PROPELLANTS

Propellants are mixtures of chemical compounds that produce large volumes of high temperature gas at controlled, predetermined rates, and can sustain combustion without requiring atmospheric oxygen for the purpose. Principal applications are in launching projectiles from guns, rockets, and missile systems. Propellant-actuated devices are used to drive turbines, move pistons, operate rocket vanes, start aircraft engines, eject pilots, jettison stores from jet aircraft, pump fluids, shear bolts and wires, and act as sources of heat in special devices. Propellants are applicable wherever a well-controlled force must be generated for a relatively short period of time. Solid propellants are compact, have a long storage life, and may be handled and used without exceptional precautions.

1. General Characteristics

1.1. Gun Propellants

Solid gun propellants are employed in the form of dense cylindrical or spherical grains, elongated hollow or split sticks, or as sheets of plasticized nitrocellulose. Gun propellants are almost always based on nitrocellulose to provide mechanical strength. These also may contain inert or energetic liquid plasticizers (qv) or a combination of the two to improve physical and processing characteristics, high explosives to increase available energy, stabilizers to prolong storage life, and a small amount of inorganic additives to facilitate handling, improve ignitibility, and decrease muzzle flash. Single-based propellants, used exclusively in guns, derive energy primarily from nitrocellulose [9004-70-0]. Double-based nitrocellulose propellants contain liquid energetic plasticizers such as nitroglycerin [55-63-0], and are used in rockets as well as guns. Triple-based propellants contain crystalline additives, eg, nitroguanidine [556-88-7], as well as nitrocellulose and energetic additives. Both double- and triple-based propellants are used in guns and rockets. Low sensitivity propellants (LOVA) have also been developed for use in guns; these contain a high energy component, eg, cyclotrimethylene trinitramine (RDX) [121-82-4] in a polymeric binder. Gun propellants are made mostly by an extrusion process that produces small grains in large numbers. Nitrocellulose serves on the energetic binder. Typical components of nitrocellulose propellants and their functions are

nitrocellulose	energetic binder
polyglycol diols	nonenergetic binder
nitroglycerin, metriol trinitrate, diethylene glycol dinitrate, triethylene glycol dinitrate, dinitro-toluene	plasticizers, energetic
dimethyl, diethyl, or dibutyl phthalates, triacetin	plasticizers, fuels
diphenylamine, diethyl centralite, 2-nitrodi-phenylamine, acardite, diethyl diphenylurea	stabilizers
lead salts, eg, lead stannate, lead stearate, lead salicylate	ballistic modifiers in rocket propellants
carbon black	opacifier
lead stearate, graphite, wax	lubricants
potassium sulfate, potassium nitrate, cryolite (potassium aluminum fluoride)	flash reducers in gun propellants
ammonium perchlorate, ammonium nitrate	oxidizers, inorganic
RDX, HMX, nitroguanidine, and other nitramines	oxidizers, organic
lead carbonate, tin	decoppering agents in gun propellants

1.2. Rocket Propellants

Solid rocket propellants are mostly based on chemically cross-linked polymeric elastomers to provide the mechanical properties required in launchings and the environmental conditions experienced in storage, shipment, and handling (see Elastomers, synthetic). Double- and triple-based nitrocellulose propellants are also employed as rocket propellants.

Polymer-based rocket propellants are generally referred to as composite propellants, and often identified by the elastomer used, eg, urethane propellants or carboxy- (CTPB) or hydroxy- (HTPB) terminated polybutadiene propellants. The cross-linked polymers act as a viscoelastic matrix to provide mechanical strength, and as a fuel to react with the oxidizers present. Ammonium perchlorate and ammonium nitrate are the most common oxidizers used; nitramines such as HMX or RDX may be added to react with the fuels and increase the impulse produced. Many other substances may be added including metallic fuels, plasticizers, stabilizers, catalysts, ballistic modifiers, and bonding agents. Typical components are listed in Table 1.

Nitrocellulose-based rocket propellant grains contain energetic liquid plasticizers such as nitroglycerin, stabilizers, ballistic modifiers, nonenergetic plasticizers, inorganic oxidizer salts, organic explosives, and metallic fuels similar to those used in gun propellants. When these latter components are included, the composition is referred to as a composite-modified double-based propellant (CMDB). Nitrocellulose-based propellants have also been made using isocyanatecurable elastomers which permit a reduction in the amount of nitrocellulose used and an increase in the nitroglycerin contents. The composition of a typical elastomer-modified composite double-base composition (EMCDB), compared to characteristic compositions of straight double-base (DB), composite-modified double-base, and conventional composite rocket propellants, can be found in Table 2.

Rocket propellants are made mostly by a casting process as distinct from the extrusion process used to make the very much smaller and more numerous gun propellant grains (1, 2).

2. Selection Criteria

2.1. Energy Considerations

The selection of gun and rocket propellants involves two principal considerations: the total amount of energy required and the mass rate at which the hot gases produced must be delivered to meet system performance

Table 1. Typical Components of Composite Rocket Propellants

Component	Characteristics
Binders	
polysulfides	reactive group (mercaptyl, —SH), is cured by oxidation reactions; low solids loading capacity and relatively low performance; mostly replaced by other binders
polyurethanes, polyethers, polyesters	reactive group (hydroxyl, —OH), is cured with isocyanates; intermediate solids loading capacity and performance
polybutadienes copolymer of butadiene and acrylic acid	reactive group (carboxy, —COOH, or hydroxyl, —OH), is cured with difunctional epoxides or aziridines; intermediate solids loading capacity and better performance than polyurethanes; less than adequate cure stability and mechanical characteristics
terpolymers of butadiene, acrylic acid, and acrylonitrile	superior physical properties and storage stability
carboxy-terminated polybutadiene	cured with difunctional epoxides or aziridines; have good solids loading capacity, high performance, and good physical properties
hydroxy-terminated polybutadiene	cured with diisocyanates; have good solids loading and performance characteristics, and good physical properties and storage stability
Oxidizers	
ammonium perchlorate	most commonly used oxidizer; it has a high density, permits a range of burning rates, but produces smoke in cold or humid atmosphere
ammonium nitrate	used in special cases only, it is hygroscopic and undergoes phase changes, has a low burning rate, and forms smokeless combustion products
high energy explosives (RDX–HMX)	have high energy and density; produce smokeless products; have a limited range of low burning rates
Fuels	
aluminum	most commonly used; has a high density; produces an increase in specific impulse and smoky and erosive products of combustion
metal hydrides	provide high impulse, but generally inadequate stability; produce smoky products and have a low density
Ballistic modifiers	
metal oxides	iron oxide most commonly used
ferrocene derivatives	permit a significant increase in burning rate
other	coolants for low burning rate and various special types of ballistic modifiers
Modifiers for physical characteristics	
plasticizers	improve physical properties at low temperatures and processibility; may vaporize or migrate; can increase energy if nitrated
bonding agents	improve adhesion of binder to solids

requirements. The energy delivered per unit mass depends on the chemical energy of the propellant components, the characteristics of the products of combustion, the chemical equilibria which prevail among the reaction products, and the efficiency with which the system converts thermal to kinetic energy. The rate at which energy is produced depends on the intrinsic burning characteristics of the propellant, its burning surface area, and the operating pressure and temperature of the system. Control of the burning surface area is obtained by using appropriate grain geometries and the required number of grains. Uncontrolled burning can result in intolerably high pressure or, in the worst case, catastrophic detonation.

The thermochemical–thermodynamic factors affecting gun and rocket performance are essentially the same. Both guns and rockets convert thermal energy into kinetic energy through physical–chemical processes. The highest energy propellants produce the largest volume of gas per unit weight of propellant at the highest flame temperature. The selection of propellant compositions for maximum performance focuses on high density compositions that form highly exothermic low molecular weight combustion products that are stable with minimum dissociation at gun or rocket operating pressures. Many practical considerations limit the attainment of the theoretical maximum performance. High flame temperature propellants used in rockets may cause

4   PROPELLANTS

Table 2. Composition of Rocket Propellants, wt%

Constituent	DB	CMDB	EMCDB	Composite
nitrocellulose	53	25	15	
nitrate ester	40	25	30	
nitramines			43	
ammonium perchlorate		30		70
aluminum		13		18
stabilizers	2	2	2	
polymeric binder		5	5	12
ballistic additives	5	5	5	

[a] Terms are defined in text.

excessive nozzle erosion and dissociation of the gaseous products at the relatively low operating pressures in rocket chambers. Use in guns may cause excessive gun tube wear and muzzle flash. The incorporation of large percentages of nitramines such as nitroguanidine in triple-base propellants or RDX in LOVA gun propellants is intended to produce the maximum energy at the lowest possible flame temperature. The isochoric adiabatic flame temperatures of propellants in use ranges from ca 2000 to 3500 K. The impetus of gun propellants is ca 822 to 1196 J/g $(275,000 - 400,000 \text{ ft·lb/lb})$. The specific impulse of high performance rocket propellants is ca $2455 - 2700$ N·s/kg $(250 - 275 \text{ lbf·s/lb})$. Factors influencing the selection of propellants for guns and rockets are as follows:

Manufacturing Characteristics
    Availability and cost of raw materials and processing equipment
    Simplicity and cost of manufacture and inspection
    Manufacturing hazards
    Propellant viscosity and flowability
    Environmental considerations
Energy Delivery Requirements
    Specific impulse or force
    Loading density in terms of required burning characteristics
    Metal parts requirements in terms of operating pressure over required temperature range
Temperature Dependence
    Ignition, pressure, burning rate, and thrust characteristics over temperature range
Mechanical Characteristics Over Temperature Range
Effects of High-Low Temperature Cycling
Reliability of Performance
    Lot-to-lot variations in burning rate and pressure
    Effect of small variations in metal parts on performance
    Effect of small variations in composition and dimensions on performance
Long-Term Storage Characteristics
    Deformation changes
    Performance changes
    Moisture absorption

Exudation or migration of plasticizer
Effects of Mechanical Characteristics
Long-term storage
High–low temperature cycling
Acceleration forces
Rough handling
Case bonding
Compatibility
With process equipment
With personnel (toxicity)
With metal and plastic parts and other components
Of reaction products with personnel, metal parts, and electronic equipment
Erosive effects of reaction products
System Requirements
Smokeless exhaust
Combustion stability
Effect of exhaust plume on radar
Absence of ignition peaks or reinforcing pressure waves
Minimum gun smoke, flash, and blast pressure
Detonation-free in event of malfunction
Minimum sensitivity to fire, high velocity fragments, and other evolved stimuli

2.2. Performance Calculations

The energy evolved by a propellant may be estimated from the percentage composition, reaction products, the heats of formation of the reactants and the products, the propellant density, and the gases and solids produced. The composition and flame temperatures of the products are determined from the applicable enthalpy–temperature and chemical equilibrium functions of the various molecular species and the operating conditions in the combustion chamber. The most important thermodynamic–thermochemical characteristics of propellant combustion products, in addition to gas volume and flame temperature, are heat capacity, heat capacity ratio, and the covolume of the gases at high pressures. Rigorous calculations require the solution of numerous equations which describe the mass and enthalpy balance and the chemical equilibria of the reaction products at elevated temperatures and pressures. Many computer programs have been developed for predicting rocket or gun performance. Simplified first approximation techniques are also available (3–15).

2.3. Mechanical Characteristics

2.3.1. Rocket Propellants

Large rocket grains in particular must have adequate mechanical properties to enable them to withstand the stresses imposed during handling and firing. These must be capable of performing satisfactorily after undergoing the thermal stresses produced during long-term exposure and cycling at temperature extremes. The development of high energy rocket propellants emphasizes maximum toughness and low shock and impact sensitivity. The mechanical properties depend primarily on the characteristics of the binder, the percentage of solids present, and the particle size distribution of the solids.

Rocket propellants are subjected to a large number of tests and inspections to establish mechanical and physical characteristics. Well-established laboratory methods determine the tensile and compressive strengths, the modulus in tension and compression, elongation under tension, and deformation under compression. Empirical techniques correlate these data and field performance. High rate of load application of tensile forces simulate those generated during ignition. Low rate tests simulate the stresses produced by differential thermal expansion. Compression test data are related to the forces experienced by rocket grains supported at the aft end of the motor. Drop tests of loaded rocket motors and vibrational, centrifugal, and sled tests that impose acceleration forces comparable to those expected in use are among the techniques employed. The linear coefficient of thermal expansion is important in rocket systems in which the propellant is coated with an inhibitor or bonded to the motor. Typical values are $3.6 - 7.2 \times 10^{-5}$ m/(m·K). Thermal diffusivities generally range between 7.7 and 15.5×10^8 m^2/s. Thermal conductivities are ca 0.22–0.33 W/(m·K) ($0.13 - 0.19$ Btu·ft/(h·ft^2·°F)). Specific heat values are ca 1.26×10^3 J/(kg·K) (0.3 Btu/(lb·°F)). Low thermal conductivity may cause severe thermal stresses that sometimes lead to cracking in large rocket grains when abrupt changes in storage temperatures occur.

Rocket propellants must not contain sizable cracks, pores, or cavities. They are inspected using x-rays and ultrasonics, and firings are conducted in strand burners, interrupted burners, and in reduced or full-scale rocket motors (see also Nondestructive evaluation) (16–20).

2.3.2. Gun Propellants

Although the stresses on individual gun propellant grains are less severe because of the small size, these propellants must withstand much higher weapon pressures and accelerations. Formulation options are usually more limited for gun propellants than for rocket propellants because the products of combustion must not foul or corrode a gun, should have a low flame temperature, and should exhibit minimum flash and smoke characteristics. Gun propellants are examined microscopically for porosity, are tested for mechanical characteristics, and fired in closed bombs to determine the burning characteristics.

2.4. Shelf Life Characteristics

The chemical safe life of all standard propellants is measured in years. Both gun and rocket propellants contain chemical stabilizers that combine with the products of decomposition to prevent autocatalytic breakdown of the propellant composition. The useful service life of gun propellants may be as long as 25 to 50 years. The useful service life of rocket propellants may be significantly less than the chemical safe life if gassing occurs, motor bonding deteriorates, or significant physical changes take place. Generally such effects are produced by high temperature storage or high–low temperature cycling, particularly if moisture is present. Relatively little degradation occurs at ambient temperature conditions. Gassing can produce internal pressures which may crack a large rocket grain or cause propellant–inhibitor or propellant–motor bond failure. The likelihood of performance failure in standard rocket systems as a result of gassing is low because of the use of chemical stabilizers and the selection of compatible inhibitors, cements, and insulation materials.

The procedures used for estimating the service life of solid rocket and gun propulsion systems include physical and chemical tests after storage at elevated temperatures under simulated field conditions, modeling and simulation of propellant strains and bond line characteristics, measurements of stabilizer content, periodic surveillance tests of systems received after storage in the field, and extrapolation of the service life from the detailed data obtained (21–33).

3. The Burning Process

The mass rate of a propellant grain burning at a given pressure and temperature depends on the amount of heat evolved during decomposition and the amount of heat transferred to the burning surfaces of the propellant from the hot gases above it. This rate is also influenced by the tangential velocity of the propellant gases and the radiation from the surroundings. Propellants burn in parallel layers so that the surface recedes in all directions normal to the original surface. The geometry of the grain on completion of burning is similar to its geometry at the start. Propellant burning at high gun pressures proceeds more smoothly and is less subject to erratic behavior than burning at very low pressures because the conditions are appropriate for maximum energy transfer in minimum time. The burning rate at gun pressures usually varies somewhat less than the first power of the pressure. It changes more slowly at rocket pressures of 3.45–10.34 MPa (500–1500 psi), often to less than the square root of the pressure.

The composition of the propellant determines the rate of exothermic molecular breakdown at a given temperature and pressure. As the reaction rate increases, the rates of heat production and transfer increase with associated increases in the linear burning rate of the propellant. The heat evolved per gram of propellant in an inert atmosphere is its heat of explosion, Q. It may be readily calculated or experimentally determined in a calorimetric bomb. Values range from ca 2.09 kJ/g (500 cal/g) for cool propellants to ca 6.27 kJ/g (1.5 kcal/g) for maximum energy propellants. The flame temperatures and the burning rates of uncatalyzed propellants of similar compositions are generally linearly related to the calorific values except at very low pressures. The presence of volatile solvents or water significantly reduces the propellant burning rate. The addition of crystalline oxidizers such as ammonium perchlorate or RDX also modifies the burning rate to a degree that depends on the physical and chemical characteristics of the compound and the percentage present. The burning rate of many propellants increases ca 0.1 to 0.4%/°C as the temperature of the propellant increases.

The operating pressure of the system is the dominant influence on the burning rate of propellants. Photographic evidence shows that increasing the pressure decreases the distance between the flame zone in the gas phase and the propellant surface. The rate of heat transfer to the propellant surface increases accordingly. The reaction rate among the gaseous components of the zones above the propellant also increases in accordance with established relationships between pressure and the rate of gas reactions in equilibrium. The velocity of the gases passing over the propellant at the dynamic conditions prevailing in a rocket motor or in a gun tube may further increase the burning rate (erosive burning). When a turbulent flow of gas occurs behind the reaction zone, part of the turbulence may penetrate the zone and increase heat transfer to the propellant surface (34–38).

3.1. Mechanism of Burning

3.1.1. Nitrocellulose-Based Propellants

Much of the information available on the burning process of nitrocellulose propellants is based on the decomposition of nitrate esters and the reaction of oxides of nitrogen with the products of decomposition. A one-dimensional physiocochemical description of a model of the burning of a double-base propellant at low (rocket) pressures is often used, and more complex models have been developed. The three reaction zones identified (Table 3) are (*1*) the foam zone where molecular bond breakage, primarily the O–N bond in cellulose nitrate–nitroglycerin-type propellants, occurs. Large volatile molecules are produced, such as aldehydes, alcohols, and low molecular weight oxygenated compounds. The rate of bond breakage depends on temperature in accordance with the applicable Arrhenius equation. (*2*) The fizz zone which is above the foam zone and results from partial reaction among the materials ejected from the foam surface. Aldehydes and alcohols are converted to smaller molecules; nitrogen, water, carbon monoxide, carbon dioxide, and nitric oxide are also formed. About half the total heat evolved by the propellant is liberated in the fizz zone, which is prominent at low pressures and disappears at high pressure. And (*3*), the flame zone, where thermodynamic equilibrium

is established. This zone defines the flame temperature of the propellant, which may range from can 1500 K for cool propellant to 3500 K for very hot ones. Here nitric oxide reacts with the reaction products formed in the fizz zone to produce carbon monoxide, carbon dioxide, hydrogen, water, nitrogen, and a small percentage of other molecules.

Table 3. One-Dimensional Model of Propellant Burning Process[a]

Parameter	Foam	Fizz	Flame	Final
zone description	solid-phase reaction	nonluminous gas-phase reaction	luminous flame reaction	final flame equilibrium
thickness[b], cm	10^{-2}	5×10^{-3}	10^{-3}	
temperature[b], K	300–600	600–1500	1500–3000	>3000

[a] Propellant is a solid at ambient temperature.
[b] Approximate value.

Because the gaseous products are in thermodynamic equilibrium at the flame temperature, quite accurate calculations of gas composition, maximum temperature, and other thermodynamic properties may be readily derived from the propellant formulation and the thermochemical characteristics of its components. Typical values of these characteristics for many nitrocellulose gun propellants are given in Table 4.

Table 4. Thermochemical, Thermodynamic, and Performance Characteristics of Nitrocellulose Gun Propellants[a]

Characteristics	Designation												
	M1	M2	M5	M6	M8	M9	M10	M15	M17	M26	M30	M31	IMR
heat of explosion, J/g[b]	3140	4522	4354	3182	5192	5422	3936	3350	4019	4082	4082	3370	3601
heat of formation, $-\Delta H_f$, J/g[b]	2261	2366	2407	2261	1989	1989	2533	1256	1361	2114	1549	1465	2366
flame temperature, Tv, K	2435	3370	3290	2580	3760	3800	3040	2555	2975	3130	3000	2600	2835
impetus, J/g[b]	911	1121	1091	956	1181	1142	1031	980	1088	1082	1065	1000	1007
heat capacity, C_V, J/(g·K)[b]	1.46	1.51	1.46	1.46	1.42	1.51	1.42	1.51	1.51	1.46	1.51	1.52	1.46
mean heat capacity products, J/(mol·K)[b]	1.84	1.76	1.76	1.80	1.76	1.72	1.80	1.88	1.88	1.80	1.80	1.88	1.80
mean mol wt of products, g/mol	22.0	25.1	25.4	22.6	26.8	26.4	24.6	21.5	23.1	24.1	23.4	21.6	23.9
specific heat ratio of gases	1.26	1.22	1.22	1.25	1.21	1.21	1.23	1.25	1.24	1.24	1.24	1.25	1.24
gas volume, mol/g	0.045	0.040	0.040	0.044	0.038	0.038	0.041	0.046	0.043	0.042	0.042	0.044	0.042
burning rate at 20°C and 137.9 MPa,[c] cm/s	7.6	12.7	14.0	8.4	17.8	23.0	11.4	10.2	14.0	11.4	12.2	7.9	
pressure exponent	0.66	0.73		0.66	0.81	0.85	0.67	0.66	0.60	0.85	0.70	0.65	
combustion product composition, mol/g $\times 10^2$													
CO	2.33	1.54	1.61	2.24	1.28	1.13	1.81	1.45	1.15	1.89			
CO_2	0.19	0.51	0.48	0.22	0.66	0.74	0.40	0.14	0.25	0.33			
H_2	0.88	0.31	0.34	0.78	0.19	0.15	0.44	0.92	0.57	0.52			
H_2O	0.64	1.10	1.08	0.72	0.11	0.09	0.99	0.83	1.07	0.95			
N_2	0.44	1.49	0.48	0.45	0.54	0.54	0.46	1.29	1.30	0.50			

[a] At loading density of 0.2 g/cm^3.
[b] To convert J to cal, divide by 4.184.
[c] To convert MPa to psi, multiply by 145.

Calculations of the burning rates are not as rewarding. A number of models have been developed that consider the gas-phase reactions and the rate of energy transfer from the gas phase to the propellant surface

to be rate determining. Surface models and combination surface–gas-phase models have also been developed. Although the surface–gas-phase models have shown approximate agreement between calculated and experimental burning rates, the correlation is not good enough for design purposes.

3.1.2. Additives

Although the burning rate of nitrocellulose propellants at high gun pressures is not significantly affected by the presence of additives, the addition of 1 to 2% of some metallic salts such as lead acetyl salicylate, lead stearate [1072-35-1], and lead stannate [1344-41-8] to double-based propellants increases their burning rates at much lower rocket pressures (see Lead compounds). The effect decreases to that of the unleaded propellant as the pressure increases so that burning rate–pressure curves having very low pressure exponents are obtained only over limited pressure regions. It has been estimated that reducing the value of the pressure exponent, n, from 0.6 to 0.1 is equivalent to increasing the specific impulse by 15 seconds. The addition of solid oxidizers and metallic fuels tends to eliminate this catalytic effect. In plateau propellants, so named because of the shape of the log pressure–log burning rate curve, the catalytic effect disappears slowly, whereas in mesa propellants the catalytic effect disappears rapidly. The extent of the rate increase is affected markedly by the type and quantity of other components present (39–45).

3.1.3. Composite Propellants

A number of analytical models have been developed to quantitatively define the burning characteristics of composite propellants. The granular diffusion model postulates that the primary reaction zone of ammonium perchlorate propellants lies almost entirely in the gas phase. This zone is less than 0.01 cm thick at rocket pressures, and its thickness decreases as the pressure increases. The oxidant and fuel are decomposed and converted into gases by pyrolysis or sublimation as a result of energy transferred primarily by thermal conduction from the gas phase to the propellant surface. The gases evolved leave pockets on the surface. Pocket size is related to the particle size of the solid components. As burning occurs, the aluminum powder accumulates on the surface of the propellant and then agglomerates as clusters to form molten droplets up to 20 times the diameter of the individual particles in the propellant.

The Beckstead-Derr-Price model (Fig. 1) considers both the gas-phase and condensed-phase reactions. It assumes heat release from the condensed phase, an oxidizer flame, a primary diffusion flame between the fuel and oxidizer decomposition products, and a final diffusion flame between the fuel decomposition products and the products of the oxidizer flame. Examination of the physical phenomena reveals an irregular surface on top of the unheated bulk of the propellant that consists of the binder undergoing pyrolysis, decomposing oxidizer particles, and an agglomeration of metallic particles. The oxidizer and fuel decomposition products mix and react exothermically in the three-dimensional zone above the surface for a distance that depends on the propellant composition, its microstructure, and the ambient pressure and gas velocity. If aluminum is present, additional heat is subsequently produced at a comparatively large distance from the surface. Only small aluminum particles ignite and burn close enough to the surface to influence the propellant burn rate. The temperature of the surface is ca 500 to 1000°C compared to ca 300°C for double-base propellants.

The burning rates of composite propellants containing ammonium perchlorate can be significantly modified by changes in the particle size of the ammonium perchlorate. The burning rates of propellants containing ammonium nitrate or the nitramines, RDX or HMX, have high pressure exponents and are only slightly affected by particle size changes. Catalysts such as the oxides and chromates of iron, , and chromium also affect the burning rate of ammonium perchlorate propellants. However, these may have an adverse effect on the shelf life of the propellants (46–55).
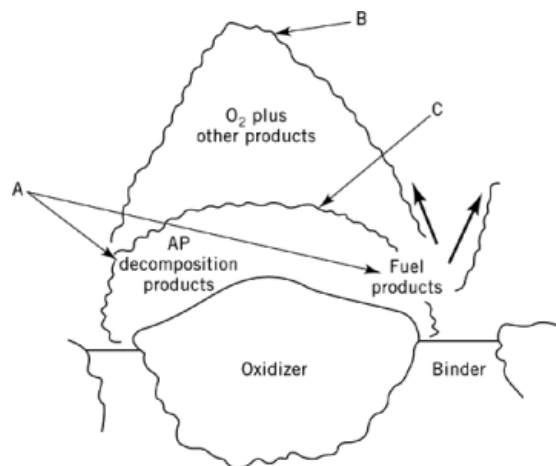
Fig. 1. The postulated flame structure for an AP composite propellant, showing A, the primary flame, where gases are from AP decomposition and fuel pyrolysis, the temperature is presumably the propellant flame temperature, and heat transfer is three-dimensional; followed by B, the final diffusion flame, where gases are O_2 from the AP flame reacting with products from fuel pyrolysis, the temperature is the propellant flame temperature, and heat transfer is three-dimensional; and C, the AP monopropellant flame where gases are products from the AP surface decomposition, the temperature is the adiabatic flame temperature for pure AP, and heat transfer is approximately one-dimensional. AP=ammonium perchlorate .

3.2. Burning-Rate Equations

The design of propellants for gun or rocket performance requires a knowledge of the exact rate at which the products of combustion are produced under the prevailing conditions of pressure and temperature. Although burning rates may be estimated by various computational procedures, the required accuracy can only be obtained experimentally. Burning-rate equations have been developed to describe the performance of solid propellants based on the assumption that all the exposed propellant surfaces are ignited simultaneously and burn at the same linear rate. For example:

$$r = a + bP \qquad (1)$$

$$r = cP^n \qquad (2)$$

where r is the linear burning rate, P is the pressure, n is the pressure exponent, and a, b, and c are constants that vary with temperature. Equation 1 is often used for propellants burning at high gun pressures, whereas equation 2 is associated with low pressure rocket systems.

3.3. Experimental Determination of the Burning Rate

Experimental determinations of the burning rate are made with the closed tomb for gun propellants and the strand burner for rocket propellants. The closed bomb is essentially a heavy-walled cylinder capable of withstanding pressures to 689 MPa (100,000 psi). It is equipped with a piezoelectric pressure gauge and the associated apparatus required to measure the total chamber pressure, which is directly related to the force of the propellant. It also measures the rate of pressure rise as a function of pressure which can then be related to

the linear burning rate of the propellant via its geometry. Other devices, such as the Dynagun and the Hi–Low bomb, have also been developed for the measurement of gun propellant performance.

The strand burner is a bomb pressurized with an inert gas-to-rocket pressure and equipped with auxiliary apparatus consisting primarily of electrical timers for determining the time to burn an accurately known distance on the propellant strand being tested. Tests are run on thin strands of propellant as extruded or machined from a grain. The data are directly converted to burning rates (56–63).

3.4. Burning Control

In order to produce propellant gas at a predetermined rate, a propellant composition is selected having the required burning rate for the operating pressures in the gun or rocket. The geometry of the propellant is then designed so that the necessary burning surface is available to provide the required mass rate of gas evolution. The individual propellant grains range from very small and numerous, eg, spherical grain dia = 0.01 cm, used for small arms, to very large, eg, dia = 3 to 5 m, and of complex geometry used for rocket boosters. Control of the total burning surface is achieved by establishing the number of grains to be used, the geometrical configuration, and, in the case of rocket propellants, the cementing of noncombustible inhibitors on grain surfaces to prevent burning, or by bonding the exterior of the propellant grain surface to the motor wall. The effect of grain shape on performance of gun and rocket propellants is shown in Figures 2 and 3, respectively. Propellant grains designed to provide a relatively uniform rate of gas evolution during the burning process have neutral geometries and undergo neutral burning. End burning grains are neutral burning, and single-perforated cylinders are almost neutral burning. Grains that increase in surface area during burning, eg, the seven or nineteen perforated grains used in large-caliber gun propellant charges, are said to burn progressively. Grains that decrease in surface area, eg, spherical grains, but regressively. Regressive burning in a gun is often undesirable, thus liquid or solid deterrents such as dibutyl phthalate, dinitrotoluene, and diphenylamine may be applied to the surface of the spherical grains used in small-caliber weapons. The geometry of rocket propellant grains is tailored to meet the specific performance required. It varies considerably, and may be much more complex than that of gun propellants.

3.5. Uncontrolled Burning

Because propellants contain potentially explosive components, a controllable burning process may change under certain exceptional conditions to uncontrollable burning with consequences comparable to a detonation. The transition from deflagration to detonation in explosives and propellants has been intensively studied, and the available evidence indicates that detonation is most likely to occur when the burning conditions can lead to the initiation and maintenance of a high pressure shock wave. If mechanical breakup of a rocket propellant occurs during the burning process, the large burning surface produced results in a high rate of gas evolution with correspondingly high pressures. An increasingly steep pressure front may evolve, accompanied by a pressure wave that transforms to a shock wave. Steady-state detonation can occur shortly thereafter. Detonation may also occur if fragments produced during grain breakup ricochet and rebound with sufficient kinetic energy to initiate an impact-sensitive propellant composition. Uncontrolled burning in rocket propellants is most likely to occur when using high energy propellants that have a large crystalline filler content of high energy explosives such as RDX or HMX and energetic plasticizer. It may occur in gun propellants if high loading densities are used to attain maximum velocities and ignition is not rapid, uniform, and nearly simultaneous in the charge; if the grains can be substantially compacted; or if the entire propellant charge is accelerated by localized ignition occurring at the charge base. A very high rate of pressure increase may then develop which produces a stress wave that is reflected from the base of the projectile back into the burning charge, reinforcing existing pressure waves and possibly leading to high pressure shock waves. The potential for transition from burning to detonation in a gun is minimized by designing for nearly simultaneous ignition; selecting propellants that
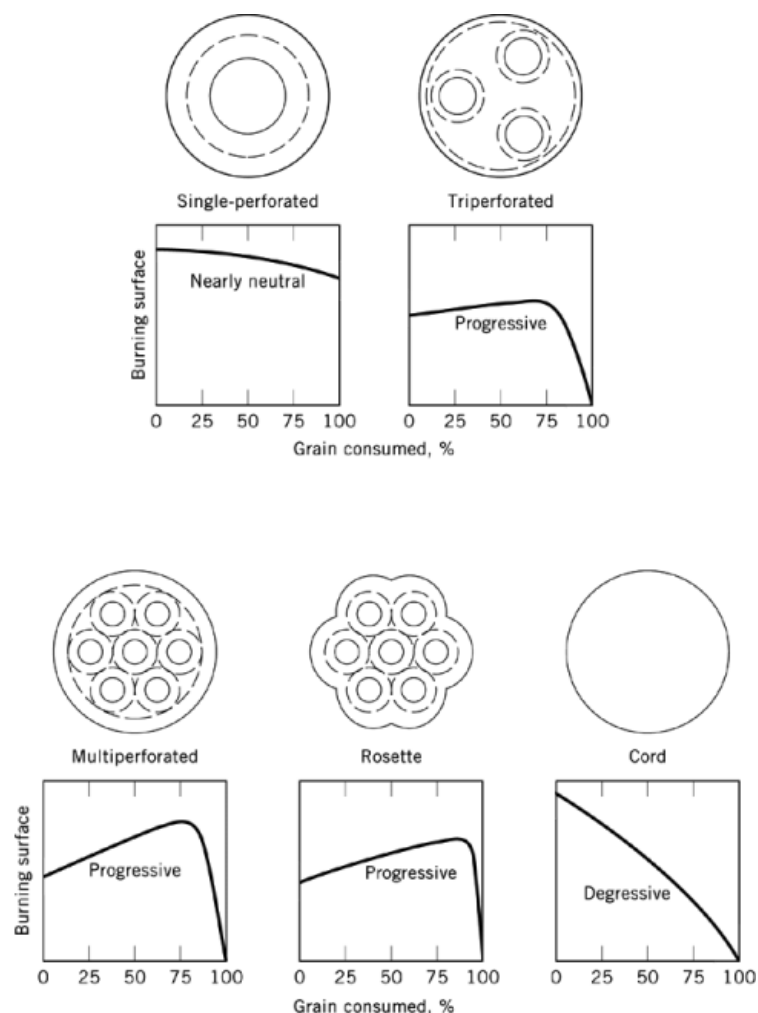
Fig. 2.   Effect of grain shape on surface exposed during burning of gun propellants. Cross section of grains are shown.

have high mechanical strength at all temperatures; and using compact, well-supported charges. Firing of gun and rocket propellants at low temperatures, eg, $-50°C$, are more likely to produce failures than at ambient or higher temperatures (64–72).

4. Component Characteristics

4.1. Rocket Propellants

4.1.1. Binders

Composite propellants are broadly classified in terms of the binder used because it is the fuel that reacts with the oxidizer and has a fundamental effect on the stability properties of the propellant. The most commonly used binders are polymers that chemically cross-link during the curing process. These polymers generally show
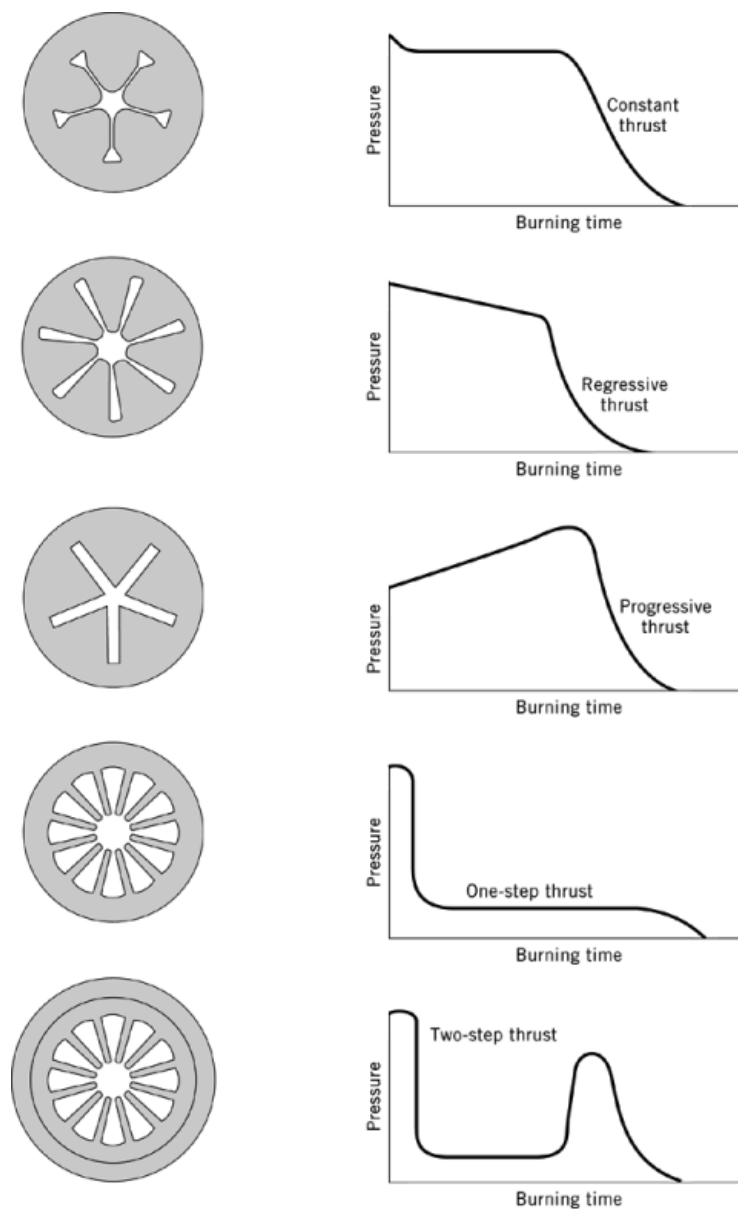
Fig. 3.   Effect of grain shape on pressure–time traces of rocket propellants. Cross section of grains are shown.

better mechanical properties at temperature extremes than plasticized binders. The mechanical properties depend on the number of cross-links and dangling chains. Thus the degree of cross-linking must be controlled to provide for polymer strength at elevated temperature, while allowing for the required elasticity at low temperature. The addition of trifunctional components to the composition and control of the ratio of trifunctional to bifunctional units establishes the number of branch points in the polymer and prevents excessive cross-linking.

A large number of polymeric compounds have been investigated, but most modern propellants utilize prepolymers that are hydroxy-functional polybutadienes (HTPB), carboxy-functional polybutadienes (CTPB), or a family of polyethylene oxides (PEGs) to form urethanes. **Typical cure reactions** are

$$RCH_2OH + R'NCO \longrightarrow RCH_2OOCNHR'$$

alcohol   isocyante   urethane
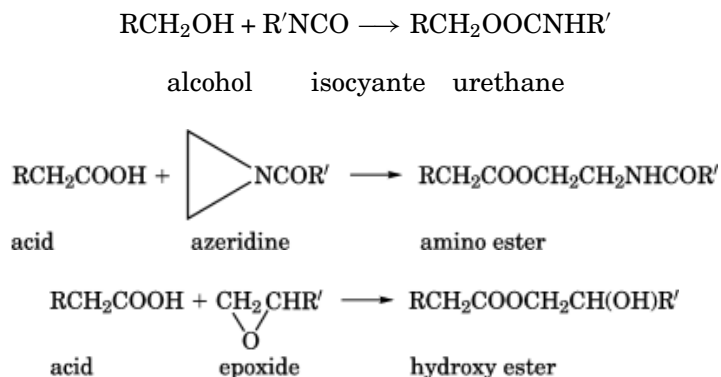
Considerable work has also been conducted to try to find thermoplastic elastomers that can be used to simplify processing by enabling dry blending and melt casting instead of the conventional mixing and curing process (see Elastomers, synthetic).

Thermoplastic elastomers are copolymers in which a thermoplastic segment is linked to an elastomer to produce copolymers having a central elastomeric core and thermoplastic ends. Mechanical strength is obtained by physical molecular linkages rather than by the chemical bonds obtained by curing at elevated temperatures. Ionomers (qv) are also under investigation. These materials produce a nonchemically cured composite matrix by linking polymers having ionic end groups and metal ions in the polymer matrix to effect the linkage.

Binders must be fluid prepolymers even when filled with 85 to 90% granular material. They must not react with the crystalline filler or other components, and should polymerize or cross-link without the formation of gaseous reaction products. Binders must be chemically and physically stable over long periods of time under severe environmental and operational conditions. They must form a durable and tough coating around the oxidizer and metallic ingredients and be capable of bonding to the interior wall of the motor after it has been suitably prepared by coating with an insulating liner and a bonding polymer. The rheological characteristics of the binder–filler and its pot life are also critical (73–78).

4.1.2. Plasticizers

Plasticizers are added to the binders to improve processability and flexibility at low temperatures. The plasticizer must have a very low melting point, dissolve in the polymer, and if possible provide oxygen in the combustion process to minimize any reduction in the specific impulse of the propellant. Many of the plasticizers used are esters of long-chain aliphatic alcohols and long-chain aliphatic acids. Typical compounds used with polybutadiene binders are isodecyl pelargonate [109-32-0] (mp -80°C) and diisooctyl adipate (mp -70°C). High energy plasticizers are designed to increase the energy level of the propellant. Typical nitrato- or nitroesters that have been investigated include nitroglycerin, butanetriol trinitrate [41407-09-4], trimethylethane trinitrate, bis(dinitropropylethyl) formal (FEFO), and a 1:1 mixture of bis(dinitropropyl) acetol and formal. Unfortunately many of the high energy plasticizers also tend to increase the propellant sensitivity.

4.1.3. Oxidizers

The characteristics of the oxidizer affect the ballistic and mechanical properties of a composite propellant as well as the processability. Oxidizers are selected to provide the best combination of available oxygen, high density, low heat of formation, and maximum gas volume in reaction with binders. Increases in oxidizer content

increase the density, the adiabatic flame temperature, and the specific impulse of a propellant up to a maximum. The most commonly used inorganic oxidizer in both composite and nitrocellulose-based rocket propellant is ammonium perchlorate. The primary combustion products of an ammonium perchlorate propellant and a polymeric binder containing C, H, and O are CO_2, H_2, O_2, and HCl. Ammonium nitrate has been used in slow burning propellants, and where a smokeless exhaust is required. Nitramines such as RDX and HMX have also been used where maximum energy is essential.

Characteristics of common inorganic oxidizers are listed in Table 5. In any homologous series, potassium perchlorate-containing propellants burn fastest; ammonium nitrate propellants burn slowest (79, 80).

Table 5. Properties of Inorganic Oxidizers

Oxidizer	Available oxygen	Melting point, °C	Density, g/cm^3	Heat of formation, kJ/mol^a	Heat capacity, J/(mol·K)^a	Gas, moles per 100 g^b
potassium perchlorate^c	46.0		2.53	−433.4	112.5	0
ammonium perchlorate	34.0	dec	1.95	−290.3	128.0	2.55
ammonium nitrate^d	20.0	169	1.72	−365.2	137.2	3.75
lithium perchlorate	60.6	236	2.43	−368.6	104.6	0

^{a} To convert J to cal, divide by 4.184.
^{b} Gas produced by oxidizer other than that formed by reaction of oxygen and fuel components.
^{c} Propellants with potassium perchlorate have relatively high burning rates (1.75 cm/s at 6.9 MPa (1000 psi) and 21°C) and high burning rate exponents (0.6–0.7).
^{d} Propellants with ammonium nitrate have very low burning rates (0.01 cm/s).

Ammonium perchlorate (AP) (see PERCHLORIC ACID AND PERCHLORATES) is hygroscopic between ca 75 to 95% relative humidity, and begins to deliquesce above 95%. AP starts to decompose at 439°C, and the decomposition may be catalyzed by metallic salts such as iron oxide and copper chromite at a lower temperature. Very finely divided ammonium perchlorate is more sensitive to impact and friction than the coarse material, and the presence of hydrocarbons greatly increases the likelihood of a detonable reaction. The burning rate of ammonium perchlorate propellants is also influenced by the particle size of the oxidizer, eg, the rate may increase by a factor of six by decreasing the average diameter from 400 to 1 μm. Bimodal and even trimodal distributions are used to load the binder with the maximum oxidizer content. Average particle size and particle size distribution affect the burning rate as well as the presence of other ingredients such as aluminum and catalysts. Particle size distribution of the perchlorate has a negligible effect on the pressure exponent and no effect on the specific impulse of the propellant (79–84).

4.1.4. Metallic Fuels

Aluminum is most commonly used to increase the impulse of both composite and nitrocellulose-base propellants because of its highly exothermic reaction with the oxidizer. Its heat of reaction with oxygen is 10.25 kJ/g (2.450 kcal/g). Materials such as aluminum hydride, beryllium, beryllium hydride, and boron offer theoretical advantages in increased impulse, but are not used because of increased cost, toxicity, or long-term instability, or because actual performance does not live up to calculated performance. Increasing the aluminum content of a propellant increases its density. The flame temperature and specific impulse sharply approach a maximum near the stoichiometric ratio of metal–oxidizer–binder. The aluminum increases the hydrogen content of the reaction products and, by minimizing the formation of water vapor, reduces the energy losses caused by dissociation of water at elevated temperatures. Incorporation of aluminum staples to replace a small part of the aluminum powder may quadruple the burning rate while maintaining the specific impulse. The presence of aluminum in rocket propellants also reduces or eliminates combustion instability caused by the formation of pressure waves in the motor chamber.

Aluminum-containing propellants deliver less than the calculated impulse because of two-phase flow losses in the nozzle caused by aluminum oxide particles. Combustion of the aluminum must occur in the residence time in the chamber to meet impulse expectations. As the residence time increases, the unburned metal decreases, and the specific impulse increases. The solid reaction products also show a velocity lag during nozzle expansion, and may fail to attain thermal equilibrium with the gas exhaust. An overall efficiency loss of 5 to 8% from theoretical may result from these phenomena. However, these losses are more than offset by the increase in energy produced by metal oxidation (85–87).

4.2. Liquid Propellants

4.2.1. Rocket Propellants

Liquid propellants have long been used to obtain maximum controllability of rocket performance and, where required, maximum impulse. Three classes of rocket monopropellants exist that differ in the chemical reactions that release energy: (*1*) those consisting of, eg, hydrogen peroxide, H_2O_2; ethylene oxide, C_2H_4O; and nitroethane, $CH_3CH_2NO_2$; that can undergo internal oxidation–reduction reactions; (*2*) those consisting of unstable molecules such as hydrazine, N_2H_2, and acetylene, C_2H_2; and (*3*) those consisting of stable mixtures of two or more compounds that are mutually compatible. These mixtures include methyl nitrate and methyl alcohol, CH_3NO_3/CH_3OH; hydrazine, hydrazine nitrate, and water, $N_2H_4/N_2NO_3/H_4/H_2O$. Hydrazine, which freezes at 275 K, is mixed with hydrazine nitrate and water (68:20:12) to meet low temperature requirements. Table 6 lists common and experimental liquid rocket bipropellants. Among the most commonly used are liquid oxygen and liquid hydrogen for maximum energy, nitrogen tetroxide and monomethyl hydrazine, and liquid oxygen and hydrocarbon fuels such as JP4.

Table 6. Liquid Rocket Bipropellants

Oxidant	Fuel	Ratio oxidant/fuel	Specific impulse, s[a]
O_2	H_2	4.0	341
O_2	B_2H_6	2.0	344
O_2	N_2H_4	0.90	313
O_2	JP4	2.60	301
F_2	H_2	9.00	410
F_2	JP4	2.40	317
F_2	N_2H_4	2.30	363
IRFNA[b]	C_2H_5OH	2.50	219
IRFNA[b]	UDMH[c]	3.00	288
H_2O_2	C_2H_5OH	4.0	230
H_2O_2	JP4	6.5	233
H_2O_2	N_2H_4		245
N_2O_4	N_2H_4		249
ClF_3	H_2	11.50	318
ClF_3	N_2H_4		292

[a] Calculated values.
[b] IRFNA contains 20–40% lithium nitrate, 55–75% red fuming nitric acid (RFNA), and 4–5% SiO_2; $mp = -54°C$.
[c] UDMH = unsymmetrical dimethylhydrazine.

4.2.2. Gun Propellants

Liquid propellants for guns have been investigated in two different types of systems: bulk and regenerative loading. Bulk loading involves insertion in the gun breech of the required quantity of propellant as a single unit, similar to a solid propellant charge, and subsequent ignition of the mass. The lack of reliable ignition and uniform combustion led to the abandonment of bulk loading.
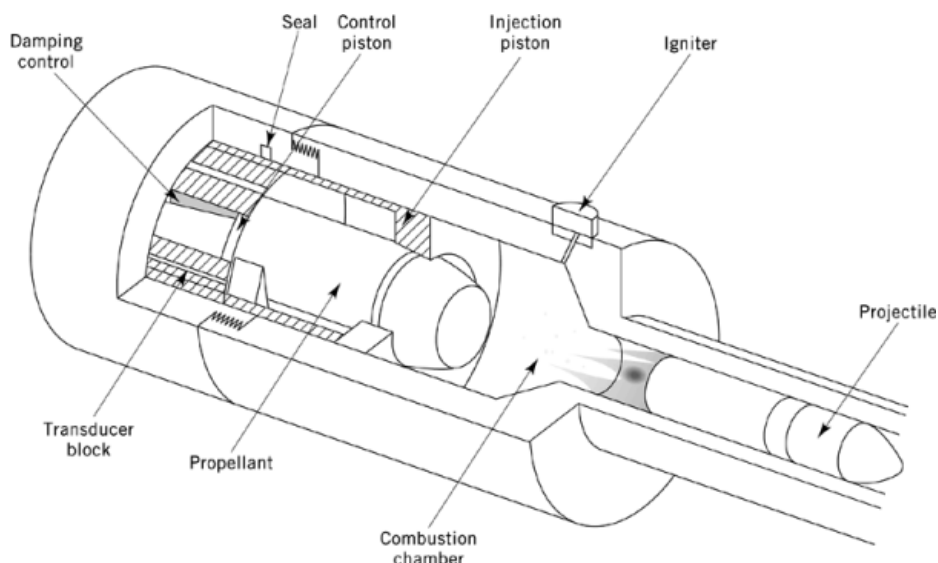
Fig. 4.   155-mm regenerative LP gun.

Regenerative loading requires continuous injection and combustion of the liquid propellant. Typical components of a regenerative liquid propellant gun are shown in Figure 4. Regenerative loading has progressed to the stage in the United States where extensive firings have been successfully conducted in guns up to 155 mm in caliber. A monopropellant mixture is used that consists of hydroxyl ammonium nitrate, triethylene ammonium nitrate, and water (20:63:17). This mixture is difficult to ignite accidentally, very stable, and biodegradable. The products of combustion are approximately 71% H_2O, 17% N_2, and 12% CO_2. Its flame temperature is 2590 K, freezing point $-100°C$, impetus 934 J/g (223 cal/g), specific heat ratio of the combustion gases, 1:22. It has low flammability and shock sensitivity, and does not detonate when subjected to the standard tests for insensitive munitions. The propellant is readily decomposed by transition metals and by nitric acid, and care must be taken to avoid contamination with ferrous materials (88–92).

4.3. Low Sensitivity Propellants

The initiation of gun and rocket propellants by fire, high velocity steel fragments and bullets, shaped charges, or electrostatic discharge, and the propagation of the resultant detonation shockwaves has resulted in catastrophic events on board military ships and on the battlefield, and has created problems in maintaining required safety distances in the storage of military materiel. As a result, gun and rocket propellants have been formulated to have minimum sensitivity to external stimuli and maximum energy content. Low sensitivity rocket propellants have also been designed to exhibit minimum smoke signatures.

4.3.1. Gun Propellants

Low sensitivity gun propellants, often referred to as LOVA (low vulnerability ammunition), use RDX or HMX as the principal energy components, and desensitizing binders such as cellulose acetate butyrate or thermoplastic elastomers (TPE) including polyacetal–polyurethane block copolymers, polystyrene–polyacrylate copolymers, and glycidyl azide polymers (GAP) to provide the required mechanical characteristics. Other high energy, low sensitivity plasticizers investigated include bis-dinitropropyl acetal formal, *n*-butyl-2 nitratoethyl-nitramine, and 1,3,3-trinitroazetidine. The weight percent composition and characteristics of a typical LOVA

propellant, such as M43, for use with tank ammunition is 76% RDX, 12% cellulose acetate butyrate, 7.6% bis-2,2-dinitropropyl acetal/formal, 0.5% neoalkoxy tri(dioctylphosphato)titanate, 4.0% nitrocellulose, 12.6% N, and 0.4% ethyl centralite [85-98-3]; heat of explosion 196 J/g (820 cal/g); impetus 1070 J/g (256 cal/g); and flame temperature 3065 K.

4.3.2. Rocket Propellants

Ammonium nitrate is the most common low cost oxidizer used to reduce sensitivity in solid rocket propellants. It is used extensively in formulations for gas generators. The propellants are cool, clean burning, and insensitive but have relatively low impulse. When processed and maintained at very low relative humidities, the volume changes characteristic of ammonium nitrate do not occur. Introducing 8–10% of potassium nitrate into the crystal lattice also eliminates phase transitions within the normal operating temperature range. The specific impulse of ammonium nitrate compositions may be increased by the use of energetic polymeric binders, such as polyglycidylazide or the addition of low concentrations of nitramine compounds such as RDX or HMX, although at some sacrifice of sensitivity (93–101).

4.3.3. Minimum Signature Propellants

Rocket propellants may produce undesirable smoke-forming combustion products in the exhaust plumes, ie, these products become visible signatures of the location of the source of smoke, and can interfere with optical guidance systems. Smoke formation is caused primarily by particulate matter, such as aluminum oxide, from aluminum in the rocket propellant, or to a lesser extent by compounds of iron, lead, or copper. This is referred to as primary smoke. Ionizing gases such as HCl serve as nucleation centers for the condensation of water vapor. Water in the propellant combustion products produces the secondary smoke that forms the contrails associated with missile flight.

Primary smoke can be nearly eliminated by deletion of aluminum from the compositions or reduction in the amount added from ca 20 to 1.2%. Aluminum, added primarily to increase specific impulse, may be replaced by high energy nitramine compounds such as RDX or HMX and energetic polymeric binders such as nitrate ester plasticized polyesters. These compounds tend to increase the sensitivity of the propellants. Very dry ammonium nitrate or phase stabilized ammonium nitrate, neither of which undergoes volume changes in the useful temperature range, may be used where lower specific impulses can be accepted. Ammonium nitrate is clean burning, has low sensitivity, and low cost. The inclusion of glycidyl azide polymers as an energetic binder component has been proposed to offset the reduced specific impulse.

Secondary smoke is produced mostly by the condensation of water in humid or cold air. The presence of hydrogen chloride or hydrogen fluoride in the combustion products increases the extent and rate of condensation. Composition modifications to reduce primary smoke may reduce secondary smoke to some extent, but complete elimination is unlikely. The relatively small amount of smoke produced in gun firings by modern nitrocellulose propellants, although undesirable, is acceptable (102–109).

5. Nonconventional Methods of Gun Propulsion

Advanced gun propulsion programs are pursued primarily to obtain projectile velocities considerably greater than the approximately 1.5–2.0 km velocity obtainable using conventional propellants and guns that rely on traditional interior ballistics. Hypervelocities would offer the possibility of achieving extraterrestrial orbits using gun-type systems instead of missiles. The advanced propulsion programs are of three types: those using chemical propellants for accelerating projectiles by unusual methods; those using electrical sources of energy; and those combining these two procedures.

5.1. The Traveling Charge

Conventional chemical propellants are designed to produce hot, high pressure gases at the breech of a weapon to accelerate the projectile down the bore of the weapon tube. A significant limitation in attainable velocity occurs because of the energy lost in accelerating the propellant gases as well as the projectile. Utilizing the traveling charge enables a theoretical increase of 10–20% in propulsion efficiency to be attained at velocities exceeding two kilometers per second. This is accomplished by attaching to the projectile a propellant having a very high (ca 100–500 m/s) burning rate to produce hot gases at a sufficient rate to maintain a constant thrust and pressure on the projectile base. The decrease in the work to accelerate the combustion gases combined with the impulse from the burning propellant accounts for the increased efficiency obtained by the traveling charge. The lower breech chamber pressures and increased downbore pressures characteristic of the traveling charge also produce a flatter, more efficient pressure-time trace similar to that obtainable with a rocket propellant. The required very high burning rate propellants have been experimentally obtained by inducing high porosity in the propellant during its manufacture, or by brittle break up of the propellant or incorporation of compounds such as decaborane, $B_{10}H_{14}$, in the propellant composition. The necessary predictability and controllability of very high burning rate propellants has not been achieved as of this writing (110–116).
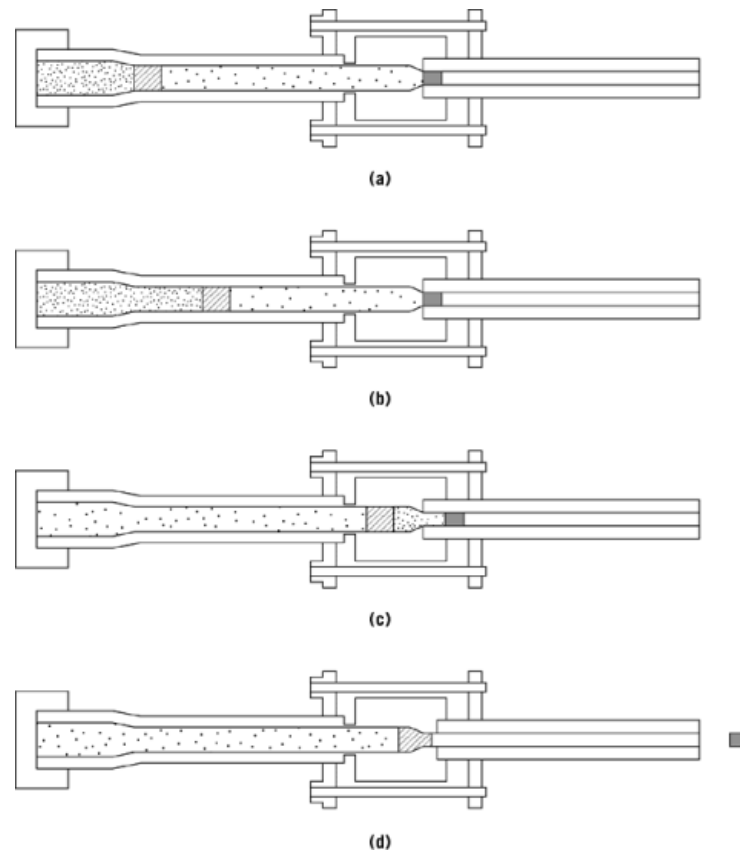
5.2. The Two-Stage Light Gas Gun

The light gas gun, designed to accelerate small projectiles to velocities up to 6.1 km/s, is an experimental tool used primarily to investigate hypervelocity penetrator/target interaction phenomena. The gun (Fig. 5) consists of a necked-down compression tube and a launch tube. The compression tube contains a firing chamber at the breech end filled with conventional propellant, a piston that closes the firing chamber, and a projectile that seals the mouth of the compression tube. Before firing, the front end of the compression tube is evacuated and filled with hydrogen or helium. The launch tube is also evacuated to minimize resistance to the projectile as it accelerates down the tube.

On firing, the gases from the propellant accelerate the piston that compresses the light gas in front of it. At a preestablished pressure, the projectile is propelled down the launch tube accelerated by the low molecular weight gas which follows the projectile to the mouth of the tube. The target material is placed in front of the launch tube, and appropriate instrumentation used to establish the characteristics of the interface reaction between projectile and target (117–120).

5.3. The Ram Accelerator

High velocities are obtained by causing combustion to occur continuously in the RAM accelerator as the projectile travels down the tube. The RAM accelerator consists of a subcaliber projectile similar to the centerbody of a conventional ramjet. The subcaliber projectile is initially accelerated in a conventional tube to velocities of about 1 m/s by a conventional propellant, or for experimental purposes by a light gas gun. As the projectile moves forward in the tube, it is further accelerated by the combustion of a reactive, premixed fuel–oxidizer gas mixture introduced under pressure into a long, eg, 10–20 m, accelerator tube. The gas that flows around the projectile is thermally choked so that it is initiated by the projectile and provides additional propulsive energy to the projectile. Diaphragms are used to seal off the end of the accelerator tube and individual sections into which different gaseous mixtures may be introduced. Gas mixtures of oxygen and methane, ethylene, or hydrogen have been used as fuels with inert gases such as argon and helium as diluents. Acceleration of the projectile depends on the propellant energy evolved, and the ratio of the mass of propellant gas to projectile mass. Velocities up to 10 km/s may theoretically be obtained (121–123).

Fig. 5.   Two-stage light gas gun showing the ▨ piston and ▪ projectile where =propellant charge and =light gas : (**a**), before firing; (**b**), after firing propellant charge; (**c**), as piston nears necked-down mouth of the launch tube; (**d**), after completion of firing cycle. Piston is removed from neck of launch tube before refiring or launch tube is replaced.

5.4. Electric Guns

Electric gun approaches that have been under considerable study include the electromagnetic (EM) gun and the electrothermal–chemical (ETC) gun. These use electrical pulse power to generate the energy required to achieve increased velocity and/or muzzle energy. The most commonly used energy storage devices are pulsed rotating machines or capacitors. The electromagnetic guns use intense magnetic fields, require special launchers, and can achieve maximum projectile velocities. The electrothermal guns use electrical energy to create a plasma, which adds energy to conventional propellant gun systems and produces greater control of the interior ballistic process.

EM guns, which offer the possibility of obtaining very high velocities with relatively short length accelerators, fall into two basic classes: railguns and coilguns. These differ in the geometry of achieving confined magnetic fields, and of coupling the resultant forces to achieve projectile acceleration, as shown in Figure 6. As a rule, railguns are conceptually and geometrically simpler, and have lower impedance, ie, require higher current and lower voltage for a specific propulsion task. They have received more developmental attention, despite the potential for greater energy efficiency from coilguns.

In the direct current electromagnetic railgun, a prime power source provides the energy to a pulsed power generator that produces electric pulses compatible with gun firing times. The current flows in one rail, across
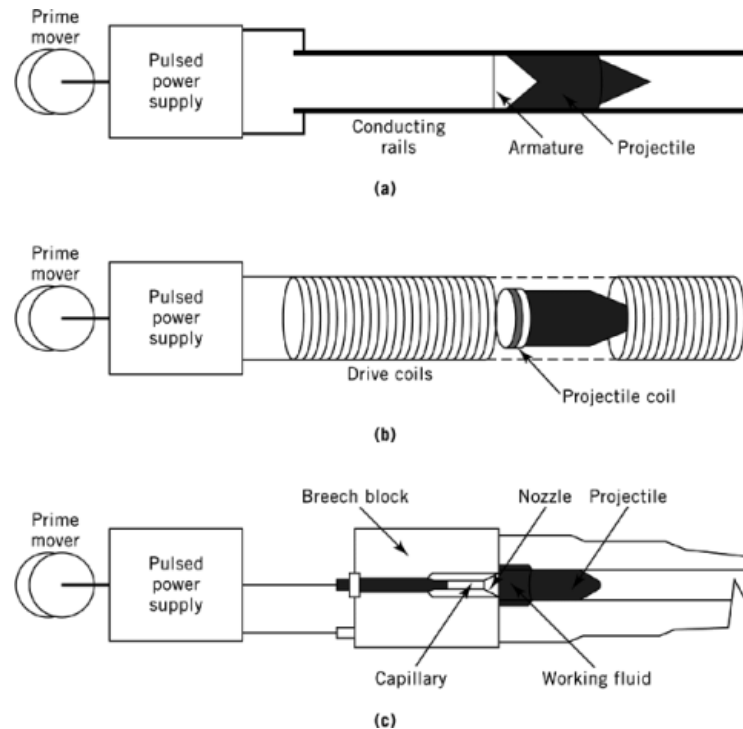
Fig. 6. Electric gun classes: (**a**), electromagnetic railgun; (**b**), electromagnetic coilgun; and (**c**), electrothermal gun.

an armature on the projectile, and back through the second rail. The gun barrel and armature constitute a one-turn coil. The current generates a magnetic field inside the gun tube; the interaction between the field and the current generates a Lorentz force which accelerates the projectile.

The electromagnetic coilgun requires pulse power on the same scale as the railgun. The current alternating in the multicoil barrel generates a changing magnetic field at the site of the projectile coil. The current in the projectile coil is attracted and/or repelled by suitably activated barrel coils. A sequence of Lorentz forces is produced like a surfboard riding a magnetic field wave.

Electrothermal–chemical propulsion is based on control of the propellant combustion process to produce a constant breech pressure–time relationship until all propellant is consumed. This contrasts with a peak pressure–time relationship produced by conventional solid propellant. The overall procedure provides high energy electrical pulses produced by a pulsed power generator. The electrical pulses generate a thermal plasma in a cartridge that initiates and controls the propellant burning process that accelerates the projectile down the bore of the tube. The velocity of the projectile depends on the electrical energy produced by the cartridge and the chemical energy of the propellant. The plasma cartridge delivers 10–20% additional energy to the propulsion system. Typically, the plasma is produced by using a high voltage, high current source to explode a foil or wire which pyrolyzes a plastic liner to yield a high (10,000–15,000 K) temperature low mass output of ionized species and hydrogen. A current continues to flow as long as the ionized species exists. Electrothermal propellants under investigation include metal–water mixes, peroxide–hydrocarbon mixes, and metal–metal hydride and water formulations (124–132).

6. Manufacture of Solid Propellants

6.1. Gun Propellants

Large numbers of small perforated grains or long sticks are used in gun propellant charges to provide the high mass rate of burning required to accelerate projectiles to maximum velocity in the relatively short distances of travel in gun tubes. These geometries are produced in enormous quantities most often by plasticizing nitrocellulose in simple mixers and extruding the soft propellant mix, which can be readily cut to the specification grain lengths and dried to a hard, horn-like texture. Stick propellant is made in the same way as granular propellant, but cut to form long strands on extrusion. Uniformity of performance is obtained by control of the composition, the volatile material present, the grain dimensions, and by blending on a large scale. Some variation in burning characteristics is permissible, because gun propellant charges can be modified to a limited extent to meet ballistic requirements by the addition or removal of propellant grains. Gun propellants are best evaluated by composition analysis, measurements of the heat of explosion, the grain dimensions, the mechanical characteristics, and the closed-bomb characteristics of relative force and quickness followed by confirmatory weapon firings.

Batch processes, which have been widely used in the manufacture of gun propellants, offer advantages of flexibility of operations and low capital investment. However, highly automated continuous and semicontinuous processes are rapidly replacing the batch processes and have been developed for single-, double-, and triple-base gun propellants and ball powder. These latter procedures offer increased safety, reduced lot to lot variation, lower labor requirements, decreased overall costs, and fewer pollution problems. Continuous processes often incorporate a variety of in-process monitoring sensors (qv) and analytical devices, automatic sampling, nondestructive testing (qv), and a high degree of automation and feedback controls. Twin-screw extruders are widely used as part of the automation process. Special procedures for increasing safety and reducing cost of gun propellants involve conducting mixing, conveying, and cutting operations under water (133–142).

6.2. Extruded Nitrocellulose Propellants

Nitrocellulose propellants are made with or without incorporation of a solvent as plasticizer by five processes:

Process	Propellant use
solvent extrusion	cannon
	fast-burning rockets
	casting powder
	ignition powder
	rifles, small-caliber weapons, expulsion charges
solvent emulsion	rifles
	small-caliber weapons
solventless extrusion	small rockets
	cannon
solventless rolling	mortars
casting	small rockets
	large rockets

All five processes require plasticization of the nitrocellulose to eliminate its fibrous structure and cause it to burn predictably in parallel layers. Mechanical working of the ingredients contributes to plasticization and uniformity of composition. The compositions of representative nitrocellulose-based gun propellants are shown in Table 7.

Table 7. Gun Propellant Composition[a], wt %

Component	M1[b]	M2	M5	M6	M8	M9	M10	M15	M17	M26	M30	M31[c]	IMR
nitrocellulose (% N)	85.0	77.5	82.0	87.0	52.2	57.8	98.0	20.0	22.0	67.5	28.0	20.0	100.0
	(13.15)	(13.25)	(13.25)	(13.15)	(13.25)	(13.25)	(13.15)	(13.15)	(13.15)	(13.15)	(12.6)	(12.6)	(13.15)
nitroglycerin		19.5	15.0		43.0	40.0		19.0	21.5	25.0	22.5	19.0	
nitroguanidine								54.7	54.7		47.7	54.7	
ethyl centralite		0.6	0.6		0.6	0.7		6.0	1.5	6.0	1.5		
diphenylamine	1.0[d]						1.0						0.7[d]
dinitrotoluene	10.0			10.0									8.0[e]
dibutylphthalate	5.0			3.0	3.0							4.5	
potassium nitrate		0.7	0.7		1.2	1.50				0.75			
barium nitrate		1.4	1.4							0.75			
potassium sulfate	1.0[f]			1.0[d]			1.0						1.0[d]
cryolite								0.3	0.3		0.3	0.3	
graphite		0.3	0.3			0.10[d]			0.15[d]				

[a] All compositions are solvent extruded as grains except M8 which is solventless-rolled as sheet.

[b] Also may contain 1.0 wt % basic lead carbonate.

[c] Also contains 1.5 wt % 2-nitrodiphenylamine.

[d] On added basis.

[e] Added as a coating.

[f] If required, on added basis.

6.2.1. Solvent Extrusion Batch Process

Almost all standard gun propellants and small-webbed rocket propellant grains are made by the solvent extrusion process. Grains having webs greater than ca 1.30 cm are produced by solventless or casting processes. The removal of solvents from large-web grains would require long periods of time and could introduce stresses that would lead to grain cracking. Triple-base propellants (M15, M17, M30, M31), having a high nitroguanidine content, are made similarly to double-base propellants. The manufacture of single-base propellants such as M1 and M6 compositions differs primarily in the mixing and drying operations.

In the typical process, purified, blended, and centrifuged nitrocellulose (NC) having the required nitrogen content and wet with ca 30% water is received from the nitrocellulose plant, transferred to a double-acting hydraulic dehydration press, and compressed at low pressure to remove some of the water. The remaining water is removed by pumping 95% ethyl alcohol through the nitrocellulose. The final blocks, containing ca 18% alcohol and ca 2.0% water, are broken up and screened to remove lumps or oversized particles. Mixing is conducted in a water-jacketed bladed mixer, and consists essentially of solid–solid and solid–liquid incorporation, the solution of stabilizers and possibly ballistic modifiers, and the absorption of solvents and liquid plasticizers by the nitrocellulose. This operation is governed by the heat generated, the heat-exchange characteristics of the operation, the method and sequence of incorporation and solvent addition, and the effects of specific equipment. The premixing operation for double- and triple-base propellants is designed to incorporate the nitroglycerin in the nitrocellulose and to begin to distribute the remaining ingredients in a slow and uniform manner. The final mixing blends the composition for an extended period of time until the ingredients are completely incorporated and plasticization occurs. The operation is generally conducted in a sigma-bladed, water-jacketed mixer to which several premix charges have been transferred. The temperature is maintained between 40 and 50°C, depending on the equipment and the colloid formation. The mix is cooled and discharged. All equipment must be grounded, and nonsparking tools used to avoid a solvent vapor–air explosion.

Single-base propellants are mixed in a similar fashion by adding the ingredients to the nitrocellulose in the mixer together with the required amounts of ether and alcohol. The mixing time is about one-half hour, and

the temperature is kept below 25°C. The partly colloidal mixture looks like moist crude sugar. A maceration step may be included to increase homogeneity.

After mixing, the dough-like composition is transferred to a vertical block screening press where it is consolidated. The block is ejected from the press. These operations remove lumps and foreign particles from the mix, increase the uniformity of ingredient distribution, and improve the colloiding of the nitrocellulose and the density of the propellant. The strands from the screening press are again consolidated in a blocking press. The blocks of propellant, whether single-, double-, or triple-base, are transferred to a vertical or horizontal graining press and extruded at relatively low pressures of 10.3–17.2 MPa (1500 to 2500 psi) through dies designed to produce the required dimensions. To ensure safety during pressing, explosive mixtures of air and solvent have to be carefully excluded during the ramming operation.

The strands of propellant are fed to a mechanical cutter and sliced to specified lengths, either as small grains or long sticks. Grains of double-, triple-, and some single-base compositions are dried in trays with warm air. The drying process for single-base propellant is entirely different from that of double- and triple-base propellant. First the alcohol–ether wet propellant is air-dried in transfer carts or large tanks to recover the solvents and reduce the volatile solvent content to ca 6%. The initial drying process is carefully controlled to prevent skin hardening or grain cracking. Temperatures are gradually raised to 50–65°C over a period of days, depending on grain size. The vapors are condensed and the solvent recovered. The propellant is then immersed in circulating water at 50–60°C. The solvent diffuses into the water, which prevents case hardening of the propellant surface and permits the solvent to be removed more rapidly than exposure to air alone would allow. After a period of time, up to ca 30 days for large single-base cannon grains, the temperature is slowly increased to reduce the solvent to a controlled minimum, depending on grain size. Final air drying at ca 55°C removes surface water.

The propellant may be tumbled in drums with a small amount of graphite to improve its flow characteristics and bulk density and to decrease the likelihood of formation of an electrostatic charge as well as to perform a degree of blending. It is then screened to remove foreign matter and blended into large lots which may range from 20 to 225 metric tons. The blending operation is essential to provide as homogeneous a lot as possible for ballistic uniformity. Although propellant grains are relatively insensitive to static electricity, propellant dust may be as sensitive as dry nitrocellulose. Fires in drying buildings and blending towers have been attributed in some cases to the electrostatic ignition of dust.

The wastewater produced in this process consists mostly of water used in cleanup and propellant conveyance and sorting operations. Techniques such as the use of activated carbon and biological treatment are being investigated for the removal of solvents and dissolved organic compounds (143).

6.2.2. Continuous Solvent–Extrusion Process

A schematic for a typical continuous process, widely used for making solvent propellant for cannons, is shown in Figure 7. This continuous process produces ca 1100 metric tons of single-base propellant per month at the U.S. Army Ammunition Plant (Radford, Virginia). Continuous processes have also been developed for double- and triple-base propellants and for stick as well as granular geometries. A principal aspect of these processes has been the extensive use of single- and double-screw extruders instead of the presses used in the batch process.

The main features in which the Radford process differs from the batch operation are in thermal dehydration and compounding. Water-wet nitrocellulose on a continuous vacuum belt filter is vacuum-dried followed by hot air transfusion (80°C) to reduce the moisture to less than 2%. After cooling, alcohol is sprayed on the nitrocellulose to a concentration of 15–20%. The alcohol-wet nitrocellulose is then transferred from a surge feeder to a compounder by a continuous weigh-belt along with the other ingredients of the composition, which are also weighed and added automatically.
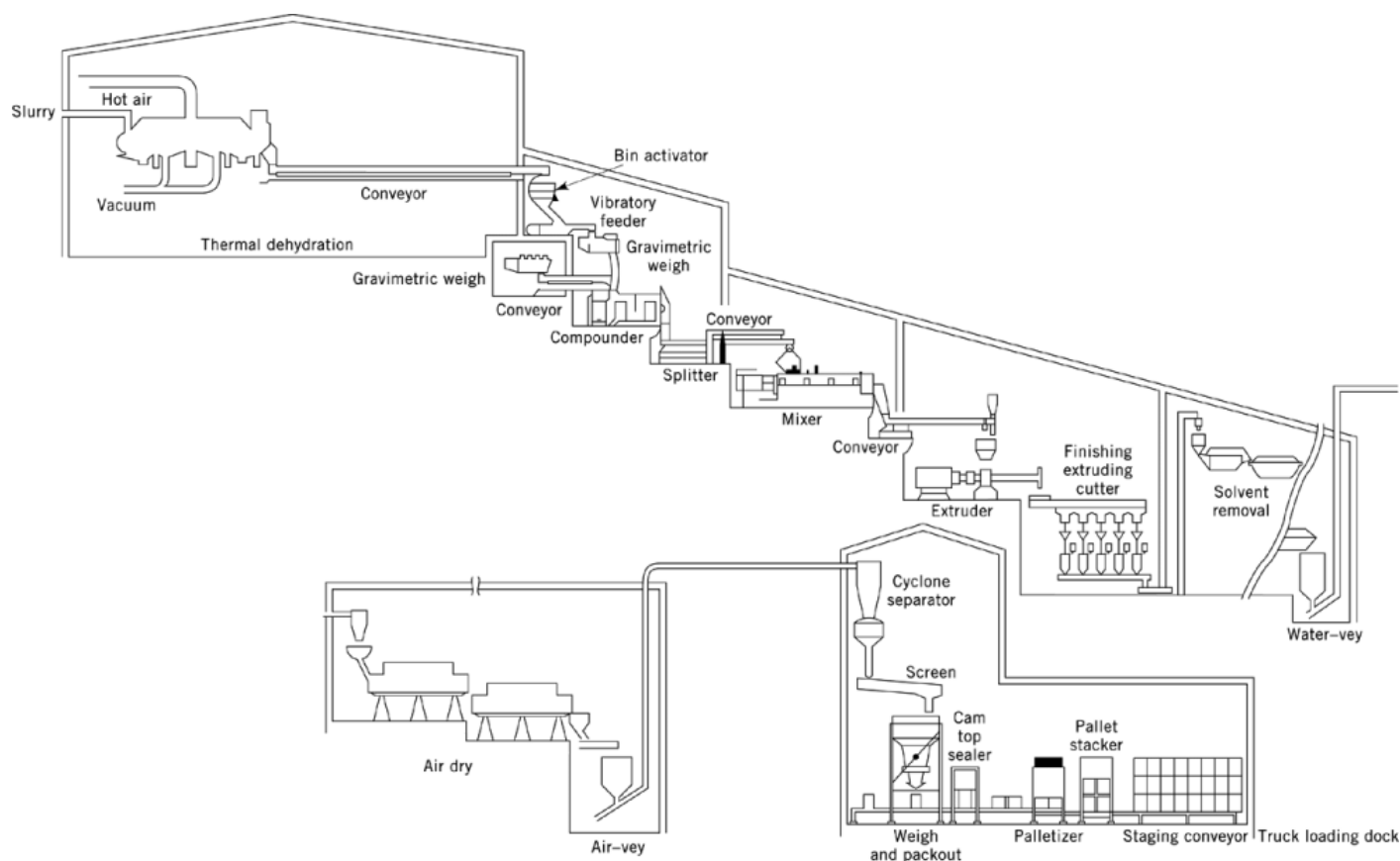
Fig. 7. Continuous process for solvent-extruded single-base propellant (automated single-base line). Vey=conveyor .(Courtesy of John Horvath, U.S.A. (Radford, Virginia).)

The compounder is a water-jacketed horizontal rotary plow that blends the ingredients to produce a homogeneous premix paste. The mixed paste is fed by a conveyor to a heavy-duty reciprocating screw mixer that is temperature controlled and specially designed to thoroughly mix and work the paste by forcing it past pins in the mixer barrel and out through a die plate. As the paste is extruded, it is cut into small pellets that are fed continuously to water-jacketed screw extruders and forced through multiple dies which provide the final shape. The strands are cooled as they are extruded to facilitate cutting by an adjustable roll-type cutter. After the cut grains are screened to remove clusters and odd sizes, the solvent is removed in the solvent recovery-water dry system where the propellant is treated first with hot inert gas and then hot water. Finally, in a series of air dryer units, the moisture content is reduced from 12 to less than 0.8%.

The entire continuous automatic process is computer controlled so that continuous performance information is available. Pressure relief is permitted wherever possible to minimize the likelihood of a detonation. Continuous-screw extrusion processes may be employed for making nitrocellulose single-, double-, and triple-base gun propellants, for some composite propellants, and for some plastic bonded explosives (144).

6.2.3. Solventless Extrusion Process

The solventless process for making double-base propellants has been used in the United States primarily for the manufacture of rocket propellant grains having web thickness from ca 1.35 to 15 cm and for thin-sheet mortar (M8) propellant. The process offers such advantages as minimal dimensional changes after extrusion, the elimination of the drying process, and better long-term ballistic uniformity because there is no loss of volatile solvent. The composition and properties of typical double-base solvent extruded rocket and mortar propellant are listed in Table 8.

Table 8. Composition and Properties of Double-Base Solventless Propellant

	Extruded for	
Parameter	Rockets	Mortar sheets
Approximate composition, wt %		
nitrocellulose[a]	51.5	52.5
nitroglycerin	43.0	43.0
potassium nitrate		1.0
diethylphthalate	3.0	3.0
ethyl centralite	1.0	0.50
potassium sulfate	1.25	
carbon black	0.20	
wax	0.05	
Thermochemical properties		
flame temperature, K		
isochoric	3660	3695
isobaric	3010	
specific impulse, N·s/kg[b]	2317	
heat of explosion, J/g[c]	5108	5209
heat of combustion, J/g[c]	9295	
gas volume, mol/g	0.038	0.037
ratio of specific heats	1.22	1.21
burning rate at 5.89 MPa[d] and 21°C, cm/s	1.52	
pressure exponent	0.68	
products' composition, wt %		
hydrogen	6.5	
water	27.0	
carbon monoxide	33.0	
carbon dioxide	18.0	
nitrogen	14.0	
other	1.5	

[a] Nitrogen content is 13.25%.
[b] To convert N·s/kg to lbf·s/lb, divide by 9.82.
[c] To convert J to cal, divide by 4.184.
[d] To convert MPa to psi, multiply by 145.

In the water-slurry process for making solventless propellants, developed in 1889, explosive and nonexplosive liquid plasticizers and water-insoluble constituents are incorporated into nitrocellulose suspended as a slurry in a large volume of hot (50°C) water. (The ratio of water to total propellant components is ca 10:1, ca 20:1 on a nitrocellulose base). After removing the excess water in a basket-type centrifugal wringer equipped with a wire-mesh screen, the resulting wet (ca 15% water) mass is partially dried at ambient temperature. During this aging process, the nitrocellulose absorbs and is partially gelatinized by the plasticizers. Water-soluble salts are then incorporated during a blending operation in a rotating drum.

The rolling operations that follow take place first on hot (95°C) differential-speed rolls which dry and colloid the paste and convert it into sheet form, and then on even-speed rolls which produce smoothly surfaced

propellant sheets in which all ingredients have been uniformly incorporated. The roll gap in the differential rolls is adjustable to produce sheets of various thicknesses, and rolling is continued until the moisture is reduced to a predetermined level, usually less than 0.5%. The sheet is then cut off the roll. Differential rolling is potentially hazardous, and fires are not uncommon, although detonations are not apt to occur. Operations are conducted by remote control.

Typical even-speed rolls, about the same dimensions as the differential rolls, are highly polished, heated to ca 60°C, and revolved at ca 10 rpm. If rocket propellant grains are being made, the sheet is slit into strips and rolled to form carpet rolls. A charge of large enough diameter is made to fit snugly into an extrusion press, which may be jacketed for temperature control and equipped with vacuum pumps for removal of air. The diameter of the press bore may be up to 60 cm, and the press may be horizontal or vertical with pressures up to 103 MPa (15,000 psi) used for extrusion. The press is loaded with the propellant, evacuated, and extrusion is begun. On extrusion, the strand is cut into the required grain lengths. The grains may be solid or have central perforations of various shapes, depending on the configuration of the die pin. The grains are visually inspected, annealed at elevated temperatures, and inspected by x-ray (143, 145).

6.3. Ball Powder

Ball powder, typically used in small-caliber weapons such as 5.56-mm, 7.62-mm, and 20-mm projectiles, has also been proposed for large-caliber weapons. The product consists of spherically shaped or flattened ellipsoidal grains, ca 0.04–0.09 cm in diameter. The process permits the recovery and use of nitrocellulose from obsolete granular propellant. It eliminates the need for the conventional mixers, extruders, and cutters used to make granular and stick propellant, and is relatively inexpensive to operate. The process is safe because mixing and extrusion take place in the presence of water. The operations are flexible so that either single- or double-base ball propellants may be produced. The use of surface layer deterrents on ball powder reduces flame temperatures during the initial stages of burning and thereby reduces barrel erosion at the time when maximum gun pressures occur. Typical composition and characteristics are shown in Table 9. The product has desirable flow characteristics because of particle shape so that small arms ammunition can be rapidly loaded by high speed automatic equipment. LOVA compositions using ball powder have been investigated, as well as procedures for achieving higher loading density by compaction of the grains.

6.3.1. Batch Process

A flow chart for the ball powder batch operation is shown in Figure 8. Water-wet fresh or extracted nitrocellulose is transferred as a slurry to a graining still. Calcium carbonate is added to neutralize any free acid released by the dissolved nitrocellulose. Ethyl acetate is added as are other soluble components such as diphenylamine. The contents are heated to ca 70°C and agitated. When the proper viscosity of the lacquer is attained, a protective colloid such as animal glue is added to form an emulsion of nitrocellulose globules. Sodium sulfate is added ca one-half hour after the beginning of globule formation to extract water from the lacquer by establishing an osmotic pressure differential between the water-laden nitrocellulose globules and the concentrated salt solution in the still. Under these conditions, small spheres of dissolved nitrocellulose and the other soluble ingredients are formed. The ethyl acetate is distilled at 70–100°C, leaving spherical particles. This graining operation requires ca 1 to 1.5 h. Grain density and size are determined by the concentration of salt in solution, the temperature and time of the dehydration, agitation speed, and the rate of distillation of the ethyl acetate.

After graining, the slurry is water-washed and then wet-screened. Over- and undersize grains are returned to the graining operation for reworking. Nitroglycerin or an organic coating material are added following the transfer of the screened ball powder as a water slurry to a coating still. The water level is adjusted, the temperature increased to 60–65°C, and a solution of nitroglycerin in ethyl acetate added with slow agitation to form an emulsion. The ethyl acetate is distilled under vacuum at 70 to 85°C, leaving the nitroglycerin present in a gradient of decreasing concentration from the surface toward the center of the spheres. If a deterrent is

Table 9. Composition and Properties of Ball Powder Propellants

Parameter	Value
Composition, wt %	
graphite[a]	0.4
potassium nitrate	1.0–1.5
sodium sulfate[a]	0.5
calcium carbonate[a]	1.0
nitroglycerin	8.0–12.0
diphenylamine	0.75–1.50
dibutyl phthalate	3.5–7.5
total volatiles[a]	2.0
residual solvents[a]	1.2
dust and foreign matter[a]	0.1
dinitrotoluene	as required
nitrocellulose	remainder
nitrogen, %	13.0–13.2
Physical properties	
hygroscopicity	1.75
granulation	
through no. 20 (840 μm) sieve, %[b]	95
through no. 40 (420 μm) sieve, %[a]	50
through no. 45 (350 μm) sieve, %[a]	3
bulk density, g/cm^3	0.95–1.0
Thermochemical properties	
heat of explosion, J/g[c]	3350–3768
flame temperature, K	2700–3000
volume of gaseous products at STP mol/g	0.04
impetus, J/g[d]	1000

[a] Value given is maximum value.
[b] Value given is minimum value.
[c] To convert J to cal, divide by 4.184.
[d] To convert J/g to ft·lb/lb, multiply by 335.

used, such as dinitrotoluene in dibutylphthalate, it is then transferred to the still, the slurry is slowly agitated at ca 75°C, cooled, transferred to a wash tub, and water-washed. The coating cycle may take ca 24 to 30 h, depending on the propellant.

Rolling may be used for shape and size modifications to increase burning surface area of the propellant. A thick water slurry of the spheres is passed through a set of appropriately spaced even-speed polishing rolls, rotating toward each other. Centrifuging the slurry reduces excess moisture to ca 6%. Surface ballistic modifiers such as dinitrotoluene, tin oxide, potassium nitrate, or small amounts of other water-soluble salts are added as an alcohol slurry. The alcohol is removed with hot air, and graphite is added to glaze the propellant. The moisture content is adjusted by the addition of water, if required, or drying.

The propellant is dry-screened to remove dust and foreign material, and excess graphite. Unacceptable propellant from the dry-screen operation may be returned to the graining stage for reworking. The product is blended in large rotating barrels for ballistic uniformity.

6.4. Continuous Process

In the continuous process, developed by Olin Corp. and now used more extensively than the batch process, the nitrocellulose and stabilizing additives are dissolved in the solvent in a continuous-screw mixer to form a dough-type lacquer, which is pumped continuously through filters to the graining operation. The lacquer is

```
┌─────────────────────┐
│      NC slurry       │
└─────────────────────┘
           │
           ▼
┌─────────────────────┐     ┌─────────────────────┐     ┌─────────────────────┐
│ Hardening in stills  │     │Nitroglycerin coating │     │  Salt, coat, and glaze│
├─────────────────────┤     ├─────────────────────┤     ├─────────────────────┤
│                      │     │  Impregnate with NG in│     │  Coat with tin dioxide│
│                      │     │     ethyl acetate    │     │ and/or potassium nitrate│
│   Prepare NC         │     │                      │     │                      │
│ lacquer using EA,    │     │  Vacuum distill to   │     │  Glaze with graphite │
│   CaCO₃, DPA,        │     │     remove EA        │     └─────────────────────┘
│ colloid, and Na₂SO₄  │     │                      │                │
│                      │     │  Apply deterrent,    │                ▼
│  Form grains, shape  │     │  dibutyl phthalate   │     ┌─────────────────────┐
│                      │     │                      │     │     Dry screen       │
│  Densify spheres     │     │ Time/temperature heat│     ├─────────────────────┤
│                      │     │     treatment        │     │  Remove "overs" and  │
│  Wash colloid and    │     └─────────────────────┘     │    excess dust       │
│     Na₂SO₄           │                │                 └─────────────────────┘
│                      │                ▼                            │
│                      │     ┌─────────────────────┐                ▼
└─────────────────────┘     │   Roll and dewater   │     ┌─────────────────────┐
           │                ├─────────────────────┤     │      Blending        │
           ▼                │  Roll to specific web│     ├─────────────────────┤
┌─────────────────────┐     │                      │     │  Preblend, 5 circles │
│   Size separation    │     │   Centrifuge into    │     │ into 60 bags, 85 kg ea│
├─────────────────────┤     │   circle buggies for │     │                      │
│  Screen into specific│     │    movement to the   │     │  Final blend, cross  │
│ cuts and weigh charge│     │      dry line        │     │ blend of 15 preblends│
│   for NG coating     │     └─────────────────────┘     │ to get a 75,000 kg lot│
└─────────────────────┘                │                 └─────────────────────┘
           │                           ▼                            │
           │                ┌─────────────────────┐                ▼
           │                │      Tray dry        │     ┌─────────────────────┐
           │                ├─────────────────────┤     │      Packing         │
           │                │   Load powder into   │     ├─────────────────────┤
           │                │   trays and dry with │     │   Pack into M-24s    │
           │                │   hot air in ovens   │     │ (copper-lined wooden │
           │                └─────────────────────┘     │  boxes) or fiber drums,│
           │                           │                 │   150 per container  │
           └───────────────────────────┘                 └─────────────────────┘
```

Fig. 8.   Ball powder batch process. NC=nitrocellulose, EA=ethyl acetate, DPA=diphenylamine, NG=nitroglycerine.

extruded as cylindrical strands that are cut with a rotary knife into grains having a length to diameter ratio of ca 1.5 to 1. The cut cylinders are flushed away from the exit side of the graining plate using a solution of water, colloid, and salt, and are transferred to the shaping and dehydration lines. Automatic controls and monitors are used throughout.

The shaping and dehydration line is a long bank of pipes connected by short-radius U-shaped bends that are hot-water jacketed to provide a gradually increasing temperature of ca 60 to 80°C. On passage through the pipe, the viscosity of the particles decreases, and they become spherical and are dehydrated by the dissolved salt present to ca 10% entrained water. The large percentage of entrained solvent is removed by passing the lacquer–water through a series of evaporators. The propellant slurry is then passed over a screen and vacuum filtered in series to recycle the salt and colloid solution and to wash residual colloid from the grains. After washing, the propellant may be vacuum-dried to remove excess water. It is size classified on a series of continuously rotating screens, and may then be impregnated with nitroglycerin; ethyl acetate is removed by vacuum distillation. The product is coated with deterrent, and rolled if necessary, by the same methods used in the batch process. Moisture is removed by a series of continuous vibrated semifluidized-bed dryers. Surface coatings are applied in a continuous drum or a batch barrel blender. Blending is carried out in a static internal tube-type blender or a large barrel blender. The propellant is packed in drums for shipment.

The wastewater in the ball powder processes arises primarily from the washing and wet-screening process. Wash and screen waters are passed through clarifiers to remove suspended solids. The overflow from the clarifiers may be accumulated in lagoons. The wash waters contain a considerable amount of protective colloid, organic solvent, and sodium sulfate, and have to be treated before they are discharged into local streams. The colloid foams in the effluent and increases the BOD by accumulating on the bottom of the collection ponds. Cooling water can be completely recycled, and it is possible to design the washing and wet screening operations to decrease the contaminants in the plant effluent (146).

6.5. Rocket Propellants

The manufacture of propellants for rocket systems poses problems that do not exist with gun propellants. Rocket grains are generally much larger and may have more complex shapes. Each rocket grain must be made free of flaws to avoid the possibility of internal burning and breakup. In-process variations of a minor and not readily identifiable nature may produce significant changes in performance. Once the rocket grain is produced, it cannot be readily changed if it does not meet requirements. Differences in lot performance cannot be blended out as with gun propellants. Many propellant compositions have been developed to meet specific needs (147).

The most common method for producing large rocket grains involves casting a prepared mix into a mold and causing it to solidify using a solvation process, as for nitrocellulose-based propellants, or a polymerization process, as for composite propellants. Extrusion procedures may be used for the smaller (dia $_{<15-20}$ cm), rocket grains but are not feasible for large grains. The difficulty of controlling the curing operation during extrusion, and particularly the relatively limited numbers of grains required as compared to gun propellant requirements, limits the applicability of extrusion to large-volume tactical rocket applications (133).

6.6. Cast Propellants

6.6.1. Nitrocellulose-Based

Cast nitrocellulose propellant is made by a two-step process. In the first stage, casting powder is produced by procedures that are almost identical to those used for the manufacture of conventional solvent-extruded small-grain gun propellants. The second stage consolidates the casting powder by filling the interstices of the granules with a fluid plasticizer that diffuses into the powder and causes swelling and ultimate coalescence of the granules into a monolithic grain. The plasticizer generally consists of a mixture of an explosive energy-producing liquid such as nitroglycerin and an inert fluid such as triacetin. The process of consolidation is a physical one. No chemical reaction occurs, and there is virtually no shrinkage during curing.

A typical high performance composite-modified double-base cast rocket propellant starts with a single- or a double-base casting powder consisting of 30% nitrocellulose, 10% plasticizer, 30% solid oxidizer, 28% metallic fuel, and 2% stabilizer. The final propellant composition contains ca 22% nitrocellulose, 32% plasticizer, 24% solid oxidizer, 20% fuel, and ca 2% stabilizer. The type and percentage of nitrocellulose significantly affects the mechanical characteristics of the propellant. Tensile strength and the modulus of elasticity increase, and elongation decreases as the percentage of nitrocellulose increases from 12.0 to 13.15%. The mechanical properties improve at a 12.6% nitrogen content of the nitrocellulose which is most commonly used. Tougher propellants having favorable heats of formation and a satisfactory carbon–hydrogen–oxygen balance are obtained using low molecular weight nitrocellulose as a binder and the addition of compounds such as poly(ethylene glycol).

Because double-base propellants cannot be directly bonded to the walls of a rocket motor to maximize the propellant weight in the motor, an adhesive resin is sprayed into the interior while the motor is rotated. A small amount of casting powder may also be sprayed into the tacky resin. The liner is cured and becomes an integral part of the propellant charge after casting. The motor is fitted with the required casting attachments, placed in a casting pit if necessary, and the casting powder dispenser and associated equipment are installed.

The casting powder flows from a hopper through a distributor screen and a screen plate to disperse the powder uniformly into the motor. A high velocity air stream may also be used to carry the powder into the motor.

The fluid plasticizer (solvent) consists of an energetic compound, eg, nitroglycerin, an inert carrier, and a stabilizer. The system is evacuated to remove volatiles, moisture, and air, and the plasticizer is then pressurized and passed slowly upward through the powder bed while the powder is held stationary by a pressure plate on the powder column. Casting solvent may also be added from the top of the mold.

The cast-loaded rocket motor is cured at 45 to 60°C for as long as two weeks, depending on grain size. The gelatinizing solvent and the casting grains mutually diffuse so that the final rocket grain is a tough, pore-free, sturdy structure. The compositions of several typical cast double-base and composite-modified double-base propellants are given in Table 10. Cast propellant may also be made similarly in plastic inhibitor cases or uninhibited for use in cartridge loaded applications (148–150).

6.6.2. Polymer-Based

The advantages of polymeric-based cast propellants are the extensive range of performance characteristics, excellent thermal and mechanical stability, and relatively low cost. Maximum performance is obtained by the use of maximum energy propellants, maximum loading density in the rocket motor, and lightweight graphite composite cases. The facilities used in composite propellant manufacture do not compete with those required for making nitrocellulose propellants. A number of programs have been developed to convert batch to continuous processes with varying degrees of success. However, batch processes are generally employed, although various operations may be automated and made semicontinuous. Polymer-based propellants have also been made for small and medium size rocket motors using injection flow forming techniques and die extrusion processes (151).

The manufacturing operations for making different composite propellants are very similar, although a variety of polymeric binders may be used. Processing variations, even small ones, may have a significant effect on the mechanical properties of a propellant and the volumetric loading in the motor. Because the viscous propellant mix must flow uniformly and rapidly into all parts of the rocket motor assembly during the casting operation, the processibility of a formulation is fundamentally related to its rheological characteristics. These depend primarily on the cure characteristics of the polymeric binder, the volume of solids loaded into the binder, and the particle shape and size distribution of the solids. Relative humidity control at 40% or less is used in most of the process operations because degradation of the polymer, the liner insulation, and the bond between the liner and the propellant as well as shorter pot life and increased mix viscosity may occur in the presence of moisture. The perchlorate and the other components of the system may also be significantly affected.

A flow chart of a typical batch process is shown in Figure 9. The oxidizer most commonly used is ammonium perchlorate which is rigidly controlled for moisture, impurities, and particle size and shape, and may contain a flow additive such as tricalcium phosphate. Slow and high speed grinding are accomplished by hammer mills which may be coupled to an air classifier to provide the range of particle size distributions required. Fluid energy pulverizers are also used. Typical particle size ranges from 3–9 μm for microatomizers to 20–160 μm for micropulverizers. The oxidizer is blended, screened, and transferred to a storage hopper for subsequent use.

In the premix operation, a uniform slurry of all components, except the oxidizer, is prepared. The premixes may contain cross-linking, wetting, opacifying, and antifoaming agents, plasticizers, metallic fuels, catalysts, and curing compounds. Automated techniques ensure formulation uniformity and reproducibility. The polymer and other large-volume fluids required are pumped from the storage tanks to weigh tanks and then to the premix vessels. These may be up to 5000 L in capacity and equipped with turbine-driven agitators designed for the specific materials being handled. The secondary liquid components, including a portion of the curing agent, are weighed, added, and mixed at a controlled temperature after first purging the premix vessel with nitrogen. The necessary solids other than the oxidizer are screened and added, followed by further mixing under nitrogen, and finally under vacuum to remove entrapped gases. Batch mixers are temperature controlled and designed

Table 10. Composition and Properties of Nitrocellulose-Based Cast Propellants

Parameter	Low energy	High energy	
	A	B	C
Composition, wt%			
nitrocellulose, 12.6% N	59.0	20.0	22.0
nitroglycerin	24.0	30.0	30.0
triacetin	9.0	6.0	5.0
dioctylphthalate	3.0		
aluminum		20.0	21.0
HMX		11.0	
stabilizer	2.0	2.0	2.0
ammonium perchlorate		11.0	20.0
lead stearate	3.0		
Ballistic properties			
specific impulse, N·s/kg[a]	2062	2651	2602
burning rate at 6.9 MPa[b] and 20°C, cm/s	0.65	1.40	2.00
pressure exponent		0.45	0.40
pressure coefficient		0.025	0.04
Thermochemical–thermodynamic properties			
heat of explosion, J/g[c]	2931	7718	7432
heat of formation, $-\Delta H_f$, J/g[c]		1570	1842
flame temperature, K	1925	3850	3900
mean heat capacity, J/(g·K)[c]			
products	1.80	1.76	1.76
gases	1.80	1.26	1.21
mean molecular weight, g/mol			
products	21.8	27.9	28.9
gases	21.8	30.9	21.0
specific heat ratio, gas	1.27	1.18	1.17
Combustion products composition, mol / 100 g			
C	2.12		
CO_2	0.31	0.05	0.07
CO	2.12	1.30	1.15
H_2	1.06	0.75	0.66
H_2O	0.66	0.27	0.33
N_2	0.43	0.49	0.38
Pb	0.004		
Al_2O_3		0.35	0.37
H		0.20	0.23
OH		0.05	
other		0.5	0.10[d]

[a] To convert from N·s/kg to lbf·s/lb, divide by 9.82.
[b] To convert MPa to psi, multiply by 145.
[c] To convert J to cal, divide by 4.184.
[d] HCl.

to deaerate the viscous mass while imparting a shear action to ensure thorough and rapid incorporation of solids. They include relatively conventional horizontal mixers such as the sigma-blade dough mixer used in making nitrocellulose propellants, mixers with heavy-duty bear claw blades, and ribbon mixers. Vertical change-can planetary mixers are commonly used to meet requirements for increased mix capacity. Mixing times and temperatures are tightly controlled to maximize mix uniformity and minimize viscosity changes without accelerating the cure reactions to the stage where the pot life is excessively reduced. The mix temperature
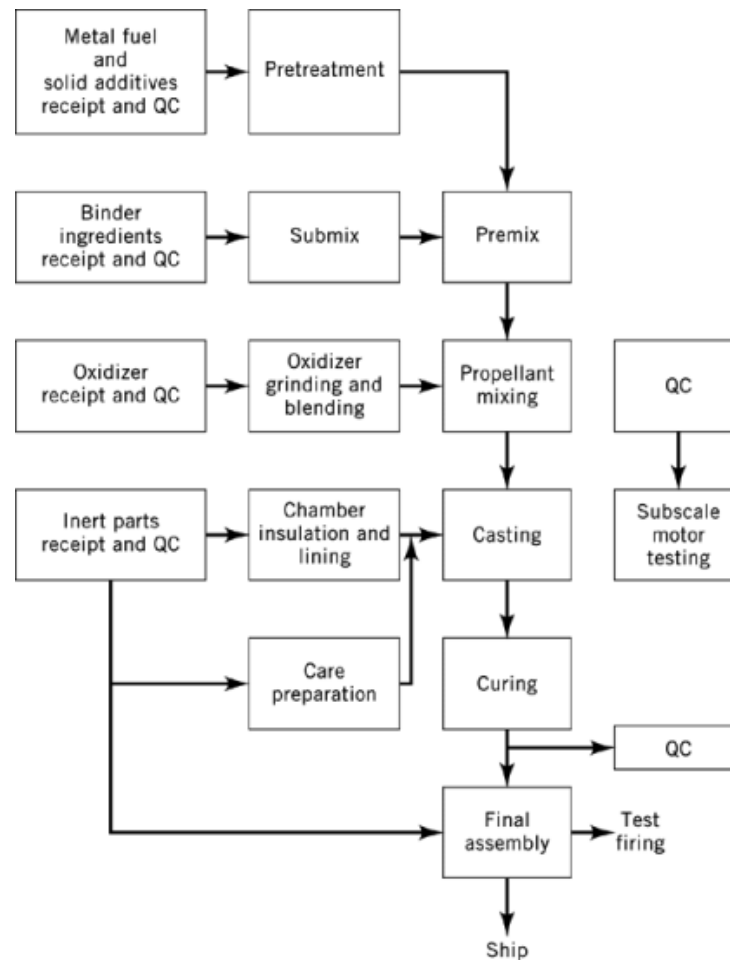
Fig. 9.   Batch process for cast-composite polymer-based propellants. QC=quality control.

increases as a result of work input on the viscous mass and the exothermicity of the initial cure reaction. The required quantity of the premix is transferred to the mixer bowl, which is moved into position and assembled to the mixer. Mixing is begun after purging with nitrogen. When the process control conditions have been attained, the oxidizer is added followed by the curing agent. Mixing then proceeds under vacuum.

Propellants cast into rockets are commonly case-bonded to the motors to achieve maximum volumetric loading density. The interior of the motor is thoroughly cleaned, coated using an insulating material, and then lined with a composition to which the propellant binder adheres under the environmental stresses of the system. The insulation material is generally a rubber-type composition, filled with silica, titanium dioxide, or potassium titanate. Silica-filled nitrate rubber and vulcanizable ethylene–propylene rubber have been used. The liner generally consists of the same base polymer as is used in the propellant. It is usually applied in a thin layer, and may be partially or fully cured before the propellant is poured into the rocket.

Table 11. Composition and Properties of Polymer-Based Cast Composite Propellants

Parameter	Poly-sulfide	Poly-urethane	CTPB	CTPB	HTPB	PBAN	PBAA	Buta-diene
Composition, wt %								
ammonium perchlorate	63.0	70.0	73.0	63.0	70.0	69.0	68.0	80[b]
binder	36.0	21.0	12.0	10.0	12.0	11.0	15.0	14
aluminum		8.0	15.0	17.0	18.0	15.0	16.0	
other	1.2[c]	1.0		10.0[d]		5.0[e, f]	5.0[f]	6
Ballistic properties								
specific impulse, N·s/kg[g]	2259	2406	2602	2602	2553	2602	2553	1866
burning rate at 6.9 MPa[h] and 20°C, cm/s	0.90	0.80	0.98	0.75	0.60	1.37	1.70	0.30
pressure exponent, n	0.45	0.20	0.30	0.30	0.30	0.33	0.20	0.50
pressure coefficient, c	0.012	0.07	0.06	0.03	0.03	0.06	0.14	0.004
Thermochemical–thermodynamic properties[i]								
heat of explosion, J/g[j]		4543	6280		6448	5966		2721
heat of formation, $-\Delta H_f$, J/g[j]	2156	2470	1842	1549		1999	1842	3768
flame temperature, T_P, K	2375	2850	3500	3650	3450	3400	3300	1000
mean heat capacity, J/(g·K)[j]			1.80					
products	2.34			1.80	1.84			2.01
gases	2.34			1.97	1.97			2.01
mean molecular weight								
products	25.2			26.9				19.5
gases	25.2	24.8	28.1	20.5		28.1	27.2	19.3
specific heat ratio, gas	1.20			1.19	1.19			
Combustion products, composition, mol / 100 g[k]								
CO_2	0.28	0.15	0.08	0.06		0.07		0.37
CO	0.80	1.02	0.79	0.78	0.95	0.89	0.96	0.93
H_2	0.55	0.94	0.88	0.85	1.15	0.96	1.14	1.40
H_2O	1.17	1.00	0.73	0.57	0.41	0.64	0.38	1.37
N_2	0.23	0.31	0.30	0.40	0.30	0.30	0.28	1.00
Al_2O_3		0.14	0.26	0.29	0.30	0.26	0.25	
HCl	0.50	0.58	0.50	0.42	0.47	0.48	0.43	
H_2S	0.10							
H			0.12	0.17	0.13	0.10	0.09	
$AlCl + AlCl_2$			0.04		0.03	0.03		

[a]   CTPB = carboxy − terminated polybutadiene; HTPB = hydroxy − terminated polybutadiene; PBAN = polybutadiene − acrylic acid − acrylonitrile; and PBAA = polybutadiene − acrylic acid.
[b] Ammonium nitrate.
[c] 1.0 wt % MgO, 0.2 wt % added sulfur.
[d] HMX.
[e] 4.0 wt % dioctyl adipate.
[f] 1.0 wt % iron catalyst.
[g] To convert N·s/kg to lbf·s/kg, divide by 9.82.
[h] To convert MPa to psi, multiply by 145.
[i] All gas volumes at standard temperature and pressure.
[j] To convert J to cal, divide by 4.184.
[k] Principal products only.

In the cast loading of large booster rockets, the motor is fixed in a vertical position and surrounded with necessary handling gear to facilitate subsequent operations. Very large motors are inserted in huge cylindrical pits. A shroud or similar enclosure may be used to surround the motor so that dry, warm air can be passed into it to preheat the motor and control the temperature of the casting and curing operation. The central mandrel required for grain geometry is inserted into the motor with controls for rigid alignment to close tolerances. The exact casting technique used depends on the rheological characteristics of the propellant and the quantity being processed. Several methods are commonly used for large grains including bayonet, bottom, and vacuum casting.

Upon completion of the casting operation, the motor is maintained at a closely controlled temperature–time regime to cure the propellant. Composite propellants are usually cured between 40 to 60°C. After curing, the core is withdrawn from the motor, and the associated casting equipment removed. The final physical characteristics of the propellant are highly dependent on the cure conditions, which in turn depend on the characteristics of the composition and the thermal conductivities of the metal and motor lining. Completeness of the cure is best determined by measuring the mechanical properties of the propellant. The reaction is finished when no change occurs on additional curing. The formulations and characteristics of a number of composite propellants are shown in Table 11 (151–163).

6.6.3. Safety

The facilities for the manufacture of composite cast nitrocellulose-based propellants incorporate the latest techniques for hazard detection and prevention and for damage control. The processes are monitored and controlled from central stations. Closed-circuit television is used for direct observation and deluge sprinkler systems having frangible seals on the nozzles are installed which can rapidly respond to a fire. Battery power is available for emergencies. Pressure relief valves incorporating frangible disks, which are fragmented by small quantities of explosives, have been used in the lines to prevent pressure buildup and permit discharge if a fire occurs. Infrared detectors capable of sensing the light of burning propellant but indifferent to room light are mounted on the head of the batch mixers. Static pressure detector units to detect excess pressure may also be mounted in the mixer head. Both the light and pressure sensors can actuate a deluge system. In addition, numerous studies have been made of the factors that affect the sensitivity of the propellant and the rocket systems that utilize them (164, 165).

6.6.4. Pollution Prevention

Procedures haven been developed for recovery of composite ammonium perchlorate propellant from rocket motors, and the treatment of scrap and recovered propellant to reclaim ingredients. These include the use of high pressure water jets or compounds such as ammonia, which form fluids under pressure at elevated temperature, to remove the propellant from the motor, extraction of the ammonium perchlorate with solvents such as water or ammonia as a critical fluid, recrystallization of the perchlorate and reuse in composite propellant or in slurry explosives or conversion to perchloric acid (166, 167).

6.7. Black Powder

Black powder is mainly used as an igniter for nitrocellulose gun propellant, and to some extent in safety blasting fuse, delay fuses, and in firecrackers. Potassium nitrate black powder (74 wt %, 15.6 wt % carbon, 10.4 wt % sulfur) is used for military applications. The slower-burning, less costly, and more hygroscopic sodium nitrate black powder (71.0 wt %, 16.5 wt % carbon, 12.5 wt % sulfur) is used industrially. The reaction products of black powder are complex (Table 12) and change with the conditions of initiation, confinement, and density. The reported thermochemical and performance characteristics vary greatly and depend on the source of material, its physical form, and the method of determination. Typical values are listed in Table 13.

Table 12.   Reaction Products of Black Powder

Component	Quantity, wt %
Gases	
carbon dioxide	49
carbon monoxide	12
nitrogen	33
hydrogen sulfide	2.5
methane	0.5
water	1
hydrogen	2
Total	*44*
Solids	
potassium carbonate	61
potassium sulfate	15
potassium sulfide	14.3
potassium thiocyanate	0.2
potassium nitrate	0.3
ammonium carbonate	0.1
sulfur	9
carbon	0.1
Total	*56*

Table 13. Characteristics of Black Powder

Characteristic	Value
flame temperature, K[a]	ca 2800
gas, mol/g	0.0128–0.0159
heat of explosion, J/g[b,c]	3015–3140
impetus, J/g[b]	239–284
burning rate at 6.9 MPa[d], cm/s	ca 1 to 1.5
temperature coefficient of pressure, %/°C	0.4
pressure exponent	0.25–0.5
ignition temperature, °C	450
activation energy, kJ/mol[b]	87.9

[a] Isochoric.
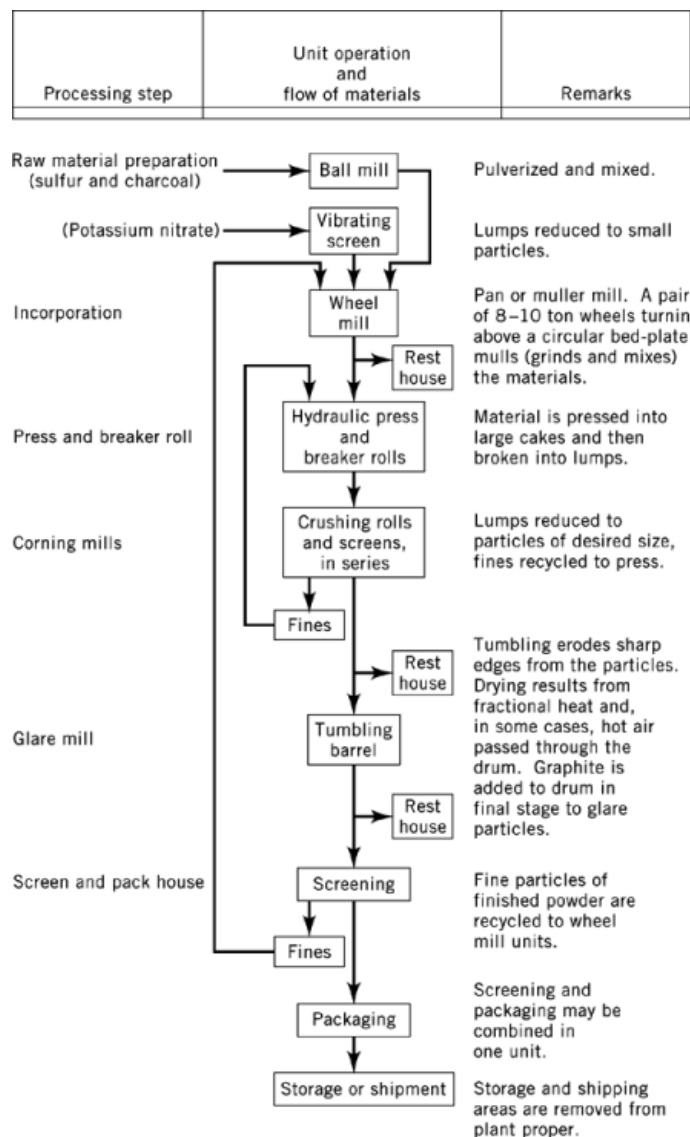[b] To convert J to cal, divide by 4.184.
[c] Water as liquid.
[d] To convert MPa to psi, multiply by 145.

The critical relative humidity of black powder is 60%. It gains ca 2% moisture in 48 h at 90% rh and 25°C. Ignitability decreases rapidly at ca 3 to 4% moisture level. The structure of black powder granules also deteriorates during cycling through high humidity atmospheres. However, it can be stored satisfactorily for many years if dry. The hygroscopicity of black powder is caused by the carbon and impurities in the potassium nitrate.

The performance of black powder is critically dependent on the degree of intimacy of the components in the product. The manufacture of black powder is essentially a procedure for bringing the ingredients into maximum mutual contact. A detailed flow chart for the conventional process is presented in Figure 10.

Typically, dry potassium nitrate is pulverized in a ball mill. Sulfur is milled into cellular charcoal to form a uniform mix in a separate ball mill. The nitrate and the sulfur–charcoal mix are screened and then loosely mixed by hand or in a tumbling machine. Magnetic separators may be used to ensure the absence of ferrous metals. The preliminary mix is transferred to an edge-runner wheel mill with large, heavy cast iron

Processing step	Unit operation and flow of materials	Remarks
Raw material preparation (sulfur and charcoal) →	Ball mill	Pulverized and mixed.
(Potassium nitrate) →	Vibrating screen	Lumps reduced to small particles.
Incorporation	Wheel mill → Rest house	Pan or muller mill. A pair of 8–10 ton wheels turning above a circular bed-plate mulls (grinds and mixes) the materials.
Press and breaker roll	Hydraulic press and breaker rolls	Material is pressed into large cakes and then broken into lumps.
Corning mills	Crushing rolls and screens, in series	Lumps reduced to particles of desired size, fines recycled to press.
	Fines	
Glare mill	Rest house → Tumbling barrel → Rest house	Tumbling erodes sharp edges from the particles. Drying results from fractional heat and, in some cases, hot air passed through the drum. Graphite is added to drum in final stage to glare particles.
Screen and pack house	Screening	Fine particles of finished powder are recycled to wheel mill units.
	Fines	
	Packaging	Screening and packaging may be combined in one unit.
	Storage or shipment	Storage and shipping areas are removed from plant proper.

Fig. 10. Process of manufacture of black powder.

wheels. A clearance between the pan and the wheels is required for safety purposes. The size of this gap also contributes to the density of the black powder granules obtained. Water is added to minimize dusting and improve incorporation of the nitrate into the charcoal. The milling operation requires ca 3 to 6 h.

The moist milled powder is transferred to a hydraulic press where it is consolidated in layers into cakes at pressures of ca 41.3 MPa (6000 psi) applied for ca 30 min. Each cake is ca 2.5 cm thick and 60 cm square. The density of the powder increases to 1.6 to 1.8 g/cm^3, depending on the pressure applied. The cakes are then transferred to a corning mill consisting of adjustable corrugated rollers that are cascaded so that a series of crushing actions occur. These are followed by automatic screening to form a product that approximates the granulation requirements. The dust and fines that have been screened are recycled to the press feed or used

in fuse powder or fireworks. Coarse material is recycled. The grains are polished and dried; graphite is added followed by blending by tumbling in a large hardwood rotating drum. From 1360 to 2265 kg powder may be tumbled at 10–20 rpm for up to 8 h. Warm air may be forced through the barrel to assure drying and to decrease cycle time. The powder is screened before packing into airtight metal drums.

A number of techniques have been developed to eliminate the hazardous wheel milling process and reduce personnel exposure by increasing automation for the continuous transport of the product from operation to operation. The jet-mill air-attrition process, which has no moving parts, has replaced the wheel-mill operation of the conventional process. Potassium nitrate, sulfur, and charcoal are automatically weighed by transferring each ingredient to a weighing and mixing bin with a vibrating transporter. Air jets are applied to the bottom of the weigh-mix bin to blend the components. The air pressure is then increased to continuously transfer the mix pneumatically to a storage bin and then to the jet mill by air injection. A high velocity stream of air entering the mill forces the particles to collide and breaks them up by attrition. The product consists of a finely divided powder. The small particles exit through a cyclone separator where they are separated from the air, which is exhausted to the atmosphere. Coarse particles drop back to the attrition section where the milling action continues. The mill may be adjusted to produce powders of different granulations.

Pressing, corning, screening, and glazing are comparable to the conventional procedures except that automation is employed wherever possible. Deluge systems that are activated by uv light sensors and can respond in milliseconds are installed for additional safety. All operations are monitored and controlled from central process control areas. The presence of operators is restricted to the receipt of raw materials and packing of the final product. The pollution aspects of black powder manufacture are relatively insignificant in view of the small quantities made. No wastewater or noxious fumes are produced (168–178).

6.7.1. Benite

Benite is an extrudable composition consisting of ca 60 parts of black powder in a matrix of ca 40 parts of plasticized nitrocellulose. It is used as a propellant igniter to reduce the residue formed compared to use of black powder alone. Benite can be extruded as strands, permitting a less obstructed flow of ignition gases and particles than granular black powder. Its approximate weight composition is nitrocellulose (13.15% N), 40%; potassium nitrate, 44%; sulfur, 6.5%; carbon, 9.5%; ethyl centralite added; 0.5%. It is made by the single-base process, followed by air-drying to remove volatile solvents (179).

6.8. Felted Nitrocellulose Compositions

A combustible case containing the propellant charge offers tactical, logistic, and performance advantages in certain types of munitions such as those used for tank weapons, mortars, and howitzers. This case is rigid and completely combustible, replacing metallic cases or flexible cases having low mechanical strength. Because nitrocellulose itself cannot be molded into a structure having the desired mechanical characteristics, inert fibers and a resin are added. A typical composition (wt %) consists of nitrocellulose (12.6% N), 55; kraft fiber, 9; acrylic fiber, 25; poly(vinyl acetate) resin, 10; and diphenylamine, 1.

The finished case has a density of ca 0.85 g/cm and a tensile strength of ca 24 MPa (3500 psi). Typical ballistic characteristics of combustible cases material are impetus, 578 J/g (138 cal/g); flame temperature, 1619 K; average molecular weight of the gaseous products, 23.3 g/mol; covolume, 1.17 mL/g; and specific heat ratio, 1.25.

Two processes may be used in the manufacture of combustible cases: the original post-impregnation process and the more recently and more widely employed beater additive process. The processes differ primarily in the point at which the required resin is added to the composition. A schematic of the beater additive process is shown in Figure 11.

The beater additive process starts with a very dilute aqueous slurry of fibrous nitrocellulose, kraft process woodpulp, and a stabilizer such as diphenylamine in a felting tank. A solution of resin such as poly(vinyl
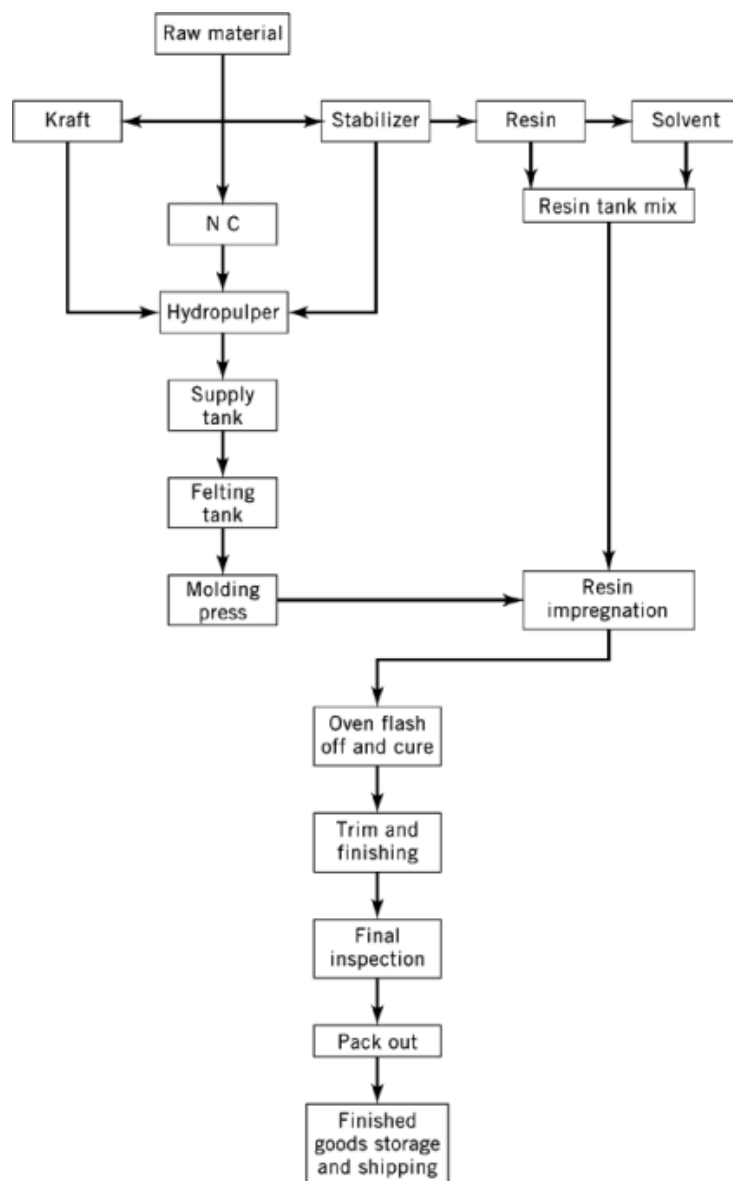
Fig. 11. Flow diagram for the beater additive process. Kraft represents the kraft process wood pulp and NC is nitrocellulose used as starting materials (182).

acetate) is added to the slurry of these components. The next step, felting, involves use of a fine metal screen in the shape of the inner dimensions of the final molded part. The screen is lowered into the slurry. A vacuum is applied which causes the fibrous materials to be deposited on the form. The form is pulled out after a required thickness of felt is deposited, and the wet, low density felt removed from the form. The felt is then molded in a matched metal mold by the application of heat and pressure which serves to remove moisture, set the resin, and press the fibers into near final shape (180–182).

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