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Ammonium Perchlorate Composite Basics

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ABSTRACT

This article addresses the theory and design of Ammonium Perchlorate / Hydroxyl-terminated Polybutadiene (AP/HTPB) composite propellant rocket motors. A discussion of the operating principles of solid motors, including motor dynamics, the combustion process of AP composite propellants, and basic nozzle theory is presented. Several grain geometries and thrust profiles are illustrated, and requirements for various casing, nozzle and adhesive materials are compared. The propellant system itself, consisting of oxidizer, binder and fuels, plasticizers, bonding agents and burn rate modifiers, is described.

Key Words: composite propellant, ammonium perchlorate, AP, specific impulse, grain geometry, HTPB, hydroxyl-terminated polybutadiene, nozzle expansion ratio, chamber pressure

Introduction

Propellants function to impart motion to an object through the conversion of potential energy into useful or kinetic energy. Two ingredients, a fuel and an oxidizer, neither of which will burn satisfactorily without the presence of the other, are necessary in a propellant system. Two main classes of propellants are recognized on the basis of physical character: liquid propellants and solid propellants. Most solid propellants belong to one or the other of two types. Homogenous propellants contain both the oxidizer and fuel in the same molecule and may also be referred to as monopropellants. These systems, consisting mostly of nitrocellulose and nitroglycerin in a colloidal mixture, are called double-based propellants. The second type is the heterogeneous or composite propellant, where the oxidizer is a finely ground inorganic salt and the fuel is plastic in nature, binding the propellant grain structure together. Black powder, the oldest of propellants, falls into this category since it uses potassium or sodium nitrate as the oxidizer and sulfur as both binder, and with charcoal, as a fuel.

Modern composite propellants first emerged in the late 1940's. These incorporate various thermoplastic and thermosetting resins or elastomers with a variety of nitrates or perchlorates as oxidizers. Perhaps the most popular of the composite propellant systems in current use consists of ammonium perchlorate, NH_4ClO_4, as the oxidizer and usually a copolymer or terpolymer of butadiene with other monomers such as acrylic acid or acrylonitrile as the binder. This article will examine the design and construction of composite propellant rocket motors using hydroxyl terminated polybutadiene (HTPB) and ammonium perchlorate (AP).

Operating Principles of Solid Propellant Rockets

As solid propellants have certain advantages over liquid propellants, composites may be more desirable for some applications than the familiar black powder formulations. All solid propellants possess a high degree of reliability by virtue of design. Once ignited, a solid rocket normally operates according to a preset thrust program, which is primarily determined by the configuration of the propellant grain. The amount of thrust which may be obtained from a given grain design is largely determined by the propellant composition.

Composite propellants burn at higher temperatures and pressures than black powder, with a net result that pound for pound, they can deliver about two and one half times the power of a black powder motor.

Propellant Characteristics

Fundamental to the design of any solid propellant rocket is a simple geometric principal: The burning surface of a solid propellant recedes in parallel layers. Because of this, solid motors are self-stabilizing. That is, should small convex or concave irregularities arise on the burning surface, as would happen if an air bubble was trapped in the propellant grain, such irregularities would disappear as burning proceeds. This is significant because as bubbles are encountered, the burning surface of the propellant and consequently the internal pressure of the motor and the burn rate of the propellant are increased. When this exceeds the design parameters of the motor, rapid overpressurization occurs, leading to a catastrophic failure.

The burning rate, r, of a solid propellant is the linear rate of propellant consumption in a direction normal to the burning surface. It typically ranges from 0.1 to 2.0 inches per second and is primarily influenced by the combustion pressure, P_c; propellant composition; and to a lesser degree by the ambient grain temperature and the velocity of gas flow past the burning surface. Burning rate may be expressed by the following equation:

$$r = aP_c^n \qquad \text{Equation 1}$$

The burning rate, r, is in inches per second; the pressure of combustion is in pounds per square inch; and a and n are constants. Propellant composition and pre-ignition temperature are the determinants for the value of the constant a, which ranges between .002 and .05. The pressure or burning rate exponent n is solely a function of the propellant formulation with negligible influence of the bulk temperature. Typical values for the burning rate exponent range from 0.2 to 0.5, but in some cases may vary between 0 and 0.9. The burning rate exponent is of critical importance in maintaining the stable operating pressure of any rocket motor.

During combustion, a rocket functions in a state of dynamic equilibrium. A stable operating pressure is maintained by a delicate balance between the rate at which gas is being generated by the burning propellant and the rate at which it is being expelled through the nozzle. This is effected by an area ratio between the propellant burning area and the nozzle throat area. This area ratio; K_n, where:

$$K_n = \frac{A_b}{A_t} \qquad \text{Equation 2}$$

and the specific formulation of a propellant and its burning rate exponent, will determine the operating pressure of a given motor. The relationship between the K_n and operating pressure of a given motor is expressed by the equation:

$$P = B\left(K_n\right)^{\frac{1}{1-n}} \qquad \text{Equation 3}$$

where P is the pressure in pounds per square inch, B is a constant for a specific propellant, and n is the same pressure or burning rate exponent as appears in the burn rate equation (Equation 1). Small changes in the value of n can lead to significant changes in the operating pressure of a rocket motor and consequently in the propellant's burn rate which was shown in Equation 1 to be pressure dependent. If n is 0.3, $(1-n)$ is .7 and $1/(1-n)$ is 1.42. A 20% increase in burning area would cause a 30% increase in pressure. But if n should be 0.8, $(1-n)$ is .2, and $1/(1-n)$ would be 5. For such a propellant, that same 20% increase in burning area would cause a 148% increase in pressure. It becomes evident that propellants with high exponents are to be avoided, as small variations in the burning surface such as when bubbles become trapped within the propellant grain or cracks are present in the grain, lead to greatly magnified variations in chamber pressure.

Specific Impulse

The quantity of energy available from a rocket propellant is determined by the chemical nature of the oxidizer and fuel molecules, as well as by the chemical nature of the reaction gas products. This is most conveniently expressed as specific impulse, I_{sp}, which is an effective measure of the performance of various propellant systems compared to one another. The higher the I_{sp} value, the more efficient the propellant. Specific impulse may be considered to be the amount of thrust which is available for each pound per second of propellant burned. It is the reciprocal of the specific consumption of propellant and is expressed in pounds of thrust per pound of propellant used per second. This is found by dividing the thrust, or total impulse (I_t) by the weight flow rate expressed in pounds.

$$I_{sp} = \frac{I_t}{W_t} \qquad \text{Equation 4}$$

The range of specific impulse for most ammonium perchlorate composite propellants may vary from near 170 to approximately 230, with a common figure around 200. In comparison, the I_{sp} of black powder is between 70 and 80, roughly two and one half times less than that of a composite propellant.

The total impulse of a rocket motor describes the total amount of energy stored in that motor. Thus, if it contained two pounds of propellant with an I_{sp} of 210, the total impulse would be: $I_t = I_{sp} \times W_t$ = 210 sec. × 2.0 lbs = 420 lb-sec. Depending on the grain design, this motor would be capable of producing 420 pounds of thrust for 1 second, 105 pounds of thrust for 4 seconds, or any combination of thrust × time which would come out with a product of 420 lb-sec.

Motor Dynamics

Regardless of the propellant system used or the I_{sp} of a given propellant, the design of a nozzle is a fundamental criterion in the construction of a rocket motor. The rocket nozzle functions to transform the heat energy of combustion into the kinetic energy of a high velocity gas stream with the maximum possible efficiency. Nozzle theory is based upon the laws of thermodynamics, gas dynamics and fluid dynamics. A basic understanding of nozzle function is of paramount importance to the proper design of rocket motors. Derivations and discussion of the fundamental laws pertaining to the conservation of matter and energy, and of the dynamic processes involved, are presented in depth in the proper texts for the interested reader to pursue. The following discussion of combustion process and nozzle theory will provide the basis for general understanding.

Combustion of Composite Propellants

The combustion of composite propellants occurs in different phases, with the oxidizer particles decomposing in the midst of the decomposing fuel matrix. Ammonium perchlorate itself does not melt, but rather undergoes an exothermic decomposition resembling that of homogenous propellants. Adjacent streams of fuel-rich and oxidizer-rich gasses rise from the surface, and immediate reaction is not possible until mixing by diffusion is complete. The combustion process takes place in three distinct zones, the foam, fizz, and flame zones. At the combustion surface, the gas velocity is relatively small and possesses little kinetic energy. It is in the flame zone that the final reaction occurs and the majority of the heat and gaseous products are evolved. There, the high pressure of the expanding gasses forces the gas particles to the rear, causing a slight decrease in potential energy at the nozzle entrance, but an increase in velocity.

Nozzle Theory

There are three basic types of rocket nozzles: subsonic, sonic, and supersonic. It is the supersonic nozzle which is of interest, consisting of three parts; a convergent section, a throat of specific diameter and therefore area, and a divergent section. Nozzles of this type are often called DeLavel nozzles, after their inventor, and may be thought of as two cones

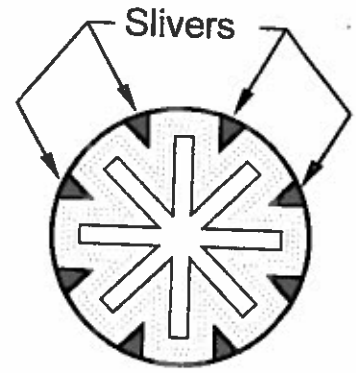
joined at their vertices by a short, straight throat section, with all transitions being smooth so as to avoid disturbances in gas flow.

When gas enters the converging portion of the nozzle, the decreasing cross-sectional area causes the flow to speed up. The maximum velocity which can be obtained in the converging portion of the nozzle occurs at the throat, and corresponds at that section to the local sonic velocity. In practice, this will not occur unless the ratio of chamber pressure to throat pressure reaches a certain minimum value, the critical pressure ratio, which corresponds to thirty-two pounds per square inch absolute or twice the ambient atmospheric pressure. Once this chamber pressure has been reached, the velocity of gas at the throat will always correspond to the critical throat velocity regardless of further chamber pressure increases.

Once the exhaust gas has reached sonic velocity, several of its major flow properties change. This may be used to advantage by the addition of a diverging section to the nozzle. Gas velocity increases into the supersonic range and pressure decreases, as expansion of the exhaust gasses takes place over the entire length of the divergent section. Optimum expansion occurs when the pressure of the exhaust gasses at the exit plane of the nozzle is equal to the ambient pressure. This will be found at a specific cross-sectional area of the nozzle exit, A_e, of a given rocket, which may be related to the throat cross-sectional area as the nozzle area expansion ratio.

$$E = \frac{A_e}{A_t} \qquad \text{Equation 5}$$

Thrust is lost when the area ratio varies in either direction from the optimum. There are upper and lower pressure limits for all propellants. Very high chamber pressures, above 6000 psia for most propellants, cause erratic and rapid burning, frequently leading to catastrophic failure of the motor. On the other hand, many propellants will not support combustion at low pressures. This may be advantageous as a safety feature, but must be taken into account when designing the grain geometry so as to minimize the unburned propellant residue or "slivers" at motor burnout. For a particular propellant grain having a fixed surface area exposed to combustion, there exists a maximum effective throat area which will maintain a chamber pressure high enough to support combustion. Most solid rockets employ nozzles which will maintain chamber pressures well above this critical limit.



It is hoped that the preceding discussion provides the basis for an appreciation of the intricacies involved with designing solid propellant systems. Let us now examine the practical application of theory.

Nozzle Design

The mechanical requirements for nozzle fabrication are quite stringent. The material utilized must exhibit good machinability or ease of fabrication while retaining excellent resistance to erosive change under the most extreme conditions. The throat section is usually made from graphite or some non-ablative material which is surrounded by insulation to keep the outside structural material cool. The inside of the exit cone in large motors is made from such materials as asbestos-phenolic backed by an external structure to contain the nozzle pressure. Fiberglass phenolic laminates and ceramics have all seen application as nozzle materials in small rocket motors, but problems with cost, fabrication, and erosion have limited their use. By far, the most simple and economic solution has been the full diameter graphite nozzle, machined from readily available rod stock which fits snugly into the

inside diameter of the motor. The major drawback of this system is that the graphite acts as a heat sink and in larger or long burning motors may cause charring of non-metallic motor casings. This difficulty may be circumvented by suspending a graphite nozzle insert of significantly smaller diameter than the motor case in a high temperature epoxy which provides insulation for the casing. Thermosetting high temperature injection molded plastics combine moderate erosion resistance with the insulating properties needed to protect the motor wall, and are currently enjoying widespread usage. These nozzles are most effectively utilized in the design of neutral burning motors. By taking advantage of the erosive nature of the nozzle in combination with a progressive grain design, a neutral thrust curve may be obtained. Their major disadvantage is the high initial cost of tool and die fabrication.

When designing a rocket nozzle, consideration must be given to the angle of convergence, the angle of divergence, the nozzle area ratio, and the nozzle throat area with its relationship to the propellant burning area, K_n. All of these parameters must be precisely calculated from complex equations in order to optimize motor performance and efficiency. However, some useful generalizations may be drawn. The convergent cone half-angle, β, varies between 15 degrees and 45 degrees, with 30 degrees being a good compromise and 45 degrees being a more space and material efficient choice. For the divergent cone, a nozzle half-angle, β, between 12 degrees and 18 degrees, has been found experimentally to be optimum, with 15 degrees being a good choice in high thrust motors.

The nozzle area expansion ratio, E, that is the ratio of nozzle exit area to throat area, deserves more attention. Expansion of the exiting gasses is ideal when the external pressure is equal to the nozzle exit pressure, and the motor delivers maximum thrust. An underexpanding nozzle will discharge the exhaust at a pressure greater than the external pressure, because the exit area is too small. Thus, the gas expansion is incomplete within the nozzle and continues outside. The nozzle exit pressure is higher than the atmospheric pressure. An overexpanding nozzle is one in which gasses are expanded to a lower pressure than the external pressure due to it having an exit area which is too large. Separation of the gas jet from the nozzle wall will result, reducing the exhaust velocity, thereby leading to a loss of thrust. The formation of shock waves is also of concern with improperly designed nozzles. It is best to design a nozzle with the optimum expansion ratio or one which underexpands the gas jet slightly. A ratio of 1:3 to 1:4 is appropriate for composite motor systems operating in the 300 psia to 400 psia range. At higher pressures, the area ratio would increase. This would also be the case for sounding rockets operating at high altitudes where the exhaust gasses must expand further so that they can match the lower atmospheric pressure at the nozzle exit plane. The upper stage nozzles of such vehicles often have exit diameters ranging from five to seven times the throat diameter.

Throat Diameter

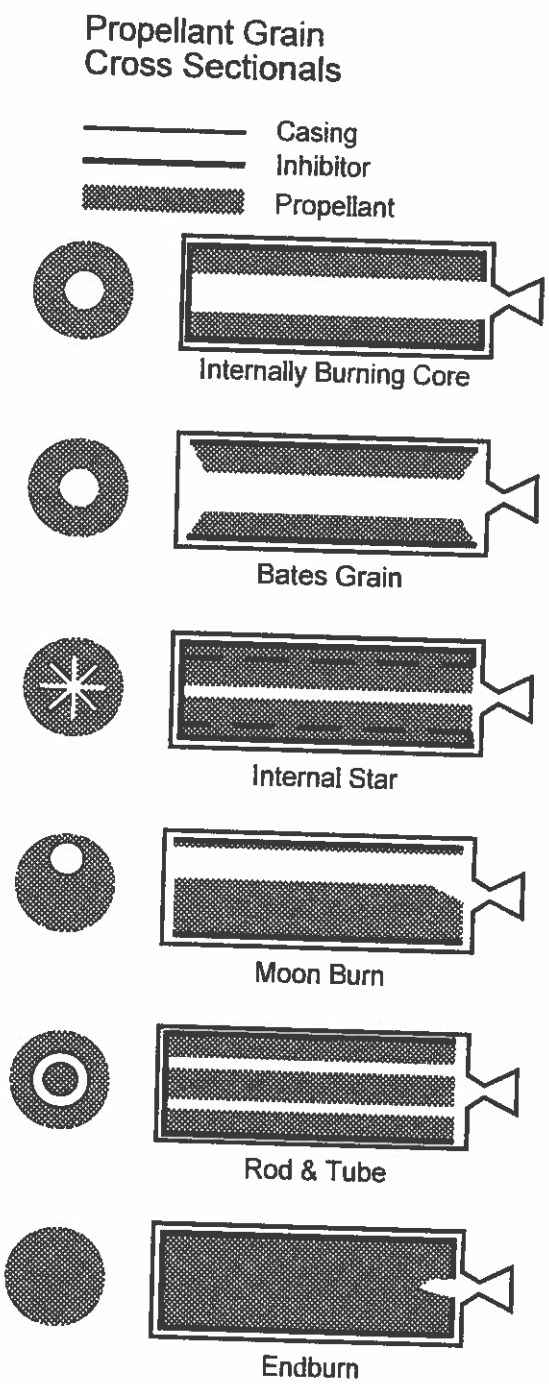
The final parameter which must be considered in nozzle design is the throat area. As has been previously discussed, the propellant characteristics of burn rate, r and pressure exponent, n must be considered when choosing the area of the throat. By substituting Equation 2 into Equation 3, the relationship of the throat area to the operating pressure and burning area is demonstrated:

$$P = B\left(\frac{A_e}{A_t}\right)^{\frac{1}{1-n}} \qquad \text{Equation 6}$$

The operating pressure is subject to the weight and strength limitations of the motor casing, while the burning area is a function of grain geometry.

Grain Geometry

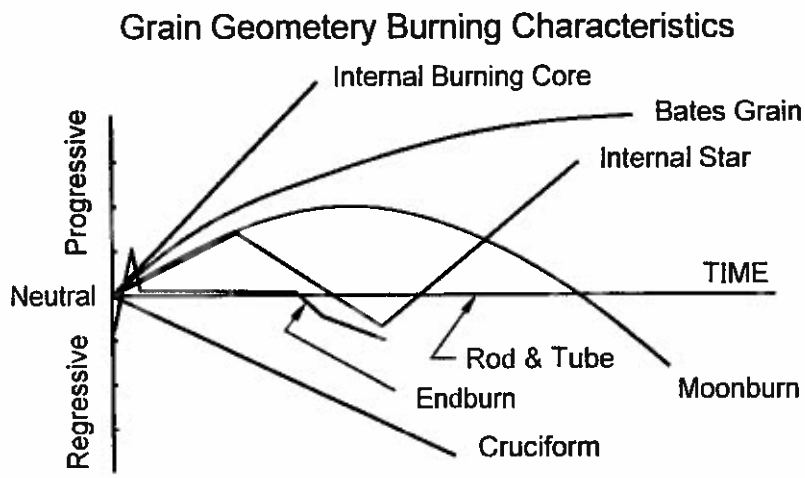
All of the many variations of grain geometry fall into three broad classes. Regressive grains have a large initial surface area which



decreases as burning progresses. Neutral burning grains will maintain a constant burning area and progressive grains exhibit an increase in burning surface as propellant is consumed. Each of these categories have inherent advantages and disadvantages. For example, a moon burning grain geometry with regressive characteristics would be useful in long burning, relatively slow traveling rockets going to high altitude. The high thrust of this initially progressive geometry would be desired at the beginning of the flight when vehicle weight is high. As the rocket gains altitude, its mass is decreasing as propellant is consumed. At the same time, the frictional resistance or drag decreases as the atmosphere thins, and the grain geometry becomes regressive as it burns out to a sustainer phase. In this way, a subsonic velocity with its lower drag coefficient may be maintained, thus optimizing vehicle altitude. When constant thrust is desired, neutral burning grains are called for. This is characteristic of an endburning charge consisting of a solid cylindrical section of propellant which is inhibited on all surfaces, except at one end, so that it will burn like a cigarette. The end is often machined into a cone shape to increase the initial surface area. Such charges have a constant burning area (unless the end is coned) and have a very long burning time, with very limited applicability for composite rockets. Hollow rod or rod and tube geometries will also provide neutral burning characteristics while exposing more propellant surface area and providing higher thrust levels than are available with endburning designs.

Progressive burning characteristics are found in internal burning case-bonded charges. An internal burning charge, as its name implies, burns outwardly from the internal perforation. It may have single or multiple ports in a variety of shapes, which provide these motors with high levels of thrust over moderately short burn times. Such motors are useful in boosting large or heavy payloads. These propellant grains may be severely stressed during motor function, particularly at the internal perforation. Moderate tensile strength (100–150 psi) and good elongation (30–70%) are necessary for case-bonded charges.

Thrust programs may be designed so as to combine the characteristics of progressive, neutral or regressive burning in a single motor. For an internal burning star grain shape, the initial surface area can be made nearly equal to the outside or final area of the grain.



During burning, the surface will increase slightly, then decrease to a minimum, then increase gradually until the points of the star reach the outer surface. At that point, there will be left semilunar sections, or slivers, which will burn out with ever decreasing area.

Progressive-regressive profiles are characteristic of moon burn grains first designed by Bill Wood, which utilize an offset core which is approximately 25% of the grain diameter. Initially, such motors are progressive core-burners up to the point where the expanding core reaches the case wall. Then, the remaining propellant, which is now in the shape of a crescent moon, burns regressively. A "D" shaped grain consisting of a solid rod with a thin slice cut off lengthwise will exhibit a similar thrust profile.

A working knowledge of the interrelationships already discussed between operating pressure, propellant burn rate, and propellant surface area leads to a second manner in which the thrust program of a given motor may be varied: changing the throat diameter. By using an ablative nozzle material which erodes at a known rate during motor function, the K_n of a motor may be changed in conjunction with the surface area of propellant burning. It is possible to design a neutral burning motor by combining a progressive grain geometry with an ablative nozzle, thus maintaining a relatively constant K_n, burn rate, and operating pressure.

Materials

Motor Casings

The combustion chamber or motor casing functions as a simple pressure vessel. High strength and low weight are of primary concern when choosing a casing material. For large rockets, steel has been a frequent choice. Aluminum is a lighter metal, but the thicker walls necessary to fabricate a casing of the same strength as steel, resulting in no net advantage. Of the metals, titanium is by far the strongest and lightest, but it is very difficult to fabricate and is an expensive alternative.

Smaller composite rocket motor casings are generally made from phenolic paper or cloth, or fiberglass. These materials are exceptionally strong and very light, and possess the added advantage of having a decreased hazard potential from shrapnel in the event of motor deflagration. Fiberglass casings may be manufactured from glass cloth or by filament winding where plastic or more commonly epoxy impregnated fiberglass is wound over a mandrel to form a tube. When the resin is cured, the mandrel is removed to make the casing. When using filament, it is desirable to maintain a 55-60 degree angle of winding so as to prevent the formation of micro-porosities extending through the walls of the finished casing. In addition, 6061-T6 aluminum tubing is

presently enjoying widespread usage in reloadable motors.

The phenolic based materials are lighter and less expensive than their fiberglass counterparts, as well as being more resistant to the high flame temperatures of composite propellants. They are also much weaker than fiberglass and therefore contraindicated for use in high pressure motors. In some cases, thin wall phenolic tubes are used as rigid liners into which propellant grains may be cast, then machined and loaded into motors.

Although not commonly considered as an appropriate material for composite motor casings, the author has recently developed a one-pound size paper casing motor (29 mm) using specially made high tensile virgin kraft tubes with ablative ceramic nozzles.

Many motor casings will incorporate a liner as insulation. Most often it is fabricated from the same binder as the propellant and filled with inert materials such as titanium dioxide, silicon dioxide, and/or other high temperature resistant materials. Asbestos free high density gasket material, (1/32") available at automotive supply stores, is an easy to use alternative when desired.

Epoxies

Epoxy compounds have received widespread utilization as the material of choice for sealing bulkhead and nozzle closures of small rocket motors. These materials are well adapted for withstanding the high heat and high pressure environment of motor function. An almost infinite number of formulations are possible based on the specific primary resin, modifying resin, and additives such as reactive diluents, bonding agents, surface active agents, fillers, and curatives.

An excellent and readily available epoxy may be found at local hobby shops which cater to radio control airplane enthusiasts: SIG One Hour Cure Epoxy is a medium viscosity clear epoxy suitable for cementing full diameter nozzles and delays.

When "floating" a nozzle of substantially smaller diameter than the motor casing, a reinforced, filled epoxy is required. These materials are commonly used for potting or encapsulating electronics components and are available in various viscosities and thermal conductivities. Biwax Corporation's Formula 411 works well for this application.

The Propellant System

Oxidizer

The primary use of ammonium perchlorate, NH_4ClO_4, is as an oxidant in solid propellants. It is also used in explosives, mines, shells, timing devices, and pyrotechnics. It is produced from anhydrous ammonia, aqueous hydrochloric acid, and sodium perchlorate. Ammonium perchlorate is a white crystalline solid with a molecular weight of 117.49 and specific gravity of 1.95. It is slightly soluble in water. Pure ammonium perchlorate is stable below 65.6 °C and undergoes an endothermic reaction at 240 °C, followed by two exothermic steps at 275 °C and 470 °C. Contamination with metallic salts such as those of copper, chromium, and iron catalyzes the second decomposition step so that it occurs at progressively lower temperatures as the impurity concentration is increased. Ammonium perchlorate is a strong oxidizer which is not explosive unless contaminated. It constitutes an extreme fire hazard in contact with oxidizable substances, organic materials, ammonium compounds, cyanides, sulfur and sulfur compounds, powdered metals, phosphorus and metal salts. Strong acids may react with perchlorates to generate perchloric acid, a dangerous explosive if allowed to contact oxidizable materials. Ammonium perchlorate crystals have piezoelectric properties, and may generate a charge upon stress deformation.

Ammonium perchlorate contains 34% available oxygen, considerably less than that of the sodium or potassium salts. Nevertheless, because of the low weight fraction of solids in their combustion gasses, propellants containing

it have overall performance characteristics exceeding that obtainable with either of the other two oxidizers. It also has the advantage of not producing smoke.

Ammonium perchlorate propellants produce hydrogen chloride and other chlorine compounds during combustion. In high humidity or a moist atmosphere, the hydrogen chloride will condense into a dangerous fog of hydrochloric acid. The exhaust gasses of these motors are toxic, as well as being highly corrosive to many materials.

Particle Size

Ammonium perchlorate is produced in three ordinance grades. The fine classified grade is available in 55 micron and 90 micron sizes, both coated with tricalcium phosphate (TCP) as an anti-caking agent. Regular–Class I is 200 microns and Coarse–Class II is 400 micron in size. The latter two grades are offered with or without the TCP and may be rotary rounded, producing spheroidal grains.

The shape of the grains and particle size of the oxidizer are of critical importance in a propellant formulation, influencing the burning rate, processing properties and the physical properties of the propellant. In general, a decrease in particle size results in an increase in burning rate, with the most significant effect in the submicron range up to about one hundred microns. The effects of crystal size are sometimes so significant that a whole series of propellants can be made with the same composition by merely varying the particle size.

Multi-Modal Propellant Systems

In practice, most composite propellants are multi-modal, consisting of several different sizes of oxidizer in specific ratios. The larger 200μ and 400μ grains are rounded to spheres so as to present the smallest possible surface area per volume of oxidizer. The smaller crystals of ground oxidizer will then fit into the interstices between the larger particles. The net result is a propellant with high solids loading which is not fuel rich and thus maximizes the I_{sp} and mechanical properties of that propellant.

Binder System

Binder

Hydroxyl terminated polybutadiene (HTPB) is a long chained clear liquid rubber polymer. First used as a binder and fuel in solid propellants by Aerojet in 1962, HTPB is chemically a polyurethane because it is cured with isocyanates. Reaction sites for cross linking are provided by hydroxyl (—OH) radicals at several points along each chain, as well as at terminal ends. It is the three dimensional matrix of the cross-linked rubber chains which impart the important mechanical properties to a propellant. The ability of a propellant to withstand high strain rates is directly related to the low temperature properties of the binder, such as elongation and brittle point. In high solids loaded propellants, a modulus of 400–700 psi with good elongation and tensile properties is required, particularly when case bonding. With a glass transition temperature near or below –100 °F, HTPB has excellent characteristics.

Table 1. Physical Data for HTPB.

Boiling point	300 °C
Specific gravity	@25 °C .90
Viscosity (Brook)	@25 °C 6000
Strain capacity	@–65 °F 25–35%

The actual mechanical properties of a specific propellant are a function of the exact formulation, i.e. by the size distribution and amount of solids, the ratio of binder to curing agent, and the amount of plasticizer.

Curative

As previously mentioned, HTPB is cured by isocyanates. Some require an elevated temperature (oven cure) of 125+ °F to activate, while others such as isophorone diisocyanate

(IPDI) or PAPI; are active at room temperature. Such curatives are usually present in the range of 8–10% of the rubber content of the propellant, based on calculation of the activity of the particular agent used. These curatives are all toxic compounds, with some more so than others. Among the room temperature curing agents, toluene diisocyanate gives the shortest pot life and is the most toxic. PAPI-901 (Dow Chemicals) and N-100 are two good choices for low toxicity and adequate pot life for room temperature curatives. Care must be taken to ensure that all propellant components are kept dry, as isocyanate groups will react with water, producing a substituted urea and liberating CO_2 in a gassing reaction.

Plasticizer

A number of very low viscosity plasticizing agents may be added to a propellant for improved wettability which will allow higher solids loading and consequently improve performance. These agents will improve the mechanical properties of a propellant, retard oxidation and embrittlement to a certain extent, and when used as a significant portion of the binder system (25–30%), will allow for some propellants to be pourable.

✣ Dioctyl adipate (Uniflex DOA, UnionCamp) is a high quality grade of Dl-2-ethylhexyl adipate which is used as a diester fluid for synthetic lubricants. This colorless liquid has low acute oral toxicity, but is considered as a high health hazard due to its mutagenic and carcinogenic effects.

✣ Dioctyl azelate (DOZ) is a similar product with a slightly higher molecular weight and lower toxicity.

✣ Isodecyl pelargonate, IPDI, (Emery 2911 Synthetic Lubricant Basestock, Emery Chemicals), is another synthetic oil of even lower viscosity than DOA, which is an excellent plasticizer.

In effect, most any low viscosity type of oil may be used as a plasticizing agent. The advantage of the aforementioned products lies in their wetting ability and ultra low viscosity.

Bonding Agents

Most published propellant formulations will contain a bonding agent. These compounds react with the surface of the ammonium perchlorate crystals (frequently releasing gaseous ammonia) and facilitate actual bonding of the rubber to the crystal. Without such an agent, the oxidizer crystals are simply retained physically within the propellant, captured in effect by a three dimensional matrix of rubber. Without a bonding agent, crystals of oxidizer which are on cut or machined surfaces of a propellant grain will be lost during processing, leaving a fuel rich surface. TEPANOL Dynamar™ Bonding Agent/ Processing Aid HX-878) is one such bonding agent and commonly comprises 0.25% of the entire propellant formulation. Bonding agents greatly improve the mechanical strength and properties of a propellant, but are not of significance in small rocket motors.

Metallic Fuels

Finely divided metals are added to almost all composite propellant formulations. These fuels provide a variety of benefits and enter into some very complex interactions during combustion. Spheroidal aluminum is perhaps the most commonly used metal in composite propellants, found in various formulations from near 1% up to around 18%. The ballistic performance of aluminized propellants is greatly increased, raising the I_{sp} in the range of up to 10% when compared to the same formulation without metal. It must be noted, however, that this effect is not significant in small rocket motors, where the metal is not in the combustion chamber long enough to be consumed, and is mostly expelled in the exhaust gasses in the molten form. The addition of aluminum to a propellant will also serve to dampen acoustic oscillations, thus minimizing the possibility of grain fracture at ignition, and also making ignition easier, especially in small motors. The net effect of aluminum on burn rate is usually not large and may be positive or negative.

When considering metallic fuels other than aluminum, those with low molecular weight are desirable. Those which might be of benefit to propellant application may be determined by considering the density and the heat of formation of the metal oxide. Beryllium heads the list and has been reportedly used, but has the problem of producing toxic combustion products. Boron, lithium and silicon all have higher heat content per gram than aluminum, and are potential additives. Magnesium has also been used, but imposes a hardship on the binder due to its lower heat content and lower density.

Burn Rate Modifiers

Numerous compounds are utilized to modify the burn rate of propellant systems. Most exert a positive catalytic effect, while some such as oxamide decrease the burn rate by insulating the heat wave and slowing the progression of combustion. Addition of inert compounds (chalk) or substituting less active oxidizers (ammonium chloride, sulfate) for a portion of the AP in a propellant will also slow the rate of burn.

By far, the majority of modifiers are catalysts which in some manner enhance the rate of burning. The effects which these compounds have on the dynamics of combustion is an exceedingly complex area of research.

At this point, it will suffice to say that catalysts exert their effects in relationship to combustion pressure and concentration. An effective range may be determined, above which the increase of catalyst percentage has diminishing returns without significant increase in burn rate.

The following is a partial listing of some frequently utilized burn rate catalysts with brief comments about each one:

Promoters

✣ Manganese Dioxide (MnO_2) — Positively catalyzes solid phase reactions. MnO_2 is a strong positive catalyst for the decomposition, but is a negative catalyst for the deflagration of AP.

✣ Iron(III) Oxide (Fe_2O_3) — An excellent and readily available catalyst. It will increase burn rate more than MnO_2 will at same level. Fe_2O_3 promotes the complete decomposition of AP at 270–280 °.

✣ Chromium(III) Oxide (Cr_2O_3) — Primarily enhances the low temperature decomposition of AP, allowing that reaction to go to completion. Chromium oxide exerts a much greater effect on burn rate than manganese dioxide, and at the 2% level is superior to iron oxide in low pressures, up to about 600 psia.

✣ Copper Chromite ($Cu_2Cr_2O_7$ or $CuO \cdot Cu Cr_2O_3$) — has a significant, but varied effect on burn rate. Analysis has shown that copper chromite catalysts differ from company to company and may not even be the same from batch to batch. Propellants containing copper chromite become brittle and do not age well.

✣ Cupric and Cuprous Oxide (Cu_2O and CuO_2) — Both catalyze the low and high temperature decomposition of AP, and promote ignition. Cupric oxide (CuO) is superior to copper chromite and even chromium oxide as a burning rate promoter.

✣ Ferrocene (Dicyclopentadinyliron, $C_{10}H_{10}Fe$) and its derivatives Catocene and N-Butylferrocene — These liquid burn rate promoters are based on two five-membered cyclopentadinyl groups with a ferrous ion (Fe^{2+}) sandwiched between. These compounds interact with aluminum during combustion. Decreasing the particle size and thus increasing the surface area of aluminum to react, will increase the burn rate of propellants containing these compounds.

Burn Rate Inhibitors

The burn rate of a propellant may be decreased by the substitution of up to 20% of the oxidizer with ammonium chloride or ammonium sulfate. The addition of zinc powder to a propellant will also slow the rate of burn, while also generating a dense, black exhaust. A fuel rich propellant or one to which an inert component such as calcium carbonate has been added, will also burn slower. The use of an

inhibiting compound which will contribute to the combustion reaction, however, seems to be the more sensible approach.

Conclusion

It is hoped that the preceding discussion provides the reader with a basic understanding of the many variables involved in the design and fabrication of composite propellant systems, and of their great potential. this is a dynamic area of technology and development, with contributions continuing to be made by amateurs and professionals alike.

A solid theoretical background is important, but in the end, any new motor or propellant design is always qualified by an extensive static testing program. For those interested, an increasing amount of information including motor and propellant development programs for PC's, and instructional manuals are becoming available. An invaluable reference source for anyone working with liquid or composite propellants, as well as for those with a more theoretical orientation is *Rocket Propulsion Elements, An Introduction to the Engineering of Rockets*, Sixth Edition, by George P. Sutton. It is available from John Wiley & Sons, Inc. Professional, Reference and Trade Group, 605 Third Avenue, New York, NY 10158-0012 USA. Many Rocketry enthusiasts have become members of the Tripoli Rocketry Association, Inc. PO Box 339, Kenner, LA 70063-0339 USA. This organization encompasses all aspects of non-professional rocketry, and is currently forming a research branch for members interested in more development.

Errata — Issue No. 2

"Errata for Issue Number 1" One of the corrections for Issue Number 1 contained further errors.

Page 14 **"An Introduction to PROPEP, A Propellant Evaluation Program for Personal Computers"** Page 15 Right column, middle of the page, one line of text was not properly superscripted, it should read:

$$p_c = c \cdot K_n^{(1/1-n)}$$

Issue No. 2:

"Introductory Chemistry for Pyrotechnists, Part 2: The Effects of Electrons"

Page 19 Left column, 2nd paragraph, lactose was incorrect. It should be:

Some elements find themselves in valence states with an excess of electrons. Lactose ($C_{12}H_{22}O_{11}$), for instance contains carbon with a valence state of zero [12(0) + 22(+1) + 11(-2) = 0].

Page 21 Table 4, Commonly Used Color Agents.

Copper(II) Carbonate should be Basic Copper Carbonate, with the empirical formula of
(I) $CuCO_3 \cdot Cu(OH)_2$,
(II) $2CuCO_3 \cdot Cu(OH)_2$ [Shimizu, p. 112]. Commercially available material is usually a mixture of (I) and (II).

Sodium Disilicate should be synthetic Ultramarine, with the empirical formula $Na_2S_2 \cdot 3NaAlSiO_4$ [Shimizu, p. 148].

[Shimizu, T. *Fireworks: The Art, Science and Technique*, Reprinted by Pyrotechnica Publications, Austin, TX, 1986.]

Events Calendar

Pyrotechnics

27th International Conference of the Institute of. Chemical Technology

June 25 – 28, 1996, Karlsruhe, Germany

Contact: Fraunhofer - Inst. für Chem. Tech.
P.O. Box 1240
D-76318 Pfinztal (Berghausen)
Germany

Phone: +49-721-4640-121
FAX: +49-721-4640-111

22nd International Pyrotechnics Society Seminar

July 15 – 19, 1996, Ft. Collins, Colorado, USA

Contact: IIT Research Institute
10 W. 35th Street
Chicago, IL 60616 USA

Phone: 312-567-4280 or 312-567-4293
FAX: 312-567-4543 or 708-790-9526

e-mail: TULIS@EAGLE.HQ.IITRI.COM

John Conkling — 1996 – One-Week Seminars

Chem. of Pyrotechnics & Explosives, Jul.21–26
Application of Pyrotechnic Principles to Solve Performance and Safety Problems, Jul28–Aug.2

Contact: Dr. John Conkling
Summer Pyrotechnic Seminars, P.O. Box 213
Chestertown, MD 21620 USA

Phone: 410-778-6825
FAX: 410-778-5013

26th International Symp. on Combustion

July 28 – August 6, Naples, Italy

Contact: The Combustion Institute
5001 Baum Boulevard, Suite 635
Pittsburgh, PA 15213-1851 USA

Phone: 412-687-1366
FAX: 412-687-0340

email: combust@telerama.lm.com

International Autumn Seminar on Propellants, Explosives and Pyrotechnics

October 7 – 10 1996, Beijing, China

Contact: Prof. Changgen Feng
Mechanics and Engineering Dept.
Beijing Institute of Technology
P.O. Box 327, Beijing 100081, China

Phone: +841-6688 ext. 2941 or 2764
FAX: +841-2889

American Defence Preparedness Association (ADPA) Pyrotechnics Section — in conjunction with **Munitions Technology Symposium IV** and **Statistical Process Control Meeting**

February 10–12, 1997, Reno, Nevada, USA.

Contact:
Jason Burkett
Olin Ordinance
10101 9th St. N.
St. Petersburg, FL 33716

Phone: 813-578-8280
FAX: 813-578-8146

e-mail: Bullet Dr@aol.com [Yes, it is a space.]

23rd International Pyrotechnics Seminar

September 30–October 4, 1997, Tsukuba, Japan

Contact: Prof. Tadao Yoshida
College of Engineering of Hosei University
3 – 7 – 2 Kajino–cho, koganei–shi
Tokyo 184 Japan

Phonr: +81-423-87-6132
FAX: +81-423-87-6381

Fireworks

Benson & Hedges International Fireworks Competition in Montreal, Canada – 1996

Dates and Competitors:

June 15 Marutamaya Ogatsu, Japan
June 20 Sunny International, China
June 23 Pirotecnica Soldi, Italy

(Continued on next page)