothetical propellant systems (Table 222) show that the metal perchlorates or ammonium nitrate give low performance, while ammonium perchlorate is higher, though not in the same range as nitronium perchlorate. Table UNI

# Theoretical Specific Impulses of Hypothetical Belid Propellant Systems (Unmetallized)

Oxidiser	Fuel	Wt % fuel	Specific lbf s lb <sup>-1</sup>	Impulse N s kg-1	Chamber Temp. ( <sup>°</sup> K)	Density (g cm <sup>-3</sup> )
LiClO,	CH	15	234.1	2295.	3060	1.94
4 NH, C10,	CH	9.5	252.8	2479	3018	1.76
4 4 NH. C10,	CH	15	246.5	2417	2950	1.66
4 4 NO_C10,	CH	21	278.6	2732	3603	1.70
2 4 NH, NO_	Polyester	20	202.8	1988	1753	1.51
4 3 NH, ClO,	Polyester	20	237.7	2330	2834	1.73
NO_C10,	Polyester	32	258.0	2530	3375	1.75
NH. C10.	Polyurethane	15	245.2	2405	2912	1.70
NH. C10.	Polysulphide	14	241.9	2372	2926	1.81
NHLCIO4	Double-base	40	250.7	2458	3051	1.73

The great majority of modern, high-performance composite propellants employ ammonium perchlorate as oxidiser. Ammonium nitrate is still used for cool-burning, gasgenerating propellant compositions, and for applications where a smokeless exhaustis required. However, only relatively low burning rates can be achieved with ammonium nitrate, and its use is hindered by the polymorphic transitions which occur in the salt with changes in temperature. The resulting changes in volume, unless they are accommedated by the binder, may have deleterious effects on the case-bond.

A number of oxidisers are known with superior energetics to ammonium perchlorate or too (Table 37), but in general the compounds are too incompatible/hygroscopic for practical application. This is particularly true of nitronium perchlorate, which is energeticall attractive and has a high density, but is extremely hygroscopic. Perchlorates of hydrazine and hydroxylamine have been considered, but they also have shortcomings which hinder their use in real systems.

- 24 -

Provided combustion efficiency is adequate, considerable improvements in specific impulse can be achieved by incorporating light metals or their hydrides in solid propellants (Table 7). These calculations show that about 17 units (lbf s lb<sup>-1</sup>) of specific impulse are gained from aluminium, 27 units from aluminium hydride, 39 units from beryllium, and 57 units from beryllium hydride.

又 Table 的

1

.

Properties of Some Solid Oxidisers

	KNO3	NaNO3	NH4NO3	NH4ClO4	NO2CIO4	N2H5C104	N2H6(C104)2	NH_OHC104
Oxygen, wt. % H., kcal mole <sup>-1</sup>	47.47 -417.76	56.47 -111.54	59.96 -87.27	54.5 -70.73	_ 66 +8.88	48.3 -42.5	54.9 -70.1	59•9 -66•5
H, kcal atom oxygen-1	- 39.3	- 37.2	-29.1	-17.7	+1.5	-10.6	- 8.8	-13.3
Density, g cm <sup>-3</sup>	2.109	2.261	1.725	1.95	2.22	1.939	2.2	(2)
Melting point, °C	333	310	169.6	5000		137	2000	81
Decomposition temp., °C	3 400	380	210	270	120	145	170	180
Molecular weight	101.11	85.01	80.05	117.5	145.47	132.51	232.98	133.5

- 26 -

Table VI

Theoretical Specific Impulses of Hypothetical Solid Propellant Systems (Metallized)

Additive (wt. %)	Binder (wt. %)	Oxidiser	Specific lbf s lb <sup>-1</sup>	Impulse Nskg <sup>-1</sup>	Chamber Temp. ( <sup>°</sup> K)	Density (g cm <sup>-3</sup> )
	CH <sub>2</sub> (15)	NH4C104	246.5	2417	2950	1.66
A1 (19)	сн <sub>2</sub> (15)	11	264.1	2590	3179	1.74
A1H <sub>3</sub> (34)	СН <sub>2</sub> (15)	8.8	274.2	2689	2546	1.53
Be (12)	СН <sub>2</sub> (15)	15	285.6	2800	3172	1.66
BeH <sub>2</sub> (25)	CH <sub>2</sub> (20)	88	304.0	2981	2644	1.14

Beryllium is more effective than aluminium by virtue of its exceptionally high heat of combustion per unit of weight. However, beryllium and certain of its compounds are highly toxic, and the formulation and testing of berylliumcontaining propellants present formidable problems. Most practical high-energy compositions contain aluminium.

Choice of binder also affects propellant performance, as well as determining the physical characteristics of the charge. Hydrocarbon binders or polymer systems which do not contain appreciable amounts of oxygen, for example polyurethane or polysulphide are preferred. Weakly-bound oxygen, found in the organic nitrates of double-base systems, is acceptable, but performance is somewhat lower if the oxygen is bound directly to carbon as in a polyester.

Ballistic performance, in terms of delivered energy and burning rate, is by no means the only criterion influencing the composition of a solid propellant. Other factors include the size and chemical stability of the charge, and its ability to withstand extremes of temperature and rough handling, and the forces of ignition and acceleration. Improved physical properties are favoured by reducing the solids loading (at the expense of performance), controlling the particle size of the solids to permit optimum packing, and by improving the binder-filler bond (for example, by adding "bonding agents") and the physical properties of the binder itself.

Lightly cross-linked, high molecular weight (3000 to 5000) polymers with a fairly broad molecular weight distribution are generally used for solid propellants. A broad distribution helps to maintain physical properties over

- 27 -

a wider temperature range, although low molecular weight material is best avoided, this may result in low strengths. Low-temperature physical properties are often improved by incorporating organic esters (for example, dioctyl adipate) as plasticisers. The level of chemical reactivity between the pre-polymer and the curing agent should be low enough to give a reasonable "pot-life" without being so low that additional cross-linking takes place during storage; such "post-cure" may cause changes to occur in physical properties.

Since

Representative performance characteristics of the major classes of solid rocket propellants are given in Table VII. Choice of propellant for a particular application depends upon numerous factors, not least being the question of safety both during manufacture and in use.

Table VII

Performance Characteristics of Solid Propellants

Type of propellant		CDB	С	HEC	CMDB
20 P Q Q D T C	$(lbf s lb^{-1})$	170-220	170-230	240	260
Specific impulse	(N\$skg <sup>-1</sup> )	1670-2160	1670-2260	2350	2550
Burning rate (mm	s <sup>-1</sup> )	5-20	1.5-35	5-35	8-25
Flame temp. ( <sup>o</sup> K)		1900-3000	1400-3000	3000-3800	<b>Over</b> 4000
Density (g cm <sup>-3</sup> )		1.50-1.63	1.58-1.77	1.66 400000000000000000000000000000000000	

CDB	cast double-base	
С	composite	
HEC	high energy composite	
CMDB	composite-modified dou	ble-base

## Liquid Propellants

## Monopropellants

Choice of liquid monopropellants is restricted to fluids which are stable at storage temperatures but are capable of undergoing exothermic decomposition to yield gaseous products at a rate suitable for rocket applications. Moreover, safety considerations limit the choice to relatively low impulse substances since, at a given level of energy, liquid explosives are much more hazardous than solids. Nevertheless monopropellant rocket motors have several advantages compared with bipropellant systems, particularly with regard to hardware requirements and operational simplicity. Altman (1960) distinguished three classes of monopropellant.

Class A - This class, in which oxidiser and fuel are in the same molecule, is exemplified by nitromethane  $(CH_3NO_2)$ , ethyl nitrate  $(C_2H_5ONO_2)$ , isopropyl nitrate  $(C_3H_5ONO_2)$ , ethylene oxide  $(C_2H_4O)$ , and hydrogen peroxide  $(H_2O_2)$ .

Class B - Compounds in class B have positive standard heats of formation, and decomposition energy is released when their atoms re-combine to form more stable molecules. Hydrazine  $(N_2H_4)$  is a well-known example.

Class C - Stable mixtures of fuel and oxidiser are grouped in class C. Mixtures which have been considered include methyl nitrate-methanol (Myrol), hydrogen peroxide-methanol, and tetranitromethane-fuel (for example, benzene). However such mixtures are generally too sensitive to be recommended as monopropellants.

## Hydrogen peroxide

Hydrogen peroxide is used in the form of high-test peroxide (HTP), a 90 per cent strength solution obtained by fractional distillation in vacuo. In use, HTP is decomposed catalytically (samarium oxide-coated silver screen) into superheated oxygen gas and water vapour.

$$H_2O_2(1) \longrightarrow H_2O(g) + \frac{1}{2}O_2 + 12.96$$
 kcal

The theoretical chamber temperature and specific impulse for 100% hydrogen peroxide are  $1250^{\circ}$ K and 146 lbf s lb<sup>-1</sup> (1432 N s kg<sup>-1</sup>) (20 to 1 pressure ratio) respectively. Presence of water lowers the chamber temperature (320°K decrease for 13% H<sub>2</sub>0), and this is advantageous for gas-generator applications requiring a cool clean exhaust. Further advantages of HTP include its high density (1.39 g cm<sup>-3</sup>) and ease of ignition. Its chief disadvantage is its thermal<sup>jn</sup> tability and tendency to react with many metals to form oxides which catalyze the decomposition reaction. Even contamination by atmospheric dust may be sufficient to promote rapid, exothermic decomposition. The liquid is usually stored in vented aluminium containers, thoroughly cleaned and pre-conditioned by treatment with concentrated nitric acid.

An early use of HTP for military purposes was in the German V-2 rocket during World War II. Alcohol and liquid oxygen were employed as the main propulsion system, and these liquids were fed into the combustion chamber by turbine-pumps driven by hot gases from hydrogen peroxide decomposition.

# Isopropyl nitrate

Isopropyl nitrate (IPN) undergoes exothermic decomposition over chromic oxide (pre-heated) to yield hot gases consisting mainly of carbon monoxide, carbon

dioxide, nitrogen and steam. The gases are used to drive a turbine for an engine starter system in which IPN is decomposed on an electrically pre-heated catalyst bed. IPN is a stable liquid and may be stored in mild steel vessels.

## Hydrazine

Hydrazine has two modes of thermal decomposition:

 $3 N_2H_4 \rightarrow 4 NH_3 + N_2 + 80.15 \text{ kcal}$  $4 NH_3 \rightarrow 2 N_2 + 6 H_2 -44.00 \text{ kcal}$ 

Dissociation of ammonia is negligible below  $400^{\circ}$ K but is almost complete at  $800^{\circ}$ K. Specific impulse remains nearly constant over the range 0 - 50% ammonia dissociated because the decomposition of ammonia produces hydrogen, and the average molecular weight of the exhaust gases decreases about as rapidly as the decrease in combustion temperature. Optimum specific impulse at low combustion temperatures is obtained in the range 30 - 50% ammonia dissociated.

Hydrazine has a fairly high freezing point (1.4°C) but this may be lowered by admixture with monomethylhydrazine (MMH) or unsymmetrical dimethylhydrazine (UDMH).

## Bipropellants

Since the qxidiser and fuel components of bipropellant systems are stored separately it is possible, in principle, to consider using much more energetic substances. However, availability and cost have to be considered as well as high energy, and shortcomings in performance can generally be overcome by suitable design. One of the most successful design features is the multi-stage rocket. This allows more efficient utilization of propellant by ensuring that the cases of empty, burnt-out motors are discarded in flight, and do not add dead-weight to the payload. Recent space projects have generally relied on liquid propulsion in conjunction with multi-stage rockets, and relatively cheap combinations such as liquid oxygen and kerosene are widely used, particularly in first-stage motors.

Theoretical studies show that specific impulse is enhanced if oxidiser and fue react to produce more heat or if the mean molecular weight of exhaust products is decreased. Only low atomic weight elements and their compounds provide useful combinations and, for oxidisers, the choice is limited to Group VI and VII elements oxygen and fluorine, and to compounds of these elements with carrier atoms such as nitorgen or chlorine. Commonly-used oxidisers for rocket applications include liquid oxygen, hydrogen peroxide, nitric acid and dinitrogen tetroxide. The high performance potential of liquid fluorine is well-known, but its use is still in an experimental stage due to its hazardous nature. Research on more advanced oxidisers has been much concerned with the chemistry of fluorine-based compounds, particularly those containing O-F, Cl-F and N-F bonds. The aim has been to make compounds with weakly-bound fluorine, and to take advantage of the high heats of combustion which are the nett result of breaking weak valency bonds and forming strong bonds (Table  $\frac{VIII}{WUX}$ ). However, the compounds which have been investigated are generally too unstable or too explosive for practical purposes.

Table VIII

Average Bond Energies (kcal mole<sup>-1</sup>)

Desirable in oxidisers	F-F 38	0-0 37
	0-F 50	N-0 48
	C1-F 45-60	C1-0 48
м, s	N-F 66	
Morginal value	P-F 65-119	
Marginal Vario	S-F 67- 86	s-0 60-80
Underinable in oxidisers	C-F 115	C-0 81
Undebilable in oxiderour	Si-F 132	P-0≯80
1 .		07
Desirable. in products	H-F 134	Li-0 85
	Li-F 137	B-0 109
	A1-F 140	H-0 110
	Be-F 149	Be-0 118
	B-F 154	Al-0 168

Choice of fuels is also restricted by atomic weight considerations to members of the first and second periods of Groups I to IV. Conventional liquid fuels are usually based on compounds containing C-H or N-H bonds such as kerosene, alcohol, aniline, and methylhydrazine. Boron hydrides and their derivatives compounds with much higher heats of combustion than hydrocarbons - have also been considered, but the fuels are toxic and air- and moisture sensitive. Moreover, the formation of boric oxide as a combustion product creates difficulties in engine design.

Liquid hydrogen is outstanding as a high performance liquid fuel, apart from its low boiling point  $(-252.8^{\circ}C)$  and low density  $(0.07 \text{ g cm}^{-3})$ . A very high specific impulse is obtainable in combination with liquid oxygen, but this is offset by the additional structure weight and aerodynamic drag associated with the larger vehicles required to carry the low density fuel. This means that the advantages of using liquid hydrogen are best realised in applications outside the Earth's

- 31 -

atmosphere; for instance, in the upper stages of space rockets. Evaporation losses from liquid hydrogen are minimised by storing the fuel in the para form.

Theoretical specific impulses of conventional liquid systems which involve only the elements C, H, O and N, range from 150 lbf s lb<sup>-1</sup> (1470 N s kg<sup>-1</sup>) for 90 per cent hydrogen peroxide, up to 300 lbf s lb<sup>-1</sup> (2940 N s kg<sup>-1</sup>) for liquid oxygen-kerosene (Table WWWA). The highest performing members of the storable bipropellant group are combinations of dinitrogen tetroxide and hydrazine derivatives, and to achieve higher specific impulses it is necessary to use the cryogenic oxidiser, liquid oxygen. IX

Table 1

# Theoretical Performance of Liquid Propellant Systems

Propellant		Density	Specific	impulse	Flame temperatur		
		g cm <sup>-3</sup>	lbf s lb <sup>-1</sup>	Nskg <sup>-1</sup>	°ĸ		
Monopropellants					4070		
90% H <sub>2</sub> 0 <sub>2</sub> N <sub>2</sub> H <sub>4</sub>		1.39 1.01	151 191	1481	890		
Storable bipropellants							
90% H_0_/JP-4		1.29	, 266	2608	2800		
WFNAª/ JP-4		1.33	268	2628	3230		
IRFNA/ MAFD		1.31	270	2648	3030		
IRFNA/ UDMHC		1.25	277	2716	3230		
N O. /50% N.H. + 50% Me	NH	1.21	288	2824	3360		
N <sub>2</sub> O <sub>4</sub> /MeN <sub>2</sub> H <sub>3</sub>	2	1.21	288	2824	3370		
Cyryogenic bipropellant	3						
0./EtOH (92.5%)		0.99	287	2814	3370		
2 /RP-1	1	1.02	301	2952	3650		
02/H2		0.28	391	3834	3010		
Advanced cryogenic big	propellants						
(30% F_)FLOX <sup>d</sup> /RP-1		1.09	321	3148	3980		
OF_/RP-1		1.34	350	3432	4350		
OF /MeN_H_		1.25	351	3442	4350		
OF /B H.		0.87	364	3569	3970		
2 2 6 F /N H		1.31	364 -	3569	4640		
F2/H2 F2/H2	e i	0.46	410	4021	3950	•	

aWFNA = White fuming nitric acid

b IRFNA/MAF = Inhibited red fuming nitric acid/mixed amine fuel

c<sub>UDMH</sub> = <u>unsym</u>-Dimethylhydrazine

d<sub>FLOX</sub> = Liquid fluorine/oxygen

#### Oxidisers

X

Table 14

The properties of some conventional liquid oxidisers based on oxygen are shown X in Table 22 together with those of more advanced oxidisers, including fluorine.

Physical and Thermodynamic Properties of Liquid Oxidisers

		MP	BP	Density			∆ Hf		
Compound	Formula	°C	°c -	State	g cm <sup>-3</sup>	°C	State	kcal mole-1 at 25°0	
Ovygen	0	-218.4	-183.0	(1)	1.142	-182	(g)	0	
Hydrogen peroxide	H <sub>2</sub> O <sub>2</sub>	-0.41	150.2	(1)	1.463	20	{ (g }	-32.5	
Nitric acid	HNO	-42	86	(1)	1.502	25	-\is	-41.4	
Dinitrogen tetroxide	N204	-11.2	21.2	(1)	1.45	20	(g) (l)	2.3 0 <sup>±</sup> 0.5	
Fluorine	F2	-223	-188	(1)	1.50	-188	(g) (l)	-3.0	
Chlorine trifluoride	CIF3	-83	11.3	(1)	1.809	25	{(g) (1)	-39 <sup>±</sup> 1 -44.4	
Oxygen difluoride	QF2	-223.8	-144.8.	(1)	1.528	-147.3	(g)	8	

## Liquid Oxygen

Liquid oxygen is produced very cheaply by fractional distillation of liquid air. It is a very efficient liquid oxidiser on a weight basis and is non-toxic and noncorrosive. One disadvantage is that it is highly reactive with most organic materials and therefore constitutes a serious fire hazard. Oxygen equipment must be kept clean and free of contaminants, and personnel wear goggles and leather gloves when handling the liquid to avoid low temperature "burns".

#### Hydrogen Peroxide

Because of its tendency to undergo slow decomposition hydrogen peroxide has found little application as a bipropellant oxidiser. It is however employed as a monopropellant and gas generator.

#### Nitric Acid

Nitric acid is a widely-used, storable liquid oxidiser which is cheap and readily available. It is generally used in two forms: white fuming nitric acid (WFNA) containing less than 2% water, and red fuming nitric acid (RFNA), consisting of nitric acid with about 14% dissolved nitrogen dioxide; the colour of the latter may be orange or dark red. Both forms may be treated with 0.5% hydrofluoric acid to reduce the corrosivity of the acid and to permit long term storage in aluminium or stainless steel tanks (Table  $\frac{XI}{4}$ ).

# Table XI

Specifications for Nitric Acids

Weight %	WFNA		RFNA	
	I	IA	III ·	IIIA
HNO_	97.4 min	96.6 min.	82.4 - 85.5	81.6 - 84.9
3 H_O	2.0 max	2.0 max	1.5 - 2.5	1.5 - 2.5
NO	.5 max	.5 max	14 = 1	14 = 1
2 Solids as nitrates	.1 max	.1 max	.1 max	.1 max
HF	613	.7 ± .1		.71

Concentrated nitric acid is very reactive and corrosive; there is a fire hazard with many organic substances including wood. Protective clothing has to be worn when the liquid is being handled, and gas masks with self-contained air supplies are often used.

# Dinitrogen Tetroxide

Dinitrogen tetroxide has been used in combination with hydrazine for rocket applications including the US Titan rocket. The oxide exists as  $N_2O_4$  in the solid state but partial dissociation to  $NO_2$  occurs in the liquid, and the equilibrium moves further in the direction of  $NO_2$  in the vapour state; at 100°C the mixture is 90%  $NO_2$ . The oxidiser is very toxic and inhalation of vapours is a serious hazard. A further disadvantage is that the liquid has a fairly high freezing point (-11.2°C); this may be lowered by adding nitric oxide, but 25% NO is required to reduce the freezing point to  $-55^{\circ}C$ .

## Liquid Fluorine

Reaction of fluorine with hydrogen to produce hydrogen fluoride gives theoretical specific impulses over 400 lbf s lb<sup>-1</sup>, and this is a very significant improvement over conventional systems. However, fluorine is the most reactive element known, and its use presents severe handling and compatibility problems. Even the protective clothing which is essential when dealing with this very corrosive and toxic substance may be attacked. Several materials are available however for storing and handling liquid fluorine: metals such as "Monel", 18-8 stainless steel, and aluminium 61 have been used for storage tanks, and polymers of the "Kel-F" and "Teflon" types are suitable as valve packings. At present it appears that fluorine will only be used for special applications where high performance is critical.

## Chlorine Trifluoride

Chlorine trifluoride resembles fluorine in being highly reactive and very toxic. Most metals are corroded although several, including Monel and nickel, form protective fluoride films which protect the metal even at elevated temperatures. The problems of handling and transporting this oxidiser are reduced to a slight extent because it may be treated as a non-cryogenic liquid.

### Oxygen Difluoride

Oxygen difluoride is also very reactive and extremely toxic. Its chemical behaviour is similar to fluorine in most respects, although it is somewhat more compatible with organic substances because its reactions involve higher energies of activation.

### Fuels

A wide range of compounds have been employed as fuels, although the majority contain C-H or N-H bonds (Table 32).

## Table XII

Physical and Thermodynamic Properties of Liquid Fuels

Compound	Formula	MP C	BP °C	Density			AHf	
				State	'g cm <sup>−3</sup>	°c	State	kcal mole <sup>-1</sup> at 25°C
RP-1	Hydrocarbons	-49	160-299	(1)	0.806	15	(1)	-5.9
Ethyl alcohol	C2H5OH	-117.3	78.5	(1)	0.789	20	(g)	-50.2
Aniline	C_H_NH	- 6.2	184.32	(1)	1.022	20	(1)	8.3
Ammonia	NH 3	- 77.7	-33.4	(1)	0.817	-79	$\frac{j(g)}{l(1)}$	- 11.0 - 16.6
Hydrazine	N2H4	1.4	113.5	(1)	1.011	20	<b>ξ</b> (g) <b>ζ</b> (1)	22.8 12.0
Unsym-Dimethyl hydrazine	(CH <sub>3</sub> )2 <sup>NNH</sup> 2	57.8	63	(1)	0.790	15.6	(1)	' 12.7
Diborane	<sup>B</sup> 2 <sup>H</sup> 6	-165.5	-92.5	(1)	0.447	-112	<b>(</b> (g) (1)	7.5
Hydrogen	Н2	-259.14	-252.8	(1)	0.071	-252.7	{(g) (1)	-2.0

#### Hydrocarbon Fuels

Petroleum fractions selected on the basis of low volatility and freezing point, and high flash point, are among the cheapest and most widely used fuels for jet or liquid rocket engines. Specifications for these complex mixtures usually refer to

- 36 -

boiling range, density, heating value and limits of composition. Examples include JP-4 which contains 25% aromatics (by volume) and boils over the range  $93 - 288^{\circ}C$ , and HP=4 beiling from 160 - 299°C (Table 2007). These fuels give specific impulses of about 300 lbf s lb<sup>-1</sup> (2940 N s kg<sup>-1</sup>) with liquid oxygen. This is rather lower than the theoretical performance obtainable from lower molecular weight hydrocarbons  $(C_1 - C_4)$  or from olefins  $(C_2 - C_3)$ , but the former are cryogenic, and the latter tend to polymerize on storage.

Table XIII		
Typical Data for Petroleum Fuels		
Distillation	JP-4	RP-1
10% ( <sup>°</sup> C)	102	199
50% ( <sup>°</sup> C)	159	219
`90% ( <sup>°</sup> C)	218	242
Volume %		
Aromatics	25	5
Olefins	5	1
Flashpoint (°C)	-74	> 44
Freezing point (°C)	< -60	-49
Viscosity at -40°C (centistokes)	. 3.5	13.8
H combustion (kcal g <sup>-1</sup> )	10.39	10.38
Density at 15°C (g cm <sup>-3</sup> )	0.773	0.806

The higher boiling point petroleum fractions have excellent handling and storage characteristics, and JP-4 and RP-1 are standard fuels for jet aircraft and rockets respectively.

#### Ethyl Alcohol

Both ethyl and methyl alcohol were used in early liquid rocket engines; the German V2 missile was propelled by ethyl alcohol-liquid oxygen, a combination with a theoretical specific impulse of 287 lbf s  $lb^{-1}$  (2814 N s kg<sup>-1</sup>). Petroleum fractions and hydrazine-based compounds have now replaced these relatively low density fuels.

## Aniline

Aniline reacts spontaneously with fuming nitric acid and this bipropellant system has been used in several rockets. For example the US Army "Corporal" was propelled by red fuming nitric acid and a fuel consisting of equal parts of aniline and furfuryl alcohol with 7% hydrazine. Aliphatic amines such as methylamine have been employed as fuels occasionally for special applications, but hydrazine and unsym-dimethyl hydrazine (UDMH) are generally preferred for their higher performance.

## Liquid Ammonia

Ammonia is the simplest of the N-H type fuels, but the compound has not been used extensively for rocket applications because the liquid has a very high vapour pressure. It was used in combination with liquid oxygen in the US X-15 rocket research aircraft.

# Hydrazine and unsym-Dimethyl hydrazine

A high density and an absence of carbon contribute to the high performance potential of hydrazine, but its freezing point is unsuitable. In practice the compound is usually mixed with UDMH to lower the freezing point with minimal loss of performance. A typical mixture is Aerozine-50 - a 50/50 blend of hydrazine and UDMH, used in combination with dinitrogen tetroxide in the US Titan missile. These amine fuels, hydrazine, UDMH and Aerozine-50, are insensitive to shock, but hypergolic (autoigniting) with several rocket oxidisers. They are generally employed in conjunction with nitric acid or dinitrogen tetroxide, whereas liquid hydrogen and hydrocarbon fuels are often combined with liquid oxygen.

Amine fuels are strong bases and reducing agents with characteristic fishy odours. Even low vapour concentrations of hydrazine and its derivatives are highly toxic, and strict protective measures are necessary when handling the fuels. Ammonia is stable, but hydrazine undergoes catalytic decomposition, and UDMH is susceptible to slow air oxidation. Several types of aluminium, stainless steel and nickel are suitable for use with hydrazine, and these are also satisfactory for UDMH. A wide range of non-metallic materials are also available, including Teflon, Kel-F and polythene.

Mixed amine fuels (MAF) may contain several constituents. For example, MAF-1, used in the US Bullpup engine, consists of 50.5% diethylenetriamine (DETA), 40.5% UDMH, and 9.0% acetonitrile.

## Diborane

Diborane  $(B_2H_6)$  is the simplest borane, a group of boron hydrides which includes pentaborane  $(B_5H_9)$ , boiling point 58°C, and decaborane  $(B_{10}H_{14})$ , a solid melting . at 99.5°C. The compounds offer promise of high performance, but they are costly and toxic, and some are very reactive towards air and water; diborane and pentaborane ignite spontaneously in air. A great deal of work has been done on these fuels in recent years, but their practical usage remains a difficult problem.

## Liquid Hydrogen

Liquid hydrogen is an extreme fire hazard, forming explosive mixtures with air,