## AD NUMBER

AD830265

## NEW LIMITATION CHANGE

TO

Approved for public release, distribution unlimited

FROM

Distribution authorized to U.S. Gov't. agencies and their contractors; Administrative/Operational Use; Sep 1964. Other requests shall be referred to HQ, Army Materiel Command, Attn: AMCRD-TV, Washington, DC 20315.

## AUTHORITY

USAMC ltr, 2 Jul 1973

AMC PAMPHLET AMCP 706-175

ENGINEERING DESIGN HANDBOOK

# EXPLOSIVES SERIES

# SOLID PROPELLANTS PART ONE



HEADQUARTERS, U. S. ARMY MATERIEL COMMAND SEPTEMBER 1964

136

# DISCLAIMER NOTICE

# ENGINEERING DESIGN HANDBOOK SERIES

Listed below are the Handbooks which have been published or submitted for publication. Handbooks with publication dates prior to 1 August 1962 were published as 20-series Ordnance Corps pamphlets. AMC Circular 310-38, 19 July 1963, redesignated those publications as 706-series AMC pamphlets (i.e., ORDP 20-138 was redesignated AMCP 706-138). All new, reprinted, or revised Handbooks are being published as 706-series AMC pamphlets.

General and Miscellaneous Subjects

| Number | Title |
|---|---|
| 106 | Elements of Armament Engineering, Part One, Sources of Energy |
| 107 | Elements of Armament Engineering, Part Two, Ballistics |
| 108 | Elements of Armament Engineering, Part Three, Weapon Systems and Components |
| 110 | Experimental Statistics, Section 1, Basic Concepts and Analysis of Measurement Data |
| 111 | Experimental Statistics, Section 2, Analysis of Enumerative and Classificatory Data |
| 112 | Experimental Statistics, Section 3, Planning and Analysis of Comparative Experiments |
| 113 | Experimental Statistics, Section 4, Special Topics |
| 114 | Experimental Statistics, Section 5, Tables |
| 121 | Packaging and Pack Engineering |
| 134 | Maintenance Engineering Guide for Ordnance Design |
| 135 | Inventions, Patents, and Related Matters (Revised) |
| 136 | Servomechanisms, Section 1, Theory |
| 137 | Servomechanisms, Section 2, Measurement and Signal Converters |
| 138 | Servomechanisms, Section 3, Amplification |
| 139 | Servomechanisms, Section 4, Power Elements and System Design |
| 170(C) | Armor and Its Application to Vehicles (U) |
| 250 | Guns--General (Guns Series) |
| 252 | Gun Tubes (Guns Series) |
| 270 | Propellant Actuated Devices |
| 290(C) | Warheads--General (U) |
| 331 | Compensating Elements (Fire Control Series) |
| 355 | The Automotive Assembly (Automotive Series) |

Ammunition and Explosives Series

| Number | Title |
|---|---|
| 175 | Solid Propellants, Part One |
| 176(C) | Solid Propellants, Part Two (U) |
| 177 | Properties of Explosives of Military Interest, Section 1 |
| 178(C) | Properties of Explosives of Military Interest, Section 2 (U) |
| 210 | Fuzes, General and Mechanical |
| 211(C) | Fuzes, Proximity, Electrical, Part One (U) |
| 212(S) | Fuzes, Proximity, Electrical, Part Two (U) |
| 213(S) | Fuzes, Proximity, Electrical, Part Three (U) |
| 214(S) | Fuzes, Proximity, Electrical, Part Four (U) |
| 215(C) | Fuzes, Proximity, Electrical, Part Five (U) |
| 244 | Section 1, Artillery Ammunition--General, with Table of Contents, Glossary and Index for Series |
| 245(C) | Section 2, Design for Terminal Effects (U) |
| 246 | Section 3, Design for Control of Flight Characteristics |
| 247 | Section 4, Design for Projection |
| 248 | Section 5, Inspection Aspects of Artillery Ammunition Design |
| 249 | Section 6, Manufacture of Metallic Components of Artillery Ammunition |

Ballistic Missile Series

| Number | Title |
|---|---|
| 281(S-RD) | Weapon System Effectiveness (U) |
| 282 | Propulsion and Propellants |
| 284(C) | Trajectories (U) |
| 286 | Structures |

Ballistics Series

| Number | Title |
|---|---|
| 140 | Trajectories, Differential Effects, and Data for Projectiles |
| 150 | Interior Ballistics of Guns |
| 160(S) | Elements of Terminal Ballistics, Part One, Introduction, Kill Mechanisms, and Vulnerability (U) |
| 161(S) | Elements of Terminal Ballistics, Part Two, Collection and Analysis of Data Concerning Targets (U) |
| 162(S-RD) | Elements of Terminal Ballistics, Part Three, Application to Missile and Space Targets (U) |

Carriages and Mounts Series

| Number | Title |
|---|---|
| 340 | Carriages and Mounts--General |
| 341 | Cradles |
| 342 | Recoil Systems |
| 343 | Top Carriages |
| 344 | Bottom Carriages |
| 345 | Equilibrators |
| 346 | Elevating Mechanisms |
| 347 | Traversing Mechanisms |

Materials Handbooks

| Number | Title |
|---|---|
| 301 | Aluminum and Aluminum Alloys |
| 302 | Copper and Copper Alloys |
| 303 | Magnesium and Magnesium Alloys |
| 305 | Titanium and Titanium Alloys |
| 308 | Glass |
| 309 | Plastics |
| 310 | Rubber and Rubber-Like Materials |

Military Pyrotechnics Series

| Number | Title |
|---|---|
| 186 | Part Two, Safety, Procedures and Glossary |
| 187 | Part Three, Properties of Materials Used in Pyrotechnic Compositions |

Surface-to-Air Missile Series

| Number | Title |
|---|---|
| 291 | Part One, System Integration |
| 292 | Part Two, Weapon Control |
| 293 | Part Three, Computers |
| 294(S) | Part Four, Missile Armament (U) |
| 295(S) | Part Five, Countermeasures (U) |
| 296 | Part Six, Structures and Power Sources |
| 297(S) | Part Seven, Sample Problem (U) |

HEADQUARTERS
UNITED STATES ARMY MATERIEL COMMAND
WASHINGTON, D. C. 20315

30 September 1964

AMCP 706-175, Solid Propellants, Part One, forming part of the Explosives Series of the Army Materiel Command Engineering Design Handbook Series, is published for the information and guidance of all concerned.

(AMCRD)

FOR THE COMMANDER:

SELWYN D. SMITH, JR.
Major General, USA
Chief of Staff

OFFICIAL:

R. O. DAVIDSON
Colonel, GS
Chief, Administrative Office

DISTRIBUTION: Special

# EXPLOSIVES SERIES

# SOLID PROPELLANTS
## PART ONE

By A. M. Ball

CONSISTING OF
CHAPTERS 1-10

## PREFACE

This handbook has been prepared as one of a series on Explosives. It is part of a group of handbooks covering the engineering principles and fundamental data needed in the development of Army materiel, which (as a group) constitutes the Engineering Design Handbook Series of the Army Materiel Command.

~~This~~ The handbook presents information on the design, functioning and manufacture of solid propellants for use in propelling charges for guns and rockets.

The text and illustrations for this handbook were prepared by Hercules Powder Company under subcontract to the Engineering Handbook Office of Duke University, prime contractor to the Army Research Office-Durham for the Engineering Design Handbook Series.

Agencies of the Department of Defense, having need for Handbooks, may submit requisitions or official requests directly to Publications and Reproduction Agency, Letterkenny Army Depot, Chambersburg, Pennsylvania 17201. Contractors should submit such requisitions or requests to their contracting officers.

Comments and suggestions on this handbook are welcome and should be addressed to Army Research Office-Durham, Box CM, Duke Station, Durham, North Carolina 27706.

# TABLE OF CONTENTS

## TABLE OF CONTENTS (Continued)

## TABLE OF CONTENTS (Continued)

## TABLE OF CONTENTS (Continued)

## TABLE OF CONTENTS (Continued)

# LIST OF ILLUSTRATIONS

## LIST OF ILLUSTRATIONS (Continued)

# LIST OF TABLES

# LIST OF SYMBOLS

$a$ = a constant

$a$ = acceleration

$\dot{a}$ = time rate of acceleration

$a$ (subscript) = atmospheric

$av$ (subscript) = average

$A_b$ = area of burning surface = $S$

$A_e$ = area of nozzle exit

$A_p$ = port area

$A_t$ = nozzle throat area

$b$ = a constant

$b'$ = a constant

$b''$ = a constant

$c$ (subscript) = chamber

$c^*$ = characteristic velocity

$c^*_o$ = calculated thermodynamic characteristic velocity

$C$ = concentration of polymer in solution

$C_D$ = mass flow factor = $\frac{1}{c^*}$

$C_F$ = thrust coefficient

$C_i$ = number of weight atoms of carbon in unit weight of ingredient $I$ in propellant composition

$C_p$ = molar heat capacity at constant pressure

$C_v$ = molar heat capacity at constant volume

$d$ = grain diameter

$D_e$ = diameter of nozzle exit

$D_t$ = diameter of nozzle throat

$e$ = base of natural logarithms

$e$ (subscript) = exit

$E$ = internal energy

$\Delta E$ = heat of formation = $H_f$

$f$ (subscript) = partial value contributed by fuel

$F$ = specific force or impetus

$F$ = thrust

$g$ = acceleration of gravity

$g$ (subscript) = gaseous state

$G$ = mass velocity of the gases in the port

$Ghp$ = gas horsepower

$H$ = moisture content

$H_f$ = heat of formation = $\Delta E$

$H_{ex}$ = heat of explosion = $Q$

$\Delta H$ = enthalpy change

$i$ (subscript) = partial value contributed by ingredient $I$

$I$ = ingredient in propellant composition

$I$ = total impulse

$I_{sp}$ = specific impulse

$I^o_{sp}$ = calculated thermodynamic specific impulse

$I_{sp}$ (del) = measured specific impulse at nonstandard conditions

$j$ (subscript) = partial value contributed by product

$J$ = product gas constituent

$k$ = erosion constant

$K$ = a constant

K = Kelvin (temperature)

$K$ = ratio of initial propellant burning surface to nozzle throat area = $\frac{A_b}{A_t}$

$K_1$ = erosivity constant

$l$ (subscript) = liquid state

$L$ = distance downstream from the stagnation point

$L$ = grain length

$M$ = molecular weight of combustion gases

$\frac{1}{M}$ = specific gas volume

$M_{T_p}$ = average molecular weight of combustion gases at isobaric adiabatic flame temperature

$M_{T_v}$ = average molecular weight of combustion gases at isochoric adiabatic flame temperature

$n$ = exponent in de Saint Robert burning rate equation, $r = bP^n$

$n$ = gas volume in moles produced from unit weight of propellant = $\frac{1}{M}$

$n_p$ = moles per unit weight of gas at isobaric adiabatic flame temperature

$n_v$ = moles per unit weight of gas at isochoric adiabatic flame temperature

$o$ (subscript or superscript) = calculated thermodynamic value

$o$ (subscript) = initial condition

$ox$ (subscript) = partial value contributed by oxidizer

$p$ (subscript) = constant pressure conditions

$P$ = pressure

$P_c$ = chamber pressure

## LIST OF SYMBOLS (Continued)

$Q$ = heat of explosion = $H_{ev}$
$r$ = linear burning rate
R = Rankine (temperature)
$R$ = specific gas constant = $\frac{R_o}{M}$
$R_o$ = universal gas constant
$RF$ = relative force
$RH$ = relative humidity
$RQ$ = relative quickness
$s$ (subscript) = solid state
$S$ = area of burning surface
$S$ = tensile stress
$S_b$ = tensile stress at break
$S_f$ = final area of surface after burning
$S_i$ = initial area of surface
$S_m$ = maximum stress
$t$ = time
$t_b$ = burning time
$t$ (subscript) = throat condition
$T$ = absolute temperature
$T_i$ = initial temperature
$T_i$ = pyrolysis temperature
$T_o$ = reference temperature
$T_p$ = isobaric adiabatic flame temperature
$T_t$ = temperature at throat
$T_v$ = isochoric adiabatic flame temperature
$u$ = a constant
$v$ (subscript) = constant volume conditions
$V$ = velocity
$V$ = volume
$V_p$ = volume of propellant
$W$ = weight
$\dot{W}$ = weight burning rate = $\frac{dW}{dt}$
$x$ = weight fraction
$y$ = volume fraction
$\dot{}$ (superscript dot) = time derivative

—— (overline) = average
$\alpha$ = a constant
$\alpha$ = covolume
$\alpha$ = nozzle divergence half-angle
$\beta$ = a constant
$\beta$ = volumetric coefficient of thermal expansion
$\gamma$ = ratio of specific heats = $\frac{C_p}{C_v}$
$\epsilon$ = nozzle-expansion area ratio = $\frac{A_e}{A_t}$
$\eta$ = viscosity of solution
$\eta_o$ = viscosity of solvent
$\frac{\eta}{\eta_o}$ = relative viscosity
$\lambda$ = nozzle divergence loss factor
$\Lambda$ = propellant mass ratio, ratio of propellant mass of any stage to gross mass of that stage
$\pi_{\frac{P}{r}}$ = temperature coefficient of pressure at constant pressure-rate ratio = $\left(\frac{\partial lnP}{\partial T}\right)_{\frac{P}{r}}$
$\pi_K$ = temperature coefficient of pressure at constant $K$ value = $\left(\frac{\partial lnP}{\partial T}\right)_K$
$\rho$ = density
$\frac{1}{\rho}$ = specific volume
$\sigma_p$ = temperature coefficient of burning rate at constant pressure = $\left(\frac{\partial lnr}{\partial T}\right)_P$
$\sigma_K$ = temperature coefficient of burning rate at constant $K$ value = $\left(\frac{\partial lnr}{\partial T}\right)_K$

# SOLID PROPELLANTS

## PART ONE

### CHAPTER 1

## INTRODUCTION

**1. Purpose.** This Handbook is intended to provide a general description of solid propellants used in small arms, artillery, rockets, and some other devices. It is assumed that the reader has as background the equivalent of an undergraduate degree in engineering or physical science, but no previous experience in propellants or ballistics.

**2. Definitions.** A solid propellant is a chemical or a mixture of chemicals which when ignited burns in the substantial absence of atmospheric oxygen at a controlled rate and evolves gas capable of performing work. In order to discuss certain phenomena, notably burning and detonation processes, it is necessary to define certain terms that are used with meanings differing significantly from those given in MIL-STD-444.[1]* The more important of these are:

A (solid) monopropellant is a single physical phase comprising both oxidizing and fuel elements. This is analogous to common usage in the liquid propellant field describing a single-phase liquid propellant.

A filler is a discrete material dispersed in substantial quantity in the continuous or binder phase of a composite propellant.

Deflagration is a burning process in a solid system, comprising both oxidant and fuel, in which the reaction front advances at less than sonic velocity and gaseous products if produced move away from unreacted material. Whether or not explosion occurs as a result of deflagration depends on confinement.

None of these definitions is used for the first time in this Handbook. Other definitions are introduced in the text at appropriate places. Unless otherwise noted, definitions are in accord with MIL-STD-444, Merriam-Webster's unabridged dictionary, or common usage.

*Numbers refer to items listed as References at the end of each chapter.

**3. Plan.** In Chapter 2 is described how the figures of merit—specific force for gun propellants and specific impulse or characteristic velocity for rocket propellants—are derived from thermochemical data and empirically verified. Also in Chapter 2 is discussed the mechanism of burning of propellants and the scheduling of gas evolution to meet the requirements of various engines in which propellants are used, such as guns, catapults, rockets, and gas generators. A few simple numerical examples are given by way of illustration, but detailed discussion of the ballistics of such engines is omitted as being beyond the scope of this work and available elsewhere. In Chapter 3 appears a discussion of certain physical properties of propellants as related to system requirements. In Chapters 4-9 conventional propellants are discussed, arranged according to their physical structure. Black powder is presented in Chapter 4. Crystalline monopropellants appear in Chapter 5. Plastic monopropellants, commonly known as single-base and double-base propellants, appear in Chapter 6. These common terms can be somewhat confusing, since the class contains propellants comprising, for example, cellulose acetate and nitroglycerin which are difficult to assign to either single- or double-base. Composites comprising monopropellant binder and monopropellant filler, commonly known as triple-base, appear in Chapter 7. Again the common term can be confusing, as when a nitroguanidine propellant with a single-base (nitrocellulose) binder is to be described. Manufacturing processes for the propellants of Chapters 6 and 7 are given in Chapter 8. Fuel binder composites are discussed in Chapter 9. A discussion of inert simulants, or dummies, for propellants is given in Chapter 10. Higher energy systems are discussed in ORDP 20-176, *Solid Propellants*, Part Two (C).

Literature consulted in the preparation of this Handbook includes publications early in 1960. The reader is referred to SPIA/M2,[2] in which will be found data sheets for all of the propellants developed and used within the Department of Defense including those that will appear subsequent to the publication of this Handbook.

## REFERENCES


1. MIL-STD-444, *Military Standard, Nomenclature and Definitions in the Ammunition Area*, Department of Defense, 6 February 1959.
2. SPIA/M2, *Propellant Manual*, Solid Propellant Information Agency, Johns Hopkins University, CONFIDENTIAL.

## CHAPTER 2

# EVOLUTION OF GASES BY PROPELLANTS

**4. General.** The devices in which propellants are commonly used, be they devices, such as guns that comprise moving pistons, or vented vessels acquiring momentum by discharge of gas, are devices that convert heat energy into mechanical energy. They thus fall into the general classification of heat engines. The propellant gas is then the working fluid that actuates heat engines. In solid propellant heat engines the working fluid is generated *in situ* by burning the propellant within the engine. The general problem in fitting a solid propellant to a heat engine is the generation of gas of specified properties at a specified rate which is a function of time. The specifications of gas properties and rate of generation are not usually independent of each other. Thus a given problem may be solved by using gas with one set of properties at one rate schedule or, alternately, by using a different set of gas properties on a correspondingly different rate schedule. The properties of the gas are determined by the composition of the propellant. The derivation of the gas properties from the composition is known as *thermochemistry of propellants*. The rate of gas generation is determined by the linear rate of burning and charge geometry. Of these, the linear burning rate as a function of pressure is a propellant property. System pressure and charge geometry are controlled at least in part by the end-item specification. The overall problem of selecting a propellant formulation and geometry to meet a given end-item performance specification is an exercise in *interior ballistics*. Because the propellant developer owes the ballistician both thermochemical data and rate versus pressure data, he should have a qualitative knowledge of interior ballistics in order to perform his function intelligently.

**5. Equation of state.** The classical equation of state used by ballisticians is known as the *Noble-Abel equation*. For unit mass of propellant it is usually written

$$P(V - \alpha) = RT$$

where $R$ is the gas constant per unit mass of propellant, or more generally

$$P(V - \alpha W) = \frac{WR_oT}{M} \qquad (1)$$

where $R_o$ is the universal gas constant. The term $\alpha$ is known as the covolume and may be thought of as the space occupied by the gas when compressed to the limit. It has the empirical value of about 1 cc per gram for most propellants.[1] The significance of the covolume correction may be shown by some simple numerical examples. Under standard conditions of temperature and pressure (273°K, 1 atm), 1 gram of gas of molecular weight 22.4 occupies 1000 cc. A temperature of 2730°K and a pressure of 68 atm (1000 psi) are conditions typical of rocket ballistics. Under these circumstances

$$V - \alpha = 1000 \times \frac{2730}{273} \times \frac{1}{68} = 147 \text{ cc}$$

For 1 percent accuracy, $V - \alpha$ does not differ significantly from $V$. It is customary, therefore, in rocket ballistics to ignore the covolume correction and use the perfect gas equation

$$PV = \frac{WR_oT}{M} \qquad (1a)$$

as the equation of state. On the other hand, whereas we encounter similar temperatures in gun ballistics, the pressures are higher. Taking 3000 atm (44000 psi) as typical, for 1 gram of gas

$$V - \alpha = 1000 \times \frac{2730}{273} \times \frac{1}{3000} = 3.3 \text{ cc}$$

Under these conditions, $V - \alpha$ differs significantly from $V$, and the covolume correction must be made. For precise calculations, other equations of state of greater precision than Equation 1 are used. These equations are more complex and contain constants the physical significance of which is more difficult to understand. In such calculations the departure from the perfect gas law is still called the covolume correction. The covolume if evaluated is no longer a constant but is a variable with a value still in the neighborhood of Noble-Abel's $\alpha$.

**6. Ballistic parameters.** Different systems[2-3] of interior ballistics have been developed by gun ballisticians on the one hand and by rocket ballisticians on the other. Both types of system depend on the same primary thermochemical properties of propellant gases, but use different parameters as working tools. Thus, as a measure of the ability of the combustion products of propellants to perform in their respective heat engines, gun ballisticians use the parameter *specific force* (often abbreviated to *force*), or *impetus*, $F$. Rocket ballisticians use for the same purpose *characteristic velocity*, $c^*$, or *specific impulse*, $I_{sp}$. Auxiliary power unit engineers sometimes use *gas horsepower*, *Ghp*.

**6-1. Specific force.** Specific force, $F$, is a measure of the ability of the propellant gas to perform work. It is defined by the equation

$$F = \frac{R_o T_o}{M} \qquad (2)$$

and is expressed in terms of foot-pounds per pound.

**6-2. Characteristic velocity.** Characteristic velocity, $c^*$, is not a significant physical quantity. It is defined as $\frac{P_c A_t g}{\dot{W}}$, where $P_c$ is chamber pressure, $A_t$ is nozzle throat area, and $\dot{W}$ is burning rate in pounds per second. Mathematical analysis[9] shows that it can be computed* from the thermodynamic properties of the gas as

$$c_o^* = \sqrt{\frac{gR_oT_o}{\gamma M}}\left(\frac{\gamma+1}{2}\right)^{\frac{\gamma+1}{2(\gamma-1)}} \qquad (3)$$

**6-3. Reduced characteristic velocity.** Equation 3 may be rewritten

$$\frac{c_o^*}{\sqrt{\frac{gR_oT_o}{M}}} = \left(\frac{1}{\gamma}\right)^{\frac{1}{2}}\left(\frac{\gamma+1}{2}\right)^{\frac{\gamma+1}{2(\gamma-1)}} \qquad (3a)$$

The quantity $\frac{c_o^*}{\sqrt{\frac{gR_oT_o}{M}}}$ may be called the reduced characteristic velocity; it is dimensionless and is a function only of the specific heat ratio, $\gamma$. In Table 1 are shown the values of the reduced characteristic velocity for different values of $\gamma$. The characteristic velocity is obtained by multiplying the reduced characteristic velocity by $\sqrt{\frac{gR_oT_o}{M}}$. The comparatively small change of the reduced characteristic velocity with changing $\gamma$ points out that the characteristic velocity is a stronger function of $\frac{T_o}{M}$ than of $\gamma$.

---

* Computed thermodynamic values are denoted by subscript or superscript o, to differentiate from values depending on direct measurements. See also Paragraph 8-3.

**TABLE 1. REDUCED CHARACTERISTIC VELOCITY**

| $\gamma$ | $\frac{c_o^*}{\sqrt{\frac{gR_oT_o}{M}}} = \left(\frac{1}{\gamma}\right)^{\frac{1}{2}}\left(\frac{\gamma+1}{2}\right)^{\frac{\gamma+1}{2(\gamma-1)}}$ |
|---|---|
| 1.15 | 1.566 |
| 1.20 | 1.542 |
| 1.25 | 1.520 |
| 1.30 | 1.499 |
| 1.35 | 1.479 |
| 1.40 | 1.461 |

**6-4. Specific impulse.** Specific impulse, $I_{sp}$, is defined as the impulse (force × time) delivered by burning a unit weight of propellant in a rocket chamber. From rocket ballistic theory[10] can be derived the equation

$$I_{sp} = \sqrt{\frac{2\gamma R_oT_o}{gM(\gamma-1)}\left[1-\left(\frac{P_e}{P_c}\right)^{\frac{\gamma-1}{\gamma}}\right]} \qquad (4)$$

Note that this parameter becomes a thermodynamic function of the propellant only when the ratio $\frac{P_e}{P_c}$ is specified. The current United States convention is to consider $P_e$ as one atmosphere (14.7 psi) and $P_c$ as 1000 psi unless otherwise specified. Implied in this formula is the assumption of zero half-angle of nozzle expansion. See also Paragraph 8-4.

**6-5. Reduced specific impulse.** Equation 4 may be rewritten

$$\frac{I_{sp}^o}{\sqrt{\frac{R_oT_o}{gM}}} = \sqrt{\frac{2\gamma}{\gamma-1}\left[1-\left(\frac{P_e}{P_c}\right)^{\frac{\gamma-1}{\gamma}}\right]} \qquad (4a)$$

The quantity $\frac{I_{sp}^o}{\sqrt{\frac{R_oT_o}{gM}}}$ is known as the reduced specific impulse; it is dimensionless and depends only on the pressure ratio, $\frac{P_e}{P_c}$, and the specific heat ratio, $\gamma$. A plot of the reduced specific im-

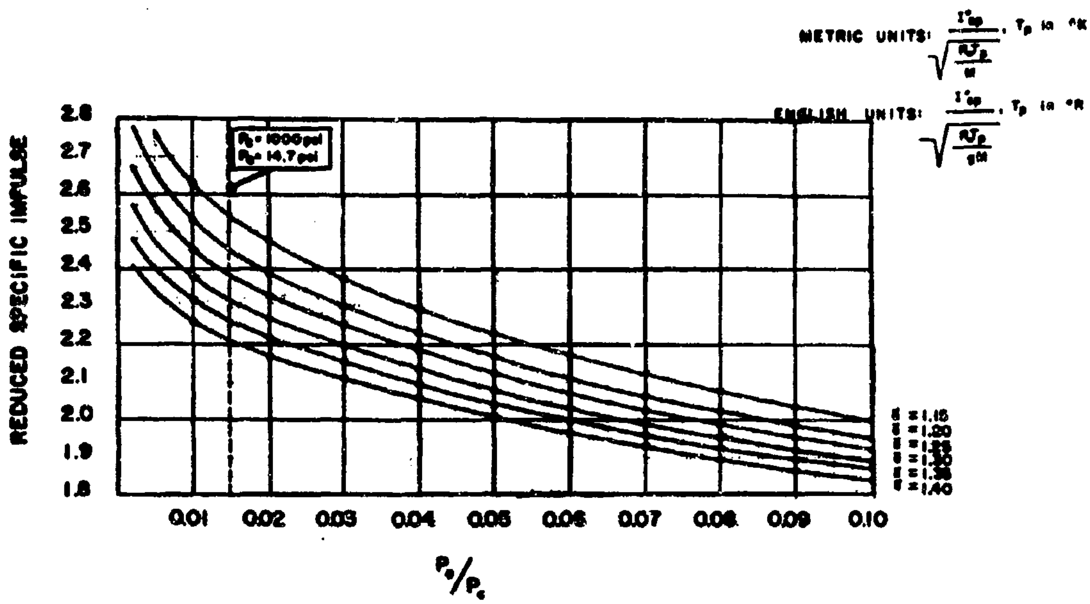



*Figure 1. Reduced Specific Impulse Versus Area Ratio and Gamma*

pulse as a function of pressure ratio for various γ's is shown in Figure 1. The use of this chart in calculating specific impulse is illustrated in the numerical example, Paragraph 7-7.

**6-6. Volume specific impulse.** The product of specific impulse and density, expressed in units of pound-seconds per cubic inch, is known as the volume specific impulse. If a proposed rocket motor has a fixed propellant envelope, it will generate impulse roughly in proportion to its volume specific impulse. Thus a propellant with lower specific impulse but higher density may sometimes outperform one with higher specific impulse and lower density. If the proposed rocket motor requires a given total impulse but has no envelope requirement, the volume of the propellant, and hence the size and weight of the (inert) chamber, will be lower the higher the volume specific impulse.

**6-7. Gas horsepower.** Gas horsepower is defined as

$$Ghp = \frac{\dot{W}}{550} \times \frac{\gamma}{\gamma - 1} \frac{R_0 T}{M}\left[1 - \left(\frac{P_2}{P_1}\right)^{\frac{\gamma-1}{\gamma}}\right] \quad (5)$$

Here again is a parameter that does not become a thermodynamic function of the propellant unless the ratio $\frac{P_2}{P_1}$ is specified. There appears to be no United States convention with respect to $\frac{P_2}{P_1}$. Gas horsepower is therefore not purely a propellant property.

**7. Thermochemistry.** Thermochemical data required for the determination of the above parameters are the burning temperatures at constant volume and at constant pressure, $T_v$ and $T_p$, respectively, specific gas volume, $\frac{1}{M}$, and, ratio of specific heats, γ. The burning temperatures and composition of the product gas are also important from the standpoint of compatibility with the surroundings. In propellants the surroundings include the inert parts of the heat engine which must remain intact through the cycle or even have a service life of many cycles.

**7-1. Specific gas volume.** Specific gas volume, $\frac{1}{M}$, is the number of weight moles of gas produced in the burning of a unit weight of propellant. In all cases where only gaseous products result, $M$ is the average molecular weight of the product gas. The gas volume is determined from the conservation equations for the elements

$$\Sigma C = [CO_2] + [CO] \quad (6a)$$
$$\Sigma H = 2[H_2] + 2[H_2O] + [HCl] \quad (6b)$$
$$\Sigma N = 2[N_2] \quad (6c)$$
$$\Sigma Cl = [HCl] \quad (6d)$$
$$\Sigma O = [CO] + 2[CO_2] + \Sigma H_2O \quad (6e)$$
$$[CO_2] + [CO] + [H_2] + [H_2O] + [N_2] + [HCl] = \frac{1}{M} \quad (7)$$
$$\frac{1}{M} = \Sigma C + \tfrac{1}{2}\Sigma N + \tfrac{1}{2}\Sigma H + \tfrac{1}{2}\Sigma Cl \quad (8)$$

In these equations, $\Sigma C$, *e.g.*, is the total number of weight atoms of carbon in a unit weight of propellant and $[CO_2]$ is the number of weight moles of $CO_2$ in the gas from the unit weight of propellant. If $x_i$ is the weight fraction of ingredient $I$ in the propellant composition and $C_i$ the number of weight atoms of carbon in unit weight of $I$, then

$$\Sigma C = \Sigma(x_i C_i) \quad (9)$$

$\Sigma H$, $\Sigma N$, and $\Sigma Cl$ are derived in the same way.

**7-2. Flame temperature at constant volume.** The flame temperature at constant volume is determined by solving the equation

$$Q = \frac{1}{M}\Sigma\left[y_j \int_{T_o}^{T_v} C_{v_j} \quad dT\right] \quad (10)$$

where $y_j$ is the mole (volume) fraction of a product gas constituent $J$, *e.g.*, $CO_2$, in the gases formed from the propellant and $C_{v_j}$ is the molar heat capacity of the same gas constituent. The *heat of explosion* or calorific value of the propellant, $Q$, usually expressed in calories per gram, is the difference at reference temperature, $T_o$, between the heat of formation of the products and the heat of formation of the propellant.

$$-Q = \Delta E_{products} - \Delta E_{propellant} \quad (11)$$

Assuming no heat effect of mixing

$$\Delta E_{propellant} = \Sigma(x_i \Delta E_i) \quad (12a)$$

where $\Delta E_i$ is the heat of formation of ingredient $I$ per gram.

$$\Delta E_{products} = \frac{1}{M}\Sigma(y_j \Delta E_j) \quad (12b)$$

where $\Delta E_j$ is the heat of formation of product $J$ per mole.

The quantities $y_j$ are derived from Equations 6a-6c and various gas equilibrium equations, of which the most important is the water gas equilibrium

$$\frac{[CO][H_2O]}{[CO_2][H_2]} = K_o T \quad (13)$$

In actual systems there may be found small quantities of constituents other than those discussed above, such as $CH_4$, $NH_3$, NO, OH, H, O, and N, as well as products of other atomic species if present in the propellant. For each such constituent there is available an equilibrium constant $K_i(T)$ similar to $K_o(T)$ (Equation 13) and an estimate of its molar heat capacity.

The constants $K_i(T)$ and the various $C_v$'s and $\Delta E$'s have been quite precisely evaluated as functions of temperature, $T$.[11]

**7-3. Flame temperature at constant pressure.** The calculation of $T_p$ is similar to that of $T_v$, except that instead of Equation 10 we must use the following

$$Q = \frac{1}{M}\Sigma\left[y_j \int_{T_o}^{T_p} C_{p_j} \quad dT\right] \quad (14)$$

where $C_{p_j}$ is the heat capacity at constant pressure of gas constituent $J$.

Since burning is now at constant pressure, enthalpy instead of heat of formation must be used.

$$-Q = \Delta H_{products} - \Delta H_{propellants} \quad (15)$$

$$\Delta H_{propellant} = \Sigma(x_i \Delta H_i) \quad (16a)$$

$$\Delta H_{products} = \Sigma(y_j \Delta H_j) \quad (16b)$$

**7-4. Ratio of specific heats.** The value of $\gamma$ for a propellant is the weighted average of the $\gamma$'s of the gas constituents

$$\gamma = \frac{\Sigma y_j C_{p_j}}{\Sigma y_j C_{v_j}} \quad (17)$$

The values of $\gamma$ used are not the ratios of heat capacities at room temperature, but the ratios at operating temperatures of the heat engines concerned.

**7-5. Exact calculation of flame temperature and product composition.** The calculation of the flame temperature and product gas composition is done by trial, starting usually with an assumed temperature. This is an iterative process and is profitably done with a machine calculator, particularly when gas equilibria other than the water gas equilibrium must be considered. Programs[12-14] have been worked out for such calculations, assuming essentially only adiabatic conditions and chemical and thermodynamic equilibria, to give results of accuracy limited only by the thermodynamic data of the individual species considered. These programs also are used for calculated specific impulse on the basis of either frozen composition flow or equilibrium flow through the nozzle. A JANAF Thermochemical Panel exists for the coordination of thermochemical data and calculating procedures.

The exact calculation, even with a sophisticated machine calculator, is time consuming. Consequently nearly every propellant development facility has for internal use a short-cut calculation yielding approximate results useful for screening and program guidance. Many of the data reported in the literature, including some SPIA/M2 data sheets, are the results of such approximate calculations and should be confirmed by exact calculations before important decisions are based on them.

Two approximate calculations that have been used by more than one facility are described in Paragraphs 7-6 and 7-8.

**7-6. Hirschfelder-Sherman calculation.**[15] It is possible[16] to calculate $Q$ from additive constants $Q_i$ which are defined as the contributions of ingredients $I$ to the heats of explosion of propellants containing them. The Hirschfelder-Sherman calculation takes as the reference temperature 2500°K. The heat of explosion, $Q$, of the propellant differs from the heat required to bring the combustion products to 2500°K by an amount $E$, which can also be calculated from additive constants $E_i$ which are properties of the ingredients $I$. Finally, the heat capacity of the product gas at 2500°K is estimated from additive constants $C_{v_i}$ which are properties of the ingredients $I$. These heat capacities are assumed constant for the interval from 2000°K to 3000°K. The burning temperature at constant volume, $T_v$, is then given by the equation

$$T_v = 2500 + \frac{E}{C_v} \tag{18}$$

The gas volume, $\frac{1}{M}$, is calculated by Equation 8, and the force, $F$, by Equation 2.

If $T_v$ is above 3000°K, a better approximation of $T_v$ is given by the relationship

$$T_v = 3000 + 6046\left\{-(C_v + 0.01185) + [(C_v + 0.01185)^2 + 3.308(10^{-4})(E - 500C_v)]^{\frac{1}{2}}\right\} \tag{19}$$

In order to calculate characteristic velocity from Equation 3 or specific impulse from Equation 4 (see also Reference 17) we need the flame temperature at constant pressure, $T_p$, and the ratio of specific heats, $\gamma$, at the working temperature. The value of $\gamma$ is given by the relationship[18]

$$\gamma = 1 + \frac{1.987}{C_v M} \tag{20}$$

from which $T_p$ is calculated by the equation

$$T_p = \frac{T_v}{\gamma} \tag{21}$$

Additive constants for a number of propellant ingredients are given in Table 2. Constants for other organic ingredients can be estimated from the relationships[18]

$$\left(\frac{1}{M}\right)_i = C_i + \tfrac{1}{2}N_i + \tfrac{1}{2}H_i \tag{8}$$

$$C_{v_i} = 1.620C_i + 3.265H_i + 5.193O_i + 3.384N_i \tag{22}$$

$$Q_i = (-\Delta E)_i - 67421[2C_i + \tfrac{1}{2}H_i - O_i] \tag{23}$$

$$E_i = (-\Delta E)_i - 132771C_i - 40026H_i + 51819O_i - 6724N_i$$

where $(-\Delta E)_i$ is the heat of combustion of ingredient $I$.

Within the range 2000° to 4000°K for $T_v$ this method gives results within a few percent of the exact method. The method should not be used for propellants with $T_v$ over 4000°K as it does not allow for dissociation to free radicals, such as H, OH, and Cl. It should also not be used for propellants yielding a substantial amount of condensed exhaust.

## TABLE 2. THERMOCHEMICAL CONSTANTS FOR HIRSCHFELDER-SHERMAN CALCULATION[2a]

| | $Q_i$ | $C_{v_i}$ | $E_i$ | $\left(\frac{1}{M}\right)_i$ |
|---|---|---|---|---|
| Acetone | −1938 | 0.5104 | −2842.5 | 0.10331 |
| Ammonium dichromate | 1290 | 0.2700 | 610 | 0.0200 |
| Ammonium nitrate | 1450 | 0.4424 | 405.1 | 0.03748 |
| Ammonium perchlorate | 1603 | 0.3167 | 800.22 | 0.2128 |
| Ammonium picrate | 539 | 0.3213 | −117 | 0.04470 |
| Asphalt | −2302 | 0.2179 | −2305 | 0.09450 |
| Bd-MVP copolymer (90% butadiene, 10% 2-methyl-5-vinylpyridine copolymer) | −2741 | 0.4132 | −3183 | 0.11544 |
| Butyl carbitol adipate | −1836 | 0.4923 | −2629 | 0.09889 |
| Butyl carbitol formal | −1802 | 0.5229 | −2652 | 0.10403 |
| Carbon black | −3330 | 0.1349 | −3187.5 | 0.08326 |
| Cellulose acetate | −1263 | 0.3953 | −1971 | 0.06929 |
| Diallyl maleate | −1358 | 0.3872 | −1957 | 0.08155 |
| Di-*n*-butyl phthalate | −2071 | 0.4258 | −2656 | 0.09701 |
| Dibutyl sebacate | −2395 | 0.5108 | −3159 | 0.1113 |
| Di-(2-ethylhexyl) azelate | −2612 | 0.5272 | −2272 | 0.11876 |
| Diethyl phthalate | −1760 | 0.3866 | −2348.7 | 0.08550 |
| Diglycol dinitrate | 1073 | 0.3857 | 232.4 | 0.04589 |
| Dinitrophenoxyethanol | -15 | 0.3369 | −633.4 | 0.05698 |
| Dioctyl phthalate | −2372 | 0.4650 | −3020 | 0.11026 |
| Diphenylamine | −2654 | 0.3471 | −3010 | 0.10637 |
| Diphenylguanidine | −2270 | 0.3476 | −2626 | 0.09941 |
| Ether | −2007 | 0.5970 | −2958 | 0.12143 |
| Ethyl alcohol | −1716 | 0.6083 | −2785 | 0.10854 |
| Ethyl centralite | −2412 | 0.3905 | −2766 | 0.10434 |
| Graphite | −3370 | 0.1349 | −3234 | 0.08326 |
| GR-I rubber | −3257 | 0.5779 | −4006 | 0.14235 |
| HMX, Cyclotetramethylenetetranitramine | 1321 | 0.3414 | 575 | 0.0405 |
| Lead stearate | −2030 | 0.3976 | −2440 | 0.09180 |
| M & V | −1827 | 0.3976 | −2440 | 0.09180 |
| N-Methyl-*p*-nitroaniline | −1095 | 0.35808 | −1625 | 0.07887 |
| Metriol trinitrate | 1189 | 0.3052 | 377 | 0.04313 |
| Mineral jelly | −3302 | 0.5811 | −475 | 0.1426 |
| Nitrocellulose, 12.2% N | 900 | 0.3478 | 137.7 | 0.04127 |
| Nitrocellulose, 12.6% N | 956 | 0.3454 | 198.9 | 0.04040 |
| Nitrocellulose, 13.15% N | 1033 | 0.3421 | 283.1 | 0.03920 |

## TABLE 2. THERMOCHEMICAL CONSTANTS FOR HIRSCHFELDER-SHERMAN CALCULATION[10] (Continued)

| | $Q_i$ | $C_{v_i}$ | $E_i$ | $\left(\frac{1}{M}\right)_i$ |
|---|---|---|---|---|
| 2-Nitrodiphenylamine | −1813 | 0.3226 | −2201 | 0.06411 |
| Nitroglycerin | 1785 | 0.3438 | 951.9 | 0.03082 |
| Nitroguanidine | 713 | 0.3710 | −68.6 | 0.04808 |
| PETN, Pentaerythritol tetranitrate | 1531 | 0.3424 | 727 | 0.0348 |
| Petrin | 1202 | 0.3703 | 374 | 0.04109 |
| Polyester | −2184 | 0.3552 | −2620 | 0.09123 |
| Polyisobutene | −3228 | 0.5798 | −3981 | 0.14299 |
| Poly (methyl acrylate) | −1404 | 0.4231 | −2111 | 0.08140 |
| Polystyrene | −2983 | 0.3739 | −3309 | 0.11523 |
| Polyurethane | −3296 | 0.4073 | −3773 | 0.10796 |
| Poly(vinyl chloride) | −1614 | 0.2080 | −1851 | 0.05600 |
| Potassium nitrate | 1434 | 0.2158 | 24.9 | 0.00989 |
| Potassium perchlorate | 1667 | 0.2000 | 800 | 0.00722 |
| Potassium sulfate | 300 | 0.1250 | −800 | 0.00574 |
| RDX, Cyclotrimethylenetrinitramine | 1360 | 0.3416 | 615 | 0.0405 |
| Sucrose octaacetate | −1121 | 0.3941 | −1825 | 0.06922 |
| Triacetin | −1284 | 0.4191 | −1973 | 0.07333 |
| Triethylene glycol dinitrate | 750 | 0.40430 | −89.24 | 0.05412 |
| Trinitrotoluene | 491 | 0.3037 | −110 | 0.04843 |

**7-7. Example calculation of $F$, $c_v^*$, $I_{sp}^\circ$ by the Hirschfelder-Sherman method.** Consider a propellant of composition:

| | |
|---|---|
| Nitrocellulose, 12.6% N | 0.50 |
| Nitroglycerin | 0.49 |
| Ethyl centralite | 0.01 |

From the composition and Table 2, we have

| Ingredient | Weight fraction | $x_iQ_i$ | $x_iC_{v_i}$ | $x_iE_i$ | $x_i/M_i$ |
|---|---|---|---|---|---|
| Nitrocellulose | 0.50 | 478 | 0.1727 | 99.5 | 0.02020 |
| Nitroglycerin | 0.49 | 875 | 0.1685 | 466.4 | 0.01510 |
| Ethyl centralite | 0.01 | −24 | 0.0039 | −27.6 | 0.00104 |
| Summations | 1.00 | 1329 | 0.3451 | 538.3 | 0.03634 |

*Isochoric flame temperature:*

$$T_v \text{ by Equation 18: } 2500 + \frac{538.3}{0.3451} = 4060°K$$

Since this is higher than 3000°K, we must calculate by Equation 19

$$T_v = 3000 + 6046\left\{-(0.3451 + 0.01185) + [(0.3451 + 0.01185)^2 + 3.308 \times 10^{-4} \times (538.3 - 500 \times 0.3451)]^{\frac{1}{2}}\right\}$$
$$= 3855°K \text{ or } 6940°R$$

*Force:*

$$F = \frac{R_0T_v}{M} = 1543 \times 6940 \times 0.03634$$
$$= 389{,}000 \text{ ft-lb/lb}$$

*Specific heat ratio:*

$$\gamma = 1 + \frac{1.987 \times 0.03634}{0.3451} = 1.2092$$

*Isobaric flame temperature:*

$$T_p = \frac{3855}{1.209} = 3188°K \text{ or } 5738°R$$

*Characteristic velocity,* $c_o^*$*:* From Table 1, the reduced characteristic velocity corresponding to $\gamma = 1.209$ is 1.540. The characteristic velocity, $c_o^*$, is then

$$c_o^* = 1.540\sqrt{32.2 \times 1543 \times 5738 \times 0.03634}$$
$$= 4950 \text{ ft/sec}$$

*Specific impulse,* $I_{sp}^*$*:* From Figure 1, the reduced specific impulse corresponding to $\gamma = 1.209$ and $\frac{P_e}{P_c} = 0.015$ is 2.445. The specific impulse, $I_{sp}^*$, is then

$$I_{sp}^* = 2.445\sqrt{\frac{1543 \times 5738 \times 0.03604}{32.2}}$$
$$= 245 \text{ lb-sec/lb}$$

**7-8. ABL short calculation for specific impulse.**[31] In order to shorten the time and complexity of the exact calculation for specific impulse of propellants with condensible exhaust, the ABL method makes a number of simplifying assumptions. Chief among them are:

(a) No product dissociation is considered.

(b) A priority system applies to the formation of the products. Thus, oxygen first oxidizes all light metal, then converts C to CO, then $H_2$ to $H_2O$, and any oxygen still not used up converts CO to $CO_2$.

(c) Certain latent heats are completely recovered during nozzle expansion.

The calculation can be performed with a desk calculator, but is usually done with a larger calculator if available.

Results of this calculation may differ from exact calculation results by as much as 3 percent.

The results do not represent either frozen flow or equilibrium flow, but agree fairly well with exact equilibrium flow calculations.

The assumption of no dissociation leads to artificial values for $T_p$.

**8. Measurement of ballistic parameters.** The empirical determination of the ballistic parameters is discussed in the next few paragraphs.

**8-1. Measurement of heat of explosion.** The heat of explosion of a propellant, $Q$, also known as the calorific value, is measured by burning in a bomb calorimeter under an inert atmosphere. Two types of calorimeters have been in common use. In the Boas calorimeter the loading density, or weight of propellant per unit volume, is fairly high, leading to pressures of some thousands of pounds. This calorimeter need not be prepressurized. In a coal calorimeter, the loading density is low and an initial inert gas pressure of some 200 to 300 psi is required. Both types of calorimeter give essentially the same values of $Q$.

For thermochemical purposes, the observed heat must be corrected for the heat of condensation of water and for shifting gas equilibrium during the cooling of the calorimeter and its contents. This correction amounts to about 10 percent and may be so approximated.[32] Uncorrected calorimetric values, denoted "water liquid," are of considerable utility as a quality assurance measure in volume production of propellants to verify that successive lots of propellant manufactured to the same formula actually duplicate each other within specified limits. The calorimeter test can be run with much less effort and more precision than a complete chemical analysis. The procedure for the calorimeter test is given in a Navy Department Bureau of Ordnance report.[33] Calorific values encountered in propellants seldom exceed 1500 cal/g and are accordingly much less than for ordinary fuels. The obvious reason for this is that ordinary fuels draw on atmospheric oxygen for their combustion reactions, whereas propellants must carry their oxidants within themselves in order to function in the absence of air.

**8-2. Measurement of specific force.** Combining Equations 1 and 2 we get

$$F = \frac{P}{W}\,(V - \alpha W) \qquad (25)$$

A direct experimental measure of $F$ should then be obtained from the pressure developed under adiabatic conditions by burning a weight, $W$, of propellant in a closed chamber of volume, $V$. Because truly adiabatic conditions can only be approached, a related concept, that of *relative force*, is used. If equal weights of two propellants with the same burning time are fired consecutively in the same closed vessel at the same initial temperature, $W$ and $(V - \alpha W)$ are constant. Then

$$F_2 = F_1 \left(\frac{P_2}{P_1}\right)$$

$F_1$, the force of the standard propellant, is arbitrarily assigned the value 100 percent, and the relative force, $RF$, of the propellant under examination becomes

$$RF = \frac{P_2}{P_1} \times 100\% \qquad (26)$$

Relative force is used in quality control of gun propellants to assure that successive lots of the same formulation duplicate each other. In developing a new propellant to replace an existing one, a measurement of relative force is useful as an indication that the relationship between calculated and delivered force is or is not similar to the relationship for the known standard propellant. The procedure and description of apparatus for the determination of relative force may be found in an Army Service Forces Directive.[24]

**8-3. Measurement of characteristic velocity.** Delivered or actual characteristic velocity, $c^*$, is defined as

$$c^* = \frac{gA_t}{W} \int P_c \, dt \qquad (27)$$

It is determined experimentally by static firing of a weight, $W$, of propellant in a vented vessel of known throat area, $A_t$, measuring the chamber pressure as a function of time, and integrating. The JANAF Solid Propellant Rocket Static Test Panel has published[25] a survey of existing static test facilities and is continuing to coordinate test procedures. Comparison of $c^*$ with $c_0^*$ gives a measure of the operating efficiency of the vented vessel. In similar heat engines with similar propellants, $\frac{c^*}{c_0^*}$ should remain nearly constant. The difference between $c_0^*$ and $c^*$ is due largely to heat losses to the motor walls.

**8-4. Measurement of specific impulse.** Delivered or actual specific impulse, $I_{sp}$, is defined as

$$I_{sp} = \frac{1}{W} \int F \, dt \qquad (28)$$

This parameter is determined also by static firing a vented vessel, but measuring thrust.[26]

Unless the operating and discharge pressures are 1000 psi and 14.7 psi, respectively, the measured $I_{sp}$ must be corrected to these values. Corrections must be applied also for the divergence half-angle of the nozzle, since the amount of impulse delivered decreases as nozzle angle increases.[27] The usual convention for half-angle is 15°. Part of the difference between $I_{sp}^0$ and $I_{sp}$ is therefore due to the divergence loss. The 15° convention is unfortunately not always observed. Some measured $I_{sp}$ data reported in the literature have been corrected to zero half-angle. In using $I_{sp}$ data, one must identify which half-angle correction has been used.

**8-5. Example calculation of $I_{sp}$ from measured $I_{sp}$ (del) at nonstandard conditions.** The following data were taken from an actual rocket firing:

Expansion ratio, $\epsilon_e = \frac{A_e}{A_t} = 2.779$
Mean chamber pressure, $P_c = 218$ psia
Nozzle divergence half-angle, $\alpha = 20°$
Specific heat ratio, $\gamma = 1.17$
$I_{sp}$ (del) = 201.3 lb-sec/lb

The correction of $I_{sp}$ (del) to standard conditions involves the parameter *thrust coefficient*, $C_F$, from interior ballistics. The thrust coefficient, defined as

$$C_F = \frac{F}{P_c A_t} = \frac{gI_{sp}}{c^*} \qquad (29)$$

measures the contribution of the nozzle to the rocket thrust. Since $c^*$ is independent of discharge conditions, for any given rocket firing $\frac{I_{sp}}{C_F}$ is a constant independent of nozzle and external conditions.

The thrust coefficient has its maximum value when expansion in the nozzle is to zero pressure (vacuum) and discharge is also to zero pressure. For any other exit pressure the vacuum thrust coefficient must be corrected by a term $\epsilon\left(\frac{P_e}{P_c}\right)$. If the ambient pressure differs from the exit pressure another correction involving $\epsilon\left(\frac{P_a}{P_c}\right)$ must be applied.

Values of $C_F$ and $\epsilon\left(\frac{P_e}{P_c}\right)$ are obtained from *Thrust Coefficient and Expansion Ratio Tables*[28] of which the tabulated $C_F$ is for vacuum discharge and zero divergence angle. The divergence angle correction[27] is made by the equation

$$\lambda = 0.5 + 0.5 \cos \alpha$$

so that the overall correction becomes

actual $C_F$ =

$$\lambda\left[C_F\,(\text{table}) - \varepsilon\left(\frac{P_e}{P_c}\right)\right] + \varepsilon\left(\frac{P_e}{P_c}\right) - \varepsilon\left(\frac{P_a}{P_c}\right)$$

For the example at hand, using the table values:

| | Firing conditions | Standard conditions |
|---|---|---|
| $C_F$ | 1.54358 | 1.75284 |
| $\varepsilon\left(\frac{P_e}{P_c}\right)$ | 0.21405 | 0.13856 |
| $\lambda$ | 0.9699 | 0.983 |

Inserting numerical values, and noting that for standard conditions $P_e = P_a$

$$C_F\,(\text{firing})^* = 0.9699(1.54358 - 0.21405) + 0.21405 - 2.779 \times \frac{14.7}{218} = 1.316$$

$$C_F\,(\text{std}) = 0.983(1.75824 - 0.13856) = 1.587$$

The corrected value of $I_{sp}$ at standard condition is, therefore,

$$201.3 \times \frac{1.587}{1.316} = 242.8 \text{ lb-sec/lb}$$

**9. Burning of propellants.** Heat will be transferred by radiation, conduction, and/or convection to the surface of a cold solid propellant suspended in a hot atmosphere. If the solid is essentially a nonconductor of heat, the heated surface will pyrolize, giving rise to gaseous products and exposing new surface to the hot atmosphere. The gas in immediate contact with the burning surface[28] will be the uncontaminated pyrolytic products of the surface, at the temperature of pyrolysis. Moving out from the surface the gases are raised to the temperature of the hot atmosphere and undergo reactions among themselves and with the atmosphere so that the hot atmosphere continues to exist in a state of equilibrium among the several chemical species present. If the solid is a monopropellant and the hot atmosphere comprises its combustion products at flame temperature, the primary pyrolytic products are given off already premixed and in proportions such that the final reaction of the products among themselves will bring the gas to flame temperature and thus duplicate the hot atmosphere in temperature and composition.

Although the temperature rise and composition changes are continuous from the unchanged propellant to the products at flame temperature, it is convenient for analysis to break the process down into several phases as represented by Figure 2. Region A represents the unheated interior portion of the solid. In region B a thin layer of the solid is being heated to pyrolysis temperature, $T_i$. In region C pyrolysis is taking place and gaseous products are being formed. The pyrolytic reactions may or may not involve the formation of liquid intermediates (foam zone). A layer of primary gaseous pyrolytic products at temperature $T_i$ is region D. In region E (fizz zone) these gases are heated to ignition temperature. In this process they may undergo low temperature reactions of an exothermic character and produce some heat. The bulk of the heat is generated in the flame zone, region F, to yield finally burned gas at temperature $T$ in region G.

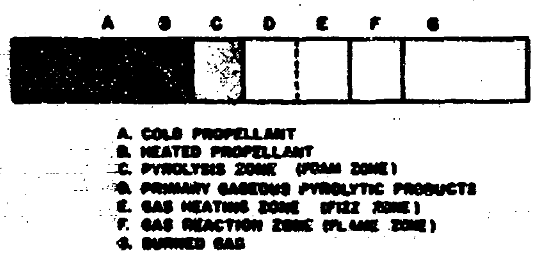



*Figure 2. Burning of Solid Monopropellant*

At operating pressures in the neighborhood of several hundred pounds per square inch and higher, the thickness of the regions B through F is small, perhaps of the order of $10^{-3}$ inches in total. By operating at greatly reduced pressures one can broaden these regions. The foam zone, fizz zone, and flame zone have been observed in experiments of this type.[30]

The linear rate of burning of the monopropellant depends on the rate at which the surface receives heat from the surrounding combustion products. All exposed surfaces that can "see" the

*Since this value is a theoretical value derived from approximate measured parameters, it does not necessarily agree with a value of $C_F$ calculated by Equation 29 from measured $I_{sp}$ and $c^*$.

hot combustion products should receive heat at the same rate and therefore burn at the same rate. The burning surface should recede by parallel layers. This conclusion, known as *Piobert's Law*[31] and first announced for black powder, has been verified for monopropellants under both rocket and gun conditions by examination and measurement of partially burned grains. It appears also to hold for composite propellants, although the explanation cannot be as simple.

The rate of regression of a burning propellant surface, measured normal to the surface, is known as the *linear burning rate*, $r$. It is usually expressed in terms of inches per second. When $r$ is multiplied by the area of the burning surface, $S$, and by the density we have, finally, the *weight—or mass—burning rate*, expressed as pounds per second

$$W = rS\rho \qquad (30)$$

Several factors are recognized as affecting the burning rate. Among these are pressure at which burning is taking place, initial temperature of the propellant, gas velocity over the burning surface, and composition of the propellant.

**9-1. Effect of pressure.** Increasing the pressure at which burning takes place should increase the rate of heat transfer from the flame to the propellant by increasing the density of the gas phase and thereby decreasing the thickness of regions D and E through which the heat must be transferred. The influence of pressure has been studied in both closed bombs and vented vessels over a period of years, and empirical equations in various forms developed by different schools of ballisticians.

de Saint Robert equation[32] $r = bP^n$ (31a)

Muraour equation[33] $r = a + bP$ (31b)

Summerfield equation[32] $\frac{1}{r} = \frac{a}{P} + b\left(\frac{1}{P}\right)^{1/3}$ (31c)

If the $\log P - \log r$ relation for a propellant is plotted we get a family of curves resembling Figure 3 from propellants behaving according to Equation 31a, from which the values of $b$ and $n$ can be evaluated. The constant $n$ is the slope of the log rate versus log pressure line. At gun pressures, 10,000 to 50,000 psi, nearly all propellants follow Equation 31a, with $n$ = approximately 0.9.[34] At rocket pressures, below 2000 psi, $n$ for the same propellant is generally lower than at gun pressures. In this region will be found propellants giving the normal straight line log rate versus log pressure relationship, but also many propellants deviating widely from it. Two types of curves are worthy of special mention.

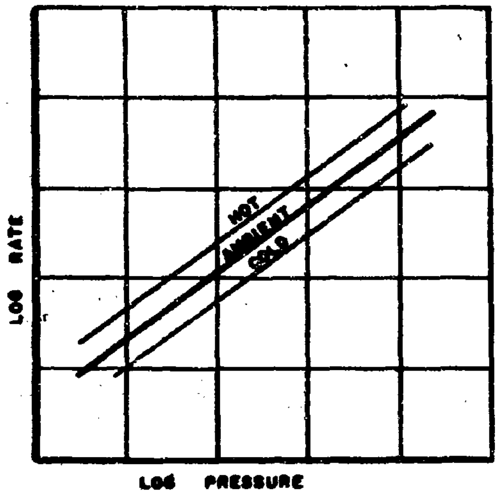



*Figure 3. Rate-Pressure Relationship of Propellants for Which $r = bP^n$*

Propellants showing a region of markedly reduced $n$, as shown in Figure 4, are known as

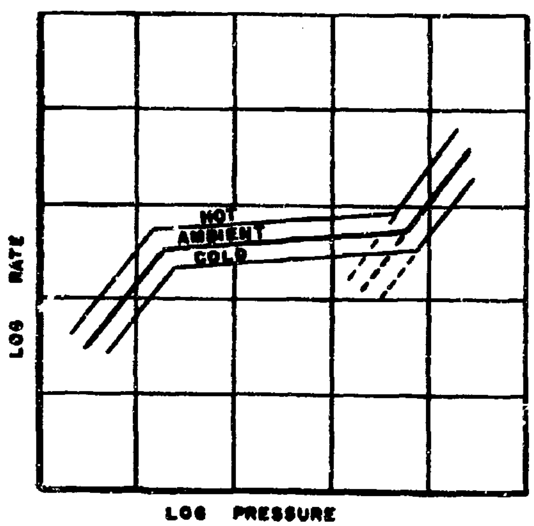



*Figure 4. Rate-Pressure Relationship of Plateau Propellants*

"plateau" propellants.[28] This behavior is shown by certain nitrocellulose system propellants containing small amounts of lead compounds and by some fuel binder ammonium perchlorate composites. The effect of the lead compounds is to increase the burning rate in the plateau region and at lower pressures, as shown by the fact that without the lead the propellant would show a normal curve coinciding with the high pressure branch of the plateau propellant's curve and continuing normally into the lower pressure region (dotted line, Figure 4). The mechanism of plateau formation has not been fully elucidated. From Equation 31a the pressure in a vented vessel is of the form[30]

$$P = \text{const}\, x \left(\frac{bS}{A_t}\right)^{\frac{1}{1-n}} \qquad (32)$$

from which it is apparent that a low value of $n$ is desirable in rocket propellants to decrease the sensitivity of the operating pressure to small changes in $b$ (a function of propellant ambient temperature); $S$, the burning area; and $A_t$, the throat area. In practical terms, a low value of $n$ permits design of lighter weight rocket motor chambers by decreasing the requirement for high safety factors to take care of deviations of $b$, $S$, or $A_t$ from design values.

As a low value of $n$ is desirable, a negative value is even more desirable. Propellants are known which show negative values of $n$ over short pressure ranges, as shown in Figure 5.[27] They are known, from the shape of the curves, as "mesa" propellants. In the region of negative slope, should the pressure increase as a result of sudden exposure of additional burning surface or by partial constriction of the throat the rate would drop immediately to restore the balance. The close approach of the isotherms also contributes to a low temperature coefficient of performance for vented vessels designed to operate in this region. Crossing of isotherms indicates a region of negative temperature coefficient.

**9-2. Effect of temperature.** As can be seen from the isotherms of Figures 3, 4, and 5, the initial temperature of the propellant has a significant effect on the linear burning rate. If all of the heat transferred to the propellant surface from the combustion products were used to raise that surface to a temperature $T'$, at which vaporization or

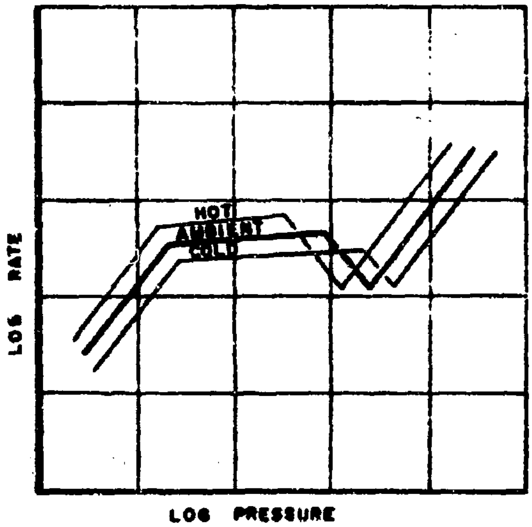



*Figure 5. Rate-Pressure Relationship of Mesa Propellants*

reaction becomes appreciable, one would expect the temperature-rate relationship to assume the form

$$r = \frac{b'P^n}{(T' - T_i)} \qquad (33)$$

where $b'$ is a constant and $T_i$ is any initial temperature. By measuring the linear burning rates at the same pressure for the same propellant at two initial temperatures one could calculate $T'$. Another frequently used relationship is

$$r = b''P^n e^{u(T_i - T_0)} \qquad (34)$$

where $b''$ and $u$ are constants and $T_0$ is a reference initial temperature. A linear relationship has also been noted.[28] The existence of regions of negative temperature coefficient described above is not consistent with either of these relationships, so the effect of propellant temperature on linear burning rate remains largely an empirical relationship.

In the SPIA/M2 data sheets four temperature coefficients may be found. Of these the temperature coefficient of burning rate at constant pressure, $\sigma_p = \left(\frac{\partial \ln r}{\partial T}\right)_P$, is estimated from the rate-pressure curves (Figures 3, 4 or 5) using the intersections of the curves for the different temperatures with a vertical line at the constant pressure of interest.

Since for a real rocket motor the working pressure is not the same at different grain temperatures, this parameter does not have real significance. The temperature coefficient of burning rate at constant $K$ value, $\sigma_K = \left(\frac{\partial \ln r}{\partial T}\right)_K$ is determined empirically by static-firing rocket motors at different grain temperatures and dividing the known web dimensions by the burning times to get the rates. Since neither the burning surface nor the nozzle throat area changes appreciably with ambient temperature, the assumption of constant $K$ value between rocket motors of the same design at different temperatures is good. The temperature coefficient of pressure at constant $\frac{P}{r}$ value, $\pi_{\frac{P}{r}} = \left(\frac{\partial \ln P}{\partial T}\right)_{\frac{P}{r}}$ is determined from the rate-pressure curves, using the intersections of the curves for the different temperatures with 45° lines which are lines of constant $\frac{P}{r}$. In real rocket motors the assumption of constant $\frac{P}{r}$ with changing temperature is better than the assumption of constant pressure, but this parameter still has only qualitative value. The more significant temperature coefficient of pressure at constant $K$ value, $\pi_K = \left(\frac{\partial \ln P}{\partial T}\right)_K$, is again determined empirically by static firing at different temperatures. All four of these parameters are expressed in units of percent per degree, usually Fahrenheit. Low values of these coefficients are desirable.

**9-3. Effect of gas velocity. Erosive burning.** When burning occurs inside tubes of propellant such as the perforations of gun propellant and the interior surfaces of rocket propellant, it is found that the linear burning rate at and near the exit of the tube exceeds the normal rate. The shape of the "eroded" region suggests a velocity effect, and indeed the erosion law may be written

$$r = bP^n(1 + K_1\frac{V}{C}) \qquad (35)$$

where $V$ is the local gas velocity in the tube and $C$ is the velocity of sound in the combustion products. In the case of a single internal-burning rocket grain in a rocket[39] motor, $VA_p = CA_t$ where $A_p$ is the "port area" or the exit area of the tube and $A_t$ is the nozzle throat area, so Equation 35 becomes

$$r = bP^n(1 + K_1\frac{A_t}{A_p}) \qquad (35a)$$

which is in a more convenient form for use by rocket designers. The constant $K_1$ is called the "erosivity constant" and is a measure of the susceptibility of a propellant to erosion. Its value is of the order of 0.5 to 1.0. Equation 35 will be recognized as a linear approximation, applicable over the range of gas velocities for which the constant $K_1$ has been developed. A theoretical treatment of erosion[40] has been based on the transition from laminar flow to turbulent flow of the combustion products within the perforation.

An erosive burning law

$$r = bP^n + \frac{\alpha G^{0.8} e^{-\frac{\beta r \rho}{G}}}{L^{0.2}} \qquad (36)$$

has been developed[41] from consideration of heat transfer to the propellant walls from the hot gas passing down the perforation. In this equation, $\alpha$ and $\beta$ are constants characteristic to the propellant burned, $G$ is the mass velocity of the gases in the port, and $L$ is the distance downstream from the stagnation point.

**9-4. Effect of composition.** As the driving force for the burning of propellant is the temperature of the combustion products, all theories agree that hot propellants should have a higher linear burning rate than cool ones. This is found quite generally true at gun pressures and also at rocket pressures where the rate-pressure relationship is "normal." This is a matter of no more than academic interest to the users of gun propellants who do not have the problem of reconciling grain geometry to charge envelope requirements. In rocket design on the other hand, where, in general, single grains are used, it is necessary to be able to control burning temperatures and rates independently in order to meet simultaneously performance and envelope requirements. To this end rocket compositions quite commonly contain additives known as burning rate catalysts which generally increase or decrease the normal burning rate of the propellant. The choice of catalysts and their proportions in the composition are determined by experiment. Temperature coefficients and erosivity constants are also properties of the compositions.

**9-5. Burning rate of composite propellants.** A composite propellant has been defined as a solid propellant system comprising two or more solid phases intimately mixed. In all important cases, with the possible exception of black powder, one of these phases is continuous and forms the matrix or binder in which the other phase or phases is dispersed. When a composite propellant burns, the burning surface comprises a web of binder filled with exposed surfaces of filler material. Each exposed material burns at its own linear rate at any given pressure and starting temperature and has its own pressure index and temperature coefficient. A perfect match between the burning rates of binder and filler would be a coincidence, and easily disturbed by a change in burning pressure. In general the filler surface will recede faster or slower than the binder, giving rise to an irregular and time-dependent boundary between regions C and D. Figure 6 shows the case of filler burning more rapidly than binder. Area I shows a filler particle not yet exposed. Area II shows a filler particle partially burned, while at Area III is a pocket left by a filler particle completely consumed. The net effect of the faster-burning filler is to increase the instantaneous burning surface of the binder. We can no longer measure the burning area, only its projection on a plane parallel to the original burning surface. By increasing the actual burning area, we attain a greater apparent linear rate, referred to the projected area. In spite of the lower apparent burning rate of the binder, the burning rate of the composite propellant approaches the linear rate of the fast-burning filler.

The case of filler burning more slowly than binder is shown in Figure 7. In Area I we have again a filler particle not yet uncovered, in Area II a filler particle burning at a slower rate than the surrounding binder, and in Area III an incompletely burned filler particle completing its combustion in the gas phase outside the piece of propellant. In this instance the linear burning rate of the composite should approximate that of pure binder.

As the linear burning rate of the composite tends to follow the burning rate of the faster-burning phase, it is to be expected that the temperature

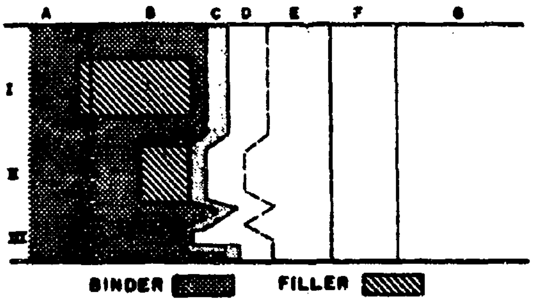



*Figure 6. Burning of Composite Propellant—Filler Rate Faster Than Binder*

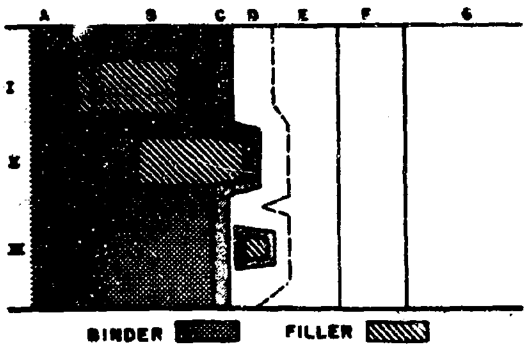



*Figure 7. Burning of Composite Propellant—Filler Rate Slower Than Binder*

coefficient and pressure index should also tend to follow the corresponding figures for the faster-burning phase.

In a two-phase filler-binder composite various combinations of monopropellants, fuels, and oxidizers are possible. If both binder and filler are monopropellants, region D is all combustible mixture, although of a mixture of compositions. If the binder is a monopropellant and the filler is either oxidant or fuel, region D is a continuum of combustible mixture containing pockets of fuel gas or oxidizer gas, and a diffusion process as well as heating must occur in region E before the combustion reactions can be completed. If the binder is fuel or oxidant and the filler is monopropellant, region D becomes a continuum of fuel gas or oxidizer gas containing pockets of combustible mixture. If the binder is fuel and the filler oxidant or vice versa, region D contains no combustible mixture.

A diffusion step is required to mix the fuel-rich gas with oxidizer-rich gas before the reactions to produce the flame temperature can be completed. With larger filler particle size the distance either gas must move to accomplish diffusion is longer and, therefore, the distance between region D and region F should be greater than with smaller filler particle size. This may explain qualitatively the observed slower burning rates of fuel binder composites with large filler particle size.

The requirement of a diffusion step before a combustible continuum is achieved is no essential handicap in a burning regime. It is interesting to note, however, that propellants with this requirement propagate detonation in the solid less readily than do monopropellants.

The preceding discussion of the burning relationships applies to steady state burning and assumes no pores, cracks, or fissures with components perpendicular to the burning surface. Two important problems are recognized in connection with burning.

**9-6. Problem of unstable burning.** For as long as modern rockets have been under investigation in the United States and undoubtedly earlier elsewhere, some rockets have exhibited a tendency to develop irregular pressure peaks at some time during their burning cycles. In severe cases this has led to rupture of the motor chamber. With pressure-time instrumentation of sufficiently low time constants these pressure irregularities have been shown to exhibit frequencies identified with axial, radial, and/or tangential vibration modes of the burning cavity. In separate instances the phenomenon has been overcome by "resonance rods"[42] placed inside the grain perforation, radial holes[43] through the web, slots[43] or baffles[43,44] within the grain, and most recently by adding small quantities of finely-divided aluminum[45] to the composition. In each case a "quick-fix" has been accomplished but no real explanation has been given for the phenomenon. Considerable light has been shed very recently on this question by the appreciation that the propellant grain does not behave as a rigid body but has acoustic properties similar to those of the gas in the burning cavity.[39]

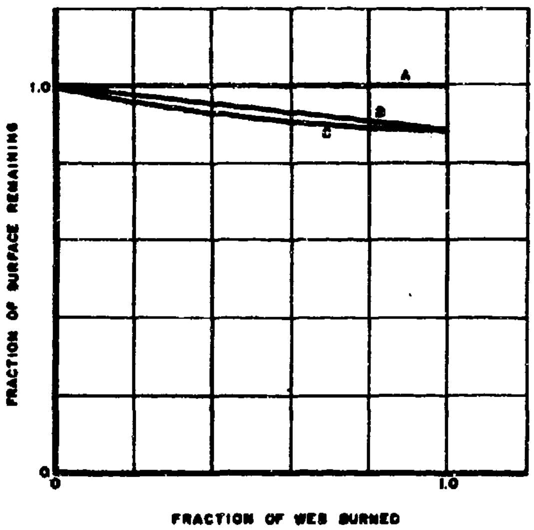
**9-7. Transition from deflagration to detonation.** With the advent of very large, high performance rocket engines the question has been raised whether and under what circumstances a rocket motor can proceed spontaneously from a burning regime to detonation. This question has been and is being investigated intensively.

It is presumed that burning can give rise to shock and that the shock thus produced can occasion detonation in the propellant. That continuous monopropellants can be detonated by shock has been well documented.[46,47] The necessary conditions are that the shock intensity be sufficiently great and that the propellant be present in cross section greater than its critical diameter. That burning of a properly consolidated rocket grain can give rise to shock has not been demonstrated. A theoretical study[48] indicates that only when the pressure rises exponentially in a few microseconds to several thousand atmospheres can coalescence of pressure waves give rise to shock as a result of burning. In an improperly consolidated propellant, on the other hand, with regions of interconnected porosity it is comparatively easy to attain a condition of shock which will result in detonation. Unfortunately much of the literature which purports to study the transition from deflagration to detonation actually reports studies of the transition from shock to detonation.[49]

**10. Propellant grain.** A single piece of propellant is known as a *grain*. The exposed portion of the grain surface at any time during burning is the *burning surface*. Any portion of the surface which is covered by adhered nonburning material is *inhibited*. The shortest distance, normal to a burning surface, that the grain burns until it loses its structural integrity is the *burning distance*. The thickness of the propellant wall so consumed is the *web*. If a grain burns on only one side, as is the case with case-bonded or otherwise inhibited grains, the web is equal to the burning distance. If two parallel surfaces burn toward each other, as in uninhibited single- or multiple-perforated grains, the web is twice the burning distance. The relationship between web and burning distance is thus not single valued. The dimensions of the grain taken collectively are known as the *granulation* when referred to multiple-grain or bulk charges, or as *configuration* when referred to a single grain.

A grain that maintains its burning surface constant, or approximately constant, during burning has *neutral* geometry. Simple neutral geometries include sheets, squares, or disks with webs small compared with surface dimensions or with edges inhibited, long tubes, or tubes with ends inhibited.

A grain whose burning surface increases during the burning has *progressive* geometry. Examples of progressive geometry are tubes with outer surface inhibited and burning only on the perforation surface, also grains with multiple perforations. A grain whose burning surface decreases as burning progresses has *degressive* geometry. Such geometries include spheres, cubes, also cylinders and cords of any cross section. The burning surface is plotted against fraction of web burned for several geometries in Figures 8-14. The portions of the grain remaining at burn-through, shown shaded in




A. LONG TUBE, END-INHIBITED TUBE, SHEET, END-BURNER
B. SHORT TUBE, WEB = 0.1 LENGTH, STRIP WEB = 0.1 WIDTH
C. DISK, WEB = 0.05 DIAMETER

*Figure 8. Neutral Geometry*

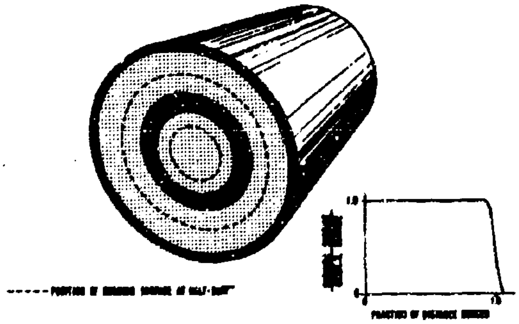


*Figure 9. Rod and Shell Grain*

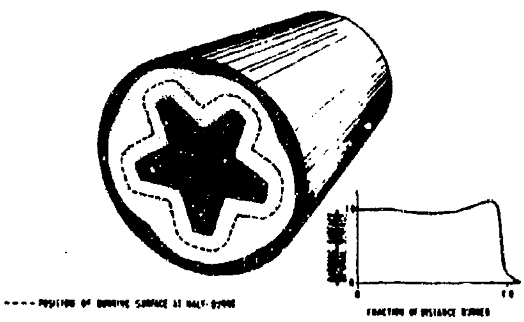


*Figure 10. Star-Perforated Grain*

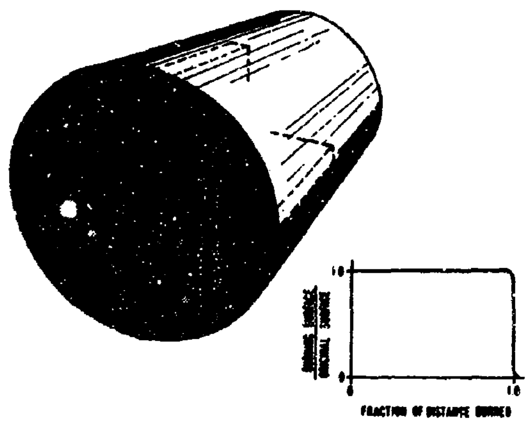
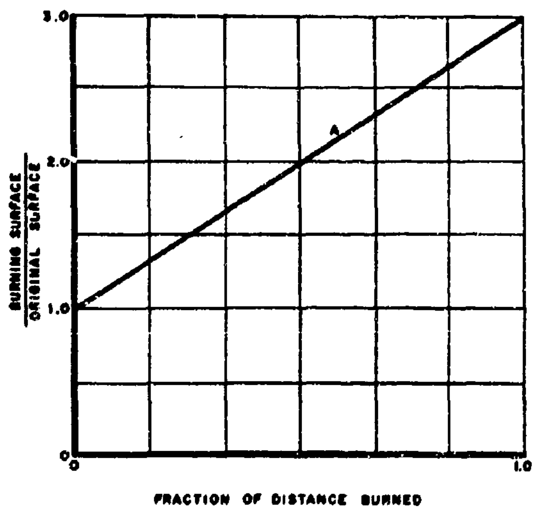


*Figure 11. Slotted-Tube Grain*




A. INTERNAL BURNING TUBE, PERFORATION $1/3$ DIAM

*Figure 12. Progressive Geometry*

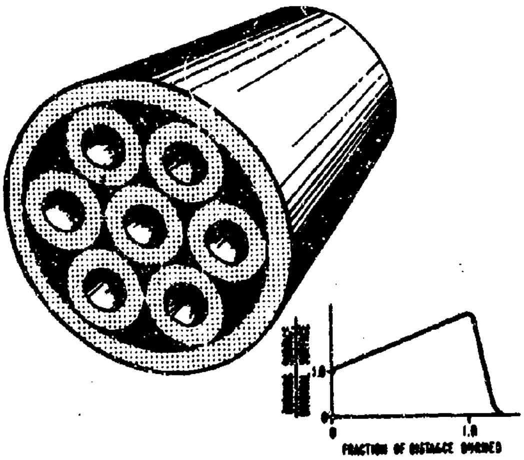


*Figure 13. Multiple-Perforated Cylinder*

Figures 10 and 13 are known as *slivers.*

The terms neutrality, progressivity, and degressivity are also applied to the weight burning rate, $\dot{W}$. Since $\dot{W}$ is proportional to both linear rate and burning surface, factors affecting the rate can affect the progressivity just as well as can geometric factors. In this sense a dual-composition grain in which the first composition exposed burns more slowly than the second can be progressive in spite of a degressive geometry. Such grains are used for small arms charges. The slow-burning outer composition is created by *coating* or applying a plasticizer to the outside of the grain and causing it to penetrate only part way through the web, leaving the interior of the web unchanged. Dual-composition grains may also be used in rockets to create a boost-sustain situation. In this case the fast-burning composition is first exposed and the slow-burning one later. Erosive burning is sometimes used to speed up the early burning of a normally progressive geometry and attain essentially neutral burning. Finally, pressure changes that affect the rate contribute to progressivity. In this sense all closed bomb burning is at least initially progressive, regardless of geometry, and burning of a progressive or degressive geometry in a vented vessel is more progressive or degressive than is indicated by the geometry.

**11. Scheduling of mass rate.** Let us now consider some of the operating cycles for engines in which propellants are used.

**11-1. Gun.** The pressure-time relationship in a gun is shown in Figure 15. The propellant on ignition starts to burn essentially in a closed chamber. When the pressure has built up to a sufficient level, known as shot-start pressure, the frictional and other forces tending to hold the projectile in place are overcome and the projectile starts to move. As the projectile moves the volume of the burning chamber increases, requiring generation of more gas to maintain the pressure level. During the early portion of the projectile travel the quasi-constant volume of the burning chamber permits continued pressure build-up. By the time the projectile has traveled only a few calibers (distance equal to the diameter of the gun tube), the rate of addition of volume has caught up with the rate of generation of gas, and the pressure has attained its maximum value. The remaining portion of the propellant is consumed at decreasing pressure, after which the gases expand adiabatically until the projectile leaves the muzzle. The entire cycle is accomplished in a matter of milliseconds.

The gun cycle can be fairly precisely analyzed, but the analysis is complicated and requires machine calculation. It is obvious that the mass rate of burning is very high and that the propellant must have either a very high linear burning rate or a very large burning surface (Equation 30). Because propellants do not have very high linear

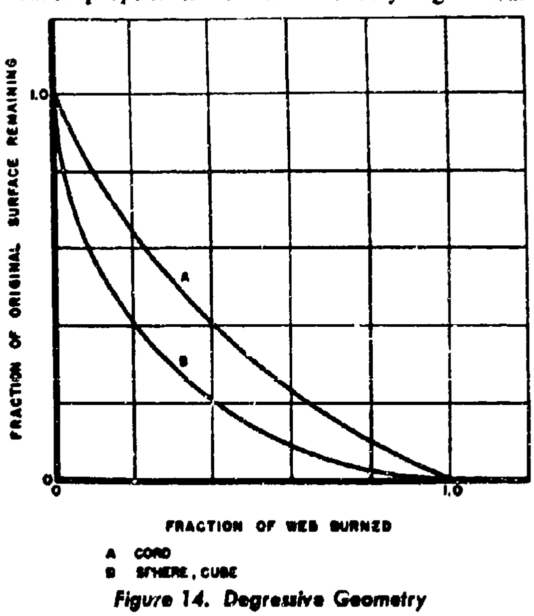



*Figure 14. Degressive Geometry*

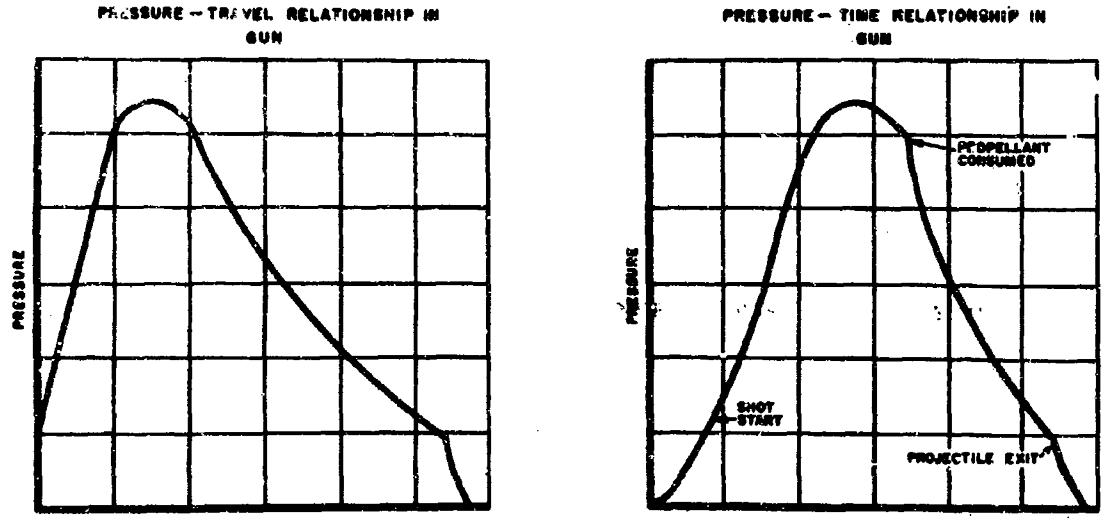



*Figure 15. Gun Cycle*

burning rates, even at gun pressures, we are left with the requirement of a very large surface. The geometric problem of accommodating a charge of very large surface in the gun chamber or cartridge case is very much easier to solve by breaking up the charge into a number of grains than by keeping it in one piece, and we find gun propellant charges are indeed multiple-grain charges. In Europe where charges are hand loaded, gun propellant charges are often made up of long strips or cords approaching the full length of the cartridge case. In the United States where charges are machine-loaded, the shorter single- and multiple-perforated cylinder form is preferred. Geometric progressivity is not vital; guns have been quite successfully fired using degressive cord charges. There are, however, marginal advantages to progressive or neutral burning geometries which tend to shift the position of the peak pressure to a later time and, therefore, to a larger burning volume than when a cord-form charge is used.

The practice in the United States in designing a propellant charge for a new gun or in designing a new propellant charge for an existing gun is to select a propellant composition on the basis of its force, $F$, and flame temperature, $T_v$, and establish the optimum granulation empirically. Having established a given lot of propellant as the standard, additional lots that are manufactured must match the standard by actual comparison firing in the gun. For quality control purposes, firing in the closed bomb (Figures 16 and 17) can yield a relative quickness, *RQ*, along with the relative force *RF* (see Paragraph 8-2). In this determination the bomb is instrumented to record directly $\frac{dP}{dt}$ versus pressure. The test propellant is fired in comparison with the standard propellant, and *RQ* is determined[11] as the ratio of $\frac{dP}{dt}$ for the test propellant to $\frac{dP}{dt}$ for the standard at one or more pressure levels.

**11-2. Catapult.** The function of the catapult is to accelerate a load attached to a piston to a final velocity without exceeding a maximum acceleration. The ideal catapult should operate at constant pressure to afford constant acceleration. The ideal travel-time curve for the catapult is shown in Figure 18. The same curve may be used to show the volume of the burning cavity and the required progressivity of the charge. It may be observed not only that an extremely high progressivity is required, but that the required progressivity is not linear. For personnel catapults there is an added requirement that the rate of acceleration, $\dot{a}$, (jerk) not exceed a specified value. This sets an upper limit on the slope of the rising portion of the pressure-time curve, Figure 18. Catapult grains may be designed in the form of multiple-perforated

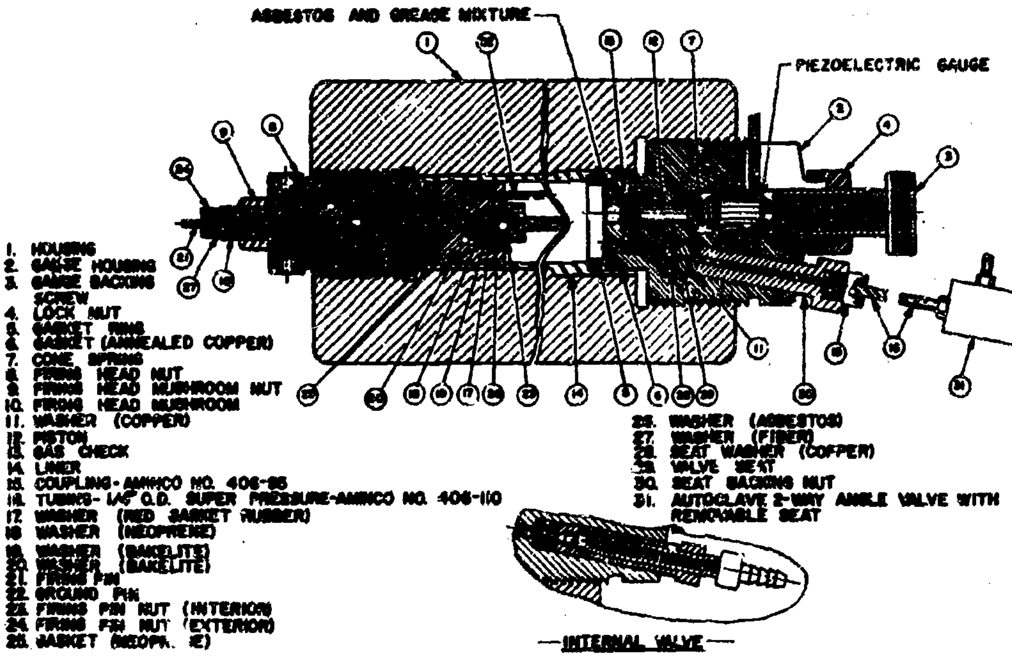



*Figure 16. Closed Bomb Assembly*

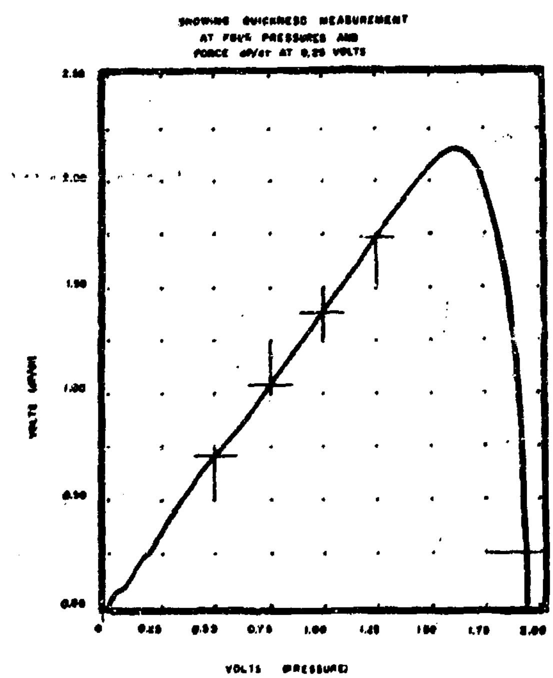



*Figure 17. Closed Bomb Record*

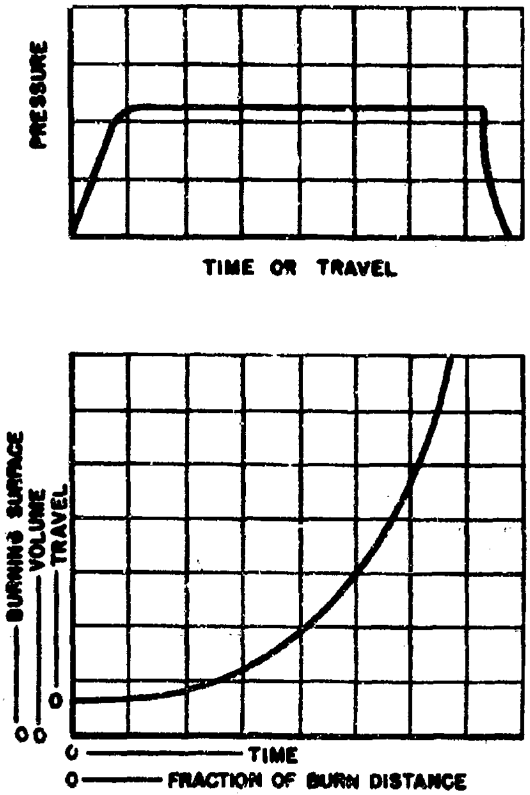



*Figure 18. Catapult Cycle*

cylinders inhibited externally, or rhomboid prisms burning from the corner edges. A fuller treatment of the ballistics of the catapult is given in reports by the Atlantic Research Corporation.[51]

**11-3. Rocket motor.** The design requirements for a rocket motor propellant charge usually call for burning at a constant mass rate equal to the mass rate of discharge required to impart the design thrust, and for the design duration which may be from tens of milliseconds to tens of seconds. The burning pressure should at least approximate a constant level. The pressure versus time record of the burning of a rocket grain usually resembles Figure 19.

**11-4. Calculation of a rocket propellant charge.** A rocket motor is required to maintain an average sea level thrust of 2000 lb for 20 sec at a design operating temperature of 70°F. The total impulse, $I$, required is 20 × 2000 or 40000 lb-sec.

At this point in the design a propellant must be selected. For this example, OIO propellant (see SPIA/M2) which has the following characteristics is chosen:

$I_{sp} = 212$ lb-sec/lb at 1000 psia and optimum expansion

$C_D = 0.00741$

$\gamma = 1.25$

$r = 0.27$ at 1000 psia and 70°F

$\rho = 0.0557$ lb/in$^3$

A chamber pressure is now chosen in the region of plateau burning of the propellant, so that changes in the burning surface of the propellant will cause only minimum variations in pressure and thrust. The pressure selected is 1000 psia.

Because of heat loss to the rocket motor and other inefficiencies, a delivered specific impulse with optimum expansion of 95 percent of the theoretical specific impulse is assumed. The weight of propellant required is

$$W = \frac{I}{I_{sp}} = \frac{40{,}000}{212(0.95)} = 198.5 \text{ lb}$$

The weight flow rate is

$$\dot{W} = \frac{W}{t_b} = \frac{198.5}{20} = 9.93 \text{ lb/sec}$$

At a chamber pressure of 1000 psia

$$A_t = \frac{\dot{W}}{C_D P_c} = \frac{9.93}{(0.00741)(1000)} = 1.40 \text{ in}^2$$

or $$D_t = 1.34 \text{ in}$$

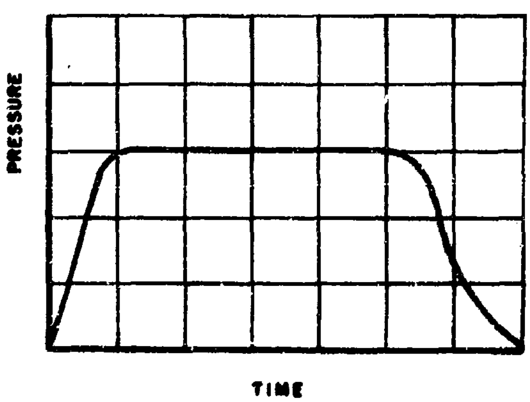



*Figure 19. Rocket Motor Cycle*

The optimum expansion ratio of $\frac{A_e}{A_t}$ obtained from the *Thrust Coefficient and Expansion Ratio Tables*[31] is found to be 8.4:1.
Therefore

$$A_e = 8.4(1.40) = 11.75 \text{ in}^2$$
$$D_e = 3.87 \text{ in}$$

The average propellant surface during burning is

$$S_{av} = \frac{\dot{W}}{r\rho} = \frac{9.93}{(0.27)(0.0557)} = 659 \text{ in}^2$$

If a nearly neutral thrust is desired, then the surface during burning should be as constant as possible, *i.e.*, $S_i = S_f = S_{av}$. The propellant burning distance is equal to

$$rt_b = (0.27)(20) = 5.4 \text{ in}$$

At this point some type of grain design, such as a star-type, slotted cylinder, cruciform, rod and tube, etc., should be initially chosen. The design requirements can be met with a slotted cylinder.

An important parameter in grain design is the ratio of the port area in an internal burning grain to the nozzle throat area. For this illustration the port-to-throat ratio is set at the minimum of 1.5:1 to prevent erosive burning of the grain.*

Therefore the port area

$$A_{p_{min}} = 1.5A_t = 1.5(1.40) = 2.10 \text{ in}^2$$

The use of a minimum port area will result in the smallest possible space envelope for the rocket motor. With a port diameter of 1.64 in and a burning distance of 5.40 in, the outer diameter of the propellant is 12.44 in. The volume of propellant required is

$$V_p = \frac{W}{\rho} = \frac{198.5}{0.0557} = 3560 \text{ in}^3$$

The required grain length is approximately

$$L = \frac{3560}{(0.785)(12.44^2 - 1.64^2)} = 29.8 \text{ in}$$

*In more sophisticated design work the port-to-throat ratio frequently is chosen as low as 1:1, accepting erosive burning. In the early stages of burning (until the port-to-throat ratio equals 1.5), a portion of the propellant will burn at a higher rate than normal for the existing pressure, and the grain geometry must compensate for this. The design problem becomes thus more difficult, but by no means impossible.

Continuing with this design, the surface area without slots and with the ends of the grain uninhibited, is

$$S = 2\left(\frac{\pi}{4}\right)(OD^2 - ID^2) + \pi(ID)(L)$$
$$= 2(0.785)(12.44^2 - 1.64^2) + 3.14(1.64)(29.8)$$
$$= 393 \text{ in}^2$$

The surface of the slots is therefore

$$S_{slots} = 659 - 393 = 266 \text{ in}^2$$

Using four slots at 90°, 5.40 in high, and 0.10 in wide, the slot length becomes

$$L_{slot} = \frac{266}{8(5.40)} = 6.15 \text{ in}$$

Disregarding the void volume of the slots for the moment

$$S_f = 3.14(12.44)(29.8 - 6.15 - 5.4)$$
$$= 714 \text{ in}^2$$

Within the accuracy of the calculations this design appears slightly progressive. The volume of the slots is

$$V_{slots} = 6.15(5.40)(0.1)(4) = 13.3 \text{ in}^3$$

and the actual propellant length is

$$L = 29.8 + \frac{13.3}{(0.785)(12.44^2 - 1.64^2)} = 29.9 \text{ in}$$

In an actual problem the design should be checked for undesirable variations of burning surface by plotting the calculated burning surface as a function of burning time. Final verification of the design would be accomplished by fabrication and static test of the grain.

While it is comparatively easy to design a rocket grain to fit the performance requirements of a design problem, it is often quite another thing to fit the grain into the required envelope. Where a gun charge designer can select a propellant composition and determine the proper granulation, a rocket charge designer is often forced by envelope requirements to start with a grain geometry and develop a propellant composition to give the required burning rate. For this reason there are nearly as many active rocket propellant compositions as there are rockets. The propellant geometries and significant performance parameters of most solid propellant rocket motors used by the United States military services are summarized in the SPIA Jato Manual.[11]

**11-5. Gas generator.** Gas generators are required to provide for a certain duration (a) a specific volumetric flow rate, or (b) a specific mass flow rate, or (c) a specific gas horsepower. In addition, a maximum gas temperature is usually specified, and the exhaust gases from the propellant must be clean.

**11-6. Calculation of a gas generator propellant charge.** Assume a gas generator must be designed to provide 20 gas horsepower for 30 seconds. The maximum allowable flame temperature, $T_g$, is 1900°K. OGK propellant (see SPIA/M2), which meets the temperature requirement, has the following characteristics:

$$\gamma = 1.25$$

$$T_g = 1888°K = 3398°R$$

$$\frac{1}{M} = 0.04576 \text{ moles}$$

$$r = 0.28 \text{ in/sec at 1000 psia}$$

$$\rho = 0.055 \text{ lb/in}^3$$

If the nozzle exit pressure is 50 psia, substituting in Equation 5

$$20 = \frac{\dot{W}}{550} \times \frac{1.25}{0.25} \times 1543 \times 3388 \times 0.04576\left[1 - \left(\frac{50}{1000}\right)^{\frac{0.25}{1.25}}\right]$$

$$\dot{W} = 0.0254 \text{ lb/sec}$$

Using a single-end burning grain design

$$S = \frac{\dot{W}}{r\rho} = \frac{0.0254}{(0.28)(0.055)} = 1.65 \text{ in}^2$$

The propellant diameter is 1.45 in. The propellant length is

$$L = rt_b = (0.28 \times 30) = 8.4 \text{ in}$$

If a certain mass rate of flow is required, the design proceeds as above. If a volumetric flow rate is defined, this can be converted to a mass flow rate by using a variation of the perfect gas law

$$\rho = \frac{PM}{R_0 T} \tag{37}$$

REFERENCES


1. J. Corner, *Theory of the Interior Ballistics of Guns*, p. 101, John Wiley & Sons, Inc., New York, New York, 1950.
2. Allegany Ballistics Laboratory, George Washington University, *Rocket Fundamentals*, ABL-SR4, OSRD 3992, 1944 (SPIA Abstract No. 0576B).
3. M. Barrere, A. Laumotte, B. F. DeVeubeke and J. Vandenkerckhove, *Rocket Propulsion*, Elsevier Publishing Company, Inc., New York, New York, 1960.
4. J. Corner, *loc. cit.*
5. C. Cranz, *Innere Ballistik (Lehrbuch der Ballistik*, Bd. 2), Julius Springer, Berlin, Germany, 1926.
6. F. R. W. Hunt, Editor, *Internal Ballistics*, Philosophical Library, Inc., New York, New York, 1951.
7. G. P. Sutton, *Rocket Propulsion Elements. An Introduction to the Engineering of Rockets*, 2nd edition, John Wiley & Sons, Inc., New York, New York, 1956.
8. R. N. Wimpress, *Internal Ballistics of Solid-Fuel Rockets. Military Rockets Using Dry-Processed Double-Base Propellant as Fuel*, McGraw-Hill Book Company, Inc., New York, New York, 1950.
9. M. Barrere, *et al.*, *loc. cit.*, p. 98.
10. Allegany Ballistics Laboratory, George Washington University, *loc. cit.*, p. 24.
11. F. D. Rossini, D. D. Wagman, W. H. Evans, S. Levine and I. Jaffe, *Selected Values of Chemical Thermodynamic Properties*, Circular of the National Bureau of Standards 500, U. S. Government Printing Office, Washington, D. C., 1952.
12. S. L. Levy and O. A. Reynolds, *Rocket Propellant Performance Computations Program for the IBM 650 Computer*, Allied Chemical Corporation, General Chemical Division, 16 May 1960, Contract DA-30-069-ORD-2638.
13. T. O. Dobbins, *Thermodynamics of Rocket Propulsion and Theoretical Evaluation of Some Prototype Propellant Compositions*, WADC TR-59-757 (Project 3148), Wright Air Development Center, Dayton, Ohio, December 1959.
14. Joint Army-Navy-Air Force Ad Hoc Panel on Performance Calculation Methods and Thermodynamic Data, *Bulletin of the Second Meeting, 27-29 April 1959*, PCMTD2, Solid Propellant Information Agency, Applied Physics Laboratory, The Johns Hopkins University, Silver Spring, Maryland, CONFIDENTIAL.
15. J. O. Hirschfelder and J. Sherman, *Simple Calculation of Thermochemical Properties for Use in Ballistics*, NDRC A-101, OSRD 935, October 1942, CONFIDENTIAL (SPIA Abstract No. 0303A); *ibid.*, NDRC A-101 (addenda), OSRD 935 (addenda) (OSRD-1300, A-67M-A-70M), March 1943, CONFIDENTIAL (SPIA Abstract No. 0303B).
16. P. de Pauw, "Die Verbrennungswärme des rauchlosen Pulvers," *Z. ges. Schiess- u. Sprengstoffw.*, **32**, 10, 36, 60 (1937).
17. A. O. Dekker, "Rapid Estimation of Specific Impulse of Solid Propellants," *Jet Propulsion*, **26**, 572 (1956).
18. Allegany Ballistics Laboratory, George Washington University, *loc. cit.*, p. 274.
19. Allegany Ballistics Laboratory, George Washington University, *loc. cit.*, p. 275.

20. Allegany Ballistics Laboratory, Hercules Powder Company, unpublished data.

21. C. A. Orlick and A. M. Jacobs, *The ABL Procedure for Calculation of the $I_{sp}$ of Propellants Which Yield a Condensible Exhaust Product*, Allegany Ballistics Laboratory, Hercules Powder Company, ABL/X-34, March 1959, Contract NOrd 16640, CONFIDENTIAL (SPIA Abstract No. 19064).

22. J. Corner, *loc. cit.*, p. 128.

23. *Standard Methods and Procedures for the Determination of Heat of Explosion of Rocket Propellant Powders*, Navy Department, Bureau of Ordnance, NAVORD OD 9375, 8 June 1953 (SPIA Abstract No. 13,318).

24. Army Service Forces, *Proof Directive 12, 3rd revision*, 12 February 1946.

25. Joint Army-Navy-Air Force Solid Propellant Rocket Static Test Panel, *Description of Static Test Facilities at Participating Organizations*, CONFIDENTIAL, Solid Propellant Information Agency, Applied Physics Laboratory, The Johns Hopkins University, Silver Spring, Maryland.

26. F. A. Warren, E. L. Anderson and P. M. Ku, *Evaluation of Solid Propellant Properties. Part I—A Survey of Current Methods*, Southwest Research Institute, Report RS 287, 31 January 1959, CONFIDENTIAL (SPIA Abstract No. 19191).

27. F. J. Malina, "Characteristics of the Rocket Motor Unit Based on the Theory of Perfect Gases," *J. Franklin Inst.*, 230, 433 (1940).

28. H. S. Seifert and J. Crum, *Thrust Coefficient and Expansion Ratio Tables*, Ramo Wooldridge Corporation, Guided Missile Research Division, 29 February 1956 (SPIA Abstract No. 17368).

29. H. Muraour, "Sur les lois de combustion des poudres colloïdales. 3° note," *Bull. soc. chim. France*, 41, 1451 (1927); *ibid.*, "Sur les lois de combustion des poudres colloïdales. 4° note," *Bull. soc. chim. France*, 47, 261 (1930); *ibid.*, "Sur une théorie de la combustion en vase clos, des poudres colloïdales," *Compt. rend.*, 192, 227 (1931); H. Muraour and W. Schumacher, "La vitesse de combustion des poudres colloïdales sous la pression atmosphérique," *Mém. poudres*, 27, 87 (1937). (Summarized in J. Corner, *loc. cit.*, pp. 43-5.)

30. B. L. Crawford, Jr., C. Huggett and J. J. McBrady, "The Mechanism of the Burning of Double-Base Propellants," *J. Phys. Chem.*, 54, 854 (1950).

31. Piobert, *Traité d'Artillerie*, 1839 as cited in J. Taylor, *Solid Propellent and Exothermic Compositions*, p. 56, Interscience Publishers, Inc., New York, New York, 1959.

32. J. Taylor, *Solid Propellent and Exothermic Compositions*, p. 56, Interscience Publishers, Inc., New York, New York, 1959.

33. M. Summerfield, *Burning Mechanism of Ammonium Perchlorate Propellants. Part II. Theory of Burning of a Composite Solid Propellant*, paper presented at American Rocket Society 13th Annual Meeting, 17-21 November 1958, New York, New York.

34. J. Corner, *loc. cit.*, p. 71.

35. W. H. Avery, R. E. Hunt and M. N. Donin, *Burning-Rate Studies of Double-Base Powder*, Allegany Ballistics Laboratory, George Washington University, ABL/P-1, OSRD 5827, January 1946, CONFIDENTIAL (SPIA Abstract No. 0514); S. Zmachinski and R. F. Preckel, *Strand-Rate Ballistic Studies of Plateau-Type Propellants*, Hercules Powder Company, ABL/P-13, December 1948, Contract NOrd 9709, CONFIDENTIAL.

36. Allegany Ballistics Laboratory, George Washington University, *loc. cit.*, p. 45.

37. J. H. Godsey and R. F. Preckel, *Strand Rate Ballistic Studies of Plateau-Type Propellants. Part IV. Characteristics of Various Ballistic Modifiers*, Allegany Ballistics Laboratory, Hercules Powder Company, ABL/P-25, April 1955, Contract NOrd 10431, CONFIDENTIAL (SPIA Abstract No. 15,209).

38. J. Corner, *loc. cit.*, p. 73.

39. F. T. McClure, R. W. Hart and J. F. Bird, *Solid Propellant Rocket Motors as Acoustic Oscillators*, Applied Physics Laboratory, The Johns Hopkins University, Report TG 335-3, 5 October 1959, Contract NOrd 7386.

40. J. Corner, "The Effect of Turbulence on Heterogeneous Reaction Rates," *Trans. Faraday Soc.*, 43, 635 (1947). (Summarized in J. Corner, *Theory of the Interior Ballistics of Guns*, p. 74, John Wiley & Sons, Inc., New York, New York, 1950.)

41. Rohm & Haas Company, Redstone Arsenal Research Division, *Quarterly Progress Report on Interior Ballistics*, Report No. P-54-9, 15 April–15 July, 1954, Contract W-01-021-ORD-334, CONFIDENTIAL (SPIA Abstract No. 14391); G. Robillard and J. M. Lenoir, *The Development of a New Erosive Burning Law*, Jet Propulsion Laboratory, California Institute of Technology, Bulletin of the Thirteenth Meeting of the Joint Army-Navy-Air Force Solid Propellant Group, Vol. II, p. 441, CONFIDENTIAL, Solid Propellant Information Agency, Applied Physics Laboratory, The Johns Hopkins University, Silver Spring, Maryland.

42. A. L. Antonio, *Development of Internal-Burning Solid Propellant Rockets*, Aerojet-General Corporation, Aerojet Report L3032/35-2, 16 November 1950, CONFIDENTIAL (SPIA Abstract No. 10731).

43. R. P. Smith and D. F. Sprenger, *Development of Internal-Burning Solid-Propellant Rockets. Fundamental Studies of Unstable Burning of Aeroplex Propellants*, Aerojet-General Corporation, Aerojet Report 606 (Final), 4 June 1952, CONFIDENTIAL (SPIA Abstract No. 12189).

44. G. E. Miles, *Investigation of Unstable Resonance Burning*, Allegany Ballistics Laboratory, Hercules Powder Company, ABL/MPR 46 (p. 7 of Monthly Progress Report 46), 1 August 1955, Contract NOrd 10431, CONFIDENTIAL (SPIA Abstract No. 15552).

45. R. L. Lou and R. C. Kriger, *Effect of Chemical Additives on Unstable Burning*, Aerojet-General Corporation, Aerojet Report L2798-18, -19 (16 October–15 December 1957), 10 January 1957, Contract NOrd 16879, CONFIDENTIAL (SPIA Abstract No. 18,003).

46. V. Philipchuk, *Double-Base Cast Propellant, Assessment of Fire and Explosion Hazard During Manufacture*, Naval Proving Ground, Report 834, 11 August 1951, CONFIDENTIAL (SPIA Abstract No. 11162).

47. Rohm & Haas Company, Redstone Arsenal Research Division, *Quarterly Progress Report on Interior Ballistics (April 15, 1956 to July 15, 1956)*, Report No. P-56-14, 10 August 1956, Contract W-01-021-ORD 334, CONFIDENTIAL (SPIA Abstract No. 16482); *ibid.*, J. R. Hyndman, W. W. Brandon, H. M. Shuey, *Deflagration-Detonation Studies of Solid Propellants*, Bulletin of the Twelfth Meeting of the Joint Army-Navy-Air Force Solid Propellant Group, Vol. II, p. 99, CONFIDENTIAL, Solid Propellant Information Agency, Applied Physics Laboratory, The Johns Hopkins University, Silver Spring, Maryland.

48. A. Macek, "Transition from Deflagration to Detonation in Cast Explosives," *J. Chem. Phys.*, 31, 162 (1959).

49. S. J. Jacobs, "Recent Advances in Condensed Media Detonations," *ARS Journal*, 30, 151 (1960).

50. L. E. Smith, Jr., C. S. Ingram and T. Walsh, *Ballistic Test Methods—Closed Bomb Test Variables. A Review of Proof Directive 12, 3rd Revision, February 13, 1946*, Sunflower Ordnance Works, Hercules Powder Company, 8 July 1959.

51. M. L. Rice, J. Hull, B. Wales and A. C. Scurlock, *A Study of Propellant Charge Requirements for the C-10 Catapult*, Atlantic Research Corporation, November 1952, Contract NOrd 10721, CONFIDENTIAL (SPIA Abstract No. 13,037); M. L. Rice, T. Davis and A. C. Scurlock, *A Comparison of Steam and Powder Catapults*, July 1954, Contract NOrd 10721, CONFIDENTIAL (SPIA Abstract No. 14,403).

52. *Jato Manual. Volume I. Early Experimental Jato Units*, Solid Propellant Information Agency, SPIA/M1, CONFIDENTIAL; *Rocket Motor Manual. Volume II (of Jato Manual). Units of Current Interest*, SPIA/M1, CONFIDENTIAL, Solid Propellant Information Agency, Applied Physics Laboratory, The Johns Hopkins University, Silver Spring, Maryland.

CHAPTER 3

# PHYSICAL PROPERTIES REQUIREMENTS

**12. General.** Just as propellants have different ballistic requirements depending on the uses to which they are put, the physical properties requirements of propellants will be different depending on use.

**13. Density.** Since in a solid propellant heat engine the propellant is always contained within the engine, the propellant must have a density high enough that the charge can be so contained. Two factors enter into the determination that the charge will fit into the chamber: the density of the propellant itself, and the volumetric efficiency of the charge geometry or the fraction of the propellant envelope occupied by propellant.

The density of a propellant is calculated from the densities of its ingredients, assuming no volume change as a result of mixing.

$$\frac{1}{\rho} = \Sigma \frac{x_i}{\rho_i} \tag{38}$$

In the case of a propellant undergoing chemical reaction during the mixing operation, as is the case of many fuel binder composites, the ingredients include the reaction products (*e.g.*, polymers) and not the reagents actually charged (monomer). In the case of a propellant manufactured with inclusion of a volatile solvent later substantially removed, that portion (residual solvent) of the solvent remaining in the finished propellant must be considered an ingredient.

Density can be measured with a mercury displacement volumeter[1] or with a pycnometer[2] or, more roughly, from the weight and dimensions of the grain. Comparison of the measured density with the calculated value gives a measure of porosity, cracks, and fissures in the propellant. Microscopic individual pores, as around crystals in composite structures, have no apparent effect on the burning of the propellant, but cracks and fissures constitute undesirable burning surface that cause excess pressure and interfere with the scheduled mass burning rate, and interconnected gross porosity can lead to detonation. In monopropellants measured density is usually very close to calculated density. In composites a difference of more than 2 percent indicates trouble.

**14. Gravimetric density.** Gravimetric density is measured on bulk gun propellants as the weight of propellant required to fill a specified container when charged at a specific rate from a hopper at a specified height.[3] (The density of propellant as loaded into cartridge cases can also be determined.[4])

This datum is influenced not only by density and dimensions but by the smoothness of the surface and the presence or absence of tailings from the cutting operation. It is used as an indication that the required charge weight can be contained in the cartridge case.

**15. Hygroscopicity.** Most propellants contain constituents that are hygroscopic and this property is passed along in some degree to the propellants. The mechanism of sorption and desorption of hygroscopic moisture probably involves a rapid attainment of the equilibrium, dependent on relative humidity, at the surface of the grain, followed by slow diffusion within the grain. The effect of hygroscopic moisture is the same as if the formula contained the same fraction of water.

Hygroscopicity of propellants for cannon is defined as the equilibrium moisture content at 90 percent relative humidity and 30°C temperature. For small arms propellants hygroscopicity is defined as the difference between the equilibrium moisture contents at 90 percent relative humidity, 30°C temperature and at 20 percent relative humidity, 30°C temperature. The procedure for small arms propellants[5] involves successive exposure of the same sample to controlled humidity atmospheres, whereas for cannon propellants[6] a single exposure and a chemical analysis for moisture are required.

Hygroscopicity of propellant charges loaded in engines has been controlled by hermetic sealing of the engine or its shipping and storage container, or by loading a desiccant either into the engine or the shipping container. Hygroscopicity of individual grains has been minimized by formulating to a minimum content of hygroscopic material and in the case of coated grains by building a layer of material of low permeability into the surface of the grain.

**16. Coefficient of thermal expansion.** At the level of about $10^{-4}$ per degree C, the thermal expansion coefficient is of little moment to multiple-grain charges. For single-grain charges loaded into chambers at small clearances, care must be taken to verify that the clearances between grain and wall do not disappear in the upper range of storage or firing temperatures because of the different expansion coefficients of propellant and chamber material. In this event the chamber wall would exert stress on the grain causing it to deform or even fracture. If the grain is enclosed in a rigid inhibitor, the coefficients of the grain and inhibitor should match as closely as possible for the same reason. If the grain is to be case-bonded to the chamber, it is not ordinarily feasible to match the expansion coefficients and the grain must be formulated to accept the stresses due to differential expansion.

**17. Thermal conductivity.** Propellants are in general very poor conductors of heat. This property is a useful one for ballistic design, as it can be safely assumed that the unburned portion of a grain will remain at its initial temperature throughout the combustion process. On the other hand, in a large grain the time required to bring the propellant to a uniform temperature following a change of environment may be several hours or even days depending on temperature differential, air circulation, and grain size. If the grain is fired while it contains a temperature gradient, the rate of gas production will reflect the temperature gradient. Thermal shock from too rapid change from very cold to very warm or vice versa may lead to cracking of the grain. The interior of grains stored in munitions in hot climates fails by a wide margin to attain the maximum diurnal temperatures.[7]

**18. Mechanical properties.** The mechanical properties of propellants must be such as to enable them to withstand the mechanical loads imposed during shipping, handling, and firing. These requirements differ widely from one engine to another. Methods for measuring physical strength and deformation are reviewed by the JANAF Panel on Physical Properties of Solid Propellants and reported in the publications of that panel. Numerical values below are as measured by standard JANAF tests.[8] Results in such tests are strong functions of the rates of loading, propellants generally appearing stronger with higher rates of loading. The rates of loading in actual rocket motors vary from low rates during storage due to temperature changes to very high rates during firing. JANAF mechanical properties test data are significant to the extent that they compare propellants under test conditions and imply that the same comparison will be valid under operating conditions.

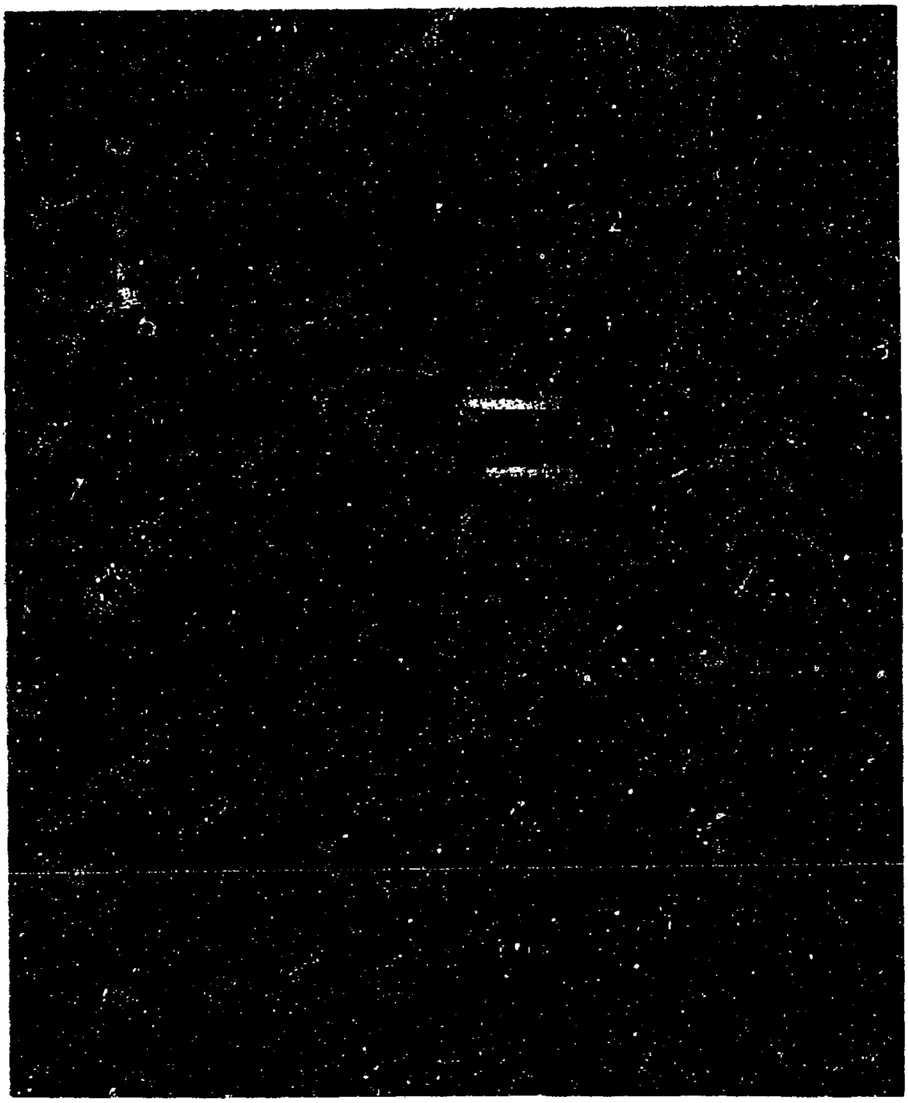
**18-1. Ultimate tensile strength.** Tensile strength is important for rocket grains supported at the head end during acceleration. For other applications it is of academic interest, or perhaps useful as a quality control measure to assure that successive lots of a given propellant resemble each other. Tensile strength ranges from about 10,000 pounds per square inch for straight polymer monopropellants to below 50 pounds per square inch for some case-bonded propellants.

**18-2. Elongation in tension.** Case-bonded grains must deform to accommodate changes in dimensions of their containing cases with changes in temperature. Although requirements vary from rocket motor to rocket motor, a minimum of 15 percent elongation at rupture at the lowest storage or operating temperature is a typical requirement for a case-bonded propellant in a large rocket. Many such propellants have reported values of 50 to 100 percent elongation at normal ambient temperature.

**18-3. Modulus in tension.** A low value of modulus is required of case-bonded grains in order to avoid distortion of the case or rupture of the adhesive bond when the motor is cooled. A typical value for modulus of a case-bonded propellant is 300 to 600 pounds per square inch per inch per inch, or dimensionally pounds per square inch.

Ultimate tensile strength, elongation, and modulus are all determined in the same test.[8] A test installation is shown in Figure 20 and a test record indicating the derivation of data in Figure 21.

**18-4. Stress relaxation.** It is advantageous in a case-bonded propellant for the stresses produced by distortion to be relaxed as the grain becomes accommodated to its new environment so that residual stresses will not lead to cracking in areas of stress concentration. The property of relaxation under tension may be measured by measuring the tensile stress at fixed elongation as a function of time.[9]



① PROPELLANT SAMPLE
② SAMPLE GRIPS
③ MOVABLE CROSSHEAD
④ FIXED CROSSHEAD
⑤ LOAD CELL
⑥ STRESS-STRAIN RECORDER
⑦ RECORDER CONTROLS
⑧ CROSSHEAD CONTROLS

*Figure 20. Tensile Test Setup*

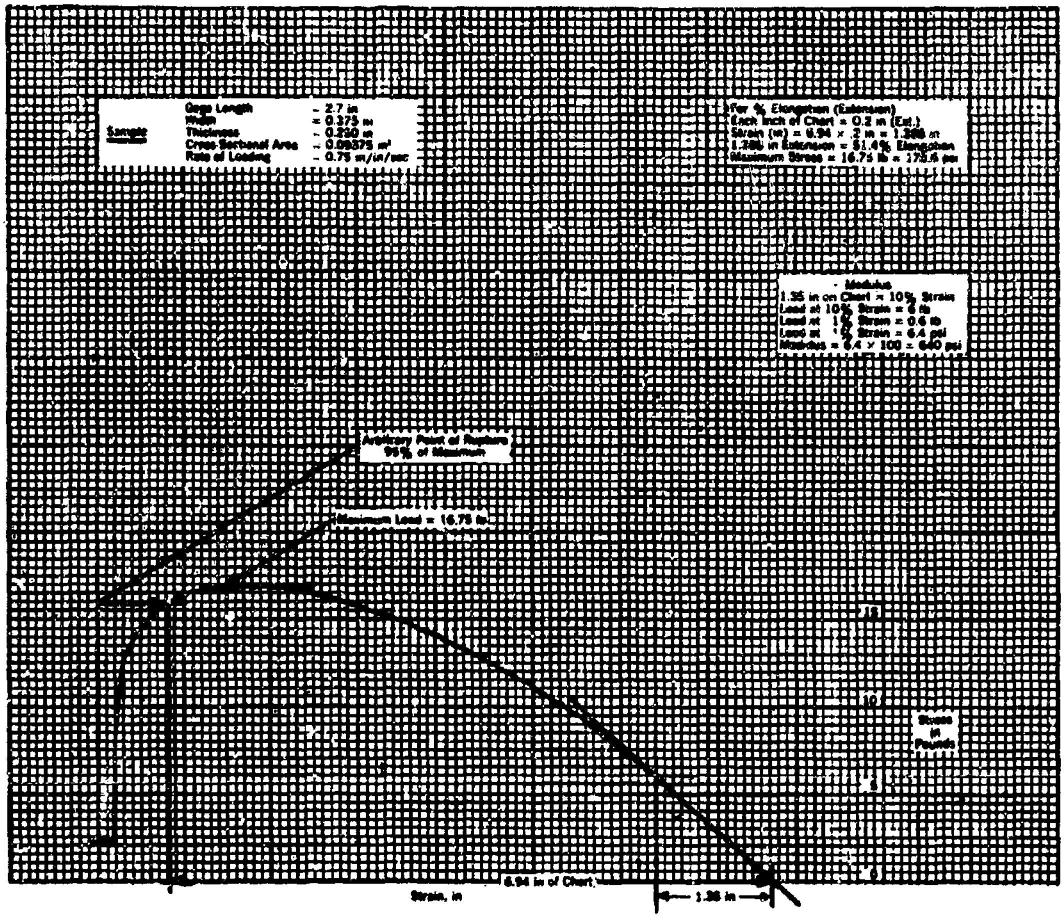



*Figure 21. Tensile Test Record Showing Derivation of Ultimate Strength, Elongation, and Modulus (Read curve from right to left)*

**18-5. Creep.** A lower limit on tensile modulus of case-bonded propellants is set by the requirement that under its own weight the propellant not deform so as to decrease port areas or substantially change shape and dimensions. Whether such deformation is elastic due to too low modulus or inelastic due to cold flow it is known as creep. Creep has been responsible also for departures from design ballistics of cartridge-loaded rocket grains. The best criterion for assessing the tendency to creep still appears to be experience.

**18-6. Compressive strength.** Cartridge-type rocket grains supported on traps or otherwise at the nozzle end are subjected to compressive stresses during firing. The magnitude of such stresses and, therefore, the compressive strength to withstand them can be computed for any instance from the designed acceleration of the rocket. Compressive strengths of propellants are usually of the same order of magnitude as ultimate tensile strength, and for design purposes the tensile strength of the propellant is frequently used with suitable safety factors. Compressive strength can be readily measured on equipment shown in Figure 20.

**18-7. Deformation at rupture in compression.** The most severe stresses on a gun propellant occur during ignition when the grains impact on the cartridge case or chamber wall and on the base of the projectile as a result of having been accelerated by the igniter gases. If the grains shatter in such impact, the added burning surface leads to excess pressures in the gun. Redesign of the igniter is the usual remedy, but the propellant is required not to be brittle. The test specified for brittleness is deformation in compression at rupture. Unless otherwise specified the required minimum value is 30 percent.[10]

**18-8. Modulus in compression.** For cartridge-loaded rocket grains the deformation due to compression during acceleration must not be great enough to cause significant departures from design geometry. This fixes a lower limit on the permissible value of compressive modulus. The value of this limit has not been precisely evaluated as high values of compressive modulus usually accompany the required compressive strength.

**18-9. Shear properties.** Case-bonded grains are stressed in shear during acceleration. The weight of the propellant must be supported by the shear strength at the bond between the propellant and the case. Per unit of propellant length, neglecting the perforation, the weight of the propellant under acceleration and therefore the total shear force is $\frac{\pi}{4}d^2\rho a$ where $d$ is the grain diameter in inches, $\rho$ the propellant density in pounds per cubic inch, and $a$ is the acceleration in $g$'s. The total shear force is applied over an area of $\pi d$. The required minimum shear strength, in pounds per square inch, is

$$\frac{\pi d^2 \rho a}{4\pi d} = \frac{d\rho a}{4}$$

Procedures for measuring shear have been reported.[11]

**18-10. Brittle temperature.** For many plastics the second-order transition temperature[12] signals the onset of brittleness. This appears to be the case with case-bonded propellants. It has not been established that the same significance of the second-order transition temperature holds for cartridge-loaded propellants which perform well at temperatures considerably below that of a second-order transition.

The second-order transition temperature may be measured[11] by noting a break in the curve of specific volume versus temperature or an abrupt decrease in mechanical properties such as impact strength at that temperature.

## REFERENCES


1. C. G. Jackson, "A Mercury Displacement Volumeter," *J. Sci. Instr.*, **6**, 261 (1929).
2. MIL-STD-286, *Propellants: Sampling, Inspection and Testing, Method 510.1.1—Specific Gravity (Pycnometer Method)*, 28 June 1956.
3. MIL-STD-286, *Propellants: Sampling, Inspection and Testing, Method 502.1—Bulk Density*, 28 June 1956.
4. MIL-STD-286, *Propellants: Sampling, Inspection and Testing, Method 507.1—Density of Loading*, 28 June 1956.
5. MIL-STD-286, *Propellants: Sampling, Inspection and Testing, Method 503.1.2—Hygroscopicity, Small Arms Propellants (Equilibrium Method)*, 28 June 1956.
6. MIL-STD-286, *Propellants: Sampling, Inspection and Testing, Method 503.2.1—Hygroscopicity, Cannon Propellants (Equilibrium Method)*, 28 June 1956.
7. J. N. Sherman and H. M. Burns, *Temperatures Produced in Solid Propellant Rockets by Exposure to Climatic Extremes*, Allegany Ballistics Laboratory, Hercules Powder Company, ABL/X-37, June 1959, Contract NOrd 16640, CONFIDENTIAL (SPIA Abstract No. 19341).

8. Joint Army-Navy-Air Force Panel on Physical Properties of Solid Propellants, *Methods for Determining the Tensile Properties of Solid Rocket Propellants. Part I. Nitrocellulose Base Propellants*, SPIA/PP8, March 1956; *Part II. Composite*, SPIA/PP8, February 1957, Solid Propellant Information Agency, Applied Physics Laboratory, The Johns Hopkins University, Silver Spring, Maryland.

9. K. H. Sweeny and K. W. Bills, Jr., *Apparatus for the Measurement of Stress Relaxation Behavior*, Aerojet-General Corporation, Bulletin of the Seventeenth Meeting of the Joint Army-Navy-Air Force Panel on Physical Properties of Propellants, SPIA/PP11, p. 91, May 1958, CONFIDENTIAL, Solid Propellant Information Agency, Applied Physics Laboratory, The Johns Hopkins University, Silver Spring, Maryland.

10. MIL-P-270A, *Propellant, Artillery*, 5 March 1959.

11. F. A. Warren, E. L. Anderson and P. M. Ku, *Evaluation of Solid Propellant Properties. Part I—A Survey of Current Methods*, Southwest Research Institute, Report RS287, 31 January 1959, CONFIDENTIAL (SPIA Abstract No. 19191).

12. F. W. Billmeyer, Jr., *Textbook of Polymer Chemistry*, p. 40, Interscience Publishers, Inc., New York, New York, 1957.

# BLACK POWDER

**19. General.** Black powder is our oldest propellant. It is older than any of the heat engines (guns, rockets) in which propellants are used, and has been used as a pyrotechnic and as a bursting charge for centuries. It is an intimate mixture of saltpeter, charcoal, and sulfur. There are two types of black powder, one made with potassium nitrate and the other with sodium nitrate.

The *potassium nitrate type* is the older, and for ordnance uses is still the more commonly used. In ordnance circles black powder is the potassium nitrate type unless otherwise designated. The name black powder is a translation of the German "Schwarzpulver," named after Berthold Schwarz who experimented with it in the fourteenth century.[1] In the English language the material was known as "gunpowder" until the use of smokeless powder in guns made it necessary to differentiate between the black and the smokeless varieties of gun propellant. Gunpowder included Musket Powder and Cannon Powder, later Rifle Powder and Sporting Gunpowder. When used for blasting, gunpowder was called Blasting Powder. The present United States terminology is "A" Blasting Powder.[2]

The *sodium nitrate type* of black powder was developed in the United States in the middle of the nineteenth century[2] and is known commercially as "B" Blasting Powder. When used for ordnance it is called sodium nitrate black powder.

**20. Appearance.** The appearance of black powder is shown in Figure 22. The grains are irregularly shaped solids, resulting from the fracture of larger pieces on the rolls of the corning mill, of roughly uniform size as a result of screening. Black powder may alternatively be pelleted into grains of uniform size and shape.

**21. Composition.** The nominal composition of black powder as available in the United States is shown in Table 3. The same compositions are used for both military and commercial grades. Selection of the charcoal has an important bearing on the quality and performance of black powder. The charcoal is not pure carbon, but contains 13 to 20 percent volatile matter and 2 to 5 percent moisture.

**22. Granulation.** The standard granulations of potassium nitrate and sodium nitrate powders are shown in Tables 4 and 5, respectively.

**23. Thermochemistry.** Lacking knowledge of the nature of the volatile matter in the charcoal, and considering that manufacturing tolerances permit 1 percent variation in the fraction of each ingredient, it is practically impossible to calculate the gas composition or volume of black powder. A rough approximation may be got by assuming that the volatile matter is largely carbon, that the potassium appears in the product as $K_2CO_3$, the nitrogen as $N_2$, the carbon as $CO + CO_2$, and that the sulfur and such hydrogen as is in the volatile matter do not make an important contribution to the gas volume. Under these assumptions the gas volume would be given by $[C] + \frac{1}{2}[N] - \frac{1}{2}[K]$. Since the [N] and [K] are present in equal numbers, the gas volume of black powder is determined roughly by the fraction of charcoal in the formula. In the United States grade of potassium nitrate type of black powder, one gram contains 0.0130 gram atoms of carbon which when burned should give 0.0130 moles or 290 cc (STP) of gas. An experimental value of the gas volume from three samples of British black powder recently examined in the Imperial Chemical Industries laboratories has been reported at 280 cc (STP).[6] The same author reports a heat of explosion, $Q$, of 720 cal/g and a calculated flame temperature,

**TABLE 3. NOMINAL COMPOSITIONS OF BLACK POWDER AVAILABLE IN THE UNITED STATES**

| | $KNO_3$ type [4] | $NaNO_3$ type [5] |
|---|---|---|
| $KNO_3$, % | 74.0 | — |
| $NaNO_3$, % | — | 72.0 ± 2 |
| Sulfur, % | 10.4 | 12.0 ± 2 |
| Charcoal, % | 15.6 | 16.0 ± 2 |
| Ash, maximum, % | 0.80 | 1.5 |
| Moisture, maximum, % | 0.50 | 0.70 |
| Specific gravity | 1.72–1.77 | 1.74–1.82 |

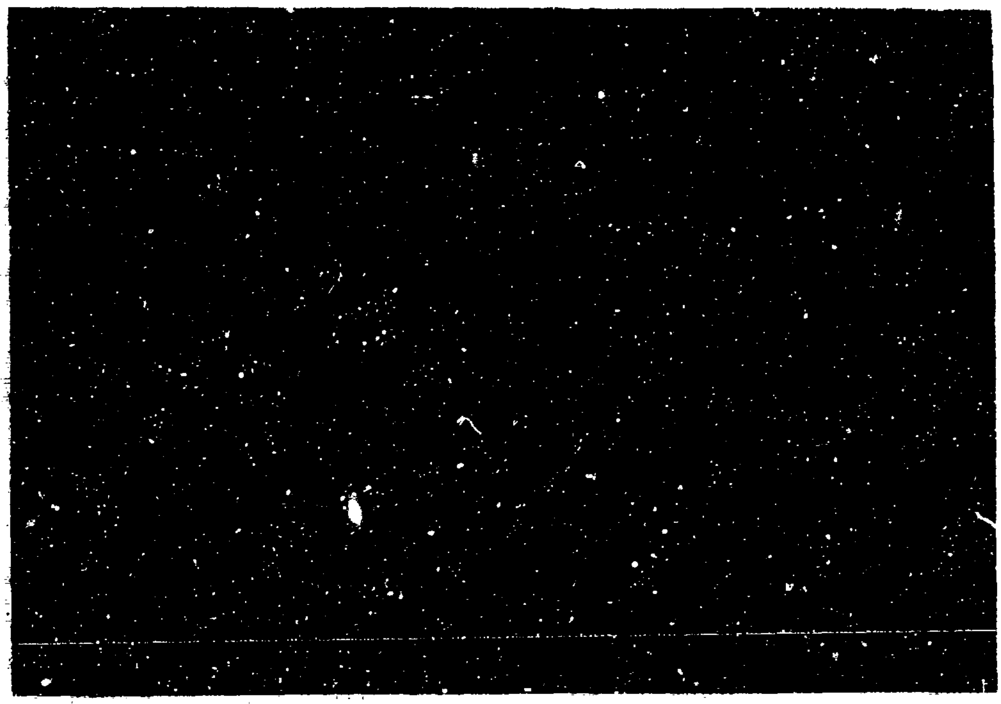


*Figure 22. Black Powder, Grade FFFFG, 8× Magnification*

## TABLE 4. GRANULATIONS OF POTASSIUM NITRATE BLACK POWDERS

| | Sieve size | Retained (maximum percent) | Sieve size | Through (maximum percent) |
|---|---|---|---|---|
| **Military grade** [4] | | | | |
| A-1 | 4 | 3.0 | 8 | 5.0 |
| A-2 | 4 | 3.0 | 12 | 5.0 |
| Cannon | 6 | 3.0 | 12 | 5.0 |
| A-3 | 12 | 3.0 | 16 | 5.0 |
| A-3a | 12 | 3.0 | 20 | 5.0 |
| Musket | 14 | 3.0 | 25 | 3.0 |
| FFG | 16 | 3.0 | 30 | 5.0 |
| A-4 | 16 | 3.0 | 40 | 5.0 |
| Shell | 16 | 3.0 | 50 | 5.0 |
| FFFG | 20 | 3.0 | 50 | 5.0 |
| A-5, Fuze | 40 | 3.0 | 100 | 5.0 |
| FFFFG | 45 | 3.0 | 140 | 5.0 |
| A-6 | 100 | 5.0 | 140 | 15.0 |
| A-7 | 100 | 3.0 | 140 | 50.0 |
| Meal | 100 | 5.0 | 200 | 50.0 |
| Sphero-hexagonal: 128 ± 2 grains per pound, 0.6-inch grain diameter | | | | |
| **Commercial grade** [2] | | | | |
| Sporting | | | | |
| Whaling | 32/64* | 3 | 4 | 12 |
| Life Saving Service | 6 | 3 | 12 | 12 |
| Cannon | 6 | 3 | 12 | 12 |
| Saluting | 10 | 3 | 20 | 12 |
| Fg | 12 | 3 | 16 | 12 |
| FFg | 16 | 3 | 30 | 12 |
| FFFg | 20 | 3 | 50 | 12 |
| FFFFg | 40 | 3 | 100 | 12 |
| "A" Blasting | | | | |
| FA | 20/64* | 3 | 5 | 12 |
| 2FA | 4 | 3 | 12 | 12 |
| 3FA | 10 | 3 | 16 | 12 |
| 4FA | 12 | 3 | 20 | 12 |
| 5FA | 20 | 3 | 50 | 12 |
| 6FA | 30 | 3 | 50 | 12 |
| 7FA | 40 | 3 | 100 | 12 |
| Meal D | 40 | 3 | — | — |
| Meal F | 100 | 3 | — | — |
| Meal XF | 140 | 3 | — | — |

* Diameter of circular perforations in plate.

## TABLE 5. GRANULATIONS OF SODIUM NITRATE BLACK POWDERS

| | Sieve size | Retained (maximum percent) | Sieve size | Through (maximum percent) |
|---|---|---|---|---|
| Military Grade [6] | | | | |
| JAN C | 9/16 inch | 0 | 3/8 inch | 0 |
| JAN B | 4 | 3 | 16 | 5 |
| JAN A | 12 | 3 | 40 | 5 |
| Commercial Grade [5] "B" Blasting | | | | |
| CCC | 40/64* | 7.5 | 32/64* | 7.5 |
| CC | 36/64 | 7.5 | 24/64 | 7.5 |
| C | 27/64 | 7.5 | 18/64 | 7.5 |
| F | 20/64 | 7.5 | 5 | 7.5 |
| FF | 4 | 7.5 | 8 | 7.5 |
| FFF | 6 | 7.5 | 16 | 7.5 |
| FFFF | 12 | 7.5 | 40 | 7.5 |
| Meal BB | 16 | 7.5 | — | — |
| Meal BD | 40 | 7.5 | — | — |

*Diameter of circular perforations in plate.

$T_v$, of 2800°C. Products identified in the combustion products include mainly $K_2CO_3$, $K_2SO_4$, $K_2S_2$, $CO_2$, $N_2$, some $H_2$, $H_2S$, $CH_4$, $NH_3$, $H_2O$, XCNS, and some unreacted $KNO_3$, C, and S.[7] As the fraction of charcoal increases and the fraction of saltpeter decreases, the gas volume should increase and $T_v$ should decrease. The force, $F$, calculated from the Imperial Chemical Industries data, is 110,000 ft-lb/lb.

The initial condensed phase reaction in the burning of black powder has been identified as the reaction of molten sulfur with occluded hydrogen[8] or oxy hydrocarbons in the charcoal,[9] or with the potassium nitrate.[9] A sulfurless grade of black powder is manufactured in Great Britain. This has a considerably higher ignition temperature than normal black powder because molten saltpeter is required to initiate its combustion.[10]

The concept of linear burning rate as presented in Paragraph 9 has little significance when applied to the irregular shapes of black powder. The term linear burning rate, when speaking of black powder, is applied to the rate of propagation along a column of the granular material, *i.e.*, a fuse.

**24. Hygroscopicity.** The hygroscopic nature of black powder has long been known and is recognized in the familiar slogan "Keep your powder dry." This hygroscopicity is primarily due to the saltpeter. It may be explained on the basis of moisture pickup at any time that the atmospheric humidity exceeds the partial pressure of water over a saturated solution of the saltpeter.

Humidity cycling results in a slow deterioration due to crystal growth of the nitrates. Submergence of black powder under water causes the saltpeter to leach out.

**25. Shelf life.** At elevated temperatures, physical changes in the sulfur can occur. The hygroscopic effects are also deleterious to shelf life. Apart from these influences, black powder is very stable thermally and under optimum conditions black powder can be stored for many years without serious deterioration.

**26. Manufacturing process.** Both types of black powder are manufactured by the process shown schematically in the flowsheet, Figure 23. The charcoal and sulfur are ground together in the pulverizer, which is essentially a ball mill using short steel cylinders for balls. The "composition dust" is discharged from the pulverizer through a "reel" or screen which rejects the coarse material. The saltpeter is added to the composition dust and

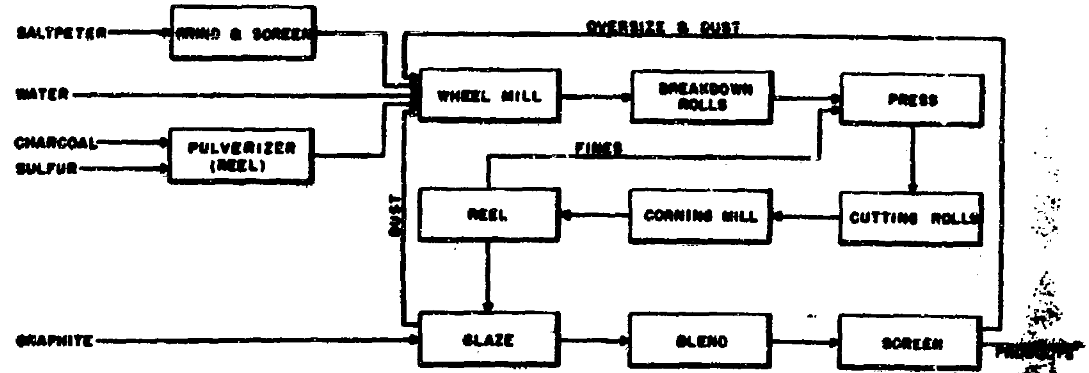



*Figure 23. Black Powder Manufacturing Process*

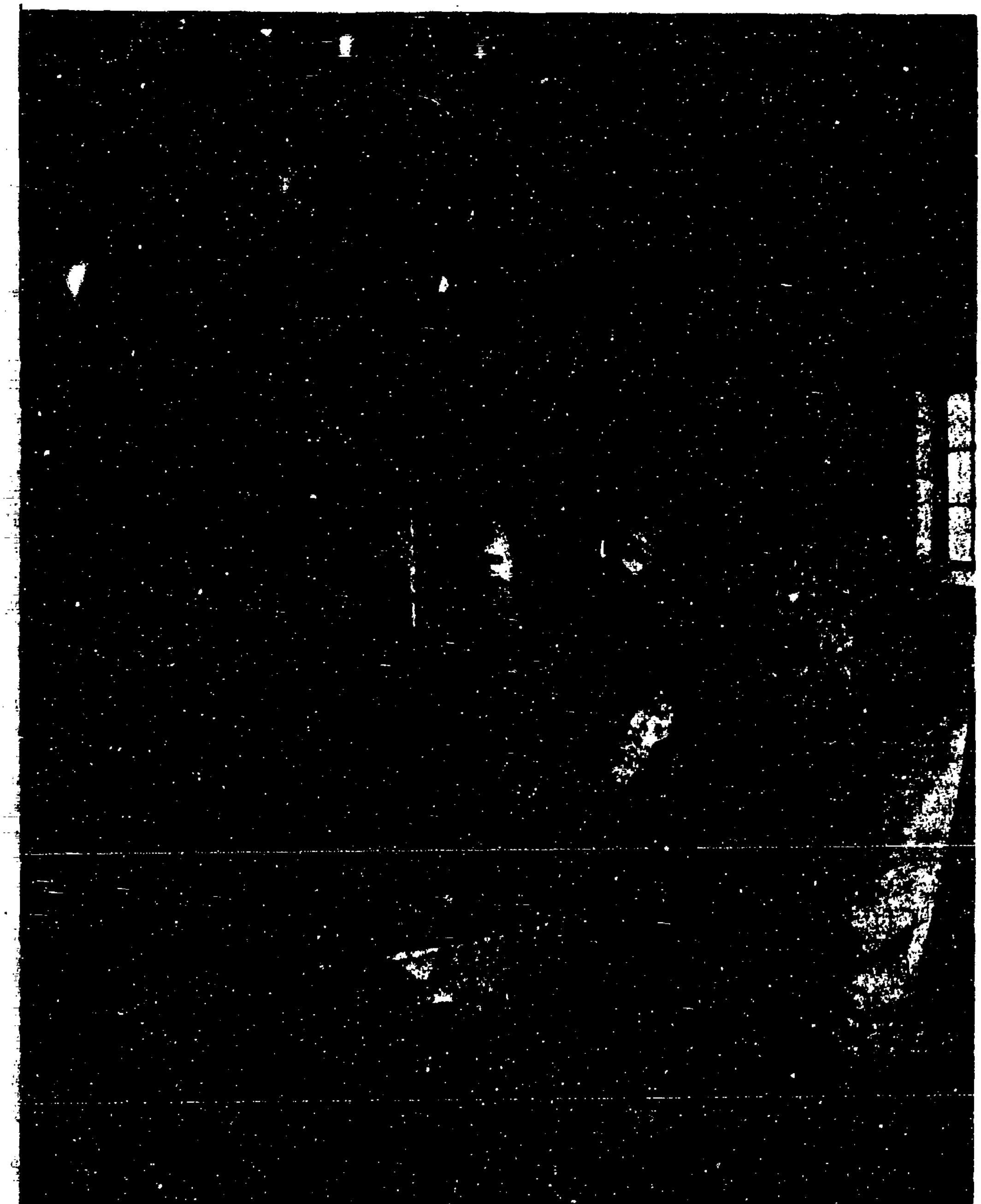
rework in the wheel mill, shown in Figure 24, along with a small quantity of water. The individual wheels of the wheel mill may weigh 10 tons and stand 7 feet high. The functions of the wheel mill include in addition to grinding and mixing the achievement of a state of "incorporation." Although incorporation is little understood, it is believed to be a state of very close contact among ingredients, perhaps without intervening films of air on particles, and accomplished by very considerable mechanical effort in the form of shearing pressure.[8] When the wheel mill cycle is complete, the wheel cake is shoveled out and transported to the press house where it is first broken down by passing through rolls, then pressed into cakes using a horizontal press shown in Figure 25.

The press cakes are broken into pieces of about ¾-inch size on the cutting rolls shown in the background of Figure 25. The size is reduced further on the corning rolls. The product from the corning mill is screened on a reel, the dust being sent back to the press. The product size and shape do not change essentially after the corning operation. The remaining operations are glazing and screening to separate the various grades produced. The glazing operation is carried out at elevated temperature in order, simultaneously, to evaporate water down to the specified level. If fuse powder is being made, two or more grades of different burning rate are produced by varying the ratio of sulfur to charcoal in the formula and these are blended to meet burning rate specifications.

**27. Uses.** With a force, $F$, of 110,000 ft-lb/lb, black powder was an effective gun propellant. The presence of solid reaction products led to large volumes of smoke and to a corrosive barrel residue requiring thorough cleaning of the gun daily or after each use. When propellants known as smokeless powders with higher force and substantially without solid products became available, black powder became obsolete for gun use. The change was not made overnight because a gun designed for black powder was not ideal for use with smokeless powder and *vice versa*. There are still a few antique sporting pieces in the hands of hobbyists who fire them, but the use of black powder as the propelling charge for guns no longer is significant.

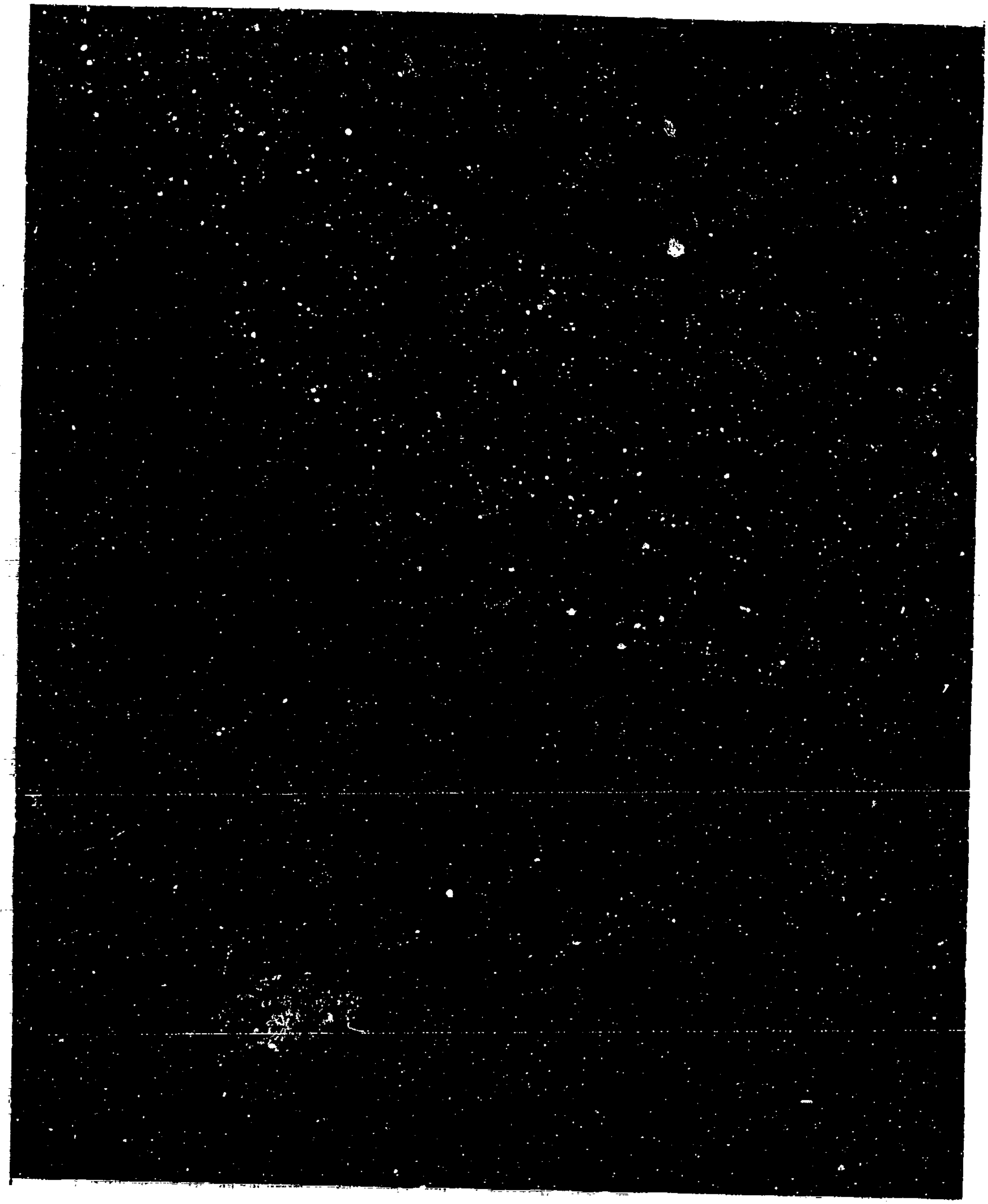
During World War II a need arose for a flash suppressant for use with certain guns, particularly the 155-mm gun. It was known that potassium salts are effective in suppression of flash. As black powder is roughly three-quarters potassium nitrate and a propellant in its own right, the use at night of an auxiliary charge of black powder was undertaken with considerable success. This use of black powder is not expected to outlive the present inventories of smokeless powder, however, since new propellants containing largely nitroguanidine have been developed which have at the same level of force lower burning temperature than those of the World War II smokeless powders. These nitroguanidine propellants exhibit much less tendency to flash, and the incorporation of small fractions of potassium salts in them generally inhibits flash completely.

Black powder was also the original rocket propellant. In the decades before World War II, except for Goddard's experiments, rocketry in the United States was confined to fireworks and small signal rockets of modest range and velocity and small payloads. For such rockets, black powder



*Courtesy of E. I. duPont de Nemours & Co., Inc.*

**Figure 24. Black Powder Wheel Mill**



Courtesy of E. I. duPont de Nemours & Co., Inc.

*Figure 25. Black Powder Press*

has been quite satisfactory. The smoke and sparks of the exhaust were desirable and there was no disadvantage connected with residue in the spent motor chamber. When military rockets were developed during World War II, first abroad and later in the United States, it was recognized that the low calorific value of black powder took it out of competition with the more energetic propellants that were available. Manufacturing processes moreover were not available to form black powder into the grain geometries required for these higher performance rockets, and it is doubtful that the physical properties of black powder would be compatible with the thermal and acceleration forces of such rockets.

As a bursting charge, black powder has been supplanted largely by more potent high explosives except for some practice bombs and projectiles where the smoke puff helps locate the impact point.

In primers for gun charges and igniters for rocket charges the easy ignitibility of black powder has made it a preferred ingredient. The high content of potassium nitrate has also been recognized as favorable for such use, because potassium salts are good emitters of radiation and radiation may be an important means of transfer of heat from the primer or the igniter to the surface of the main propellant charge.

As the first civil as well as military explosive, and for a long time the only available explosive, black powder has been extensively used for blasting. For this use the sodium nitrate black powder has been preferred ever since its introduction, in spite of somewhat greater hygroscopicity and slower burning rate, because of its lower price. Black powder does not detonate, even when initiated with a blasting cap. The observed propagation rates of 100 to 600 m/sec[1,11] when confined in steel pipes and initiated with a detonator are accounted for by shattering of the black powder by the initiator and burning at the attained pressure. Black blasting powder was first supplanted by commercial high explosives for blasting in rock because the detonation of the high explosives was very much more effective than the burning of black powder. For blasting in earth, black powder withstood the competition of high explosives for a longer time because the shock of detonation of high explosives was rapidly dissipated in earth

**TABLE 6. CONSUMPTION OF BLACK BLASTING POWDER (ALL TYPES) IN THE UNITED STATES[11]**

| Year | Pounds (thousands) |
|---|---|
| 1915 | 197,722 |
| 1920 | 254,880 |
| 1925 | 156,964 |
| 1930 | 99,873 |
| 1935 | 68,888 |
| 1940 | 59,754 |
| 1945 | 36,948 |
| 1950 | 20,655 |
| 1955 | 6,624 |
| 1956 | 5,598 |
| 1957 | 3,684 |
| 1958 | 2,492 |

whereas the slower burning black powder maintained pressure longer and gave more "heaving" of the burden. Coal miners like black powder because it breaks the coal into higher priced lump coal and produces less fines than even the low rate permissible high explosives. Unfortunately the reaction time of black powder lasts longer than the initial fracture of the coal, resulting in occasional ignition of methane (fire damp) and dust in the atmosphere of gassy mines and even of the coal itself. Use of black powder for blasting in coal mines engaged in interstate commerce is now forbidden by federal law.

The largest current use of black powder is for safety fuse. This is a column of black powder enclosed in a fabric tube. The rate of burning is carefully standardized so that the shooter can predict the length of time between lighting his fuse and the shot. Black powder has also been used as the timing element in some military fuzes. It has the disadvantage of producing a considerable volume of gas which either must be vented or it increases the pressure on the powder train and hence its burning rate. It has the further disadvantage that it is difficult to ignite at reduced pressures and impossible to ignite at pressures below 100 mm. For use at high altitudes it is necessary to assure that any device relying on the burning of black powder be pressurized.

The decline of the black powder industry in the United States is shown in Table 6.

Recognizing the obsolescence of black powder, the military forces have sponsored research on substitutes for black powder in all applications.

## REFERENCES


1. A. P. VanGelder and H. Schlatter, *History of the Explosives Industry in America*, p. 10, Columbia University Press, New York, New York, 1927.
2. C. W. Brooks (E. I. duPont de Nemours & Co., Inc.), private communication.
3. L. duPont (to E. I. duPont de Nemours & Co., Inc.), U. S. Patent 17,321 (1857).
4. JAN-P-223A, *National Military Establishment Specification Powder, Black* (12 January 1949) with *SCN No. 1* (23 March 1959).
5. JAN-P-362, *Joint Army-Navy Specification. Powder, Black, Sodium-Nitrate* (28 June 1946) with *Amendment-1* (23 December 1946).
6. J. Taylor, *Solid Propellent and Exothermic Compositions*, p. 19, Interscience Publishers, Inc., New York, New York, 1959.
7. H. Debus, "Chemische Theorie des Schiesspulvers," *Ann.*, **212**, 257 (1882); **213**, 15 (1882). (Summarized in J. Taylor, *loc. cit.*, p. 20).
8. J. D. Blackwood and F. P. Bowden, "The Initiation, Burning and Thermal Decomposition of Gunpowder," *Proc. Roy. Soc. (London)*, **A213**, 285 (1952).
9. C. Campbell and G. Weingarten, "A Thermoanalytical Study of the Ignition and Combustion Reactions of Black Powder," *Trans. Faraday Soc.*, **55**, 2221 (1959).
10. J. Taylor, *loc. cit.*, p. 21.
11. Hercules Powder Company, unpublished data.
12. U. S. Bureau of the Census, *Statistical Abstract of the United States: 1940*, 62nd edition, p. 860, Washington, D. C., 1940; *ibid., Statistical Abstract of the United States: 1959*, 80th edition, p. 815, Washington, D. C., 1959; U. S. Bureau of Mines, *Mineral Market Report No. MMS 2973*, Washington, D. C., 1959.

CHAPTER 5

# CRYSTALLINE MONOPROPELLANTS

**28. General.** The shape of black powder grains suggests crystalline material. A crystalline chemical with better thermodynamic properties than black powder should have advantages over black powder not only in ballistics but also in uniformity of composition and ease of manufacture. Such chemicals exist. They have not been exploited as propellants because they became available at a later date than nitrocellulose and smokeless powder, and the background knowledge that would have led them to be appreciated is of still more recent origin.

The list of possible monopropellants includes many chemicals used as military high explosives, as the thermochemistry of propellants is essentially the same as that for high explosives. The difference between combustion and detonation of a crystalline monopropellant is merely a difference in reaction rate.[1] Except for primary explosives, which can detonate from burning and are therefore excluded by definition from possible monopropellants, these chemicals will burn quietly when ignited. They will detonate only under the influence of a mechanical shock of severity far greater than can be found in a gun or rocket chamber. The thermal stability as well as the sensitivity of these materials have been extensively investigated in connection with their use as high explosives. In general, they exhibit long shelf life and are very stable at temperatures up to nearly their melting points.

In common with black powder grains, single crystals of monopropellants are not subject to being shaped to accurately controlled dimensions and large sizes. Again like black powder, however, they can sometimes be pelleted under sufficiently high pressure to moderately well consolidated large grains of controlled dimensions.

The densities, melting points, and ballistic parameters of several possible crystalline monopropellants are tabulated in Table 7.

**29. Nitroguanidine.** Nitroguanidine may, as an approximation, be considered to react according to the equation

$$CH_4O_2N_4 = CO + H_2 + H_2O + 2N_2 \qquad (39)$$

The gas volume, $\frac{1}{M}$, of nitroguanidine is quite high, and the fraction of nitrogen in the gas is unusually high for propellant gas. The burning temperature of nitroguanidine is some 150°K lower than that of a smokeless powder of the same force level (see M1 in SPIA/M2), indicating that nitro-

**TABLE 7. PHYSICAL AND BALLISTIC PARAMETERS OF CRYSTALLINE MONOPROPELLANTS**

| | Density (g/cc) | Melting point (°C) | $Q_v$ (cal/g) | $1/M$ (moles/lb) | $T_v$ (°K) | $T_p$ (°K) | Force (ft-lb/lb) | $I_{sp}$ (lb-sec/lb) |
|---|---|---|---|---|---|---|---|---|
| Nitroguanidine* | | | 721 | 0.0481 | 2268 | | 303,000 | |
| Nitroguanidine† | 1.715 | 246 | | | 2405 | 1819 | 321,000 | 199 |
| RDX, cyclotrimethylene-trinitramine* | 1.82 | 202 | 1360 | 0.0405 | 4020 | 3250 | 452,000 | 255 |
| HMX, cyclotetramethylene-tetranitramine* | 1.92 | 276 | 1321 | 0.0405 | 3940 | 3180 | 430,000 | 253 |
| PETN, pentaerythritol tetranitrate* | 1.77 | 140 | 1531 | 0.0348 | 4220 | 3510 | 40,900 | 250 |
| Ammonium nitrate† | 1.72 | 170 | 354 | 0.0437 | 1622 | 1245 | 197,000 | 159 |
| Ammonium perchlorate† | 1.95 | Decomposes | 335 | 0.0362 | 1849 | 1408 | 186,000 | 153 |

* *Hirschfelder-Sherman calculation* (see Paragraph 7-6).

† Exact calculation (see Paragraph 7-5).

guanidine should cause less gun barrel erosion than a comparable service gun propellant. The higher content of nitrogen in the gas should result in less tendency to flash than a service gun propellant at the same flame temperature and an even more pronounced advantage at the same level of force.

The usual crystal form of nitroguanidine is needles, resulting in quite low gravimetric density and small web. No successful work has been reported on growing crystals of size and shape that would permit using nitroguanidine as a gun propellant. The linear burning rate has apparently not been measured.

Although nitroguanidine has not found use as a monopropellant, the disadvantages of its crystal form have been overcome at the cost of some compromise of ballistic parameters by formulating nitroguanidine as filler with plastic monopropellant binders into composite propellants. Development of such composites has also permitted a continuous spectrum of force and flame temperatures in the triple-base system described in Chapter 7.

Nitroguanidine is synthesized by the fusion of calcium cyanamide or dicyandiamide with ammonium nitrate under high pressure and temperature to yield guanidine nitrate, followed by dehydration with mixed sulfuric and nitric acids[3]

$$CaNCN + NH_4NO_3 + 2H_2O = Ca(OH)_2 + NH:C(NH_2)NH_2 \cdot HNO_3 \quad (40a)$$

$$NH:C(NH_2)NHCN + 2NH_4NO_3 = 2NH:C(NH_2)NH_2 \cdot HNO_3 \quad (40b)$$

$$NH:C(NH_2)NH_2 \cdot HNO_3 - H_2O = NH:C(NH_2)NHNO_2 \quad (40c)$$

Other syntheses are known. The thiocyanate process[3] depends on the series of reactions

$$2NH_4CNS = NH:C(NH_2)NH_3CNS + H_2S \quad (41a)$$

$$NH:C(NH_2)NH_3CNS + NH_4NO_3 = NH:C(NH_2)NH_2 \cdot HNO_3 + NH_4CNS \quad (41b)$$

The Roberts process[3] proceeds through ethyl pseudourea and guanidine sulfate

$$CO(NH_2)_2 + (C_2H_5)_2SO_4 = NH:C(NH_2)OC_2H_5 + C_2H_5HSO_4 \quad (42a)$$

$$H_2SO_4 + NH:C(NH_2)OC_2H_5 + NH_3 = NH:C(NH_2)_2 \cdot H_2SO_4 + C_2H_5OH \quad (42b)$$

$$NH:C(NH_2)_2 \cdot H_2SO_4 + HNO_3 - H_2O = NH:C(NH_2)NHNO_2 + H_2SO_4 \quad (42c)$$

**30. RDX.** RDX (cyclotrimethylenetrinitramine, cyclonite, hexogen) may be considered to react according to Equation 43

$$(CH_2N_2O_2)_3 = 3CO + 3H_2O + 3N_2 \quad (43)$$

The force and specific impulse, from Table 7, are quite attractive, although the flame temperatures are higher than desirable for gun applications. RDX has been fired in sporting and small arms successfully[4] with ballistics comparing favorably with those of smokeless powder. As expected, the quickness was found to depend on the crystal size, finer crystals being quicker than coarser. The high burning temperatures may be tempered by formulating to a composite with a binder of lower burning temperature.

RDX is manufactured by the Woolwich process[5] by the nitration of hexamethylenetetramine

$$(CH_2)_6N_4 + HNO_3 = (CH_2N_2O_2)_3 + \text{gaseous products} \quad (44)$$

or by the Bachmann process[6] by reacting ammonium nitrate and nitric acid with hexamethylenetetramine under dehydrating conditions

$$(CH_2)_6N_4 + 4HNO_3 + 2NH_4NO_3 - 6H_2O = 2(CH_2N_2O_2)_3 \quad (45)$$

**31. HMX.** HMX (cyclotetramethylenetetranitramine) is homologous with RDX and may be assumed to react

$$(CH_2N_2O_2)_4 = 4CO + 4H_2O + 4N_2 \quad (46)$$

The ballistic parameters are similar to those of RDX. It is somewhat more dense than RDX and has a somewhat higher melting point (Table 7).

Like RDX, HMX can be compounded into composites such as PPL 949 (see SPIA/M2).

HMX[6] appears as a by-product to the extent of about 10% in Bachmann-process RDX. No attempt is ordinarily made to separate it from the RDX, because for most uses it is the full equivalent of RDX. By changing the conditions of operation of the Bachmann process, the fraction of HMX can be increased substantially to where isolation of the HMX is practical.

**32. PETN.** PETN (pentaerythritol tetranitrate, penthrite) may be assumed to react

$$C(CH_2NO_3)_4 = 2CO + 3CO_2 + 2N_2 + 4H_2O \quad (47)$$

With higher burning temperature and lower gas volume, the force and specific impulse of PETN are comparable to those of RDX and HMX (Table 7). Since PETN has lower density and lower melting point than RDX and HMX, these latter materials should be preferred to PETN either as monopropellants or as filler for composite propellants.

PETN is manufactured[7] by the nitration of pentaerythritol

$$C(CH_2OH)_4 + 4HNO_3 = C(CH_2NO_3)_4 + 4H_2O \quad (48)$$

**33. Ammonium nitrate.** Ammonium nitrate may be assumed to react

$$NH_4NO_3 = N_2 + 2H_2O + \tfrac{1}{2}O_2 \quad (49)$$

As a monopropellant, ammonium nitrate produces a working gas containing free oxygen. For this reason, although its force and specific impulse are somewhat modest, when compounded into composites with any incompletely oxidized binders ammonium nitrate behaves in part as an oxidant. Such composites are discussed further in Chapter 9.

Ammonium nitrate is hygroscopic at relative humidities above 40 percent. Any propellant charges comprising ammonium nitrate must be protected from humidity. Ammonium nitrate also undergoes a series of phase changes at different temperatures including one at 32.2°C,[8] all of which are accompanied by changes in density. This is destructive to the integrity of single crystals. When compounded into a composite with hydrophobic or nonhygroscopic binder, all of the ammonium nitrate crystals within the binder are protected from moisture pickup. The phase changes can also be contained, as the crystal size of the ammonium nitrate is preferably very small and the stresses produced by the volume change of the individual particles can be absorbed by the binder.

When formed into large grains by compression molding, hygroscopic effects are likewise confined to the material near the surface. Phase changes in such propellants cause them to swell somewhat on aging, but do not appear to interfere with their normal burning processes. Such grains have been studied[9] but have not found service use.

Ammonium nitrate is an article of commerce, being widely used as a fertilizer ingredient and as a constituent of commercial high explosives.

**34. Ammonium perchlorate.** Ammonium perchlorate may be assumed to react

$$NH_4ClO_4 = \tfrac{1}{2}N_2 + HCl + \tfrac{3}{2}H_2O + \tfrac{5}{4}O_2 \quad (50)$$

As a monopropellant, ammonium perchlorate is even more oxidizing than ammonium nitrate. Like ammonium nitrate, ammonium perchlorate is hygroscopic. The presence of hydrogen chloride in the products of combustion makes ammonium perchlorate unattractive for use in engines used repetitively, such as guns. For these reasons ammonium perchlorate has not been used as a monopropellant charge. It is widely used as an oxidizing filler in composite propellants for rockets, as discussed further in Chapter 9, and in ORDP 20-176.

Ammonium perchlorate is prepared by electrolytic oxidation of sodium chloride,

$$NaCl + 4H_2O = NaClO_4 + 4H_2 \quad (51a)$$

followed by metathesis with an ammonium salt

$$NaClO_4 + NH_4^+ = NH_4ClO_4 + Na^+ \quad (51b)$$

## REFERENCES


1. L. Wohler and F. J. Roth, "Ueber die Brisanz von Explosivstoffen," *Z. ges. Schiess- u. Sprengstoffw.*, **29**, 9 (1934).
2. G. B. L. Smith, V. J. Sabetta and O. F. Steinbach, Jr., "Quantitative Study of the Preparations of Guanidine Nitrate and Nitroguanidine," *Ind. Eng. Chem.*, **23**, 1124 (1931).
3. *The Synthesis and Fineness of Nitroguanidine*, Naval Powder Factory, Indian Head, Reports QR 9, 10, 15 June 1950, CONFIDENTIAL (SPIA Abstract No. 10680); *Synthesis of Nitroguanidine*, *ibid.*, Report QR 12, 15 July 1951, CONFIDENTIAL (SPIA Abstract No. 11461).
4. Hercules Powder Company, unpublished data.
5. W. M. Rinkenbach, *Explosives (High)*, in *Encyclopedia of Chemical Technology*, Vol. 6, p. 40, Interscience Publishers, Inc., New York, New York, 1951.
6. W. E. Bachmann, U. S. Patent 2,798,870 (1957).
7. E. Berlow, R. H. Barth and J. E. Snow, *The Pentaerythritols*, p. 54, Reinhold Publishing Corporation, New York, New York, 1958.
8. *International Critical Tables of Numerical Data Physics, Chemistry and Technology*, Vol. 4, p. 7, McGraw-Hill Book Company, Inc., New York, New York, 1926.
9. F. R. Groves, Jr. and L. Greiner, *Ammonium Nitrate Solid-Propellant Investigation*, Experiment Incorporated, Technical Publication 148, 8 April 1957, Contract NOrd 16890, CONFIDENTIAL.

## CHAPTER 6

# PLASTIC MONOPROPELLANTS

**35. General.** Plastic monopropellants, commonly known as smokeless powders,* have seen in use for about 75 years. The first such propellant was made by Vieille in France in 1884.[1] Vieille's product was essentially nitrocellulose, changed from its originally fibrous form to a dense plastic by colloiding with ether and alcohol, forming into grains, and subsequently removing most of the solvent. A few years later Alfred Nobel[2] introduced a different variety of smokeless powder in which nitroglycerin is used as a colloiding plasticizer for the nitrocellulose.[3] Propellants containing nitroglycerin are known as double-base because they contain two explosive ingredients in contrast to single-base propellants which contain nitrocellulose as the only explosive ingredient. Addition of fuel-type or "deterrent" plasticizers to the formulation gives the necessary flexibility for calorific value and nitrocellulose content to be varied independently, an important consideration when both ballistic qualities and physical properties may be specified. Ballistic qualities are largely determined by the calorific value, and physical properties by the polymer content. A smokeless powder, looked at in this light, is a single-phase or monopropellant comprising three ingredients: a polymer, usually nitrocellulose; an oxidant plasticizer, usually nitroglycerin; and a fuel plasticizer, for example, di-*n*-butyl phthalate. The terms single-base and double-base have lost their significance, single-base being just a special case in which the oxidant plasticizer content happens to be zero.

**36. Formulation.** The relationships within the family of nitrocellulose monopropellants are shown qualitatively in the triangular diagram of Figure 26. For ballistic purposes the scale of Figure 26 should be considered about linear in weight fractions. For physical properties it is about linear in volume fractions. In this figure the line *PH* represents all possible compositions with the same calorific value as pure polymer, *P*. Lines parallel to *PH* are lines of constant calorific value. Compositions to the left of *PH* are "cooler," have lower calorific value (lower flame temperature) than that of pure polymer. To the right of *PH*, they are "hotter," have higher calorific value (higher force or specific impulse). The line *BC* represents compositions of the minimum practical Young's modulus for propellant use. Below *BC* the propellant cannot be relied on to maintain its geometry, even when supported by being bonded to the chamber wall. The line *AB* defines the lowest calorific value that an end-item designer can profitably use. All useful nitrocellulose monopropellants are, therefore, formulated within the polygon *PABC*.

Since gun erosion limits the allowable flame temperature of a propellant, gun propellant formulas tend to fall to the left of the line *PH*, although for some applications they may be well to the right. High performance rocket propellants are found to the right of the line *PH*. Case-bondable propellants fall in the neighborhood of the line *BC*. Propellants to generate gas at moderate temperatures for aircraft starter engines and similar applications are found in the neighborhood of the line *AB*. There exists considerable overlap between the formulation areas for different types of end use. In addition to the three basic ingredients a stabilizer is universally used to increase the storage life of the propellant, and additives may be incorporated to reduce flash, to improve ignitability, to reduce metal fouling in gun barrels, to reduce the pressure exponent, *n*, to provide opacity, and for various other reasons.

**36-1. Polymer.** Nitrocellulose is the usual polymer in plastic monopropellants, but other polymers can be, and have been, used.

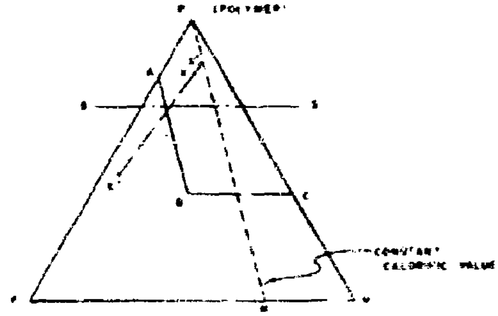
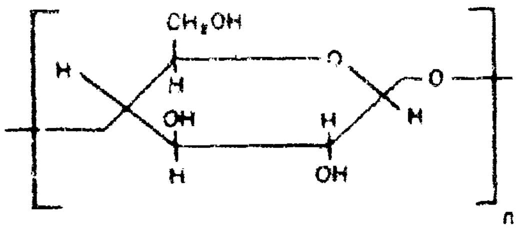


*Figure 26. Nitrocellulose Monopropellant System*

* Although the term "smokeless powder" is still current abroad and in United States commercial circles, the Department of Defense has discontinued the usage.

**34-1.1. Nitrocellulose.** Nitrocellulose is the product of partial nitration of cellulose, which is a natural polymer of empirical formula $(C_6H_{10}O_5)_n$ and structural formula



Of the three $-OH$ groups, those at the 2 and 3 positions are secondary, while that in the 6 position is primary. All of the $-OH$ groups can be nitrated, and when cellulose is completely nitrated the resulting nitrocellulose has a nitrogen content of 14.15 percent. Nitrocellulose as used in commerce, and as used in propellants is less than completely nitrated. Nitrocelluloses are characterized by nitrogen content and viscosity as independent variables. Hygroscopicity and solubility in various solvents depend primarily on the nitrogen content. Significant commercial grades of nitrocellulose are those used for lacquers at 12 percent nitrogen, for dynamite at 12 percent nitrogen, and for plastics at 11 percent nitrogen. The grades of significance to propellants in the United States are guncotton or high grade at 13.4 percent nitrogen, pyrocellulose at 12.6 percent nitrogen, and one as yet not officially named at 12.2 percent nitrogen.[4] Foreign propellants frequently contain nitrocellulose of lower substitution than 12 percent nitrogen. Guncotton is not used as the only nitrocellulose in American propellants, but is commonly blended with pyrocellulose to yield a "military blend" at about 13.15 percent nitrogen or a blend at 13.25 percent nitrogen. All fibrous nitrocelluloses look alike, and indeed look much like the original cellulose. While there could be merit in separately formulating two nitrocelluloses into a propellant, the elimination of possible confusion between different grades of nitrocellulose and the opportunity of adjusting the ratio of the nitrocelluloses while in the fibrous state to an exact blended nitrogen content argue strongly for blending.

**34-1.1.1. Nitrogen content.** As indicated in Table 2, the contribution of the nitrocellulose to the calorific value, flame temperature, and therefore force, specific impulse, or characteristic velocity of the propellant is higher the higher the nitrogen content.

**34-1.1.2. Solubility.** Nitrocellulose at 12.2 percent or 12.6 percent nitrogen is completely soluble, *i.e.*, miscible in all proportions, in a mixture of 2 parts by volume ether and 1 part alcohol, used in the required solubility determination.[4] At 13.4 percent nitrogen only a small fraction of the nitrocellulose enters the solvent phase. No attempt is made to measure the solvent content of the nitrocellulose phase. Neither the high solvent fraction nor the proportion of ether and alcohol used in this determination is representative of the system involved in the manufacture of propellants, where the nitrocellulose imbibes all of the solvent and no separate solvent phase is present. Nevertheless, as shown in Figure 27, under the microscope individual fibers can be seen to have maintained their identity in unplasticized propellant made from military blend with ether-alcohol solvent. Introduction of plasticizer into the formula usually obliterates this phenomenon completely. The reason for this is that imbibition of solvent plus plasticizer so softens the nitrocellulose fibers that the fibrous structure is destroyed by the mechanical forces acting during mixing and subsequent operations. Solubility of nitrocellulose in nitroglycerin follows generally the solubility in ether-alcohol. Solvents when used to fabricate double-base propellants usually contain acetone, in which all of the military grades of nitrocellulose are soluble. Determination of ether-alcohol solubility has little real significance either to the manufacture or performance of a propellant. It does serve to indicate that a given lot of nitrocellulose resembles the particular nitrocellulose used when the propellant was originally standardized.

**34-1.1.3. Hygroscopicity.** The moisture content of nitrocellulose in equilibrium with a saturated atmosphere at 25°C has been expressed[4] by the equation

$$H = \frac{405.8 - 28.7N}{31.11 - N} \qquad (52)$$

where $N$ is the percent nitrogen in the nitrocellulose. From this equation have been calculated the values shown in Table 8 for the nitrocelluloses used in propellants.

Courtesy of E. I. du Pont de Nemours & Company, Inc.

Figure 27. Cross Section of Grain of IMR Smokeless Powder for Small Arms, Photographed in Ultraviolet Light, 112× Magnification

**TABLE 8. HYGROSCOPICITY OF NITROCELLULOSE**

| Nitrogen in Nitrocellulose (percent) | Water (percent) |
|---|---|
| 13.40 | 1.19 |
| 13.15 | 1.57 |
| 12.60 | 2.38 |
| 12.20 | 2.93 |

The nature of this relationship may be explained on the basis that it is the unnitrated −OH groups of the nitrocellulose that sorb moisture.

**36-1.1.4. Viscosity.** Viscosity in very dilute solution is a quantitative measure of the average molecular weight of a polymer, as shown by the equation[3]

$$\lim C \to 0 \quad \frac{1}{C}\left(\frac{\eta}{\eta_s} - 1\right) = \frac{DP}{200} \qquad (53)$$

where $\eta$ is the measured viscosity of the solution, $\eta_s$ is the viscosity of the solvent, $C$ is the concentration of the nitrocellulose in the solution, and $DP$ is the degree of polymerization. The value 200 is empirical and varies slightly with the degree of substitution and with the solvent used. The figure shown here is used for acetone solution. The left member of Equation 53 is known as the intrinsic viscosity. The ratio $\frac{\eta}{\eta_s}$ is called the relative viscosity.

At higher concentration secondary effects, not completely identified, influence the viscosity. For example, two nitrocelluloses of different origin, showing the same intrinsic viscosity, may have widely differing measured viscosities in more concentrated solution. For propellant use viscosity is measured[4] by timing the fall of a $\frac{5}{16}$-inch steel ball through a 10 percent solution of nitrocellulose in acetone. Typical values of nitrocellulose viscosity for propellants are 6 to 25 seconds, but nitrocelluloses of higher and lower viscosities are sometimes used. The conditions of the viscosity determination are not representative of any conditions present during propellant manufacture. The determination has as its principal significance the assurance that the nitrocellulose examined resembles that used in the standardized propellant.

**36-1.2. Other polymers.** The polymer in the propellant need not be nitrocellulose. Other energetic polymers may be used such as poly(vinyl nitrate), poly(petrin acrylate), poly(trinitroethyl acrylate), and even fuel-type polymers such as cellulose acetate or poly(methyl methacrylate). In these cases the negative or deficient contribution on the part of the polymer to the force of the propellant is overcome by the use of oxidant plasticizers such as nitroglycerin and other nitrate esters. Cool polymers if used must be physically compatible with the hot plasticizers. This accounts for the fact that the cool polymers cited above are all esters.

Cellulose acetates, like nitrocellulose, are derived from cellulose, are not completely esterified, and are characterized by degree of esterification (expressed as percent combined acetic acid) and by viscosity. Also like nitrocellulose, a cellulose acetate in a propellant has its highest degree of polymerization at the time of introduction into the mixer.

Synthetic polymers may be polymerized in advance of introduction, in which case characterization is possible. Alternatively, they can be polymerized *in situ* after mixing.

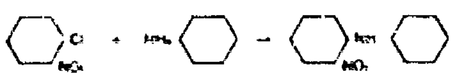
**36-2. Stabilizer.** In common with other organic chemicals, nitrocellulose tends to deteriorate with age by a process known as thermal decomposition. In the case of nitrocellulose, thermal decomposition starts with the splitting off of $NO_2$ from the nitrate groups[5] This $NO_2$ reacts immediately with organic material in the propellant (including nitrocellulose) and is evolved as NO. The secondary reaction of the $NO_2$ with the nitrocellulose accelerates the thermal decomposition. Hence thermal decomposition should be minimized by adding to the formula a chemical that will react with the $NO_2$ to give a stable product and thus prevent secondary reaction of $NO_2$ with nitrocellulose. The other product resulting from the loss of the $NO_2$ is a bound free radical which also tends to react further to more stable products. An additive to remove the free radical character of the residue should also result in stabilizing the propellant. Nitroglycerin behaves in a manner similar to that of nitrocellulose and can be stabilized in the same way. The stabilizers in current use in the United States are diphenylamine, 2-nitrodiphenylamine, and ethyl centralite. These are all weak bases, but they function by being nitrated rather than by formation of salts. Other stabilizers that have been proposed include N-ethylaniline, carbazole, β-nerolin, and N-methyl-p-nitroaniline. Mineral jelly, an unsaturated aliphatic, functions as the stabilizer in some British propellants.

**36-2.1. Diphenylamine.** Diphenylamine, $(C_6H_5)_2NH$, is prepared by subjecting aniline to high temperature in an autoclave.

$$2C_6H_5NH_2 = (C_6H_5)_2NH + NH_3 \qquad (54)$$

Its history in the aging of propellants has been traced.[1] The first reaction product is diphenylnitrosoamine, $(C_6H_5)_2NNO$, followed by ring nitration. Diphenylamine is sufficiently basic to attack nitroglycerin, so that its main use is in single-base propellants.

**36-2.2. 2-Nitrodiphenylamine.** 2-Nitrodiphenylamine is less basic than diphenylamine and is inert toward nitroglycerin while still being a good stabilizer. It is preferred to diphenylamine as a stabilizer for double-base propellants. It is made by reacting 1-chloro-2-nitrobenzene with aniline.


(55)

**36-2.3. Ethyl centralite.** Ethyl centralite, centralite-1, or centralite for short, is *sym*-diethyldiphenylurea, $CO[N(C_2H_5)(C_6H_5)]_2$. It is made by reacting phosgene with N-ethyl- or N,N-diethylaniline. Its reaction history is considerably more complicated than that of diphenylamine, ending up with nitrated anilines.[2] The methyl analog, centralite-2 or *sym*-dimethyldiphenylurea, is also known and is used somewhat abroad. The centralites are considered to be somewhat less effective as stabilizers than 2-nitrodiphenylamine, but they are also quite good plasticizers. When found in propellants they are frequently used at higher fractions than the diphenylamines to take advantage of their plasticizing properties.

**36-3. Oxidant-type plasticizers.** The required properties of an oxidant-type plasticizer are that it contribute oxidizing as well as fuel elements to the composition, that it be physically compatible with the polymer, and that its vapor pressure over the composition be low enough that the composition will not change substantially over the life of the propellant.

Nitroglycerin was the original oxidant type plasticizer and it is still the most used of this type plasticizer in the United States. It is usually prepared on the propellant plant site, by the nitration of glycerin with a mixture of nitric and sulfuric acids.

Nitrate esters other than nitroglycerin have also been used. In many cases these plasticizers are cooler than the nitrocellulose, nevertheless, propellants in which they are contained are still known as double-base. Diethylene glycol dinitrate, DGN, $NO_2(OC_2H_4)_2ONO_2$, and triethylene glycol dinitrate, TGN, $NO_2(OC_2H_4)_3ONO_2$, are the most important of these nitrates. The ether bonds in these esters are considered advantageous in improving low temperature physical properties of the propellant. DGN has been used more abroad than in the United States. Other nitrates for which feasibility is established are

metriol trinitrate
$CH_3C(CH_2ONO_2)_3$

1,2,3-butanetriol trinitrate
$CH_2ONO_2CHONO_2CHONO_2CH_3$

1,2,4-butanetriol trinitrate
$CH_2ONO_2CHONO_2CH_2CH_2ONO_2$

petrin
$CH_2OHC(CH_2ONO_2)_3$

diethanolnitramine dinitrate (DINA)
$NO_2N(C_2H_4ONO_2)_2$

**36-4. Fuel-type plasticizers.** As is the case with the oxidant-type plasticizers, fuel type plasticizers must be physically compatible with the nitrocellulose and should have sufficiently low vapor pressure to remain in the propellant during its life. In contrast to the oxidant-type plasticizers, fuel-type plasticizers contribute no oxidant or only a little oxidant to the composition and thus tend to reduce the force and flame temperature of the propellant. It is difficult to draw a sharp line between chemicals which are oxidant-type plasticizers and those which are fuel-type plasticizers, this distinction is not really very important and one is perhaps better off to consider both as plasticizers. Fuel-type plasticizers are frequently the same plasticizers that are found in commercial plastics and protective coating. They are used because they are available in quantity at reasonable prices. They may be esters such as diethyl, dimethyl, di-*n*-butyl, or di-(2-ethylhexyl)phthalate, triacetin, the adipates and sebacates, nitro compounds such as dinitrotoluene, substituted ureas such as the centralites, or even mineral jelly as used in the British cordite. If the propellant is made by a process involving a volatile solvent, the residual solvent behaves as a fuel type plasticizer and differs from the rest of the fuel-type plasticizers only in that it has a higher vapor pressure than is desirable. Gradual loss of residual solvent on aging of propellants will change the ballistic characteristics. Choice among the fuel-type plasticizers is usually made on the basis of availability and cost plus the contribution to the physical properties of the propellant.

**36-5. Additives.** The combustion products of plastic monopropellants contain gases such as CO and $H_2$ which are combustible in air. If the temperature at time of discharge to the atmosphere is high enough, ignition of these exhaust products in air may take place. This phenomenon is known as *flash*, or more specifically secondary flash. Flash is undesirable in gunnery because it discloses the position of the piece and tends to interfere with the vision of the gunners, particularly during night firing. In rockets flash can likewise afford data on the position of the launcher. Flash is also responsible, at least in part, for the attenuation of radar signals to and from rocket missiles, interfering with guidance and telemetry. To avoid or diminish flash, additives are frequently included in propellant compositions to suppress this ignition. These additives may take the form of potassium salts which function as negative catalysts for the reactions of CO and hydrogen with atmospheric oxygen. Of the potassium salts available in the United States, potassium sulfate is the most frequently used, though potassium nitrate has been used in some propellants. Potassium cryolite has been used abroad in propellants mixed in water slurry since it is insoluble in water.

Potassium nitrate and barium nitrate have been used in some propellants to make the propellant more readily ignitible. Metallic tin and metallic lead are examples of additives in gun propellants to reduce metal fouling. They function by lowering the melting point of copper which is deposited in the barrel by the projectile during travel through the bore.

Certain lead and copper salts have been found effective in lowering the pressure coefficient of burning rate in double base rocket propellants. Carbon black and other pigments have been used in some propellants to provide opacity and thus prevent malfunction due to ignition below the surface at the site of minor imperfections. Metal wire either in chopped form or strung continuously parallel to the axis of end-burning grains increases the effective burning rate of grains in which they are incorporated by increasing the burning surface. Other additives of claimed virtue are found in some propellants.

Solid products in the propellant gas resulting from the incorporation of additives contribute to *smoke*, which is objectionable for reasons similar to those for flash. The amount of additive used for a given purpose, *e.g.*, flash suppression, must be considered in the light of the contribution to smoke. As discussed in the next section, carbon may also appear in smoke.

**37. Ballistic characteristics.** The calorific values, flame temperatures, and gas volumes of plastic monopropellants may be estimated from the data of Table 2 (page 7), from which can be derived the force, characteristic velocity, and specific impulse as outlined in Paragraph 8. Calorific values range downward from a maximum of about 1[illegible] calories per gram to quite low or even negative values. It is surprising perhaps that a propellant with a negative calorific value will burn to produce a useful working fluid. That it does so is due to the fact that thermodynamic equilibrium is not attained at low flame temperature and endothermic species appear in the gaseous products.

Flame temperatures, $T_v$, at constant volume may be somewhat over 7000°R for sporting or pistol propellants and may be below 2000°R for gas generator propellants.

The composition of the gaseous products may be determined as outlined in Paragraph 7. In general, only minor quantities of solid products will be found from the combustion of plastic monopropellants. The solid products are derived from the additives except that some cool-burning gas generator propellants tend to be smoky. The smoke is carbon derived from the propellant composition. Choice of fuel-type plasticizers has a considerable effect on smoke. It is claimed that long carbon chains and particularly benzene rings in the fuel-type plasticizers are more prone to smoke than are short aliphatic chains.[11]

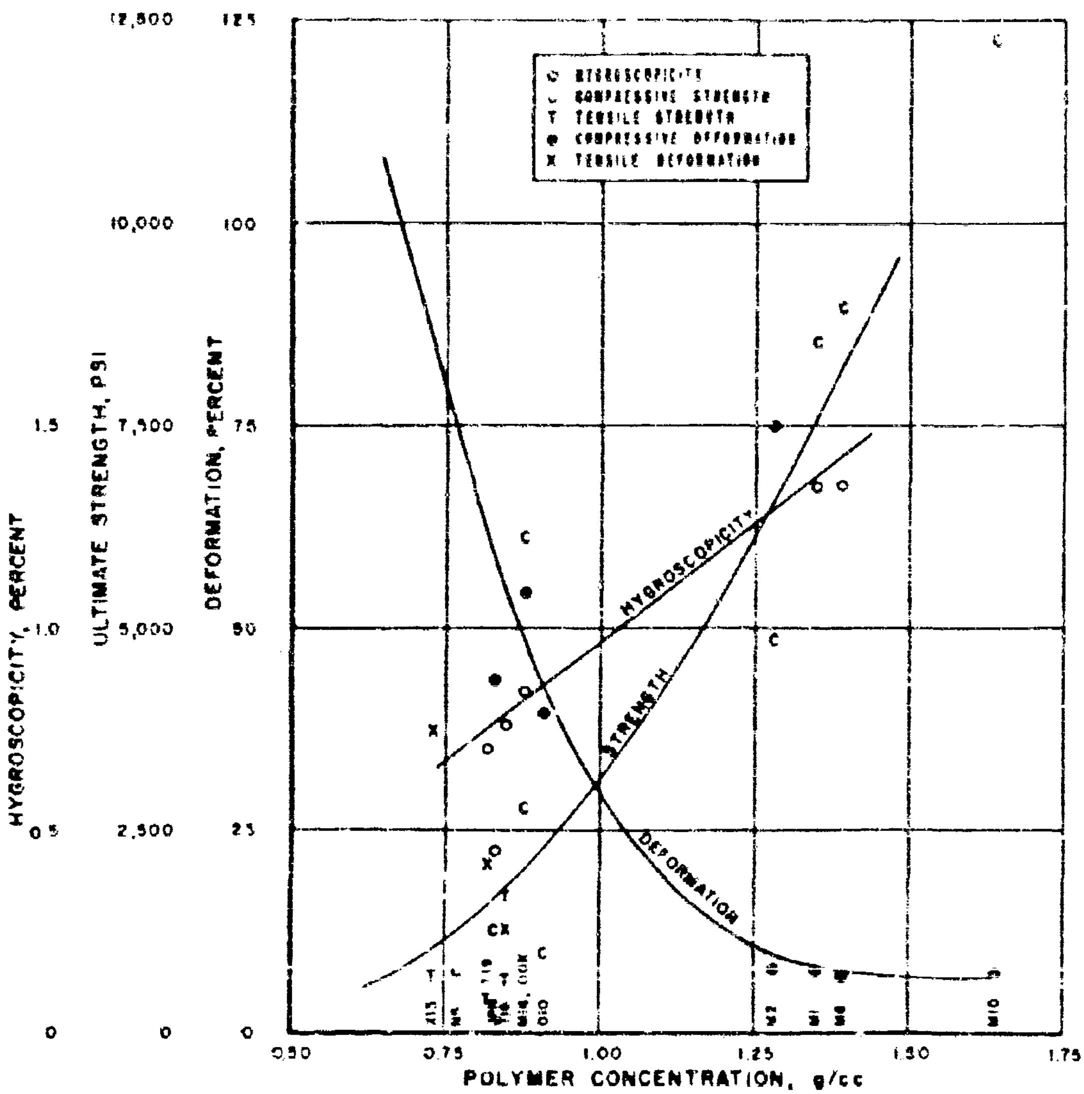



*Figure 28 Physical Properties Versus Polymer Concentration*

**38. Physical properties.** Plastic monopropellants are thermoplastic, translucent unless pigmented, and resemble generally the inert thermoplastics of commerce. Many of the physical properties are determined by the polymer content, probably best expressed in terms of concentration (weight fraction multiplied by specific gravity) of polymer in the propellant. Figure 28 presents data on the ultimate strength, deformation at rupture, and hygroscopicity typical of these propellants.

**38-1. Ultimate strength.** Unplasticized nitrocellulose has an ultimate tensile or compressive strength near 10,000 psi. As plasticizers of any description are added the strength decreases rapidly to values in the order of 2000 psi at a nitrocellulose concentration of 0.9 g/cc and continues to decrease to 500 psi at 0.7 g/cc.

**38-2. Deformation at rupture.** Unplasticized nitrocellulose is hard and somewhat brittle, rupturing in either tension or compression at less than 10 percent deformation. Plasticizers improve this property, to about 50 percent at a concentration of 0.9 g/cc and to 100 percent at 0.7 g/cc.

**38-3. Cold flow.** In common with other thermoplastics, plastic monopropellants have a tendency toward cold flow that becomes more pronounced as the polymer concentration is decreased. This tendency can be counteracted by cross-linking the polymer. Bifunctional OH-reactive chemicals such as diisocyanates and anhydrides have been used successfully.[11]

**38-4. Hygroscopicity.** The hygroscopicity of unplasticized nitrocellulose propellant is roughly the same as that of the nitrocellulose from which it is made. Upon addition of plasticizers the hygroscopicity of propellants drops off a little more rapidly than can be accounted for by simple dilution of the nitrocellulose, indicating that as a rule plasticizers tend to interfere somewhat with the sorption of water by the unnitrated OH groups of the nitrocellulose.

**38-5. Density.** The assumption seems to be generally good that no volume changes occur during the mixing of nitrocellulose propellants. Theoretical densities are computed according to the formula

$$\frac{1}{\rho} = \Sigma \frac{x_i}{\rho_i} \qquad (38)$$

where $x_i$ is the weight fraction and $\rho_i$ the density of ingredient $i$. Measured densities of propellants are quite close to the computed values.

**38-6. Vapor pressure.** Nitrocellulose itself is nonvolatile. Plasticizers in general do have measurable but low vapor pressures. Propellants in which these plasticizers are used should and actually do have vapor pressures which are the sum of the partial vapor pressures of the plasticizers and volatiles, including hygroscopic moisture and residual solvents. The vapor pressure of nitroglycerin over propellants has been extensively investigated,[11, 12] without, however, substantial agreement as to its value.

**38-7. Coefficient of thermal expansion.** Available data indicate a thermal expansion coefficient for propellants comprising largely nitrocellulose of about $10^{-4}$ in/in/°C. This is considerably greater than the expansion coefficient of chamber materials usually used. Cellulose acetate plastic has about the same expansion coefficient as nitrocellulose propellant, and this explains the use of cellulose acetate as peripheral inhibitor for many large grains. If the propellant is to be case-bonded, the existence of a considerable differential in the expansion coefficients requires that the propellant be deformable, have low modulus and large deformation (*e.g.*, BUU, SPIA/M2).

**38-8. Plasticity.** Below a nitrocellulose concentration of about 0.9 g/cc, propellants can be formed under pressure at temperatures considered safe for manufacturing operations. If the polymer concentration is much higher than this limit, volatile solvent must be used in the manufacturing process. When volatile solvents are so used, they are customarily added in sufficient amount to permit mixing and granulating at ambient temperature. This requires adding enough solvent to lower the polymer concentration to about 0.6 g/cc.

**39. Thermal properties.** The thermal decomposition of nitrocellulose propellants has been introduced in Paragraph 36-2 under the subject of stabilizer. Thermal stability of plastic monopropellants is measured by the 134.5°C heat test[14] for single-base propellants, by the 120°C heat test[14] for double-base propellants, and by the Taliani test[11] for the larger grains used in rockets and gas generators. In addition a surveillance test[14] at 150°F (65.5°C) is used to indicate the useful life of propellants. These tests are all run at elevated temperatures in order to get an end point, and are subject to the objection that the temperature coefficients of the decomposition reactions are not precisely known. In the 134.5°C heat test a life of 45 minutes is required. The 65.5°C surveillance life ranges from about 1 year for a propellant containing 40 percent nitroglycerin to about 3 years for a plasticized single-base propellant. A sample of 40 percent nitroglycerin sporting propellant stored under water since 1899 is still stable and reproduces its original ballistics.[11]

The development of supersonic aircraft carrying munitions and propellant-actuated devices has focused attention on the life of plastic monopro-

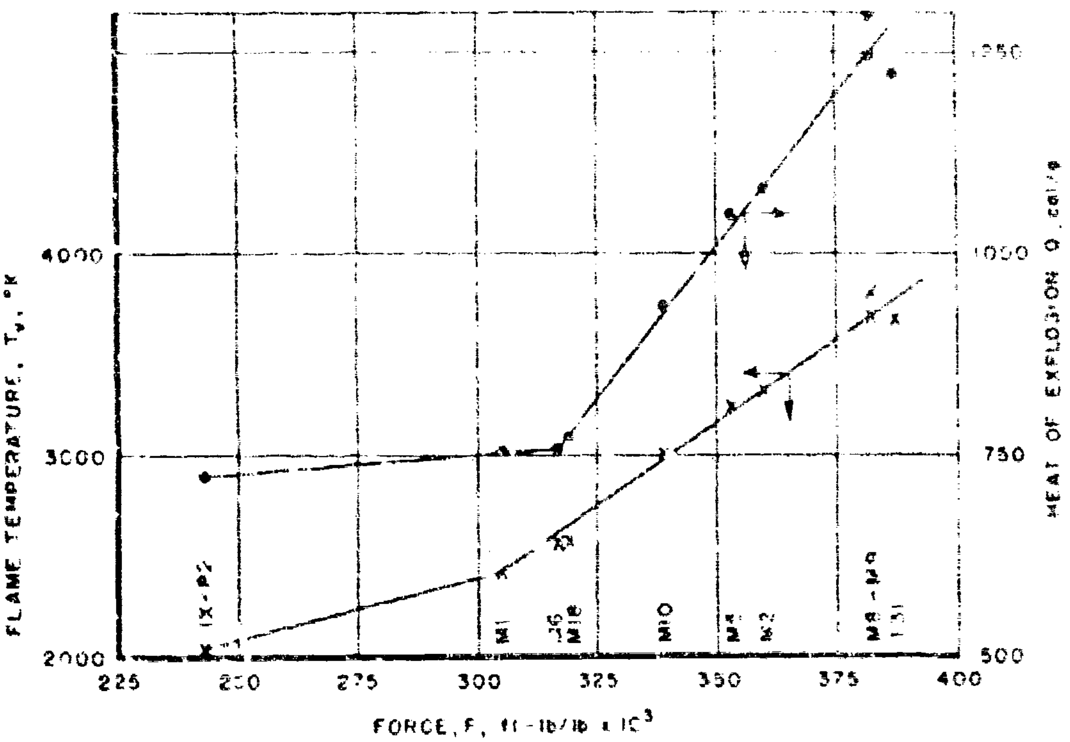



*Figure 29. Relationships among $T_v$, F, and Q for Gun Propellants*

pellants at elevated temperatures. The test for this, known as the autoignition test,[14] is comparatively new, and not many data are available. Values of 280°F for 1 hour and 250°F for 8 hours are typical of propellants containing 40 percent nitroglycerin.

**40. Uses.** Plastic monopropellants have been used in all types of engines, including guns, rocket motors, and gas generators.

**40-1. Gun propellants.** With the exception of antiques, and some signalling guns as well as moving picture and television weapons where the smoke puff is at least as important as any other effect, all guns use propellants based on nitrocellulose. Figure 29 shows the relationships among flame temperature, $T_v$, force, F, and heat of explosion, Q, of selected gun propellants from SPIA/M2 data sheets. From these data it is apparent that there is no systematic ballistic difference between single- and double-base propellants at the same force level, and indeed the force and flame temperature can be predicted reasonably from the calorific value. The accuracy of such prediction approaches that of the Hirschfelder-Sherman calculation (Paragraph 7-6). If more precision is needed, the exact calculation (Paragraph 7-5) should be performed. Experimental calorimetry becomes unreliable at values of Q somewhat below 800 cal/g, due to failure to attain chemical equilibrium at the low resulting temperature in the calorimetric bomb.

There is a difference in physical properties between single- and double-base propellants at the same force level, double-base being softer because of lower polymer content. In the United States nitrocellulose concentrations of gun propellants have been held to a minimum of about 1.8 g/cc except for thin-webbed ignition or trench mortar propellants. This has necessarily led to residual solvent, particularly in propellants of large web. That this high polymer content is not really required for functioning in guns is witnessed by the fact that gun propellants with polymer concentra-

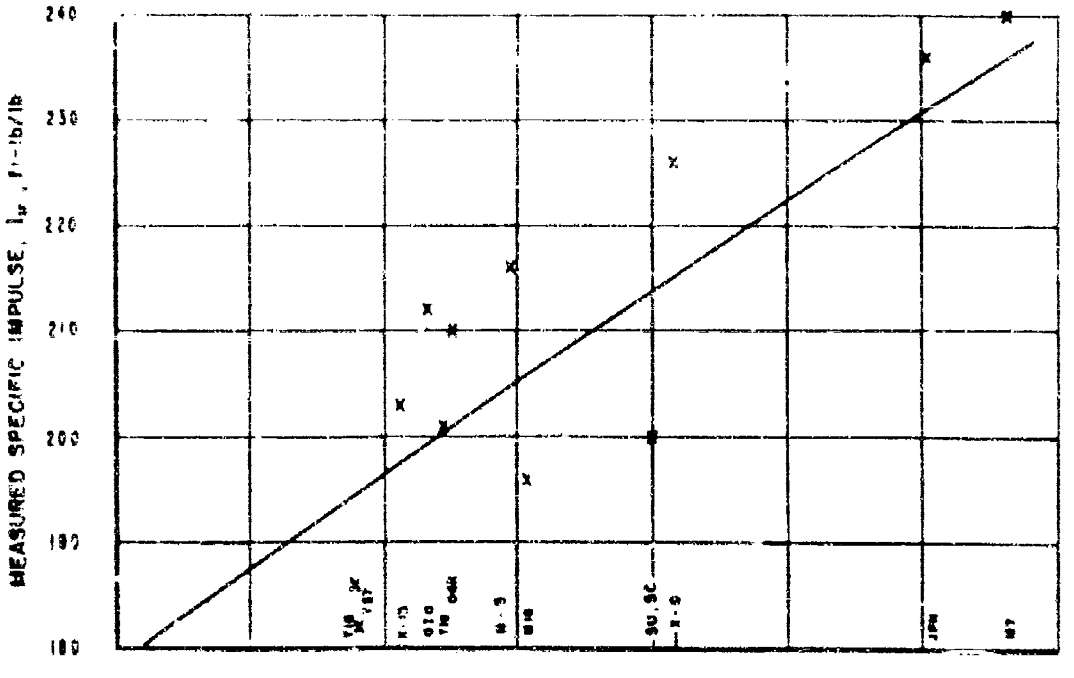



*Figure 30. Specific Impulse of Double-Base Rocket Propellants as a Function of $T_v$*

tion below 0.8 g/cc have long been used in guns abroad. British Cordite S.U. and S.C., is an example of such a propellant. Residual solvent can be dried out of large web propellants with polymer concentration as high as 1.1 g/cc,[11] and propellants with polymer concentration below 0.9 g/cc can be manufactured without volatile solvent.

**40-1.1. Propellants for cannon.** Barrel life and secondary flash are factors in the selection of propellants for cannon. Probably the most widely used cannon propellant in the United States military services is M6. Hotter propellants are used when higher muzzle energy is required than is delivered by M6. Cooler propellants are used for guns in which M6 exhibits muzzle flash or unacceptable barrel erosion.

**40-1.2. Propellants for small arms.** For many years IMR propellant was the standard propellant for small arms. Limited barrel life in high firing rate machine guns has now shown that the flame temperature, 2835°K, of IMR is too high. Cooler propellants such as M18, $T_v = 2577$°K, are now preferred. A recent study[14] has shown that other propellants of the same $T_v$ as M18 will yield comparable barrel life.

**40-1.3. Propellants for mortars.** High force has been the design goal of mortar propellants. Barrel erosion appears to be unimportant and flash can be tolerated. Flash can be eliminated by using a cooler propellant, but at the cost of increased charge weight.[11]

**40-2. Rocket and gas generator propellants.** Propellants for rockets and gas generators have usually considerably greater web than gun propellants have. For this reason the polymer concentration must be kept low in order to permit removal of volatile solvent or manufacture without volatile solvent. In Figure 30 are shown the measured spe-

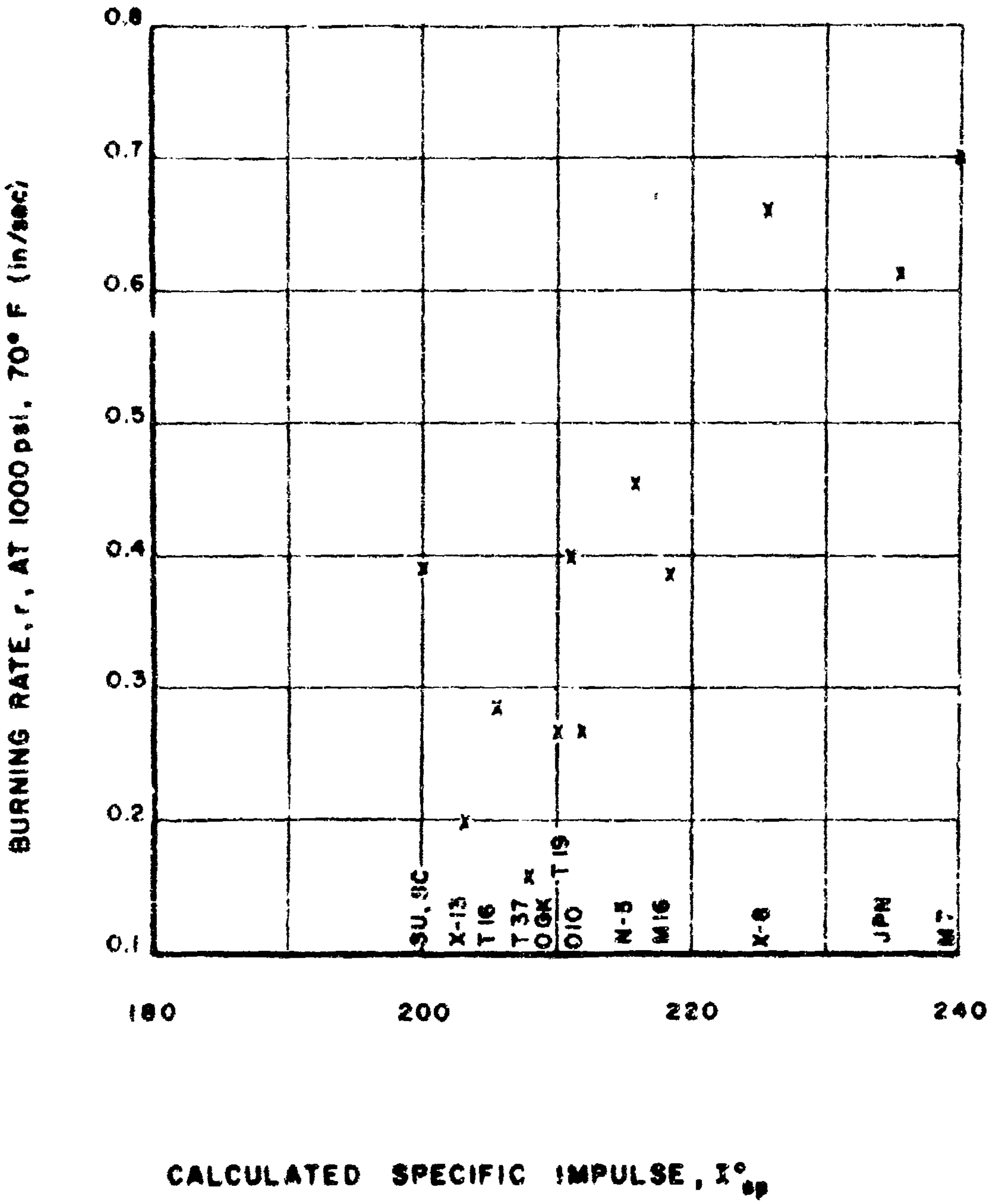



*Figure 31. Burning Rates of Double-Base Rocket and Gas Generator Propellants*

cific impulses of a number of double-base rocket propellants as a function of flame temperature, $T_v$, taken from selected SPIA/M2 data sheets. The significance of the line shown is merely that the points above the line are all high because they were either measured at higher than standard pressure or calculated, while those below the line were measured at lower than standard pressure or with insufficient expansion and should be corrected upward. These data, representing for the most part propellants in service use, were reported before the adoption of the standard practice of correcting measured specific impulses to the standard conditions described in Paragraph 8-4.

Burning rates of double-base rocket and gas generator propellants at 1000 psi, 70°F as a function of calculated specific impulse are shown in Figure 31.

**40-2.1. Propellants for rockets.** Design specifications for rockets have usually required propellant burning rates between 0.25 and 0.5 inches per second in suitable geometries. For short range applications, short burning times and high accelerations may be more important than high burnout velocity, and propellants with higher burning rate than 0.5 are used. With heavy payloads, specific impulse is frequently sacrificed to take advantage of lower flame temperature and the associated ability to use cheaper materials in the inert parts. Plastic monopropellants in service use include:

*M7* is used in the shoulder-fired rockets commonly known as bazookas. High burning rate is attained by using potassium perchlorate as a constituent in order to satisfy the requirement that burning be complete before the rocket leaves the launching tube.

*JPN* was widely used during World War II, notably in the 5.0-inch HVAR.

*X-8* is a more recent high-rate propellant less sensitive than JPN to ballistics changes with changing temperature and pressure.

*M16* is used in a booster for launching small target drone aircraft.

*N-5* is used in the 2.75-inch FFAR "Mighty Mouse."

*OIO* is used in the Honest John rocket and in the booster (first stage) motors for the Nike Ajax and Hercules, Terrier, and Talos missiles.

*OGK* is used in the Terrier sustainer motor.

*T16* is used in a line charge projector.

**40-2.2. Propellants for gas generators.** As contrasted with rocket motors, gas generators usually require smaller mass flow of propellant gas for longer times, therefore lower burning rates. The difference is qualitative, and for specialized applications a rocket motor may be best fitted with a gas generator-type propellant and *vice versa*. Other requirements for gas generator use may be cool flame temperature or high performance, depending on the application. Typical of double-base gas generator propellant compositions is *X-13*, used in the Sidewinder gas generator.

## REFERENCES


1. MIL-STD-444, *Military Standard, Nomenclature and Definitions in the Ammunition Area* (6 February 1959).
2. T. L. Davis, *The Chemistry of Powder and Explosives*. Vol. II, p. 292, John Wiley & Sons, Inc., New York, 1943.
3. A. Nobel, British Patents 1471/1888, 9361/1889. (See also T. L. Davis, *loc. cit.*, pp. 293-4.)
4. JAN-N-244 *Nitrocellulose (For Use in Explosives)* (31 July 1945) with *Amendment-1* (27 December 1945).
5. E. C. Worden, *Technology of Cellulose Esters*, Vol. I, Part 3, *Nitrocellulose—Theory and Practice*, p. 1750, D. Van Nostrand Company, New York, New York, 1921.
6. H. Staudinger, *Die hochmolekularen organischen Verbindungen*, p. 34, Julius Springer, Berlin, Germany, 1932. (Summarized in M. L. Huggins, *Physical Properties of Cellulose and Its Derivatives in Solution. Section E. Theory of the Viscosity of Dilute Solution of Long-Chain Compounds*, in E. Ott, *et al.* (editors), *Cellulose and Cellulose Derivatives*, 2nd edition, Part III, p. 1194, Interscience Publishers, Inc., New York, New York, 1955.)
7. J. Barsha, *Derivatives of Cellulose. Section B. Inorganic Esters*, in E. Ott, *et al.* (editors), *Cellulose and Cellulose Derivatives*, 2nd edition, Part II, p. 742, Interscience Publishers, Inc., New York, New York, 1954.
8. L. Pauling, *Quantitative Studies of the Stabilization of Smokeless Powders. Chemical Changes of Stabilizers in Double-Base Powders During Storage at Elevated Temperatures*, California Institute of Technology, CIT-PR-3, 1 July 1946, Contract NOrd 9652, CONFIDENTIAL (SPIA Abstract No. 1388)

9. California Institute of Technology, *Stabilization of Smokeless Powder by Ethyl Centralite. I. Transformation Products of Ethyl Centralite in Double Base Powder*, OSRD 5967, October 1945 (SPIA Abstract No 0276; see also Nos. 2398-2412).

10. E. Whitworth and C. H. Rigby (to Imperial Chemical Industries Limited), Canadian Patent 541,559 (1957).

11. J. H. Godsey, *Cast Propellants with Cross-Linked Nitrocellulose*, Allegany Ballistics Laboratory, Hercules Powder Company, ABL/MPR 44 (p. 6 of Monthly Progress Report 44), 1 June 1955, Contract NOrd 10431, CONFIDENTIAL; *Properties of Cross-Linked Propellants*, ABL/MPR 48 (p. 6 of Monthly Progress Report 48), 1 October 1955, Contract NOrd 10431, CONFIDENTIAL (SPIA Abstract No 15565).

12. W. deC. Crater, "The Vapor Pressures of Glycerol Trinitrate and Certain Glycol Dinitrates," *Ind. Eng. Chem.*, 21, 674 (1929).

13. F. M. Ernsberger, J. G. Wylie and L. Olsen, *Physical Instability of Double-Base Propellants. Part I. Vapor Pressure of Ballistite*, Naval Ordnance Test Station, NOTS 240, NAVORD 1184, 29 September 1949 (SPIA Abstract No. 10386).

14. MIL-STD-286, *Propellants. Sampling, Inspection and Testing, Method 404.1.1—Heat Tests (120° and 134.5°C)* (28 June 1956).

15. MIL-STD-286, *Propellants. Sampling, Inspection and Testing, Method 406.1 (T) Taliani Test* (28 June 1956).

16. F. A. Zihlman, *et al.*, *A Critical Evaluation of Known Methods of Stability Testing*, Naval Powder Factory, Indian Head, Technical Report 23, 3 March 1950, CONFIDENTIAL (SPIA Abstract 10299). F. A. Warren, E. L. Anderson and P. M. Ku, *Evaluation of Solid Propellant Properties Part I—A Survey of Current Methods*, Southwest Research Institute, Report RS 287, 31 January 1959, CONFIDENTIAL (SPIA Abstract No. 19191).

17. Hercules Powder Company, unpublished data.

18. MIL-D-26389 (USAF), *Data Presentation Requirements for Determining Safe Handling, Storage and Shipping Procedures. Aeronautical Rocket Motors and Components* (14 November 1958), MIL-C-25641 (USAF), *Cartridge, Gas Generating, Solid Propellant, Aircraft and Missile, Secondary Power Systems, General Specification For* (28 January 1958).

19. A. W. Baum, *Effect of Variations on Total Volatile Content of 7-8 Inch Stick Powder*, Radford Ordnance Works, Hercules Powder Company, RD 1, 19 June 1944 (SPIA Abstract No 0726); *The Modified M-2 Formulation*, RD 12, 12 February 1945 (SPIA Abstract No 1149).

20. *Research and Development of an Improved Small Arms Propellant, Non-Erosive Extruded Double Base Propellant for Caliber .50*, Hercules Powder Company, Kenvil, New Jersey, Final Report of 31 December 1956, Contract DA-36-034-ORD-1393RD (SPIA Abstract No. 17,002).

21. A. M. Ball (to Hercules Powder Company), U. S. Patent 2,577,298 (1951).

# COMPOSITES COMPRISING CRYSTALLINE MONOPROPELLANTS IN PLASTIC MONOPROPELLANT BINDERS

**41. General.** As was shown in Chapter 5, crystalline monopropellants have limited feasibility as propellants, the limitations being due to the difficulty in getting crystals of the size and shape required for many applications, and to the fact that pure chemicals do not yield a continuous spectrum of thermochemical properties. The force or characteristic velocity of a given crystalline monopropellant, while within the range of desirable values for propellants, is seldom optimum for a specific use. These deficiencies are overcome by accepting an available particle size distribution or grist of the crystalline monopropellant, and dispersing it in a plastic monopropellant. Such composites partake largely of the properties of the crystalline component. The function of the plastic is to act as a necessary diluent to permit attaining the desired geometry with acceptable physical properties, and as a modifier to vary the thermochemical properties.

The field of gun propellants is the only field in which two-monopropellant-phase composites have been widely adopted. Only those composites using nitroguanidine have been standardized by the United States military forces, although RDX composites[1] have been demonstrated feasible for gun and rocket propellants and ammonium nitrate composites[2] have been studied as rocket or gas generator propellants.

Containing three explosive ingredients; *e.g.*, nitrocellulose, nitroglycerin and nitroguanidine, these propellants are commonly known as "triple-base."

**42. Formulations.** As with any composite, each phase must be separately formulated, as well as the total composition. The important consideration of the crystalline phase is grist, or particle size and size distribution. In general the finest possible grist is preferred. In the case of nitroguanidine propellants formulated with ethyl centralite, the centralite forms a crystalline compound with the nitroguanidine,[3] which indicates that the centralite will not be in the binder phase. This might be less advantageous than to have the stabilizer in the binder phase, although such propellants have not proven unstable.

The binder will have to withstand a different set of mechanical forces during drying and temperature cycling from those encountered in a plastic monopropellant, due to the presence of the crystalline material. The binders are usually well plasticized, containing roughly equal weights of nitrocellulose and oxidant plasticizer. If stabilizers other than ethyl centralite are used they will be found in the binder phase. Potassium salts, such as the sulfate or cryolite, may be added to inhibit flash.

**43. Ballistic characteristics.** Due to the low molecular weight of the combustion products of nitroguanidine, nitroguanidine propellants at the same level of force will have lower flame temperatures $T_v$ than single-phase propellants. At the same level of flame temperature, nitroguanidine system propellants will have greater force than single-phase propellants. Advantage has been taken of this situation in the development of two separate series of propellants, for reduction of secondary muzzle flash and for increase of force.

**43-1. Nonflashing nitroguanidine propellants.** Secondary muzzle flash is due to the combustion in air of the gases issuing from the muzzle of the gun after projectile exit. These gases always contain combustibles such as $H_2$ and CO. Among the factors controlling their ignition are temperature and composition at the muzzle, lower temperatures and lower contents of combustibles decreasing the tendency to produce muzzle flash. The presence of small amounts of potassium salts also tends to diminish flash by a negative catalytic effect on the reactions of $H_2$ and CO with atmospheric oxygen.

Nonflashing nitroguanidine propellants were experimented with in this country in the 1920's, but present standard compositions are based on the British Cordite N, disclosed to us during World War II. The American M15A1 has about the same combustion temperature as the monopropel-

**TABLE 9. NONFLASHING PROPELLANTS**

| | M15A1 | T34 | Cordite N | M6 |
|---|---|---|---|---|
| Density, $\rho$ | 1.66 | 1.65 | 1.64 | 1.60 |
| Force, $F$, ft-lb/lb | 332,000 | 335,000 | 319,000 | 317,000 |
| Flame temperature, $T_v$, °K | 2546 | 2608 | 2441 | 2570 |
| Gas molecular weight, $M$ | 21.3 | 21.7 | 21.2 | 22.6 |

lant M6 and correspondingly greater force. The reduction in flash compared with M6 is therefore due largely to the reduction of the combustible fraction of the product gas. The corresponding German nitroguanidine propellant[4] is considerably cooler, employing diethylene glycol dinitrate instead of nitroglycerin as the plasticizer. Since M15A1 has greater force than M6, a somewhat cooler propellant could still be used effectively in guns chambered for M6 propellant. Three nonflashing nitroguanidine propellants are shown in comparison with M6 in Table 9.

Two avenues are open for formulating cooler nitroguanidine propellants. One is to increase the fraction of nitroguanidine in the propellant at the cost of a decreased binder fraction. This may be limited by a corresponding adverse effect on physical properties. The other course is to decrease the calorific value of the binder phase by substituting a cooler plasticizer for that presently used. Such a cooler plasticizer may be diethylene glycol dinitrate as in the German formulation or a cooler mixture of nitroglycerin and fuel-type plasticizer.

**43-2. High force nitroguanidine propellants.** For certain field uses it is desired to give a projectile the highest possible muzzle velocity. To a first approximation the muzzle velocity should be proportional to the force of the propellant. The limitation on attainment of muzzle velocity by increasing propellant force is that gun erosion is a function of combustion temperature and increases rapidly above some temperature level. An economic balance between muzzle velocity and gun wear for weapons of 3-inch or larger bore indicates that the cost in barrel life is too high to pay for added muzzle velocity if the gun chamber gas temperature is higher than about 3000°K. For rapid-fire weapons the economic chamber gas temperature is considerably lower than 3000°K.

As shown in Table 10, propellants containing nitroguanidine are considerably better than propellants without nitroguanidine in the attainment of force within a permitted maximum gas temperature. The propellants M17 and T36 contain nitroguanidine, M10 and M2 do not contain it.

High force nitroguanidine propellants were apparently originally developed in the United States.[5] Further development of this type propellant depends on the ability to increase the fraction of nitroguanidine in the propellant, presently limited by physical properties.

**44. Physical properties.** The physical properties of these composites differ considerably from those of the plastic monopropellants. They are opaque, chalky white in color unless glazed, and exhibit generally lower physical strength. As may be seen by comparison with the fuel binder composites, Chapter 9, the decrease in physical properties is not necessarily due to the volume percent of filler. It is more probably due to the shape of the nitroguanidine crystals, which are needles.

**TABLE 10. HIGH FORCE PROPELLANTS**

| | M17 | T36 | M10 | M2 |
|---|---|---|---|---|
| Density, $\rho$ | 1.67 | 1.66 | 1.67 | 1.65 |
| Force, $F$, ft-lb/lb | 364,000 | 364,500 | 339,000 | 360,000 |
| Flame temperature, $T_v$, °K | 3017 | 3040 | 3080 | 3319 |
| Gas molecular weight, $M$ | 23.1 | 23.2 | 24.6 | 25.6 |

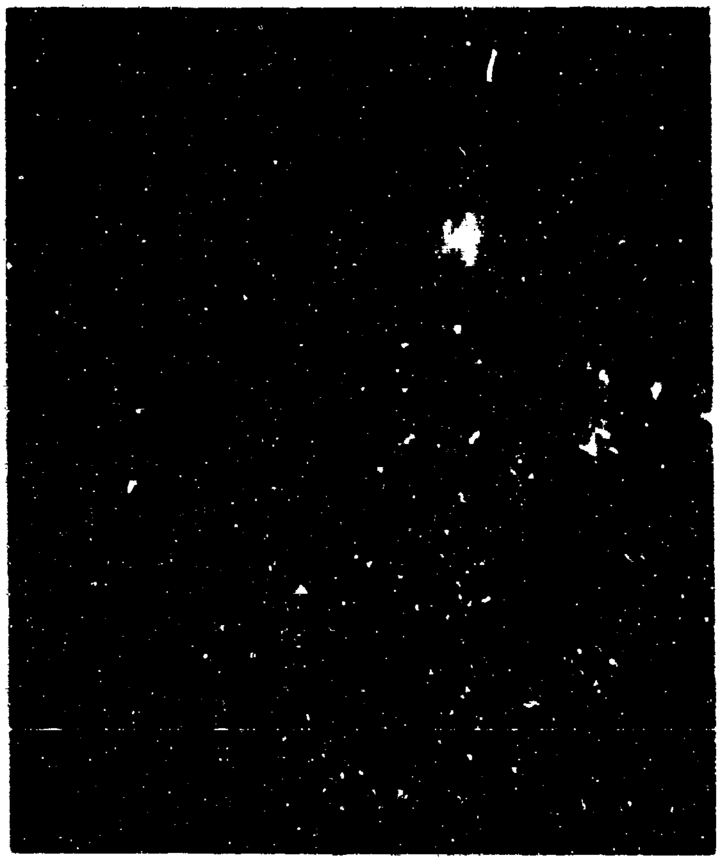


Figure 32. Cross Section of Triple-Base Gun Propellant Grain. Crossed Nicols. 32× Magnification

With an optimum crystal shape, a volume fraction of 70 percent or a weight fraction of a little more than 70 percent should be feasible without serious degradation of physical properties or manufacturability. As the nitroguanidine-filled propellants are customarily manufactured by solvent extrusion, nonparallel orientation of needles may be expected to cause bridging and to interfere with normal shrinkage during drying. The resulting residual stresses in the binder phase may explain the physical property deficiencies of these propellants. Nitroguanidine has been prepared[6] with a more favorable crystal habit which improved the manufacturability of existing formulations. It is interesting to note that in the early American studies, experimental propellants containing up to 80 percent nitroguanidine were fired in artillery pieces at Aberdeen Proving Ground.[7]

**45. Thermal properties.** The crystalline monopropellants are generally more stable than plastic monopropellants, becoming unstable only near their melting points. The aging of composites containing them is therefore due mainly to the binder, which is a plastic monopropellant. Stability tests dependent on measuring the evolution of oxides of nitrogen from a fixed weight of propellant indicate better stability for these composites than for ordinary nitrocellulose monopropellants. This indicated increased stability may not be real. Autoignition temperatures for various lengths of exposure may be expected to be higher than for the binders alone, due to this same binder dilution, provided that the melting points of the crystalline monopropellants are not too closely approached in the test.

**46. Manufacturing process.** The manufacturing process used for the nitroguanidine propellants in the United States has been uniformly solvent extrusion. The nitrocellulose concentration in the binder phase is low enough to suggest that a solventless procedure could be used. The amount of solvent used is quite low and the propellant during extrusion is very soft so that it is sometimes necessary to dry the extruded strand partially before cutting, in order not to deform the cross section at the cut. Removal of solvent from the composites is much more rapid, due possibly to diffusion of solvent within the grain along the crystal-plastic interfaces. This does not mean that drying times should be reduced. In order to make a good quality grain it is necessary to use lower drying temperatures and times comparable to those for conventional smokeless powders in order to avoid steep solvent gradients and resulting distortion and cracking.

A photomicrograph of a cross section of a nitroguanidine propellant grain[8] is shown in Figure 32.

## REFERENCES


1. E. J. Zauder, *Development of Improved Propellants*, Picatinny Arsenal, Technical Report No. 1923, 5 June 1953, Ord Proj TA1-3601, CONFIDENTIAL (SPIA Abstract No. 13,287).
2. Redstone Arsenal, *Quarterly Report [Solid Propellant and Igniter Development]*, Rept No. 3M7N24 (Oct.-Dec. 1957), 1 January 1958, CONFIDENTIAL (SPIA Abstract No. 18,085).
3. J. N. Pring (by mesne assignments to Imperial Chemical Industries, Ltd.), U. S. Patent 2,557,463 (1951).
4. R. A. Cooley, J. Waser and K. Mislow, *German Powder Development Between 1918 and 1942* (A Translation of the German Book *Die Geschutzladung* by U. Gallwitz), California Institute of Technology, 15 September 1945, NAVORD 43-45 (SPIA Abstract No. 3597).
5. A. W. Baum, J. G. Filicky and R. Winer, *Production of Nitroguanidine Propellants in Several Cannon Powder Granulations*, Radford Ordnance Works, Hercules Powder Company, Radford RD 8, 11 June 1945 (SPIA Abstract No. 1093).
6. V. Milanc, R. Evans, S. Skolnik and F. C. Thames, *Preparation of High-Bulk-Density Nitroguanidine*, Naval Powder Factory, Indian Head, Technical Report No. 66, NAVORD 3037, 14 December 1953, CONFIDENTIAL (SPIA Abstract No. 14009); J. Cohen and R. A. Henry, *A New Method for the Preparation of Nitroguanidine with High Bulk Density*, Naval Ordnance Test Station, NOTS 182, NAVORD 1062, 31 December 1948, CONFIDENTIAL (SPIA Abstract No. 3640).
7. W. F. Jackson (E. I. du Pont de Nemours & Company, Inc.), private communication.
8. C. W. Hock, *Microscopical Examination of Propellants Containing Nitroguanidine*, Hercules Powder Company, RI 3112, 25 August 1954, CONFIDENTIAL (SPIA Abstract No. 15,011).

CHAPTER 8

# MANUFACTURING PROCESSES FOR SMOKELESS POWDER

**47. General.** No one manufacturing process will produce the whole spectrum of plastic monopropellants. As is the case with commercial inert thermoplastics, a wide variety of manufacturing processes has been developed to make different propellant grains. Nearly every fabrication process used by the commercial plastics industry has been used for propellants; in fact some processes used for propellants have not yet been used by the plastics industry. For any given process the difference between use for propellants and use for inert plastics is that the consequences of a fire during processing propellants are severe and extraordinary precautions must be taken to prevent fires and to control them if they do occur. Aside from details in the design of equipment, the most striking feature of propellant manufacturing processes has been the requirement to handle the material in process in batches of finite size, separated from other operations by distances such that the loss of a charge and its containing equipment will not entail propagation to neighboring operations. This requirement has, until recently, discouraged the development of continuous processes, and is still a problem to people currently working on continuous processes.

Important processes used for nitrocellulose system propellants are solvent extrusion, solvent emulsion, rolling of sheets, solventless extrusion, the cast double-base process, and slurry casting. Since nitrocellulose is commonly manufactured also at the propellant facility, its manufacture too is described here.

**48. Nitrocellulose.** The process installed in the ordnance works, and also widely used commercially, is the Du Pont mechanical dipping process. Continuous processes have been installed by one or more commercial producers but the details have not been published. It is believed that these processes are engineering adaptations of the mechanical dipping process. The flowsheet of the Du Pont process is shown in Figure 33.

Cellulose in the form of cotton linters is dried on a moving belt in a tunnel drier to a moisture content well below 1 percent. Alternatively, sheeted wood cellulose' may be dried in the drier and then shredded. The dried cellulose and mixed nitrating acid are introduced concurrently into the nitrator (Figure 34) where the cellulose is converted to nitrocellulose. At the end of the nitration cycle, about 25 to 30 minutes, the nitrator is discharged by gravity to the centrifugal wringer (Figure 35) where the spent acid is removed. Part of the spent acid is sent back to the process for reuse after butting up with fresh acid. The remainder is reworked to remove from the system the water picked up from the nitration. The wrung nitrocellulose, wet with spent acid, is quickly drowned and transferred to the boiling tubs (Figure 36). There, for a period of several hours' depending on the degree of nitration of the nitrocellulose, it is boiled in the weak acid resulting from the dilution of the spent acid not removed in the wringing operation. This boiling treatment serves to hydrolyze any sulfate ester formed during the nitration. The nitrocellulose is next pulped, *e.g.*, in one or

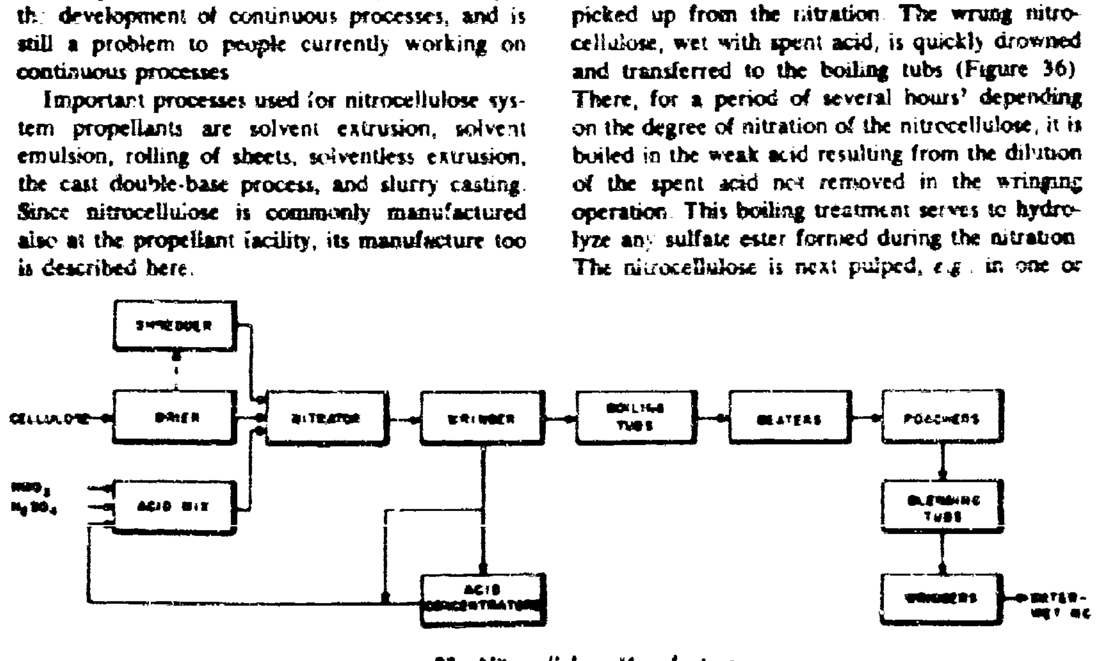
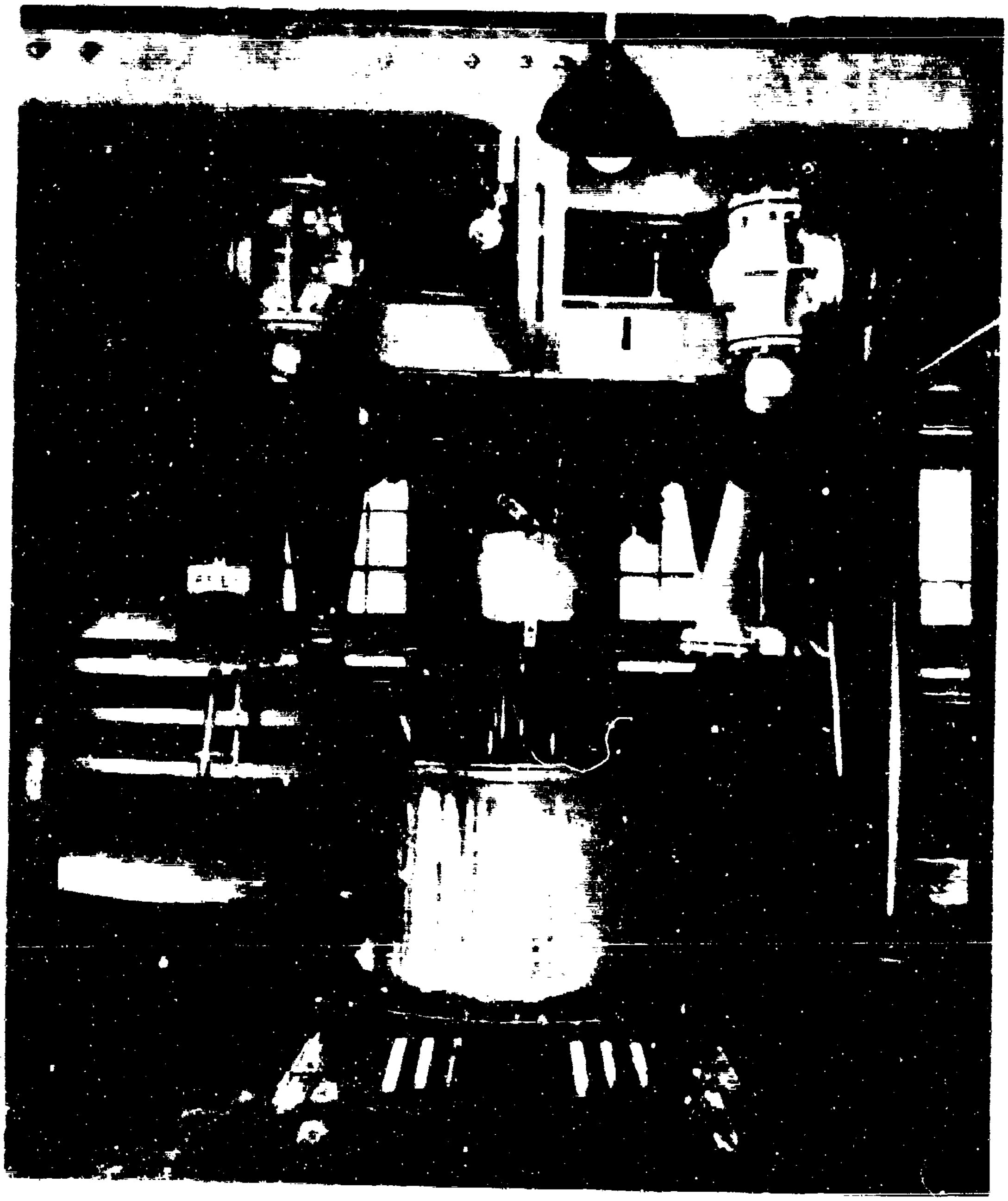
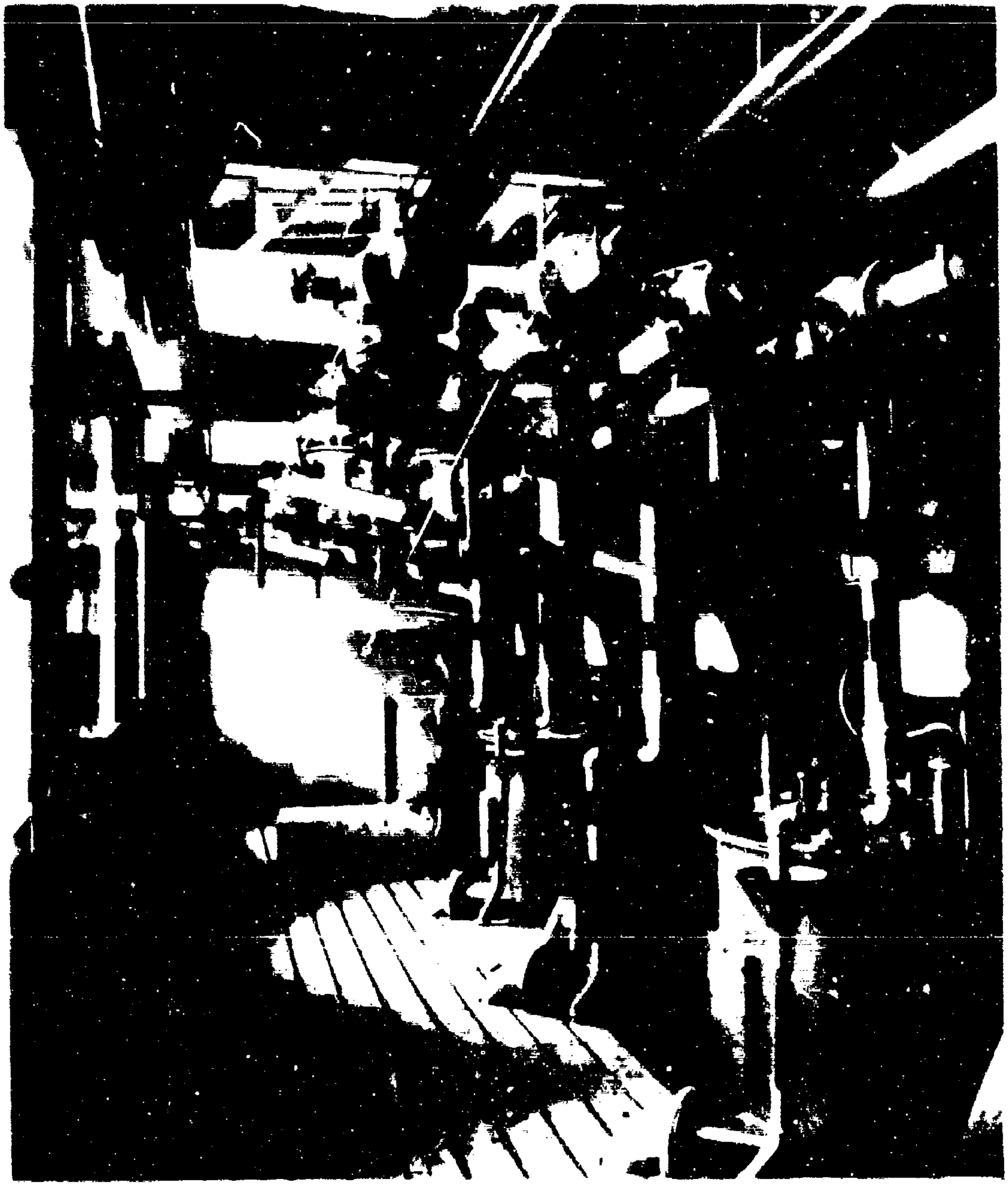



*Figure 33. Nitrocellulose Manufacture*



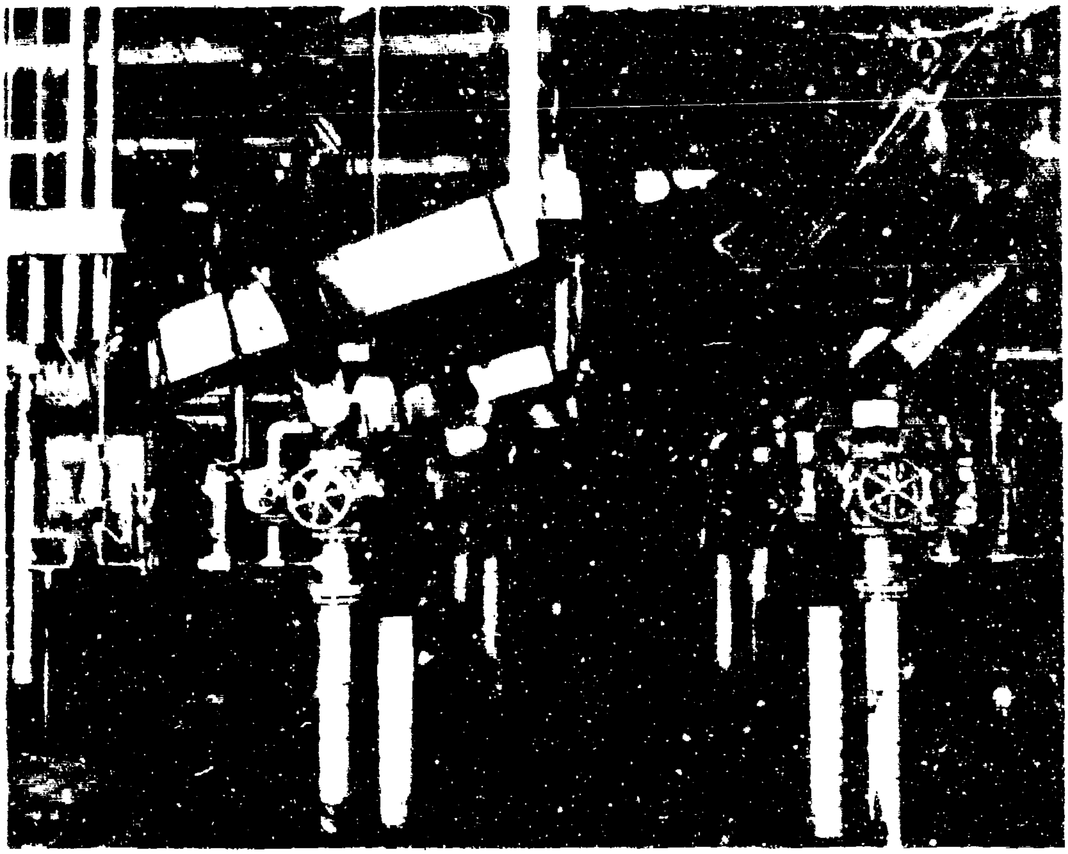
U. S. Army Photograph Radford Arsenal

Figure 34. Cellulose Nitrator



U. S. Army Photograph Radford Arsenal

Figure 35. Nitrocellulose Wringers



U. S. Army Photograph Radford Arsenal

*Figure 36 Nitrocellulose Boiling Tubs*

more Jordan engines similar to those used in the papermaking industry, and finally "poached" or boiled in a slightly alkaline solution to neutralize and remove any residual acid. Thorough washing completes the purification cycle. In order to accumulate lots of sufficient size, or to produce a mixed nitration grade such as military blend, poacher batches are blended in blending tubs. The finished nitrocellulose is centrifugally wrung to a water content of about 25 to 30 percent for transfer to propellant operations.

**48-1. Nitrogen content.** The degree of nitration is controlled by the equilibrium between the nitrocellulose and the spent acid.[1] As the acid penetrates the cellulose particle the surface is first nitrated to equilibrium with the fresh acid. The acid, becoming diluted by the residual moisture in the cellulose and also by the by-product water of the nitration reaction penetrates on through the particle, leaving behind nitrocellulose of slightly decreasing degree of substitution. The first nitration reaction is quite rapid, but subsequent equilibration in acid of different composition is much slower and is not complete by the end of the nitration operation. For this reason, careful fractionation of nitrocellulose reveals a spectrum of nitrogen contents in the nitrocellulose.

Cotton linters fibers which have thin cell walls and enough twist to keep them essentially apart in the nitrator produce a nitrocellulose of a narrower substitution spectrum than wood cellulose shreds where regions of compaction are found. The cellulose-acid ratio for wood cellulose is higher than that for cotton, resulting in a greater change of acid strength during the nitration operation. This adds to the width of the nitration spectrum for the wood nitrocellulose. Finally, while cotton cellulose is almost pure polymerized dextran, wood cellulose usually contains an admixture of other sugars such as xylan and mannan. These become nitrated and their nitrates burn like nitrated dextran but they have secondary effects on the physical strength of the polymer and its solution properties. For most purposes wood nitrocellulose is a complete substitute for cotton nitrocellulose.

Transpiration of moist air in the wringer can cause a lowering of the nitrogen level by denitration. A slight hydrolysis occurs also in the boiling operation. Both of these effects are minor in a well-conducted operation.

**48-2. Solubility.** At 12.6 percent nitrogen or 12.2 percent nitrogen nitrocellulose is miscible in all proportions with ether-alcohol. Since the nitrogen content measured is the average across a spectrum, a poorly nitrated cellulose with average nitrogen content in the soluble range may contain fractions either more or less highly substituted than are completely miscible. In such cases this would be detected by a residue in the solubility determination.[1] Guncotton contains a small fraction that is soluble, either by reason of low substitution or low degree of polymerization.

**48-3. Viscosity.** The viscosity of nitrocellulose is determined by the viscosity (degree of polymerization) of the original cellulose and by the reduction of the degree of polymerization incident to the nitrocellulose manufacturing operations. Most of this reduction occurs during the nitration step, where it is dependent on the nitration temperature. Higher nitrating temperatures result in lower viscosity nitrocelluloses.

**48-4. Significance of nitrocellulose properties.** Of the three properties discussed above only the degree of nitration has ballistic significance, affecting the molecular weight and temperature of the combustion products. In order to manufacture a propellant of a specified force, *F*, (or specific impulse) one must either have the proper nitration of the nitrocellulose or compensate for the difference between the prescribed nitrocellulose and the nitrocellulose at hand by adjusting the proportion of oxidant plasticizer and fuel plasticizer. In a volume production operation it is preferable to maintain the nitration degree of the nitrocellulose constant, by control of the nitration operation and by blending, rather than to adjust the formula. The viscosity and solubility have secondary effects in the manufacturing operations in that they affect the amount of solvent (and plasticizer) required to work the propellant. This is particularly true during the solvent extrusion operation wh[illegible] he applied pressure is constant and requires approximately constant plasticity of the green (solvent-wet) propellant. The finished dimensions of the propellant are determined by the solvent content and the die dimensions, so that if the plasticity is controlled by varying solvent content the dimensional control is forfeited. Similarly for solventless extrusions the finished dimensions are controlled by extrusion temperature and die size, and if temperatures are changed to control plasticity during extrusion, control of dimensions is less good. For these reasons nitrocellulose specifications call for control of solubility and viscosity as well as control of degree of nitration.

**49. Solvent extrusion.** In Figure 26 (page 45), the line *SS* divides the polygon *PABC* into two regions. Below *SS* the physical properties of the system are such that the composition can be worked and formed at tenable temperatures. Above the line *SS* they cannot be so worked. A composition *X* in the upper region can be made only by a process using a volatile solvent which is subsequently removed. A propellant made by a volatile solvent process always contains some residual solvent, and residual solvent is one form of fuel plasticizer. One should first establish a composition *X′* such that the addition of the residual solvent to *X′* will produce *X*. To the composition *X′* is added enough volatile solvent to enable the propellant to be processed. This results in the composition *X″* in the mixer which is well below the line *SS*. Composition *X″* is frequently so far to the left of line *PH* that the mix will not burn without air, and the hazard situation is thereby somewhat diminished. Solvent evaporates during processing and the composition of the material in process creeps back toward *X*. It must not cross the line *SS* until after the last forming operation has been completed. Final drying leaves the material at composition *X*. Note that *X′*, *X*, *X″*, and *F* are collinear.

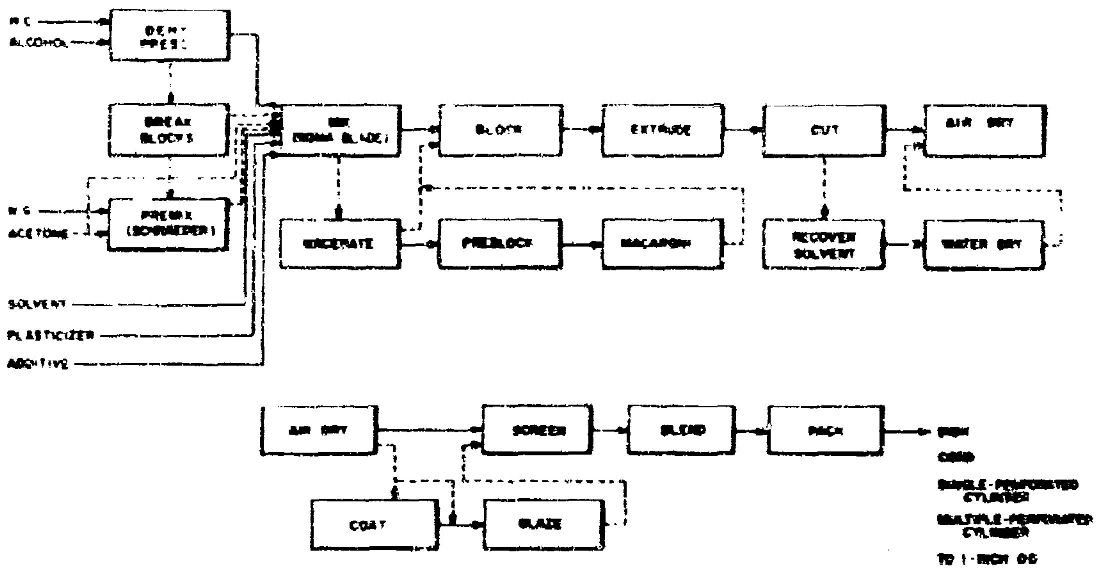



*Figure 37. Solvent Extrusion Process*

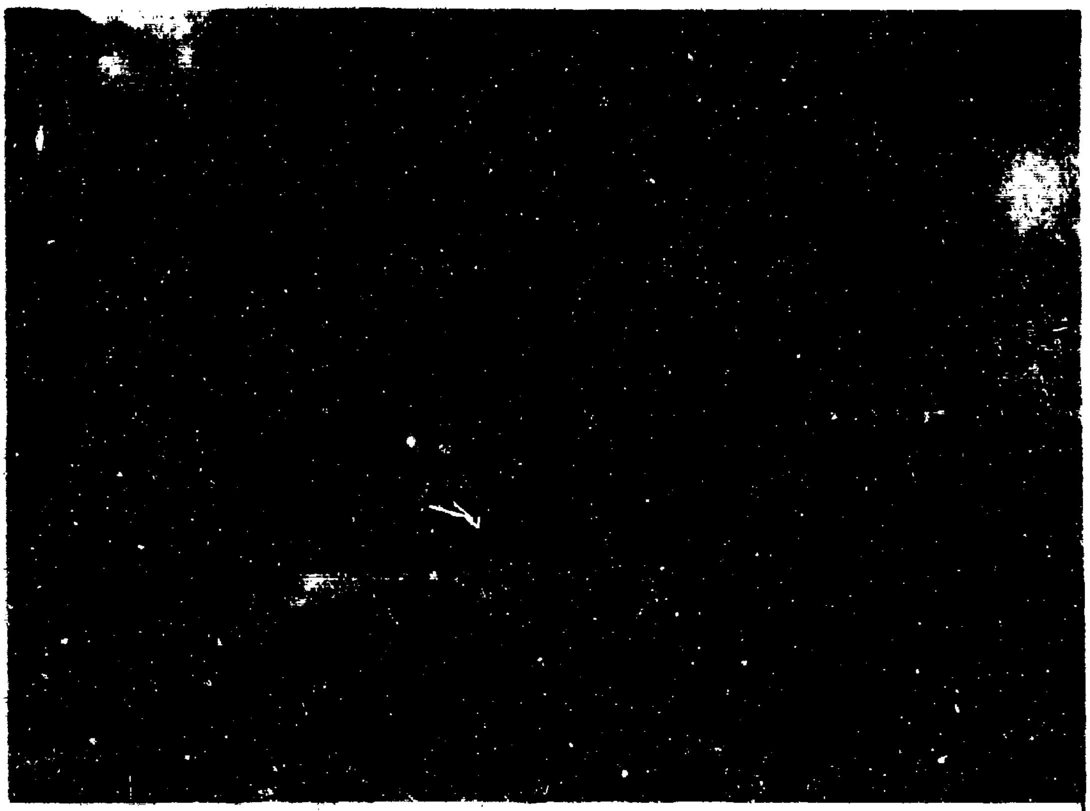
For nitrocelluloses used for propellants in the United States the position of the line *SS* corresponds roughly to a nitrocellulose concentration (weight fraction multiplied by propellant density) in the finished propellant of about 1.0 g/cc. A volatile solvent process must be used for all propellants with a greater nitrocellulose concentration than this. The solvent extrusion process is sometimes used for propellants with lower nitrocellulose concentration in order to reduce the calorific value of the mix. Because the residual solvent content increases with polymer content and with the web, the solvent extrusion process can be used only on grains with fairly thin webs. It is widely used for propellants for guns, including small arms and sporting pieces.

The flow sheet of the solvent extrusion process is shown in Figure 37.

The essential operations of the solvent extrusion process are mixing, forming, removal of solvent, and finishing. To these operations have been added a number of auxiliary operations designed to save operation time and improve the quality of the product. As indicated by the dotted lines, these auxiliary operations are not invariably used.

**49-1. Mixing.** The heart of the mixing operation is the sigma blade mixer, shown in discharge position in Figure 38. To this mixer are added all of the ingredients and solvents used in the particular propellant, and it is the function of the mixer to mix them thoroughly into a single homogeneous plastic phase. The sigma blade mixer is capable of a good mixing job but it has certain disadvantages. The shafts of the sigma blades pass through the end walls of the mixer below the upper surface of the material being mixed. The treatment of the glands through which the shafts pass is different for different types of propellant being processed. For double-base propellant it is customary to remove the packing, leaving a clearance between the shaft and the wall aperture. A small amount of the mix leaks out through this clearance and must be collected and destroyed. It is recognized that a mixer without submerged glands would be preferable.

**49-1.1. Premixing operations.** The ingredients may be added singly or in combinations. If a combined add is made, a premixing operation is required. Thus nitrocellulose is premixed with alcohol by displacing the water, present in the nitrocellulose as received, in a hydraulic press equipped to pass alcohol through the block under pressure. The dehy press has two rams. The basket is first filled with loose, water-wet nitrocellulose. The press is then closed and the nitrocellulose compressed to a "block" to express a portion of



U. S. Army Photograph Radford Arsenal

*Figure 38. Sigma Blade Mixer*

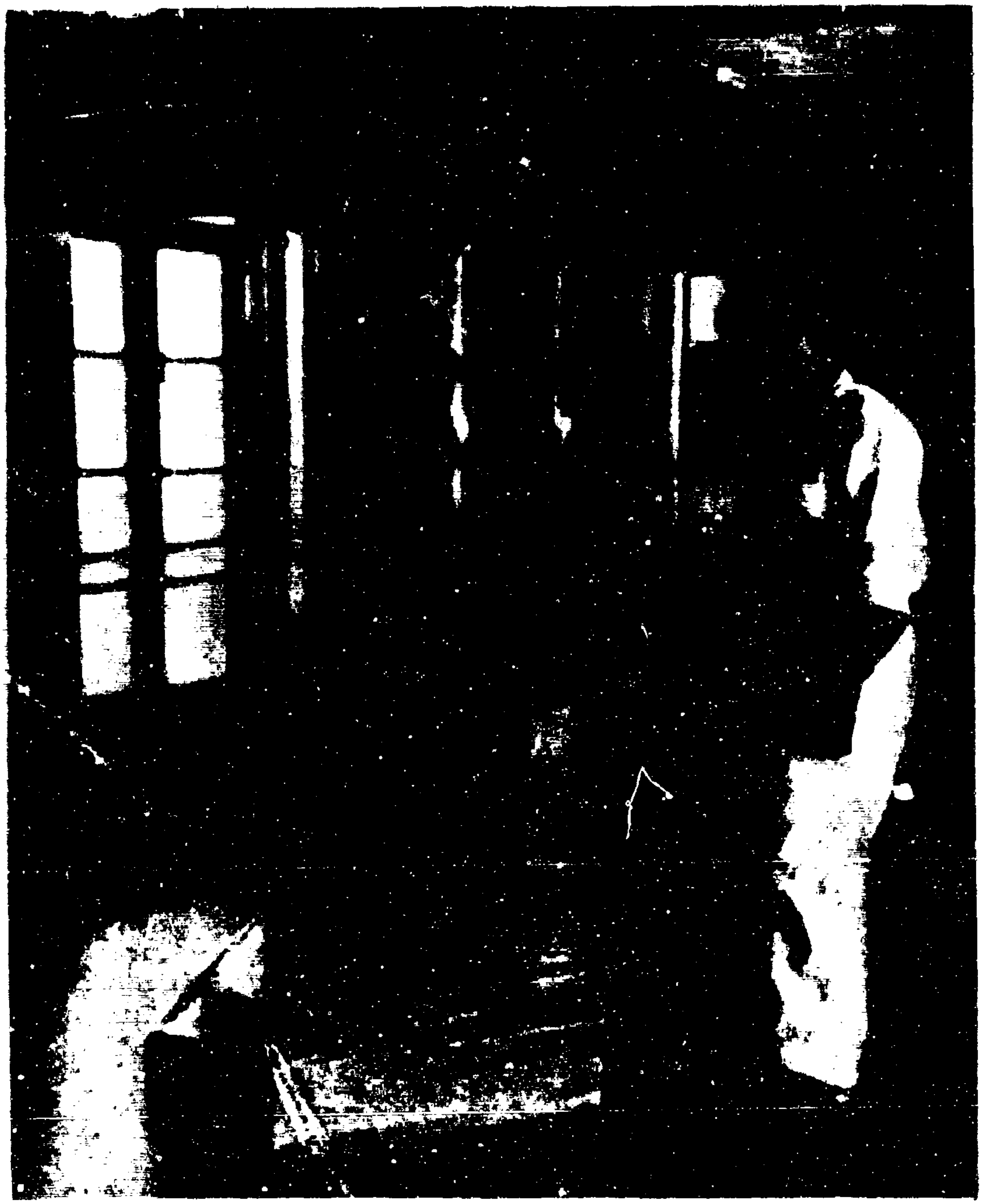
the water. Alcohol is then pumped through the block, displacing the remainder of the water. The dehydrated block is broken, sometimes in a "block breaker" or picking roll, sometimes by hand during the charging of the sigma blade mixer, sometimes by the sigma blade itself during the mixing operation.

Addition of nitroglycerin or other oxidant plasticizer to the dehydrated nitrocellulose is usually, but not always, accomplished in the Schraeder bowl shown in Figure 39. The purpose of this is to avoid the presence of a free nitroglycerin phase in the sigma blade mixer at any time. Nitrocellulose and nitroglycerin are sometimes mixed in water slurry, followed by drying and re-wetting with solvent before mixing in the sigma blade mixer.

Fuel-type plasticizers and solvent-soluble additives may be dissolved in the solvent before adding to the sigma blade mixer

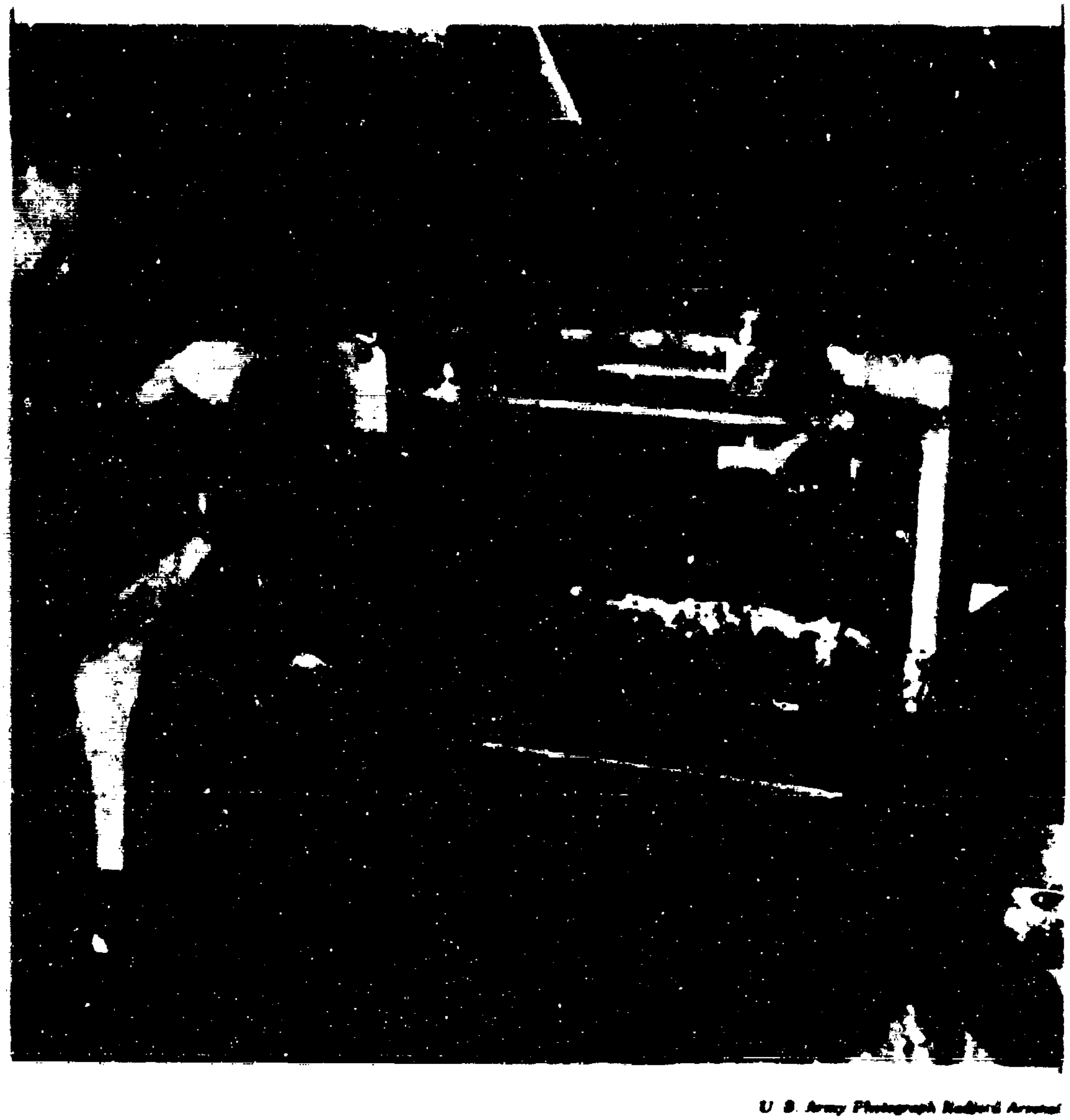
The solvents used in the United States for solvent-extrusion process propellants are usually 3 ether : 1 alcohol by weight for single-base propellants and about 1 acetone : 1 alcohol for double-base. Other solvent systems, including esters, are feasible.

**49-1.2. Post-sigma blade mixing operations.** Post-sigma blade mixing operations are also sometimes employed to shorten the sigma blade mixer cycle and to improve the quality of the mix. The macerator, shown in Figure 40, works the mix on toothed rolls, subjects it to a vigorous tearing action, and reduces the bulk density of the finished sigma blade charge, particularly if the fiber structure has not been completely destroyed at that



U. S. Army Photograph Radford Arsenal

Figure 39. Schroeder Mixer



U. S. Army Photograph Radford Arsenal

*Figure 40. Macerator*

*U. S. Army Photograph Radford Arsenal*

*Figure 41. Macaroni and Blocking Process*

point. The macaroni or screening press works the propellant by flow through screens and dies, subjecting it to shear forces. It serves also to filter out incompletely colloided particles of nitrocellulose remaining after mixing, as well as foreign bodies.

**49-2. Forming.** The cylindrical surfaces of the grain are formed by extrusion through a die, using either horizontal or vertical hydraulic presses. The die dimensions must be such as to yield a green (solvent-wet) strand of such cross section that on subsequent drying the final dimensions will be as designed. The shrinkage of propellant is almost entirely in the cross section and the volumes of propellant and solvent are approximately additive, so the desired green dimensions are readily calculated.

The charge for the finishing press is prepared by compacting in a blocking press which is a hydraulic press working against a closed end. A similar blocking operation known as preblocking precedes the macaroni operation if used. In Figure 41 are shown strands emerging from the macaroni press and entering the blocking press.

Extruded strands are cut to length, usually while still containing solvent. The equipment for this varies with the grain length. A cutting machine used for gun propellant is shown in Figure 42. The cutting knives are mounted on a rotating disk, and the strand is fed into the machine by feed rolls synchronized with the cutting head.

**49-3. Removal of solvent.** The mechanism of solvent removal involves diffusion of the solvent to the surface of the grain and evaporation from the grain. The rate of diffusion controls the drying rate, the surface of the grain being normally dry. Plasticized compositions dry more rapidly than unplasticized, and thin webs dry to lower residual solvent content than thick webs within tolerable operating cycles.

In the manufacture of single-base propellants the solvents are recovered for reuse. This is not ordinarily done with double-base propellants because the recovered solvents would be contaminated with nitroglycerin. Capital and operating costs to reclaim them safely for reuse outweigh the value of the recovered solvents. The amount of solvent used with these more highly plasticized propellants is considerably less than that used for single-base.

After most of the solvent has been removed from single-base powders, the final stages of solvent removal may be accomplished under water in order to shorten the total elapsed time. The water assists solvent diffusion by preventing premature formation of an impervious skin on the propellant surface. A final air dry removes the water.

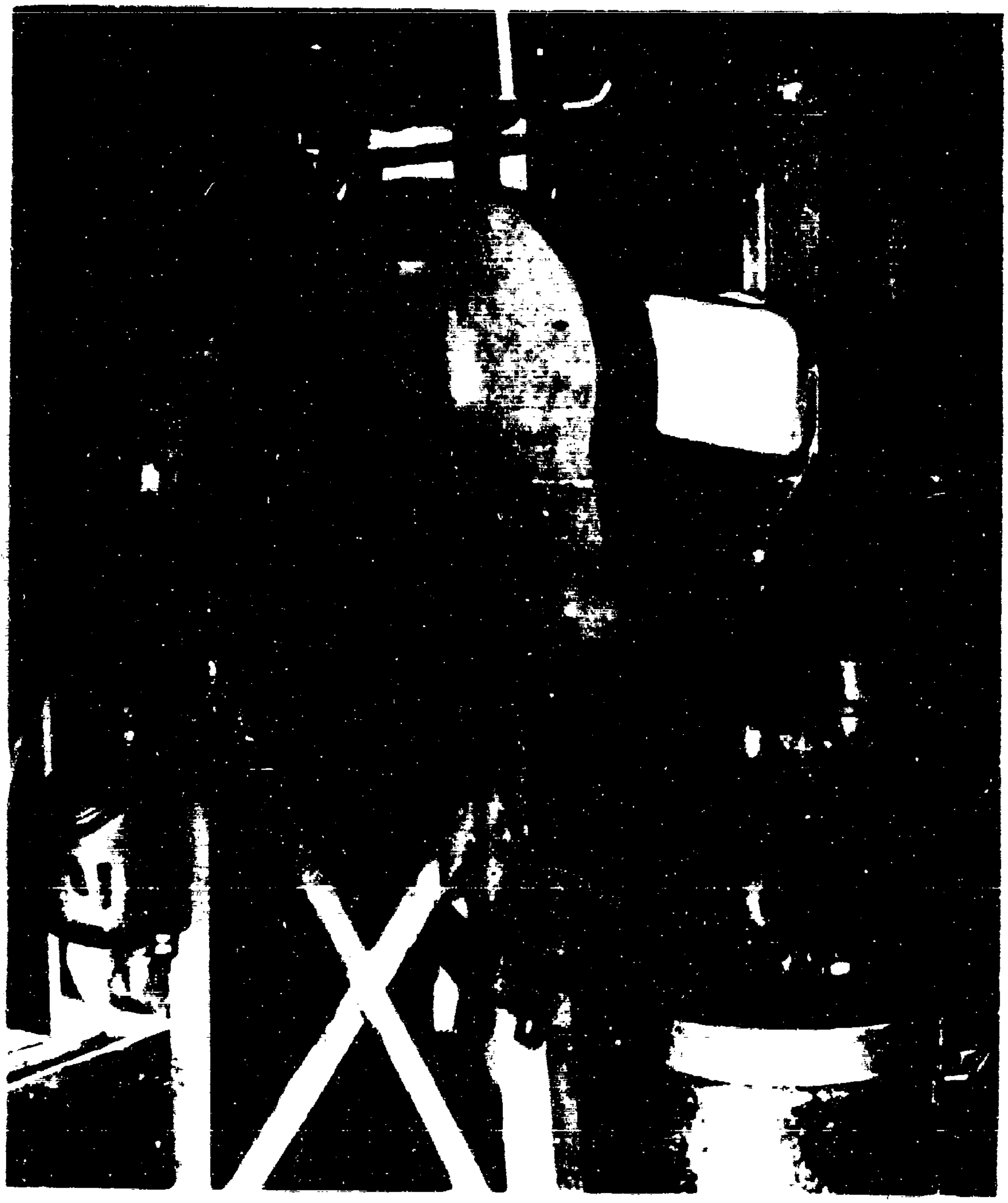
**49-4. Finishing.** Propellants for small arms may be coated with a deterrent plasticizer to retard gas evolution during early travel of the projectile. This operation is performed in a rotating "sweetie" barrel, similar to equipment used for sugar-coating pills, whence the name. The equipment is shown in Figure 43. The barrel is equipped with a warm-water jacket to heat the charge to a temperature where the coating agent will flow evenly onto the grains and be driven into the outer layers. The grain shown in Figure 27 (page 47) has been so coated.

Some propellants are "glazed" or coated lightly with graphite to decrease the accumulation of static electricity during handling and to increase the bulk density through better packing. This operation is also performed in a rotating barrel, which may be an unjacketed sweetie barrel or a larger barrel on a horizontal axis.

Propellant at this stage may contain tailings from the cutting operation, clusters of grains from the drying operations, and dusts of various descriptions from cutting, coating, and glazing. These are removed by screening. Screening is usually accomplished dry just before blending. As an alternate procedure screening may be done wet with water following the coating operation.

**49-5. Blending.** As solvent-extruded propellants are almost invariably used in multiple-grain charges, they are blended into lots containing up to 500,000 pounds. This blending may be done in a tower, in which case the entire lot is taken to the top of the tower and allowed to cascade over horizontal baffles. Alternatively blending may be done in a barrel, in which case a number of pre-blends are made, a barrel charge at a time, and the final blend is accomplished by blending in the barrel of aliquots from each preblend. For barrel blending, the glazing operation may constitute preblending.

**49-6. Propellants made by solvent extrusion.** Products of the solvent extrusion process include sporting powder in the form of disks and short tubes; single-base propellants for small arms such



U. S. Army Photograph Radford Arsenal

Figure 42. Cutting Machine

U. S. Army Photograph Radford Arsenal

*Figure 43. Sweetie Barrel*

as IMR; for cannon, including M1, M10, M12, M6, M14, IX-61; double-base gun propellants including M2, M5, M9, the British Cordites CD and WM; double-base rocket propellant M7. Data sheets for all of these propellants may be found in the *Propellant Manual* SPIA/M2. Casting powders used as intermediates in the cast double-base process may be made by solvent extrusion, as are also the triple-base gun propellants discussed in Chapter 7.

**50. Solvent emulsion (Ball Powder) process.** A second and radically different process[6,7] uses a volatile solvent to form propellant as spheres and related shapes sold as Ball Powder.* The flowsheet of this process is shown in Figure 44, and the product in Figure 45.

**50-1. Forming operations.** The process starts with the formation of spherical particles of nitrocellulose. The equipment for this operation comprises a closed, steam-jacketed vessel or "still," shown in Figure 46, equipped with paddle-baffle or double turbine agitation and an auxiliary solvent recovery system. Nitrocellulose is dispersed in a nonsolvent (water) and a solvent (ethyl acetate), a stabilizer (diphenylamine) and perhaps other additives are added. Additives introduced at this point must be insoluble in water and if crystalline they must have a particle size that is small compared to the size of the finished propellant spheres. When mixed and heated the ingredients form separate water and lacquer phases. Stabilization of reclaimed nitrocellulose[7] or even of incompletely stabilized new nitrocellulose still containing small amounts of inorganic acid can be accomplished in

* Trademark of Olin Mathieson Chemical Corporation.

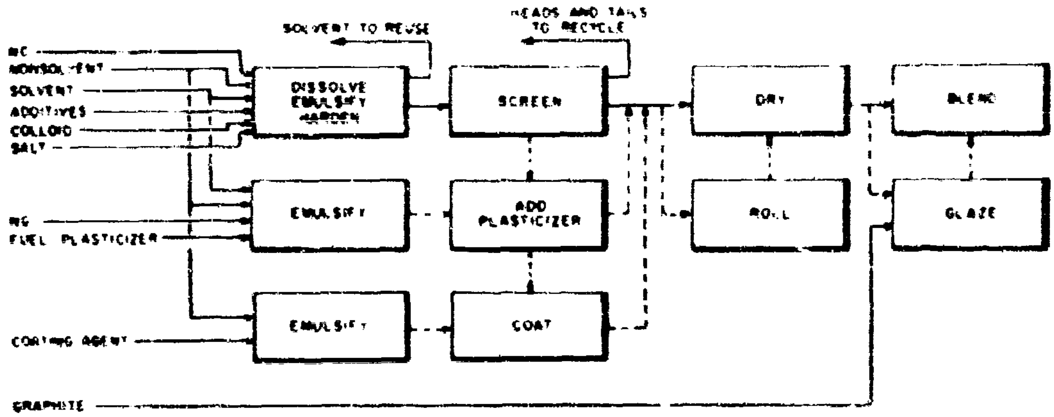



*Figure 44. Solvent Emulsion Process*

this low viscosity lacquer phase, using chalk as an additive to neutralize the acid. When a smooth lacquer has formed, a protective colloid is added to form an emulsion. The size and size distribution of the lacquer particles in this emulsion are controlled by the kind and degree of agitation. A salt is then added to draw dissolved and emulsified water by osmosis from the lacquer droplets. Omission of the salt results in a lower density product. The solvent is distilled off by raising the temperature and is recovered for reuse. When solvent removal is complete, the slurry is cooled, dewatered, and washed to remove the salt and protective colloid. The washed product is reslurried and pumped to the screening operation.

Screening is done wet on a series of vibrating or rotary screens, yielding one or more sizes for further processing to different end products. The grain size range of any cut is within about 10 to 15 percent of the average of the cut.

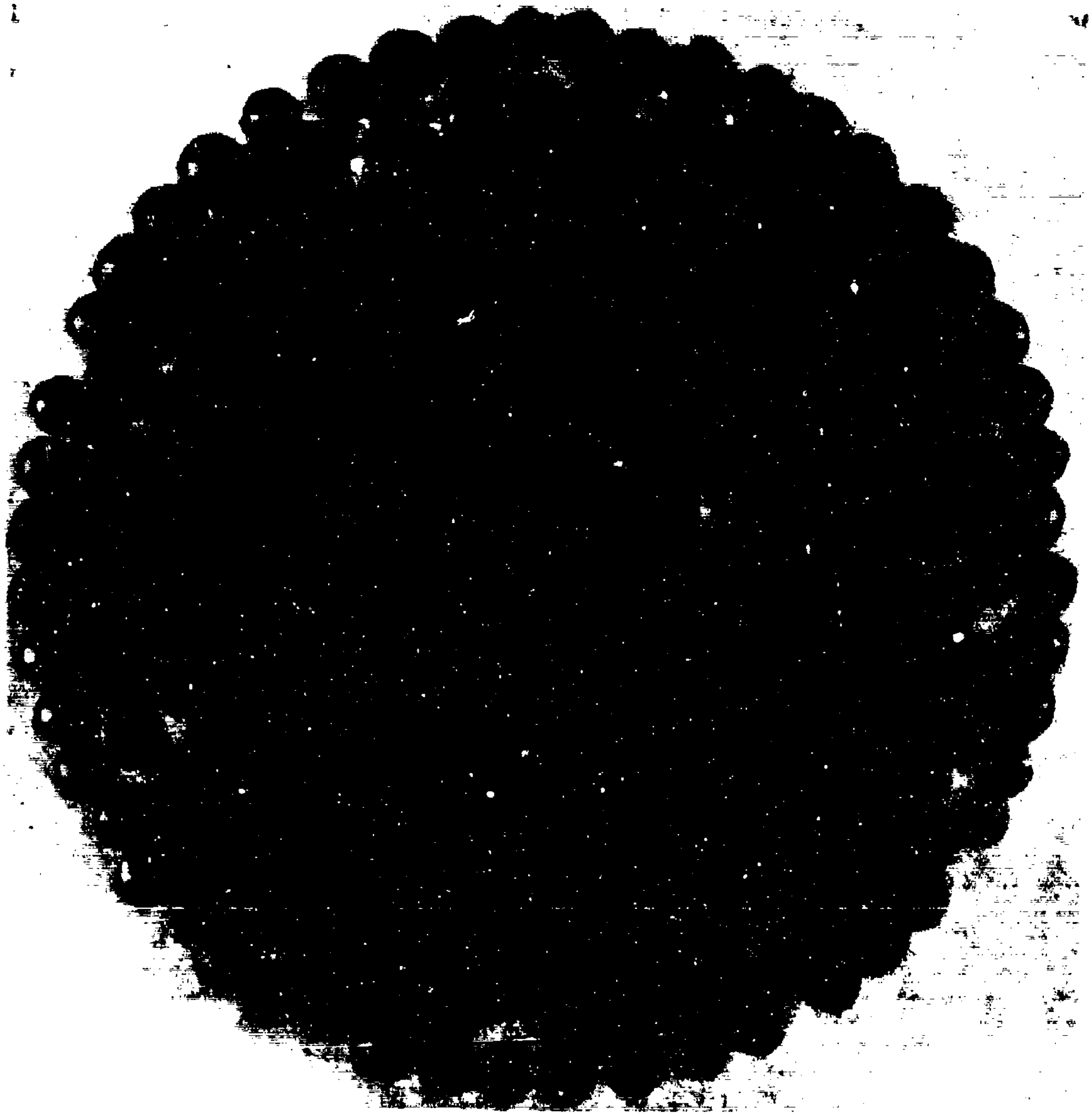
Larger spheres and more uniform sizes may be produced by a modification[8,9] of the above process in which the lacquer is made up in the absence of nonsolvent, extruded via a metering pump and orifice plate as strands into a proportionate stream of nonsolvent containing the protective colloid, and cut to square cylinders. The cylinders assume a spherical shape during transfer to the still where density adjustment (salt) and solvent removal are accomplished as described above.

Spheres 50 to 75 microns in diameter suitable for slurry casting, described below, are made[10,11] by emulsifying at high shear, heating the emulsion to a temperature well above the atmospheric boiling point, and flash evaporating the solvent. These spheres may then be plasticized as described below. They are usually coated with a small amount of casting plasticizer prior to drying to minimize accumulation of a static charge when dry.

**56-2. Incorporation of plasticizers.** Screened cuts, still in water slurry, are weighed pycnometrically and pumped into a second still. The slurry is again heated and plasticizers (fuel and/or oxidant) are added.[13,14] If nitroglycerin is used it is added in the form of solvent solution. The plasticizer, or plasticizer solution, is emulsified before addition to the slurry. Penetration of the solvent into the nitrocellulose spheres is a time-temperature function and may be controlled to leave a plasticizer gradient within the granule. When the impregnation has been completed the solvent is removed, leaving a controlled amount of solvent in the granules to facilitate the coating operation.

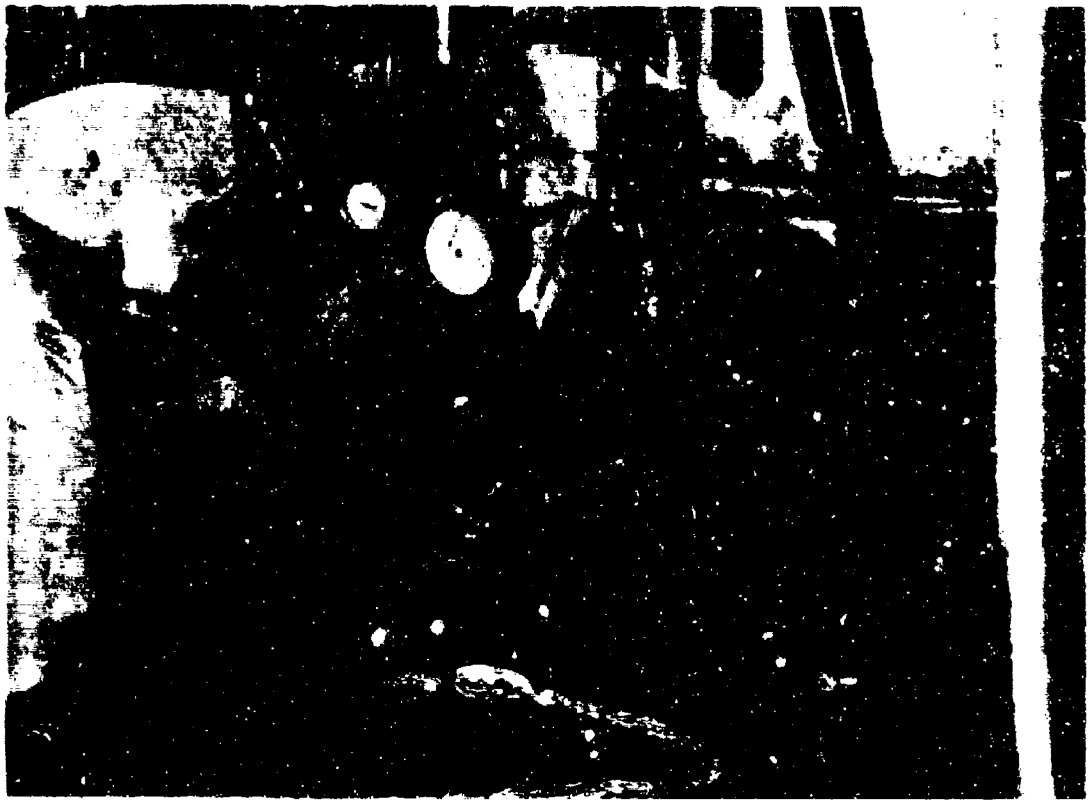
**56-3. Finishing operations.** Coating agents are again added as emulsions and the operation of coating is performed at controlled time and temperature.

In order to get more closely controlled web, the coated propellant may next be passed through sizing rolls which flatten the larger balls. The product is then dried and finished in the same way as the corresponding solvent-extruded propellants.



*Courtesy of Olin Mathieson Chemical Corporation*

*Figure 45. Ball Powder*



Courtesy of Olin Mathieson Chemical Corporation

*Figure 46. Still*

Water-soluble additives, impossible to add during the slurry operations, may be applied to the surface of the grains during the glazing operation

**51. Rolled sheet process.** If the propellant is to be used in the form of sheets, strips, cubes, or some other form of rectangular geometry, it may be suitably made by a rolled sheet process. This is basically the process originally used by Nobel, and is more extensively used abroad than in the United States. The flowsheet for this process is shown in Figure 47.

**51-1. Mixing.** A great deal of flexibility is possible within this process. Mixing may be accomplished either with or without the use of volatile solvent in a Schraeder mixer or in a sigma blade mixer, or it may take place in water slurry. If slurry mixing is used, the still fibrous mix, or paste, may be dewatered by a centrifuge, or drained off through a filter or a nutsch. Further elimination of water may be accomplished by air-drying. Final elimination of water or volatile solvent is usually accomplished during the rolling operation at the time that the propellant is consolidated to a sheet, although drying operations may be used between passes over the rolls or after the conclusion of the rolling operation.

**51-2. Rolling.** The roll mills may be even-speed (both rolls rotating at the same peripheral speed) or differential (one roll faster than the other), or a combination of differential and even speed mills may be used. Outside the United States most rolling operations are conducted on even speed rolls. In this operation the first pass forms a sheet, which is folded and or rotated for each succeeding pass. In the United States differential rolling is

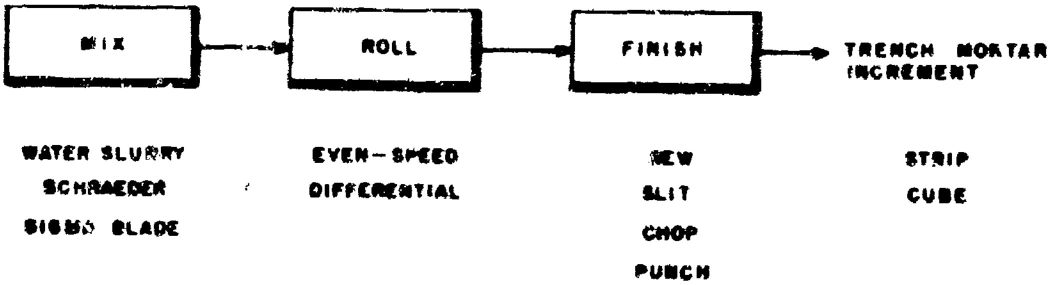
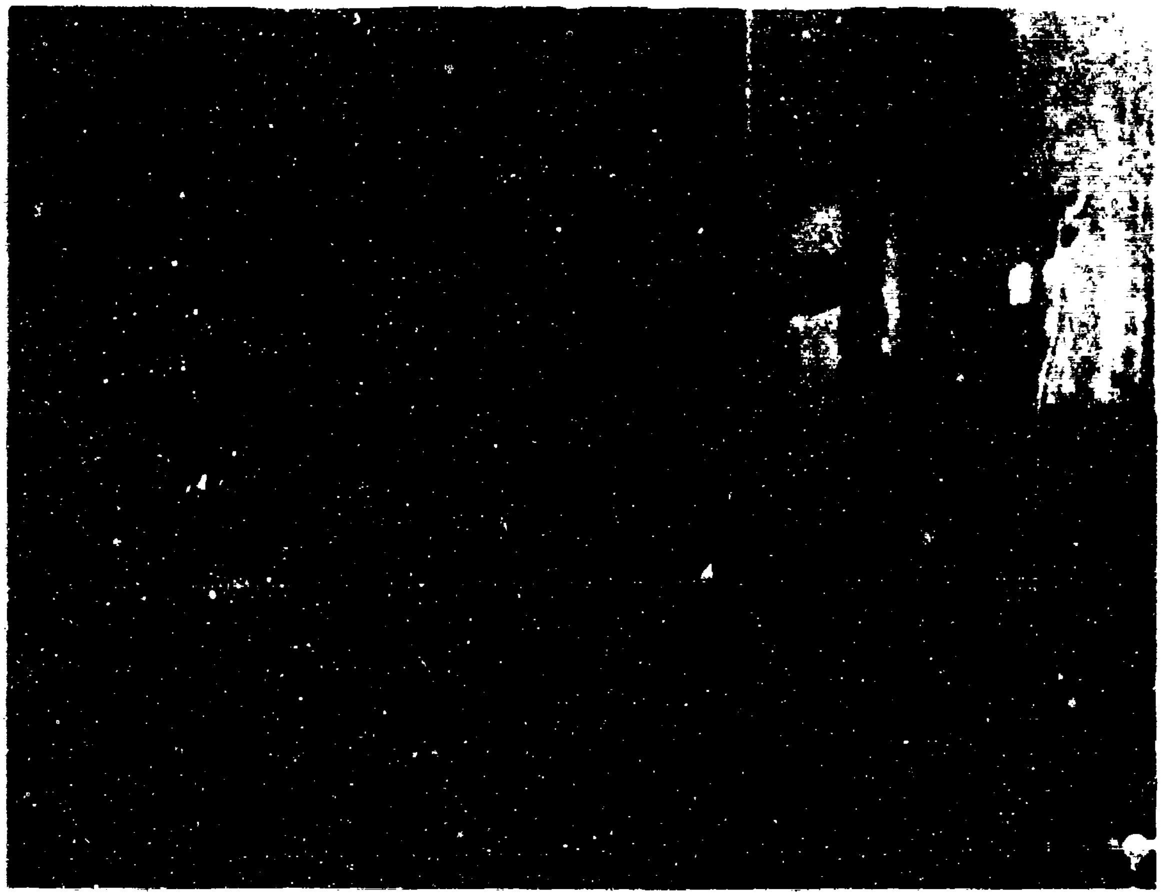



*Figure 47. Rolled Sheet Process*



*U. S. Army Photograph Sunflower Ordnance Works*

*Figure 48. Roll Mill*

U. S. Army Photograph Bedford Arsenal

Figure 49. Slitter

extensively used. The charge adheres to the cooler roll and passes repeatedly through the bite until it is stripped off. A differential roll cycle is thus properly identified by time and roll temperature instead of by number of passes. A typical roll mill is shown in Figure 48.

**51-3. Finishing.** Strip powder is made by slitting the sheet using equipment similar to that shown in Figure 49 in which rotating knives bear on the sheet as it passes over a feed roller. Cubes may be formed by cutting packages of strips with a guillotine, or by feeding sheet stock through a dicer in which slitting and chopping are done in one operation. Individual shapes such as disks may be punched from the sheets with a rule die. During World War II trench mortar increments as illustrated in Figure 50 were made from sheet powder by the sequence of operations: sewing a package of sheets together longitudinally using a sewing machine, slitting parallel to the seams, cutting across the seams, and simultaneously punching holes with a punch press.

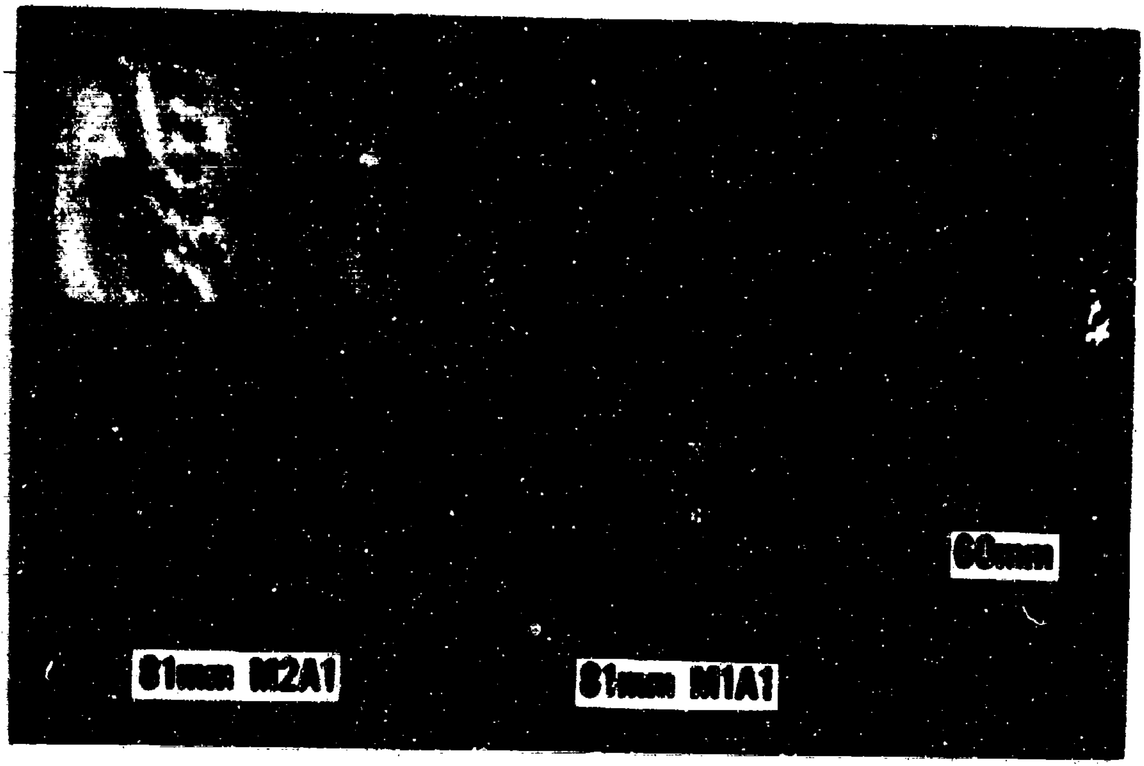
**52. Solventless extrusion process.** Propellants with a nitrocellulose concentration below 1 g/cc, particularly at webs over 0.4-inch, and in cross sections up to about 7 inches diameter may be made by the solventless extrusion process, shown in Figure 51. The existence of installed capacity and wealth of experience on the solvent extrusion process has discouraged United States use of the solventless extrusion process for webs less than 0.4-inch, although abroad webs considerably smaller have been extruded without solvent. The upper size limit has been set by the ability of a die in a 15-inch press to form a perfectly consolidated grain. Since World War II work both in the United States and abroad has indicated the possibility of extruding considerably larger grains, even exceeding the cross section of the powder basket of the press, by incorporating an expansion chamber between the basket and the die. As with most extrusion processes the products have cylindrical geometry. In the case of solventless extrusion the word cylindrical may be very broadly construed (Figure 52). Since no volatiles are present during the extrusion the die has nearly the same shape and dimensions as the strand, and cross sectional details including sharp angles can be reproduced with fidelity.

**52-1. Extrusion.** The process starts with rolled sheet, which is formed into press charges by carpet rolling (Figure 53) or by stacking disks cut from the sheet. United States practice is to use carpet rolls. The charge is brought to extrusion temperature before putting into the press (Figure 54) which is equipped with temperature controls on both the press basket and the die. The press basket is evacuated before extrusion starts. The extruded strand may be cut during the extrusion by a flying cutter which travels with the strand during the cut, or the whole strand may be extruded and cut to grain blanks between pressing cycles. The portion of the strand remaining in the die between extrusion cycles is known as the neck and is essentially compression-molded. It has different dimensions from the extruded strand due to annealing in the die between extrusions, and ordinarily is reworked. In going to larger cross sections, one may reach the point where an entire extrusion would be contained within the die. From this point on, the whole extrusion would be neck. This should result in even better dimensional fidelity than is attained in conventional extrusion.

**52-2. Finishing.** As is the case with the rolled sheet process, finishing operations are developed to meet the requirements of the product. For a gun propellant no finishing operations should be required other than cooling and equilibrating with an atmosphere of the standard relative humidity. For a rocket or gas generator grain with tight dimensional tolerances the first finishing operation is annealing to relieve residual stresses in order to stabilize dimensions. This is done by heating the grain blanks to perhaps 120°F for several hours. In its relaxation the grain becomes a little shorter and a little fatter. Without the annealing operation the same changes would take place slowly, causing the finished grain to go off dimensions.

After annealing the grain can be machined to length by sawing, and to diameter by using a lathe or dowel rod machine. Radial holes may be drilled through the web or slots milled as required.

Inhibitor patches to restrict the burning may be cemented to the grain at the ends or along the lateral surface. Inhibitors that cover the entire circumferential surface are usually wrapped. Cellulose acetate plastic wet with acetone and ethyl cellulose plastic wet with a mixture of ethyl lactate and butyl acetate are the common inhibitors




*U. S. Army Photograph Radford Arsenal*

*Figure 50. Trench Mortar Increments*

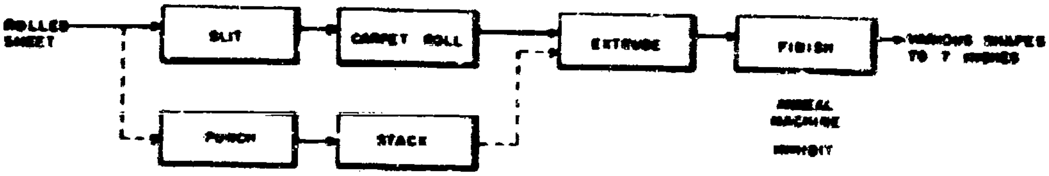
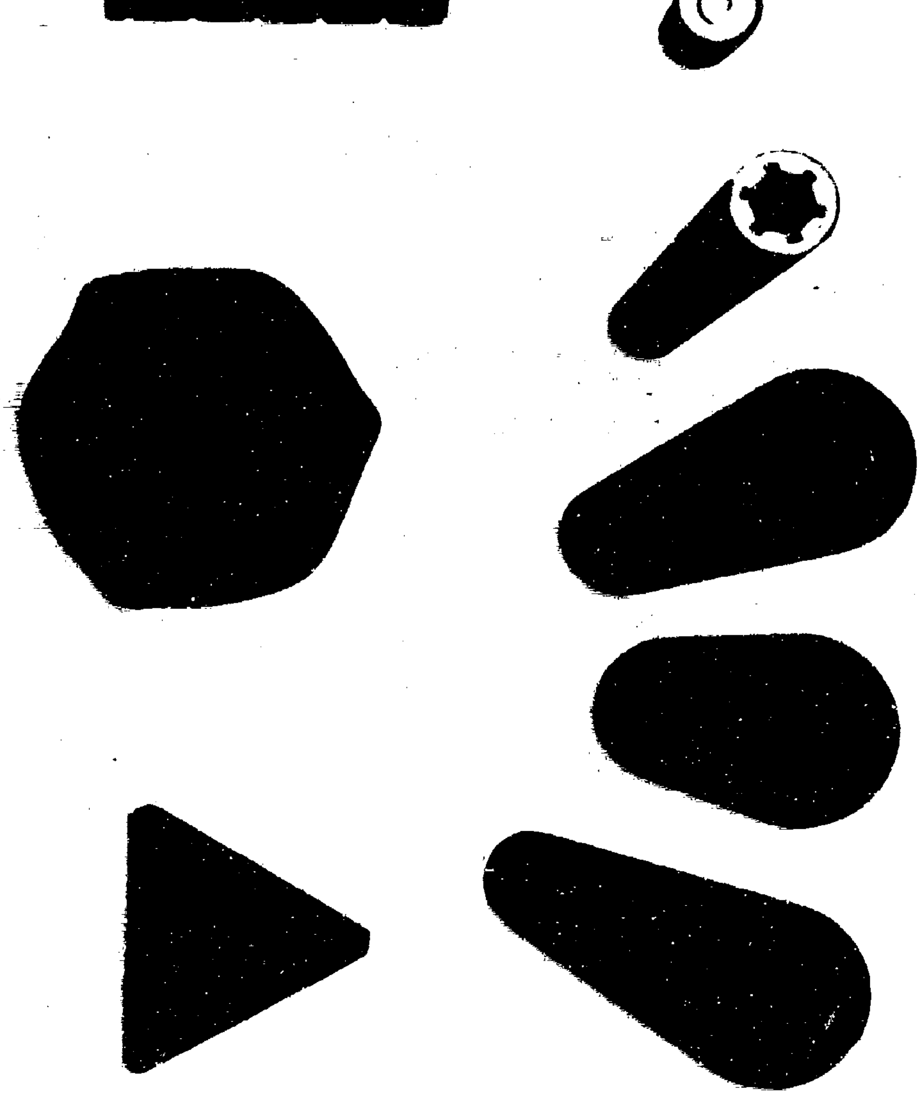
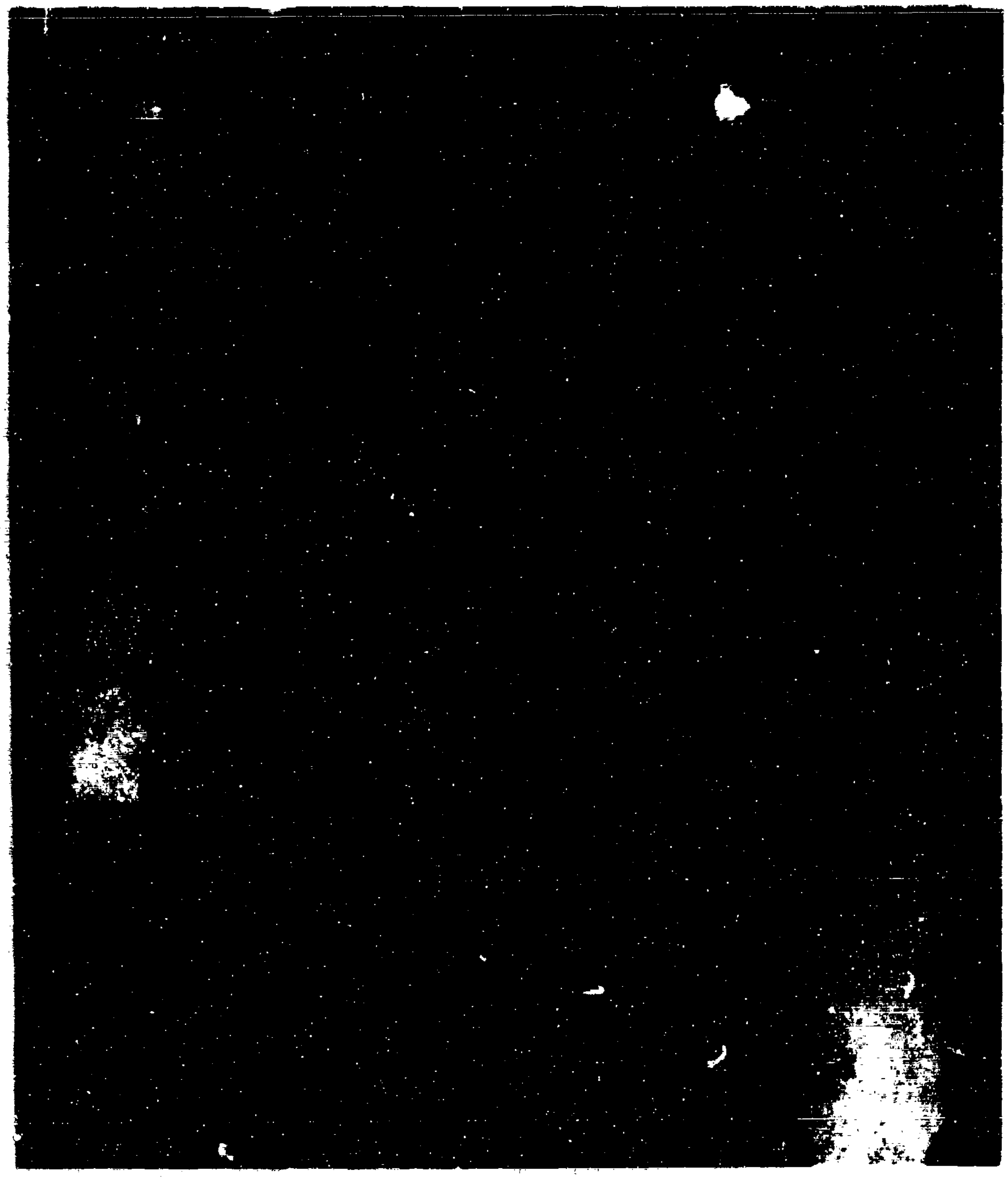



*Figure 51. Solventless Extrusion Process*



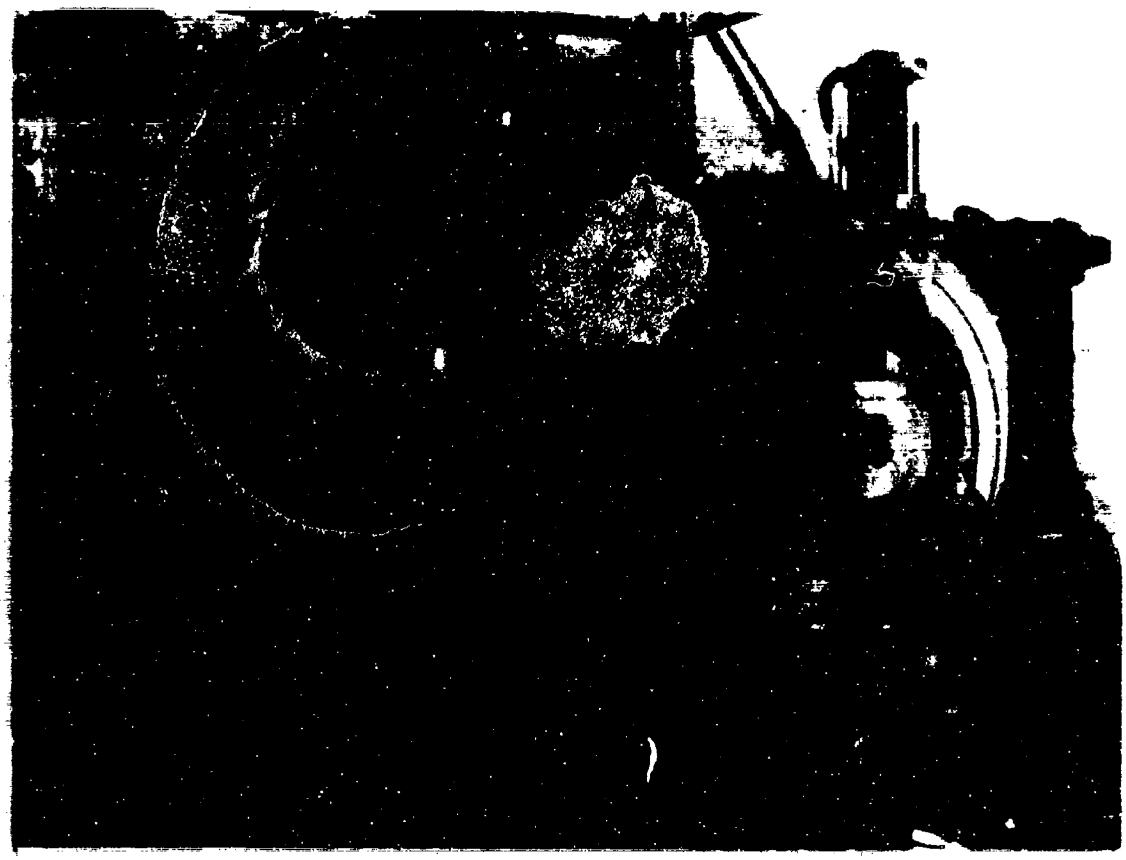
*U. S. Navy Photograph Naval Propellant Plant*

**Figure 52. Solventless Extruded Shapes**



*U. S. Army Photograph Sunflower Ordnance Works*

*Figure 33. Carpet Rolling*



*U. S. Army Photograph Sunflower Ordnance Works*

*Figure 54. Solventless Extrusion Press*

used with solventless extruded grains. The solvents are subsequently removed by diffusion and evaporation.

**52-3. Flaws.** Any imperfections in the propellant tend to be elongated in the axial direction as a result of the extrusion operation. This is usually not serious when burning of the grain is in the radial direction because no great amount of unplanned additional surface is exposed when the burning surface meets the flaw. Inspection on a statistical basis coupled with quality control throughout the operation is adequate to maintain such flaws at an acceptable minimum. When the grain produced is an end-burner, however, no axial flaws may be permitted. Great care must be taken to reject any grains containing such flaws. Flaw detection may be done with X-rays or supersonics.

**53. Cast double-base process.** The cast double-base process is used to form propellants in any geometry and in sizes from about 1 inch in diameter up to unlimited size. It uses as intermediates casting powder, which may be made either by solvent extrusion (short cylinders about 0.03-inch in diameter by 0.03-inch long) or by the Ball Powder process (spheres of similar dimension), and casting solvent, which is a mixture of plasticizers. The bulk density of the casting powders is about 1 g/cc, and the finished propellant occupies the same volume as its casting powder. This results in a maximum nitrocellulose concentration in the cast propellant of about 1 g/cc. Cast double-base propellants are therefore possible in the same range of compositions as solventless extruded propellants.

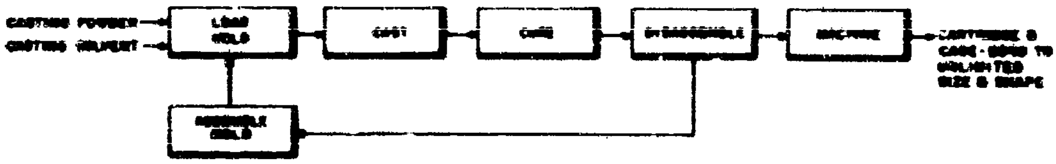


*Figure 55. Cast Double-Base Process*

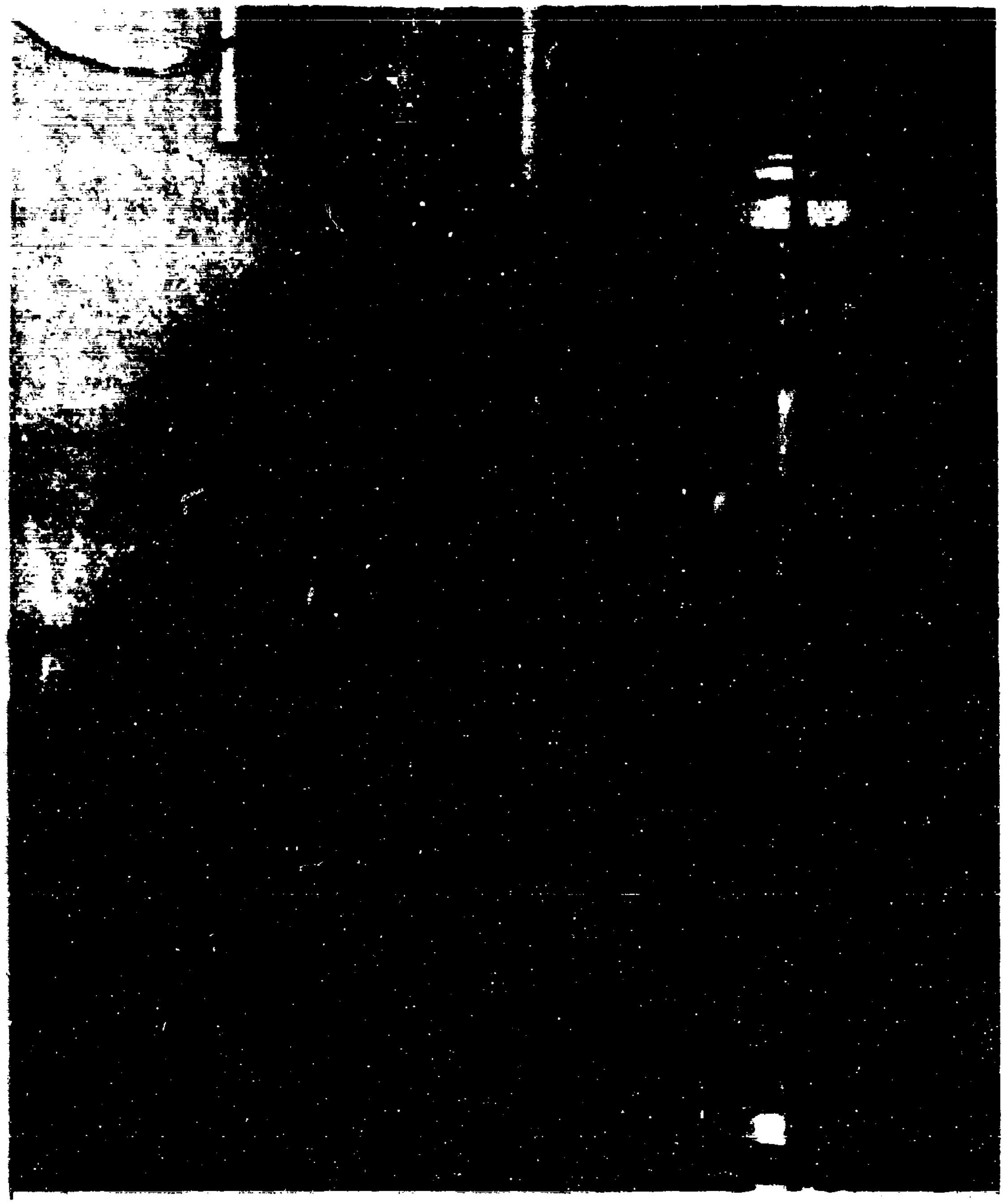
The flowsheet of the process is shown in Figure 55.

**53-1. Casting.** The casting powder is first loaded into the mold and evacuated overnight. The casting solvent, also previously evacuated, is then also introduced into the mold, usually by air pressure, where it fills the interstices between the individual casting powder grains. The casting powder imbibes the solvent and swells, causing the individual grains to coalesce to form a single grain within the mold. Due to the fact that the casting powder is glazed to dissipate static electricity and to facilitate charging, grain boundaries are visible in the finished casting, but fractures produced in tensile strength testing do not follow the grain boundaries. This indicates that the cast propellant has become really homogeneous.

The circumferential inhibitor required of cartridge-type internal burning grains is usually

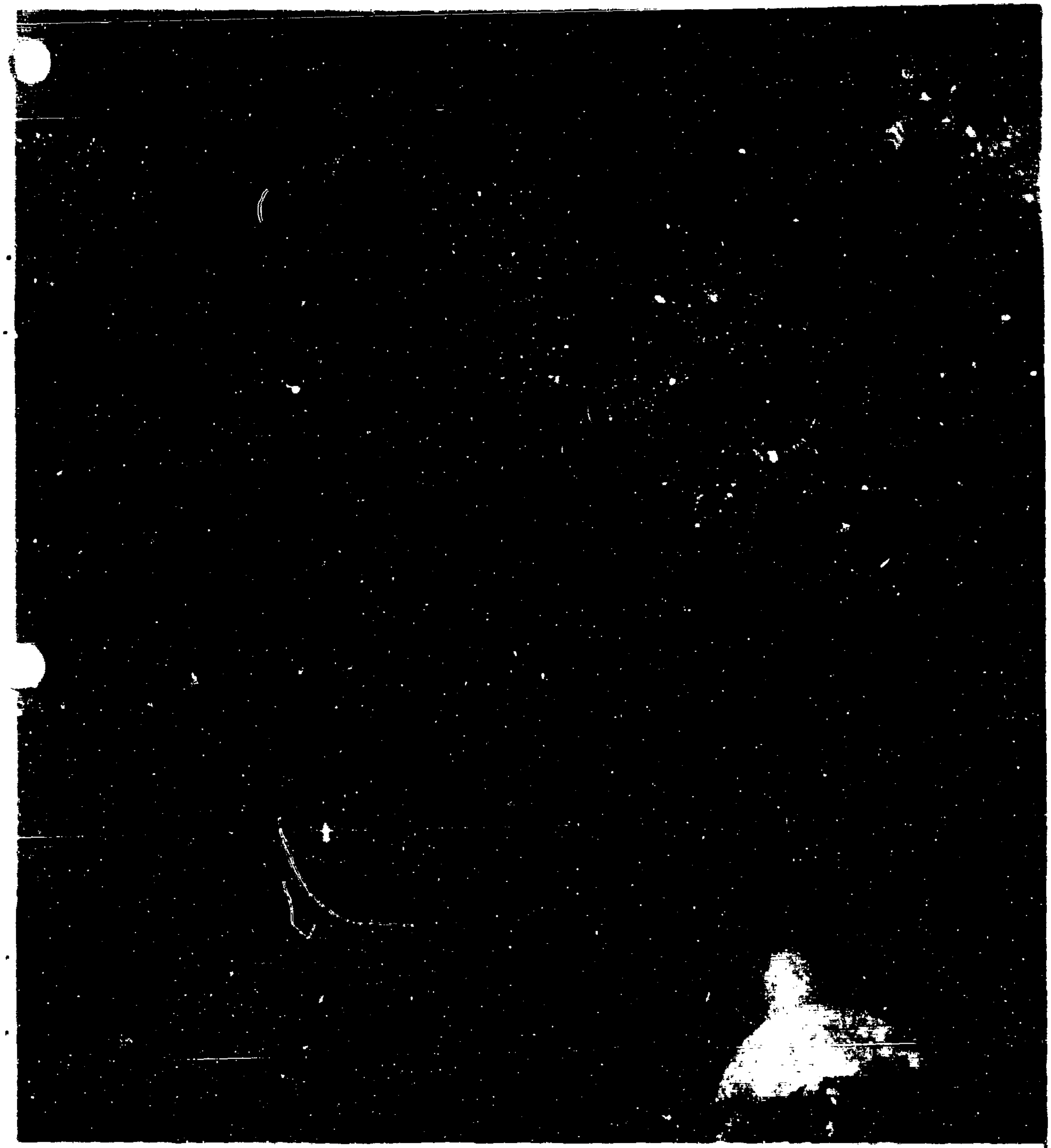
*U S Navy Photograph Allegany Ballistics Laboratory*

*Figure 56. Mold Parts*



U. S. Navy Photograph Allegany Ballistics Laboratory

Figure 57. Casting Setup



*U. S. Navy Photograph Allegany Ballistics Laboratory*

*Figure 58. Cast Grain*

prefabricated and known as the beaker. It is used as part of the mold. If a case-bonded grain is called for, the case is first lined with any required insulation and with a surface to which the propellant will bond. The case then becomes part of the mold. Typical mold parts are shown in Figure 56.

The assembled mold and accessories are shown in Figure 57. The flow of casting solvent may be upward, downward, or radial through the mold.

As a result of blending giant lots of casting powder and carefully controlling the composition of casting solvent, large lots of cast grains can be prepared with an excellent within-lot reproducibility.

**53-2. Curing.** The curing operation, during which coalescence is completed, is done at elevated temperatures (about 140°F) and requires about 3 days after the grain has come to curing temperature. After the completion of the cure the mold is disassembled and cleaned for reuse. The grain is finished by sawing to length and machining any designed surfaces not produced by the mold.

**53-3. Physical strength.** Physical strength of cast double-base propellant is comparable to that of propellant of the same composition produced by solventless extrusion. Flaws if present are randomly distributed and not elongated, so that the tolerance of flaws for end-burning castings is considerably greater than for end-burning extrusions.

A finished grain is shown in Figure 58.

**53-4. Uses of propellants made by cast double-base process.** Examples of propellants produced by casting are OGK, OIO, and BPY for cartridge applications and BUU, a case-bonded propellant. Note that these compositions must be broken down to a casting powder composition and a casting solvent in order to manufacture them.

**54. Slurry casting process.** When the total volume of the liquid ingredients exceeds about 30 percent of the volume of the composition it becomes possible to suspend the solids, including the polymer, in the mixed liquids and pour the resulting slurry directly into the mold. In this instance the solids must be supplied in a shape that has good packing density, such as spheres. As the packing density of the solids decreases, the required volume fraction of the liquid ingredients increases. It is further necessary, for the sake of pot life, that the polymer particles possess a surface that is relatively impervious to the liquid components at the temperatures of mixing and casting and yet readily soluble at curing temperature. At least three such processes have been described.[10-11]

**REFERENCES**


1. J. R. Du Pont, "Manufacture of Cellulose Nitrate for Pyroxylin Plastics," *Chem. Met. Eng.*, 26, 11 (1922).
2. R. L. Stern (to Hercules Powder Company), U. S. Patent 2,028,080 (1936).
3. JAN-N-244, *Nitrocellulose (For Use in Explosives)* (31 July 1945) with *Amendment-1* (27 December 1945)
4. E. Berl, K. R. Andress and E. Escales, *Beiträge zur Kenntnis der Mischsäure*, p. 32, J. F. Lehmann, Munich, Germany, 1937. (Summarized in J. Barsha, *Derivatives of Cellulose. Section B Inorganic Esters*, in E. Ott, *et al.* [editors], *Cellulose and Cellulose Derivatives*, 2nd edition, Part II, p. 720, Interscience Publishers, Inc., New York, New York, 1954.)
5. F. Olsen, G. C. Tibbitts and E. B. W. Kerone (to Western Cartridge Company), U. S. Patent 2,027,114 (1936).
6. H. F. Schaefer (to Western Cartridge Company), U. S. Patent 2,160,626 (1939).
7. MIL-P-3984, *Propellants, for Small Arms Ammunition, Calibers .30 to 30 MM Inclusive, Except Blank and Caliber .45* (30 November 1956).
8. J. J. O'Neill, Jr. and G. R. Cox (to Olin Mathieson Chemical Corporation), U. S. Patent 2,740,705 (1956).
9. J. J. O'Neill, Jr. and G. R. Cox (to Olin Mathieson Chemical Corporation), U. S. Patent 2,830,886 (1958).
10. R. L. Cook and E. A. Andrew (to Olin Mathieson Chemical Corporation), U. S. Patent 2,888,713 (1959).
11. E. A. Andrew (to Olin Mathieson Chemical Corporation), U. S. Patent 2,929,107 (1960).
12. G. A. McBride (to Western Cartridge Company), U. S. Patent 1,955,927 (1934).
13. W. E. Wagner (to Western Cartridge Company), U. S. Patent 2,008,889 (1935).
14. C. E. Silk (to Western Cartridge Company), U. S. Patent 2,335,804 (1943).
15. J. J. O'Neill, Jr. (to Olin Mathieson Chemical Corporation), U. S. Patent 2,916,775 (1959); E. A. Andrew (to Olin Mathieson Chemical Corporation), U. S. Patent 2,929,107 (1960).
16. A. W. Sloan and D. J. Mann (to Atlantic Research Corporation), U. S. Patents 2,931,800 and 2,931,801 (1960).
17. J. Reinhart, W. E. Stump, M. L. Bovee, P. O. Stull and A. T. Camp, *Nitrasol Propellants—Composite Propellant Formulations Based on a Plastisol Nitrocellulose-Pentaerythritol Trinitrate Binder*, Naval Ordnance Test Station, Bulletin of The Fourteenth Meeting of The Joint Army-Navy-Air Force Solid Propellant Group, Vol IV, p. 9, CONFIDENTIAL, Solid Propellant Information Agency, Applied Physics Laboratory, The Johns Hopkins University, Silver Spring, Maryland.

# FUEL BINDER COMPOSITES

**55. General.** The first fuel binder composites in the United States were developed during World War II in response to a need for grains for use in aircraft jatos. Smokeless powders had been widely used for gun propellants and had been made abroad by solventless extrusion into grains for artillery rockets, and solventless extrusion was being developed in this country. It was not immediately apparent that smokeless powder could be fabricated into grain cross sections of the size required for such jato use, such cross sections being beyond the capacity of existing or contemplated presses. The black powder art had demonstrated that a solid propellant need not be a monopropellant.

Existing black powder manufacturing techniques would not produce large grains. The existing black powder formula was less energetic than desired. Substitution of a hydrocarbon for the sulfur and charcoal of black powder put all of the fuel into the binder phase, increasing the volume fraction of binder to a point where a casting operation became feasible. At the same time oxidation of the hydrocarbon led to products (including $H_2$ and $H_2O$) of lower average molecular weight than those derived from black powder. Substitution of potassium perchlorate for potassium nitrate increased oxygen content per unit volume of filler and decreased the weight of solid residue per unit weight of propellant. The asphalt-potassium perchlorate interim propellant successfully established the position of fuel binder composites in the propellant field and encouraged further development.

The first major improvement was the substitution of a polymer system for the asphalt. The filler was mixed with binder in monomeric or partially polymerized form and cast in that condition. Polymerization was completed in the curing operation in the mold, resulting in a grain that would not cold flow under moderately warm ambient conditions as would the asphalt.

The second major improvement was the substitution of ammonium perchlorate for the potassium salt, eliminating inorganic residues and dense smoke. The gaseous combustion products, however, now contained HCl which is somewhat corrosive under conditions of high humidity. This condition has proven entirely acceptable for conditions in rocketry where the engines are expended in a single firing. It is less acceptable for some gas generator uses where the combustion gases remain in contact with metal parts that will be reused.

When considerations other than maximum performance, such as freedom from corrosive exhaust or cheapness and availability of raw materials, take precedence ammonium nitrate may be used in place of the ammonium perchlorate.

The third major development was the subsutution of an elastomeric binder for the hard polymer binder. This permitted case bonding of the propellant and elimination of the inhibitor from internal burning grains. Replacement of the inhibitor by additional propellant increases the mass fraction, or ratio of propellant weight to loaded motor weight, and thereby the performance of a rocket. Continuing need for thermal insulation negates this advantage of case bonding for end-burning grains.

**56. Choice of oxidizer.** The differences among the three oxidizers that have been widely used in fuel binder composites, potassium perchlorate, ammonium perchlorate, and ammonium nitrate are shown in Table 11. As a matter of interest,

**TABLE 11. OXIDIZERS FOR FUEL BINDER COMPOSITES**

| | $KClO_4$ | $NH_4ClO_4$ | $NH_4NO_3$ | $KNO_3$ |
|---|---|---|---|---|
| Molecular weight | 138.55 | 117.50 | 80.05 | 101.10 |
| Specific gravity, $\rho$ | 2.52 | 1.95 | 1.725 | 2.11 |
| ½ $Cl_{ox}$ | 0.0036 | 0.0043 | — | — |
| ½ $H_{ox}$ | — | 0.0170 | 0.0250 | — |
| ½ $N_{ox}$ | — | 0.0043 | 0.0125 | 0.0049 |
| $O_{ox}$ | 0.0288 | 0.0340 | 0.0375 | 0.0247 |
| Specific volume, $\frac{1}{\rho}$ | 0.397 | 0.513 | 0.580 | 0.474 |

figures are included for $KNO_3$. Following the nomenclature of Chapter 2, the items $Cl_{ox}$ is the number of gram atoms of Cl in one gram of oxidizer, $H_{ox}$, the number of gram atoms of hydrogen, etc. In the case of potassium perchlorate part of the KCl resulting from pyrolysis of the oxidizer is found to be vaporized, and part remains in the condensed phase. For the purpose of the present argument it is assumed that half of it is in the gas phase. In the case of ammonium perchlorate all of the chlorine is in the gas phase, and its contribution to the gas volume is $\frac{1}{2}Cl_{ox}$. Any hydrogen will be in the form of either $H_2$ or $H_2O$, so the contribution of the hydrogen of the oxidizer to the combustion product volume is $\frac{1}{2}H_{ox}$. The oxygen of the oxidizer will appear as CO, $CO_2$, or $H_2O$ and makes no separate contribution to the gas volume. In the case of potassium nitrate it is assumed that a solid residue of $K_2O$ will exist under operating conditions. This removes one-half atom of oxygen from the quantity available for oxidizing fuel, and the value of $O_{ox}$ under $KNO_3$ is corrected for this.

A more significant comparison of the oxidizers appears when they are formulated with a fuel. As an example, consider a series of propellants formulated at 75 weight percent oxidizers with a hypothetical fuel of composition $CH_{1.5}$ and specific gravity 1.2. Data concerning such a fuel are shown in Table 12 and for the propellants in Table 13.

**TABLE 12. HYPOTHETICAL FUEL BINDER $CH_{1.5}$**

| | |
|---|---|
| Molecular weight | 13.5 |
| $\frac{1}{2}H_f$ | 0.0556 |
| $C_f$ | 0.0740 |
| Specific volume, $\frac{1}{\rho}$ | 0.833 |

**TABLE 13. HYPOTHETICAL PROPELLANTS**

| | $KClO_4$ | $NH_4ClO_4$ | $NH_4NO_3$ | $KNO_3$ |
|---|---|---|---|---|
| Oxidizer weight | 0.75 | 0.75 | 0.75 | 0.75 |
| Binder weight | 0.25 | 0.25 | 0.25 | 0.25 |
| ΣC | 0.0185 | 0.0185 | 0.0185 | 0.0185 |
| ½N | — | 0.0032 | 0.0094 | 0.0037 |
| $\frac{1}{2}H_{ox}$ | — | 0.0128 | 0.0188 | — |
| $\frac{1}{2}H_f$ | 0.0139 | 0.0139 | 0.0139 | 0.0139 |
| ½ΣCl | 0.0027 | 0.0032 | — | — |
| $\frac{1}{M}$ | 0.0351 | 0.0516 | 0.0606 | 0.0361 |
| ΣO | 0.0216 | 0.0255 | 0.0282 | 0.0185 |
| ΣO − ΣC | 0.0031 | 0.0070 | 0.0097 | — |
| Oxidizer volume | 0.298 | 0.385 | 0.435 | 0.355 |
| Binder volume | 0.206 | 0.208 | 0.208 | 0.208 |
| Total volume | 0.506 | 0.593 | 0.643 | 0.563 |
| Specific gravity, ρ | 1.97 | 1.69 | 1.56 | 1.78 |
| Binder volume, % | 41 | 35 | 32 | 37 |

The potassium nitrate member of this series of propellants is capable of producing as much gas $\left(\frac{1}{M}\right)$ as the potassium perchlorate member but the total available oxygen is only enough to oxidize the carbon to CO. This propellant is badly underoxidized, and potassium nitrate has properly been ignored in the development of fuel binder composites.

**56-1. Potassium perchlorate.** Potassium perchlorate has the considerable disadvantage that a major part of the KCl formed in its pyrolysis remains condensed under operating conditions, resulting in a low gas volume $\left(\frac{1}{M}\right)$. The rest of the KCl condenses in the exhaust, and any propellant formulated with potassium perchlorate burns with a dense white smoke. Linear burning rates of potassium perchlorate propellants tend to be high, 0.8 to 0.9 in/sec at 1000 psi. Propellant densities also are high, 1.8 to 2.0 g/cc, reflecting the high specific gravity of potassium perchlorate. Specific impulses are generally below 200 lb-sec/lb, reflecting the low gas volume, $\left(\frac{1}{M}\right)$. The pressure exponent, $n$ (Equation 31a), tends also to be high. Due to the low specific impulse and smoky exhaust, potassium perchlorate propellants are no longer in general use.

**56-2. Ammonium perchlorate.** Ammonium perchlorate avoids most of the disadvantages of potassium perchlorate. Propellants containing ammonium perchlorate burn substantially without residue or smoke, and the oxidizer makes a substantial contribution to the gas volume. As a result of this, specific impulses have been calculated to about 250 and measured to about 240 lb-sec/sec. The (measured) specific impulses and the flame temperatures of selected ammonium perchlorate propellants taken from SPIA/M2 data sheets are shown in Figure 59.

As these propellants were made up with a variety of binders, it is apparent that specific impulse and flame temperature are largely determined by the weight loading of the oxidizer. Over the range 55 to 81 weight percent oxidizer, the flame temperatures seem to be linear and nearly proportional to the weight fraction of oxidizer. The specific impulse also rises with increasing weight

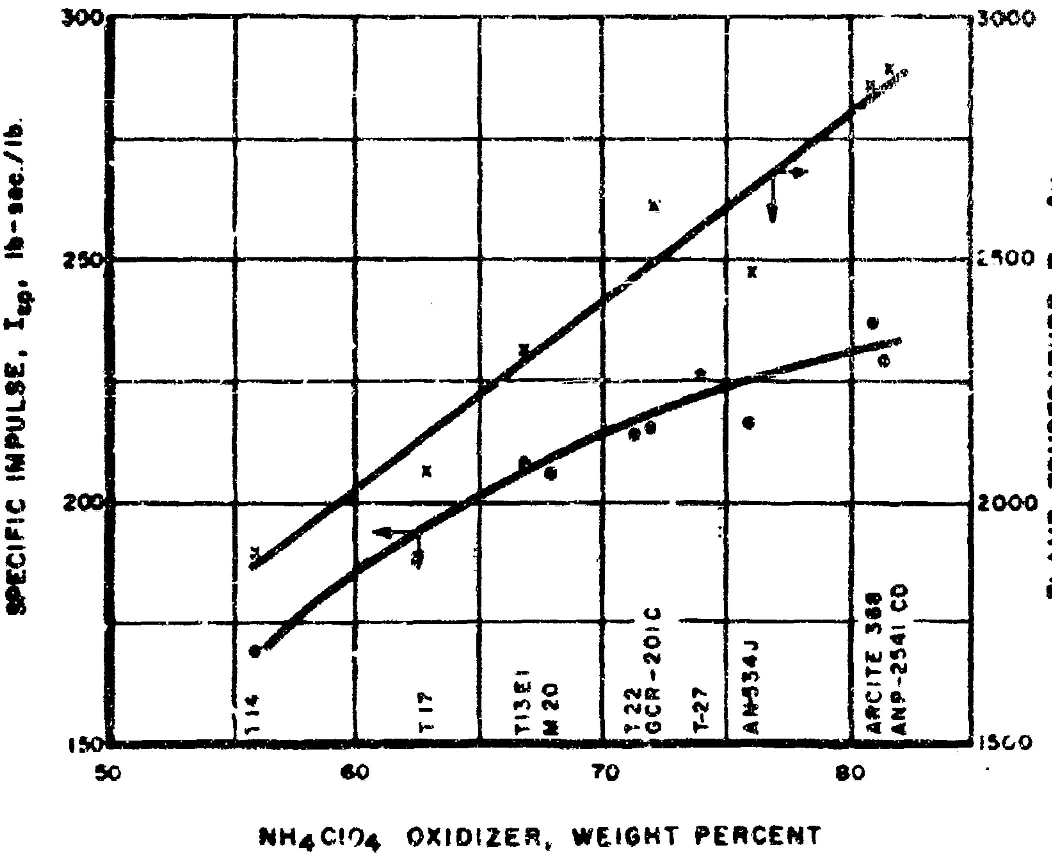



*Figure 59. Specific Impulse, $I_{sp}$, and Flame Temperature, $T_b$, of $NH_4ClO_4$-Fuel Binder Composites*

fraction of oxidizer but appears to approach a maximum of about 240 lb-sec/lb.

Comparing the two examples of potassium perchlorate propellants (ALT-161 and AK-14) with Figure 59, it appears that the potassium perchlorate propellants at about 75 percent oxidizer are equivalent in specific impulse and flame temperature to ammonium perchlorate propellants at about 60 percent oxidizer.

Burning rates of ammonium perchlorate propellants at 1000 psi and room temperature are plotted in Figure 60. They also seem to trend upward with increasing weight percent of oxidizer but are subject to other influences. It is recognized that oxidizer grist has an effect on the burning rate, coarse oxidizer leading to low burning rates in a given composition. Burning rates of ammonium perchlorate propellants have also been increased by substitution of potassium perchlorate for part of the ammonium perchlorate, but at the cost of a smoky exhaust. Burning rates may also be influenced by catalysts.

Ammonium perchlorate is a monopropellant. Its pyrolysis starts with dissociation according to the reaction[1]

$$NH_4ClO_4 \rightarrow NH_3 + HClO_4 \qquad (57)$$

leading to a combustible mixture of $NH_3$ and $HClO_4$ in the gas phase adjacent to a $NH_4ClO_4$ crystal. Subsequent features of the combustion reactions are a matter of some dispute. According to the two-temperature theory[1] the burning sur-

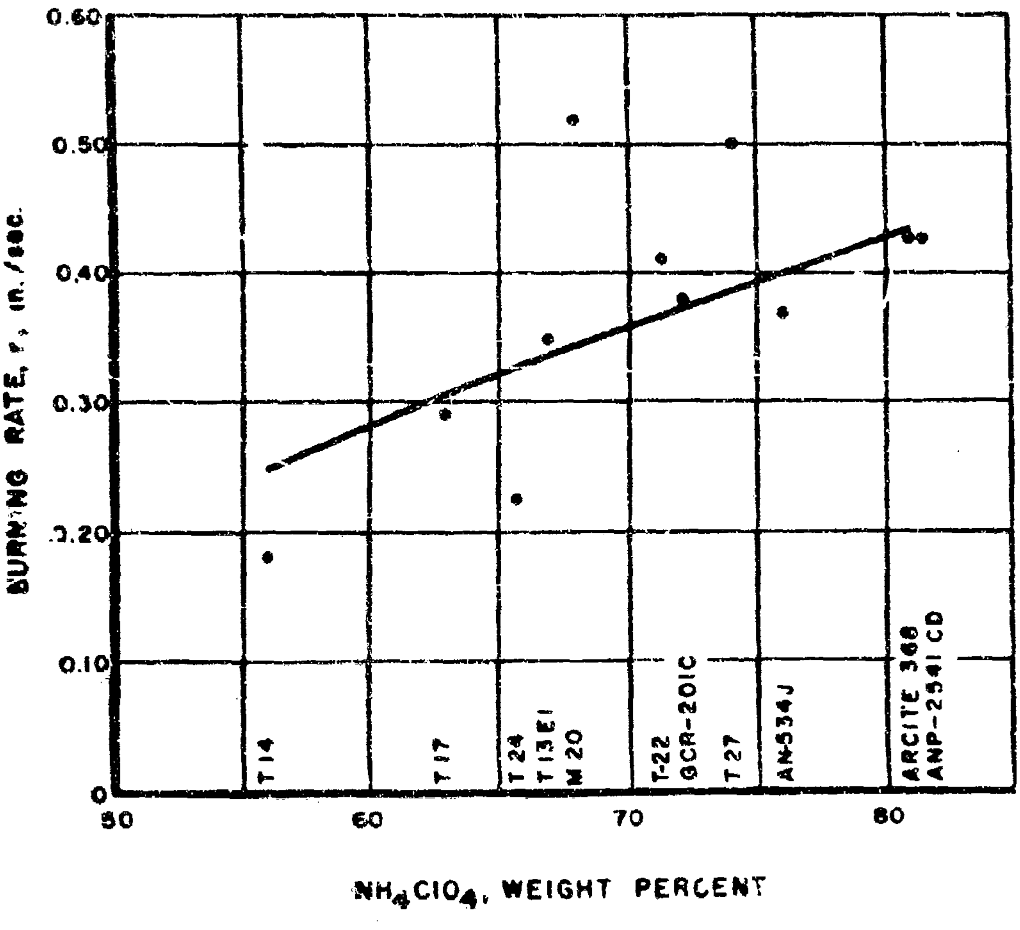



*Figure 60. Burning Rate, r, at 1000 psi, Ambient Temperature of $NH_4ClO_4$-Fuel Binder Composites*

face retreats in a plane, the linear burning rates of the binder and oxidizer are the same. This requires that the surface temperatures of burning oxidizer and binder be different. The thermal layer theory,[3] on the other hand, states that the rate-controlling step is the redox reaction of the monopropellant, in this case between the $NH_3$ and $HClO_4$, that burning surface is not plane, and that diffusion of binder pyrolytic products into the thermal layer where the redox reaction is going on may lead to perturbation depending on the relative rates of reaction between the oxidizer-binder pyrolysis products and the oxidizer pyrolysis products alone.

The reaction products of ammonium perchlorate fuel binder composites are $N_2$, CO, $CO_2$, $H_2$, $H_2O$, and HCl. Of these products only HCl deserves special mention, the others being common to smokeless powders which have long been used in various heat engines. At relative humidities above about 85 percent[3] HCl tends to condense to droplets of aqueous HCl, giving rise to smoke and to corrosion of metal surfaces. The wide use of ammonium perchlorate fuel binder composite propellants in rockets is an indication that for rocketry HCl in the exhaust is not a serious problem. If other atomic species are present in the binder, their compounds will, of course, appear

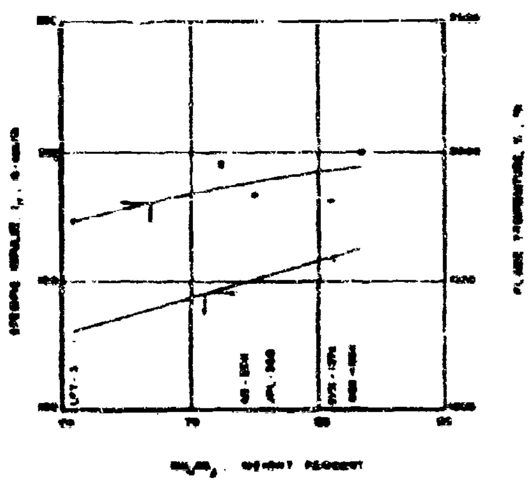


*Figure 61. Specific Impulses, $I_{sp}$, and Flame Temperatures, $T_p$, of $NH_4NO_3$-Fuel Binder Composites*

in the exhaust and may be additional sources of corrosion.

**56-3. Lithium perchlorate.** Lithium perchlorate has received some attention as an oxidizer in these composite propellants (*e.g.*, GCR-300 in SPIA/M2). This oxidizer should be superior to potassium perchlorate in that the LiCl should all be vaporized and form part of the working fluid, with the amount of available oxygen per unit weight of oxidizer higher due to lower molecular weight. Condensation of LiCl in the exhaust should lead to dense smoke as in the case of the potassium salt. Propellants containing lithium perchlorate have higher density but are more hygroscopic than corresponding ammonium perchlorate propellants.

**56-4. Ammonium nitrate.** The use of ammonium nitrate as oxidizer in fuel binder composites avoids the problem of corrosive exhaust due to HCl, at the cost of lowered specific impulse. As indicated in Table 13, the volume $\left(\frac{1}{M}\right)$ of product gas is higher than for a corresponding ammonium perchlorate propellant, so that the lower specific impulse must result from a lower flame temperature, $T_p$. This is indeed the case, as may be seen in Figure 61. The maximum specific impulse appears to be in the neighborhood of 200 lb-sec/lb, and this is attained at a flame temperature some hundreds of degrees lower than for the same specific impulse in the ammonium perchlorate system. If maximum performance is not required, quite low flame temperatures can be attained by decreasing the ammonium nitrate loading, or by incorporating thermally decomposed diluents such as cyanoguanidine.

Burning rates appear to range from 0.05 to 0.27. The combination of low temperature and low burning rate is attractive for gas generator uses. The higher rates are available through the use of catalysts such as Prussian blue (ferric ferrocyanide),[7,8] Milori blue,[7] chromium compounds such as ammonium dichromate,[8] cobalt compounds,[8] or sodium barbiturate.[10] The higher burning rates so produced[4] are useful in sustainer motors and even booster rockets.[11]

The burning mechanism of ammonium nitrate propellants has been extensively investigated. Ammonium nitrate is also a monopropellant, and its first pyrolytic product is a gaseous mixture of $NH_3$ and $HNO_3$. The rate-controlling reaction is presumed[7] to be the redox reaction

$$NH_3 + NO_2 \rightarrow NH_2 + HNO_2 \qquad (58)$$

and in the thermal layer theory the reactions of binder pyrolytic products with the ammonium nitrate pyrolytic products occur so late (so far from the burning surface) that they do not communicate heat to the burning surface. This would explain qualitatively the slow burning rates. The mechanism of catalysis has not been explained.

The combustion products of ammonium nitrate composites are $N_2$, CO, $CO_2$, $H_2$, and $H_2O$, the same as from smokeless powders, and present no new problems. They are generally in a comparatively high state of oxidation, so that even the cool formulations burn without producing much free carbon.

Ammonium nitrate is hygroscopic and, in addition, exhibits phase changes at several temperatures. Precautions must be taken to keep ammonium nitrate propellants below 40 percent relative humidity during manufacture and subsequent handling. Processing is preferably done at temperatures above 90°F to avoid cycling through the phase change at that temperature. The higher performance ammonium nitrate propellants are so formulated that their volume fraction of binder is too low to permit casting. Extrusion or compression molding processes are commonly used to fabricate such propellants.

**56-5. Mixed oxidizers.** Combinations of oxidizers are sometimes used to get burning rates outside the normal ranges for single oxidizers. The combination of potassium perchlorate[11] with ammonium perchlorate leads to higher burning rates than the arithmetic mean of the normal rates of the two oxidizers measured separately. This combination preserves the high pressure exponent (*e.g.*, T10-E3 in SPIA/M2) of the potassium perchlorate propellants, indeed in some proportions of these two oxidizers values of *n* approaching or even exceeding 1 have been observed. Ammonium nitrate, nitroguanidine, or cyclotetramethylenetetranitramine (HMX) may be used as part of the oxidizer[11] to lower the burning rate of an ammonium perchlorate propellant. Ammonium picrate comprises part of the oxidizer in the British plastic propellants.

**57. Volumetric relation of oxidizer to binder.** As shown above, the ballistic properties of a fuel-binder composite propellant are determined by the weight fraction of oxidizer. The physical properties including fluidity during manufacture are determined by the volume fraction of binder and on the choice of binder, with the shape of the oxidizer particles and their grist playing a supporting role. Roughly spherical solids can be dispersed in liquids up to about 50 volume percent without having much effect on the fluidity of the system, and with favorable grist and solid particle shape the volume fraction of the continuum may be decreased to 40 or even 35 volume percent before the presence of the solids is strongly felt in the fluidity of the system. Beyond that point the viscosity of the system increases rapidly, and a concentration is soon reached where the system will not flow. In the fuel binder composite system, casting loses its feasibility when the volume fraction of the binder goes much below 30 percent. Concurrently even with elastomeric binders the distortion at rupture approaches a low value when the volume fraction of the binder decreases below this region. For case-bonded systems, therefore, the fraction of binder must be maintained above this minimum in order that the grain maintain its integrity over a temperature range. This means that when one is formulating a high performance grain, which will therefore require a low weight fraction of binder, the preferred binder will be a low density material in order that the volume fraction of the binder be simultaneously kept high. On the other hand, at low oxidizer loading such as is preferred for low flame-temperature gas generator propellants, the binder weight fraction will be naturally higher and one might well choose a dense binder to minimize the envelope. Table 14 illustrates the effect of binder density on the weight percent oxidizer loading at a constant 30 volume percent binder basis.

**TABLE 14. OXIDIZER LOADING VERSUS BINDER DENSITY PER UNIT VOLUME**

| | | | |
|---|---|---|---|
| Binder density | 1.0 | 1.2 | 1.4 |
| Volume | 0.30 | 0.30 | 0.30 |
| Weight | 0.30 | 0.36 | 0.42 |
| $NH_4ClO_4$ volume | 0.70 | 0.70 | 0.70 |
| Weight | 1.37 | 1.37 | 1.37 |
| Propellant density, ρ | 1.67 | 1.73 | 1.79 |
| $NH_4ClO_4$, weight percent | 82 | 79 | 76 |
| Binder, weight percent | 18 | 21 | 24 |
| $NH_4NO_3$ volume | 0.70 | 0.70 | 0.70 |
| Weight | 1.21 | 1.21 | 1.21 |
| Propellant density, ρ | 1.51 | 1.57 | 1.63 |
| $NH_4NO_3$, weight percent | 80 | 77 | 74 |
| Binder, weight percent | 20 | 23 | 26 |

**58. Choice of binder.** End-item use may require either a cartridge-type grain, for ease of inspection or for repetitive use of the chamber, or a case-bonded grain for high performance. If a cartridge-type grain is called for, the propellant

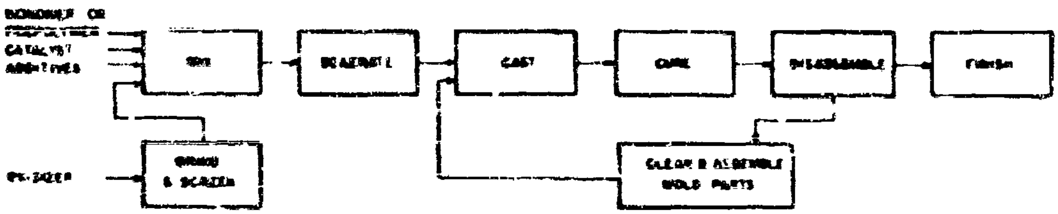


Figure 62. Slurry Casting Process

must have high modulus and some compressive strength. If the grain is to be case-bonded the stresses to which the grain will be subjected call for low modulus and high elongation.

**58-1. Asphalt.** Asphalt, the first binder used in a fuel-binder composite, produced a case-bondable propellant. As may be seen from the data sheet on ALT-161 (see SPIA/M2), the asphalt was softened with a plasticizer to decrease the modulus so that the propellant could be used over a suitable but restricted temperature range. At temperatures below about −20°F the propellant became very brittle, leading to fracture and explosion on ignition. At temperatures above about 120°F the propellant became quite soft and flowed away from its design geometry. Asphalt had the advantage of being cheap and available. The propellant manufacture was simple, the oxidizer was incorporated into the binder at elevated temperature using a sigma blade mixer and the mixture was poured into the mold or case and allowed to cool.

**58-2. Polyisobutene.** Polyisobutene, used in the British "plastic propellant," differs from asphalt chiefly in having a better temperature coefficient of physical properties. An example of such propellant is R.D. 2312 (see SPIA/M2). The oxidizer ammonium picrate is readily deformable and hence permits a lower than normal binder volume fraction. It also affords a lower burning rate than ammonium perchlorate would give as the sole oxidizer.

**58-3. Elastomeric binders.** Tensile strength enough to enable the propellant to withstand handling and firing accelerations is added to the binder properties by incorporation of a polymer, often cross-linked, into the binder. The polymer may be one of the rubbers, used with or without a plasticizer, or it may be one of the nonrubbery thermoplastics such as cellulose acetate or poly(vinyl chloride), used with enough plasticizer to bring the modulus of the propellant into the proper range.

**58-3.1. Polysulfide rubber.** The first such binder was formulated with polysulfide rubber,[11] and polysulfide rubbers have remained important constituents of case-bonded composite propellants.[11] The polymer is introduced as a partially polymerized prepolymer (liquid polymer) and polymerization is completed during the curing operation in the case or mold at elevated temperature and in the presence of a polymerization catalyst such as *p*-quinonedioxime. In order to accelerate the cure or to accomplish it at a lower temperature, a promoter such as diphenylguanidine is sometimes also used. Magnesium oxide and ferric oxide may be used to modify the burning rate, and other additives are occasionally used for various reasons.

Polysulfide propellants are fairly dense, reflecting the density of the polysulfide polymer. This feature restricts the allowable oxidizer loading. In the moderate performance range, on the other hand, a given total impulse can be contained within a smaller envelope than with a less dense propellant. At temperatures above about 0°F the tensile strain at rupture is typically 50 to 100 percent, being lower with the higher loading density. This level is generally adequate for case-bonded applications.

In more than 10 years of existence, polysulfide propellants have not shown seriously deleterious aging effects except for a change on the exposed surface of the grains that interferes with ignition. It is believed that this property has been overcome in later formulations, but this can be demonstrated only when the newer propellants have been aged.

The manufacturing process used for polysulfide propellants is the slurry casting process,[11] for which the flowsheet is shown in Figure 62.

Courtesy of Thiokol Chemical Corporation, Redstone Division

Figure 63. Sigma Blade Mixer (200 Gallon)

Reproducibility of the oxidizer grist is one of the most important quality control measures in the manufacture. The mixer may be a sigma blade mixer, equipped with bottom outlet, shown in Figure 63, or, alternatively, a vertical mixer shown in Figure 64. The ingredients are added consecutively to the mixer, starting with the prepolymer. At the conclusion of the mixing the charge is deaerated by evacuation or other means and cast into the motor case. Curing is accomplished by subjecting the loaded case to elevated temperature in a heated space (a pit is used for large charges). The mandrels are removed after the cured charge is cooled, and the charge is finished by machining any designed surfaces not produced by the mold. In general, such surfaces are chiefly the aft end of the grain. A typical mandrel is shown in Figure 65, and a motor with case-bonded grain in Figure 66.

Polysulfide-ammonium perchlorate grains from 1.5 inches to 40 inches in diameter, and in weights from 0.5 pound to 8700 pounds have been manufactured and flown in rocket motors. Examples of polysulfide-ammonium perchlorate composites in service use are

T14 used in early experimental work with large engines;

T17 used in RVA10, Sergeant (XM-12), X17, reentry vehicle (XM20), and various test vehicles in the Polaris and NASA high altitude programs,

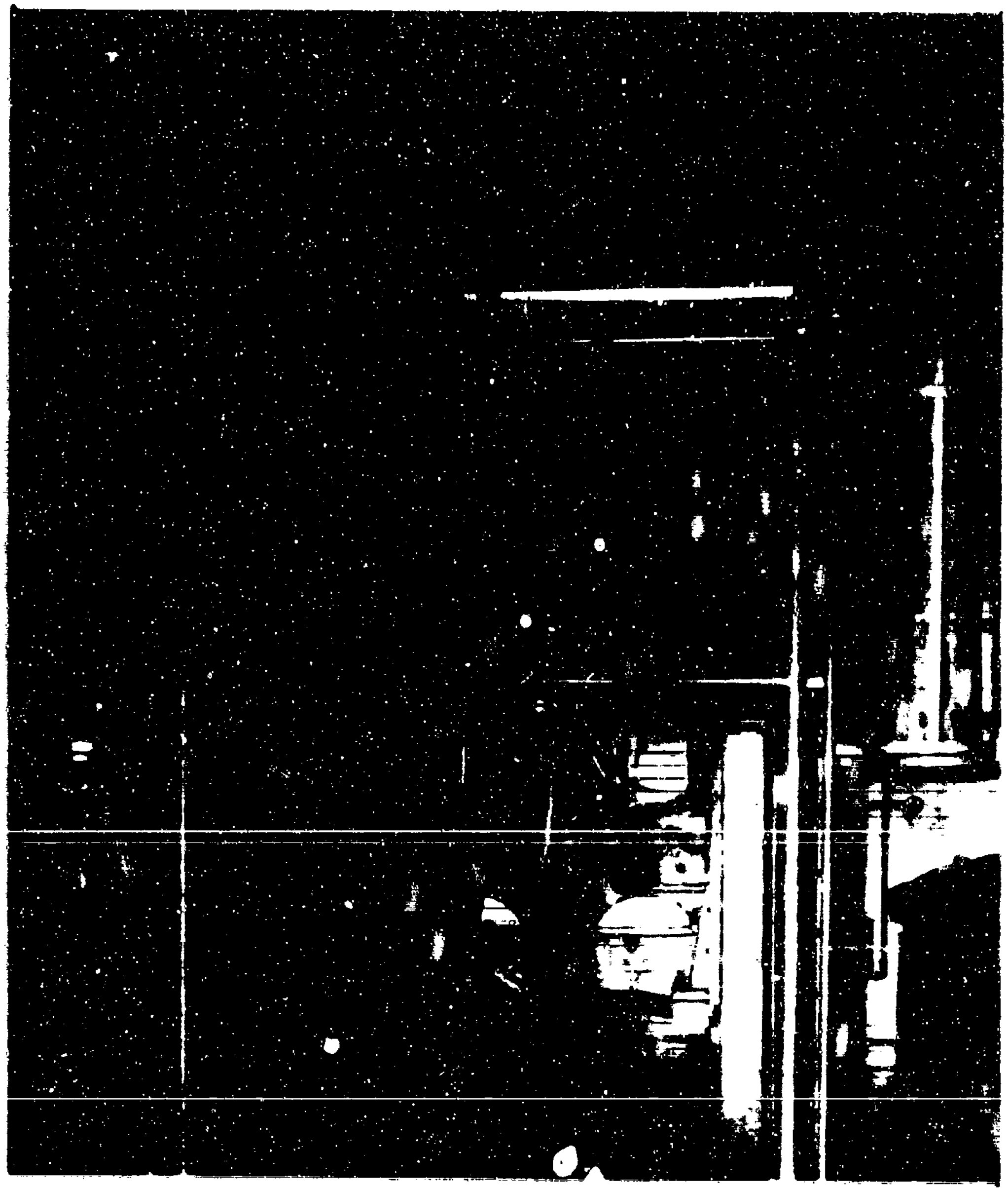
T24 used in the Honest John spinner rocket (M-7);

T13E1 used in various aerodynamic test vehicles (T-40);

T-22 used in Loki;

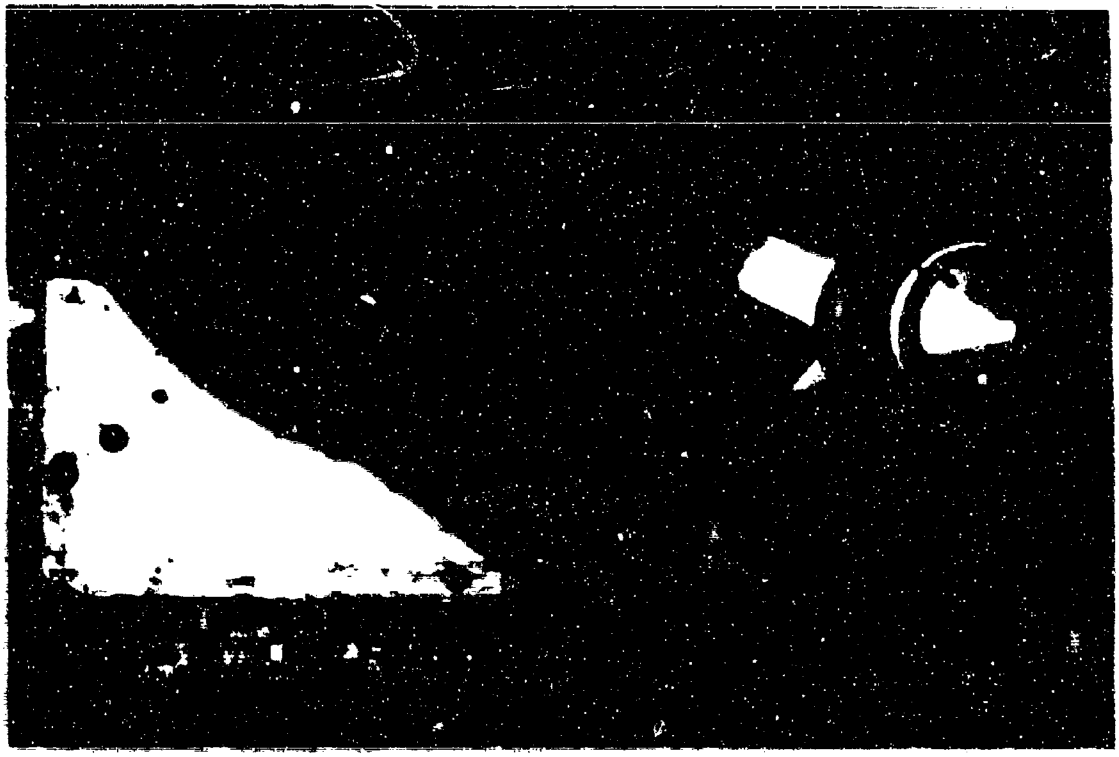
GCR-201C used in Vanguard third stage rocket, and

T27 used in Falcon (XM-46) two-level thrust motor.



*Courtesy of Thiokol Chemical Corporation, Redstone Division*

*Figure 64. Vertical Mixer (300 Gallon)*



*Courtesy of Thiokol Chemical Corporation, Redstone Division*

*Figure 65. Mandrel for Medium Size Rocket Motor*

**58-3.2. Polyurethane rubber.** Apart from the polysulfides, most synthetic rubbers are formed by vinyl-type polymerization, or addition at double bonds. Other polymerization reactions not involving production of volatile by-products are known and may be useful in preparation of propellant binder. For example, if an isocyanate is added to a compound containing an $-OH$ group, a urethane is formed according to the reaction

$$R'NCO + HOR'' = R'NHCOOR'' \qquad (59)$$

Reaction of a diisocyanate and a diol thus gives a long chain linear polyurethane, and the presence of some polyol or polyisocyanate should cause the polymer to cross-link. In order to minimize the heat of polymerization during the cure it is customary to use a long chain diol such as polypropylene glycol, $H[O\text{-}CH_2\text{-}\underset{CH_3}{CH}]_n\text{-}OH$, with a simple diisocyanate such as toluene diisocyanate. There are many long chain diols available but only relatively few diisocyanates are on the market. The polymerization reaction must be catalyzed, as by ferric acetyl acetonate, and accelerators of the polymerization are known. The polymer may be used with or without a plasticizer.

The physical properties are similar to those of polysulfide propellants at the same binder volume fraction. The density of the polyurethane propellant is naturally lower than that of a polysulfide propellant at the same oxidizer weight fraction.

The manufacturing process is the same as that for polysulfide propellant, with one important precaution. Since the isocyanates react with $-OH$ groups, it is particularly important that all ingredients be quite dry. Addition of water to isocyanates results in $-NHCOOH$ groups which tend to decompose. Polyurethane binders have been more extensively used in the aluminum-ammo-

*Courtesy of Thiokol Chemical Corporation, Redstone Division*

*Figure 66. Medium Size Case-Bonded Grain With a 5-Point Star Configuration*

nium perchlorate-binder propellants described in ORDP 20-176.

**58-3.3. Butadiene-acrylic acid copolymer rubber, PBAA.** When butadiene is copolymerized with acrylic acid and cured with an epoxide, an elastomeric binder results with properties fairly similar to those described for the polyurethanes. This binder system has a comparable density to that of the polyurethane binder, tolerates about the same weight percent of oxidizer in a case-bondable propellant, and gives performance in the same range. The manufacturing process is essentially that shown in Figure 62. PBAA binders are receiving considerable attention in the newer aluminum-ammonium perchlorate propellants, discussed in ORDP 20-176.

**58-3.4. Poly(vinyl chloride).** A nonrubbery polymer, if, sufficiently plasticized, may develop in a heavily loaded plastic about the same ultimate tensile strength, elongation, and modulus as a rubbery polymer with little or no plasticizer. This situation is taken advantage of in the poly(vinyl chloride) propellants such as Arcite 368 used in the Arcon sounding rocket motor. At a comparable density to that of the polyurethane propellants, a poly(vinyl chloride) propellant permits about the same weight fraction of oxidizer and develops about the same specific impulse. At a lower plasticizer level a stiffer binder and therefore a more rigid propellant results, with properties of compressive strength and high modulus required for a cartridge-loaded grain. Cross-linking may be accomplished by formulation with agents that react during the cure.

A novel feature of the poly(vinyl chloride) propellants is their method of manufacture. The polymer, already completely polymerized, is suspended in the plasticizer together with the oxidant and additives during the mixing operation. At ambient

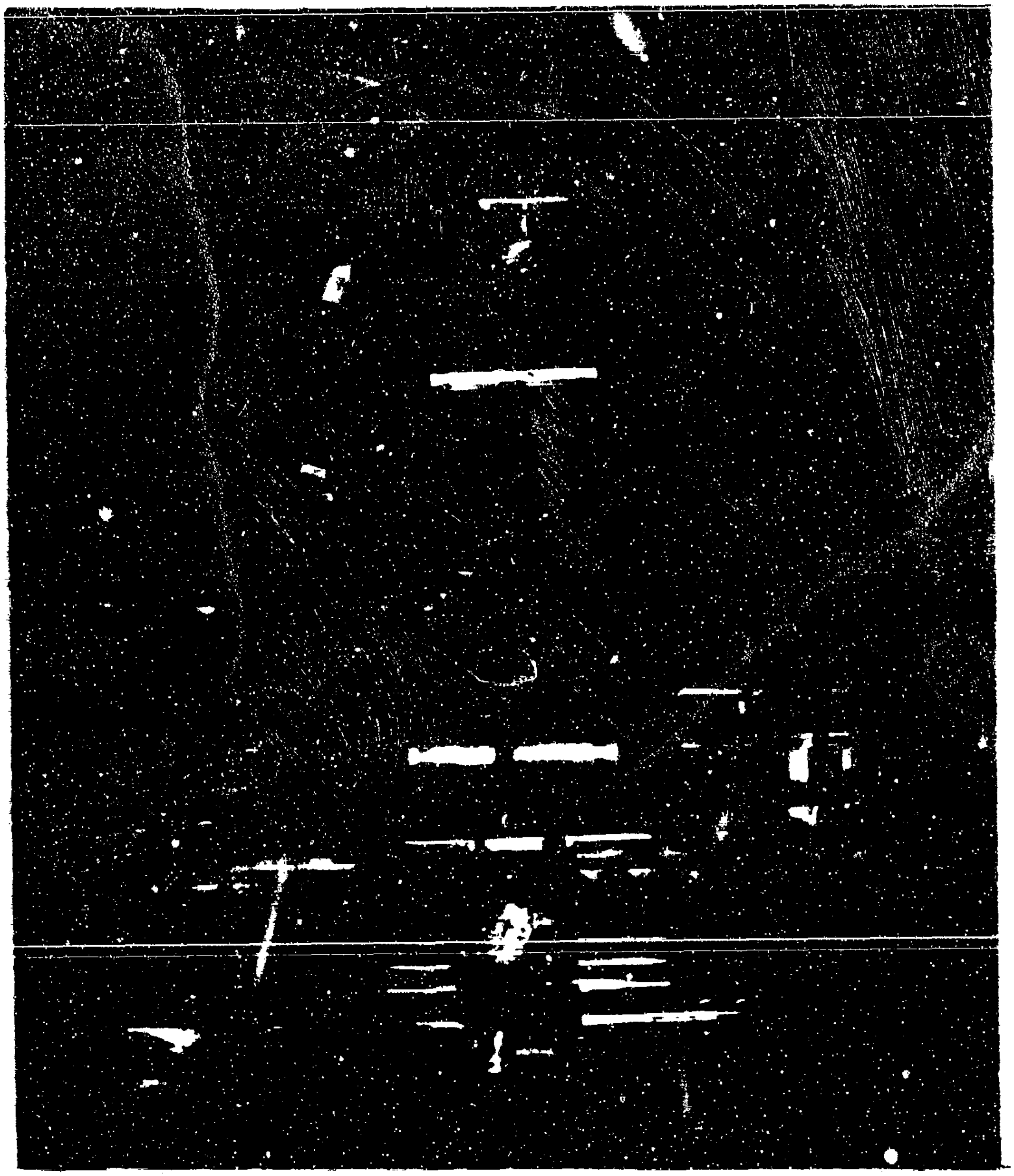


Figure 67. 1-Inch Extruder for Poly(Vinyl Chloride) Propellant

Courtesy of Atlantic Research Corporation

1. Hopper for inert propellant feed
2. Pressurized filling pot for Arcite propellant
3. "Hot" propellant feed
4. Barrel of extruder
5. Die
6. Water trough
7. Take-off rollers
8. Automatic saw
9. Extruded propellant

Courtesy of Atlantic Research Corporation

*Figure 68. Extrusion of Wired Grain*

temperature, or perhaps at a chilled mixing temperature, the polymer does not imbibe the plasticizer, so that good pot life is attainable. The still fluid mix, called plastisol, is transferred to the case or mold and the grain is cured and finished. The curing operation is mechanically the same as for the synthetic rubbers, shown in Figure 62, but it is chemically quite different. These propellants may also be extruded. A small extruder is shown in Figure 67, illustrating the essentials of this process. The extruder is operated at a temperature above 350°F, and curing takes place during the extrusion. Grains containing wires strung parallel to the axis may also be extruded, as shown in Figure 68. Since no polymerization takes place during the cure, there is no exotherm and little, if any, volume change due to curing. On the other hand, the high temperature of the curing operation entails appreciable thermal shrinkage when the cured grain is brought to ambient temperature.

**58-3.5. Elastomeric binders for cartridge-loaded grains.** Although the case-bondable binders do not in general contain so much plasticizer that they can be stiffened by eliminating plasticizer, there are at least three ways that elastomers can be adapted to such use. One such way is to bond the grain to a relatively rigid mechanical member separable from the case, which may also serve as an inhibitor. Another is to cross-link the polymer to a greater extent than is required for the readily deformable case bonds. The third method is to decrease the volume fraction of the binder to below 30 percent so that interaction of the crystalline particles carries part of the imposed load and helps resist deformation. The first two alternates would still permit fabrication of the grain by casting. The third would require other fabrication techniques. In the case of propellant CPN-127A (see SPIA/M2) used in aircraft jatos, the binder employed is a butadiene-2-methyl-5-vinyl-pyridine

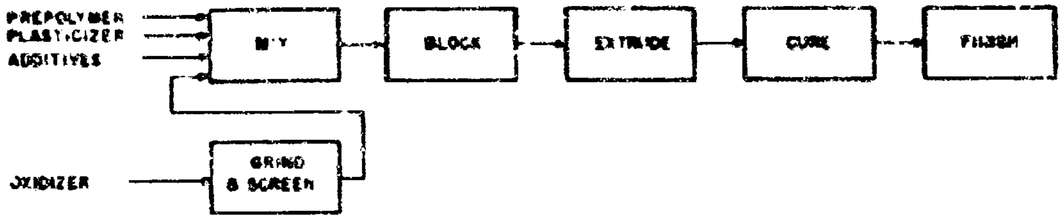



*Figure 69. Extrusion Process for Fuel Binder Composites*

copolymer plasticized with the formal of diethylene glycol monobutyl ether (Butyl Carbitol formal). The volume fraction of the binder, calculated from the composition and densities of the crystalline ingredients, is about 26 percent. The manufacturing process for this propellant is outlined in Figure 69. Mixing is done in a sigma blade mixer. The completed mix is blocked in a hydraulic press, shown in Figure 70, to form a press charge for extrusion. The extrusion press is shown in Figure 71. The extruded strand is cut to grain blanks which are then cured at elevated temperature to complete the polymerization. The cured grain blanks are finished by machining to final dimensions.[11,15]

Still another fabrication process ... used for propellant CBS-128K (see SPIA/M2), developed for the Dart and Sky Dart missiles. This propellant uses GR-I rubber plasticized with di-(2-ethylhexyl) azelate, and has a binder volume fraction even lower than CPN-127A. The flowsheet for this process is shown in Figure 72. Compounding and simultaneously curing is done on a roll mill. Disks are cut from the rolled sheet, stacked, and compression molded, as shown in Figure 73, to grain blanks. The grain blanks are machined, as shown in Figure 74, and then inhibited.

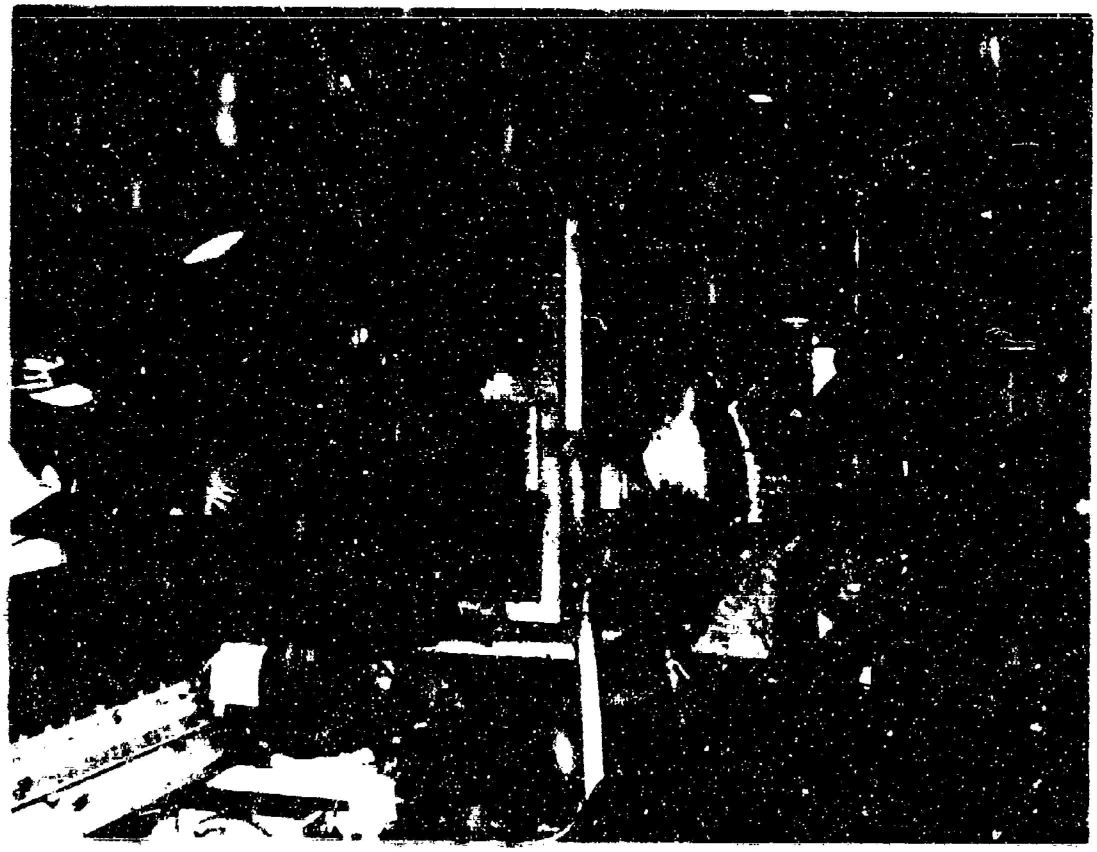
**58-4. Thermoplastic synthetic polymer binders for cartridge-loaded grains.** The use of thermoplastic polymers polymerized *in situ* predates the use of the elastomeric polymers. The binder systems are selected to give compressive strength and high modulus, thereby permitting attainment of the required physical properties in a grain produced by the slurry casting process of Figure 62. The prepolymers or monomers are mixed with the oxidizers and other additives in a sigma blade or equivalent mixer and cast into molds. Polymerization is completed at elevated temperatures in the curing operation in the molds. The molds are then disassembled and the grains finished by machining and/or inhibiting. Figures 75 and 76 show completed grains and their ... ators.

**58-5. Cellulose acetate.** Cellulose acetate is made from a natural polymer and is not available in a monomeric or prepolymer state. It has a fairly high softening temperature which can be lowered by compounding with a plasticizer, allowing the propellant to be mixed and formed at a moderately elevated temperature. In propellant LFT-3 (see SPIA/M2), used in the GAR 3 Falcon APU, the cellulose acetate is plasticized with acetyl triethyl citrate and dinitrophenoxyethanol, and stabilized with toluenediamine. The oxidizer loading is fairly low in order to maintain a desired low flame temperature. Mixing is done in a sigma blade mixer, and the grain is formed by compression molding. Larger grains may be made by bonding segments together using a polyurethane layer between the segments as well as for the peripheral inhibitor. A 50-pound individual segment as molded is shown in Figure 77 and a 1000-pound segmented grain in Figure 78.

**58-6. Other binder systems.** The above listing is by no means a complete roster of binder systems that can be used or even of systems that have been experimented with. A considerable effort has been expended on binders containing acetylenic and other endothermic groups which might add to the heat of explosion, $Q$, of the propellant at a given oxidizer loading. There is still room for binders with improved physical properties such as coefficients of expansion closer to the expansion coefficients of the materials used for rocket motor case manufacture, lower brittle temperatures, and less temperature dependence of modulus, compressive and tensile strength, and elongation at rupture. It is expected that new binder systems will continue to appear.

*Courtesy of Rocketdyne Division of North American Aviation, Inc*

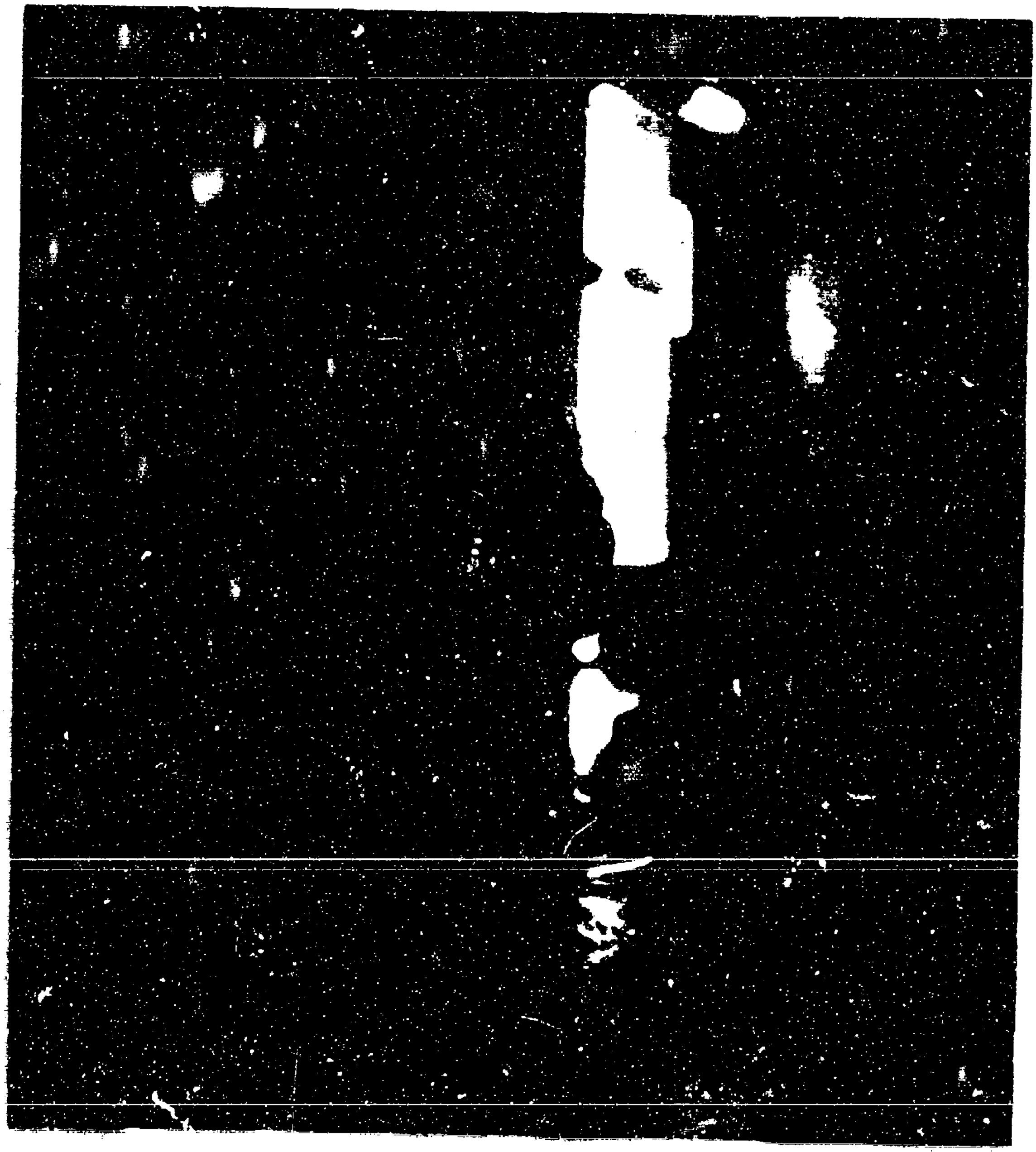
*Figure 70. Blocking Press*



Courtesy of Rocketdyne Division of North American Aviation, Inc.

Figure 71. Extrusion Press


Figure 72. Compression Molding Process for Fuel Binder Composites



Courtesy of Grand Central Rocket Company

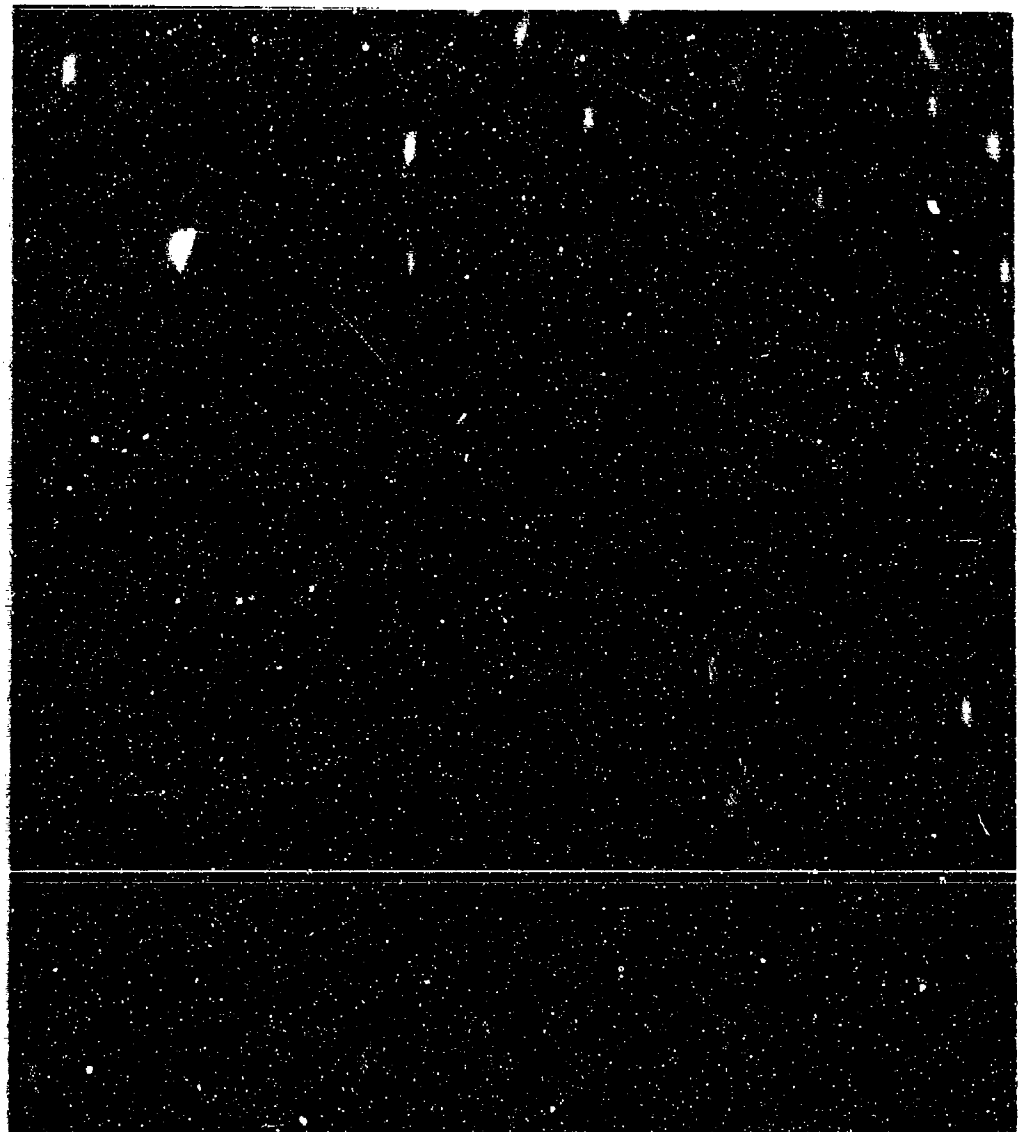
Figure 73. Compressing Stacked Disks

*Courtesy of Grand Central Rocket Company*

*Figure 74. Machining Outside Diameter of Grain*

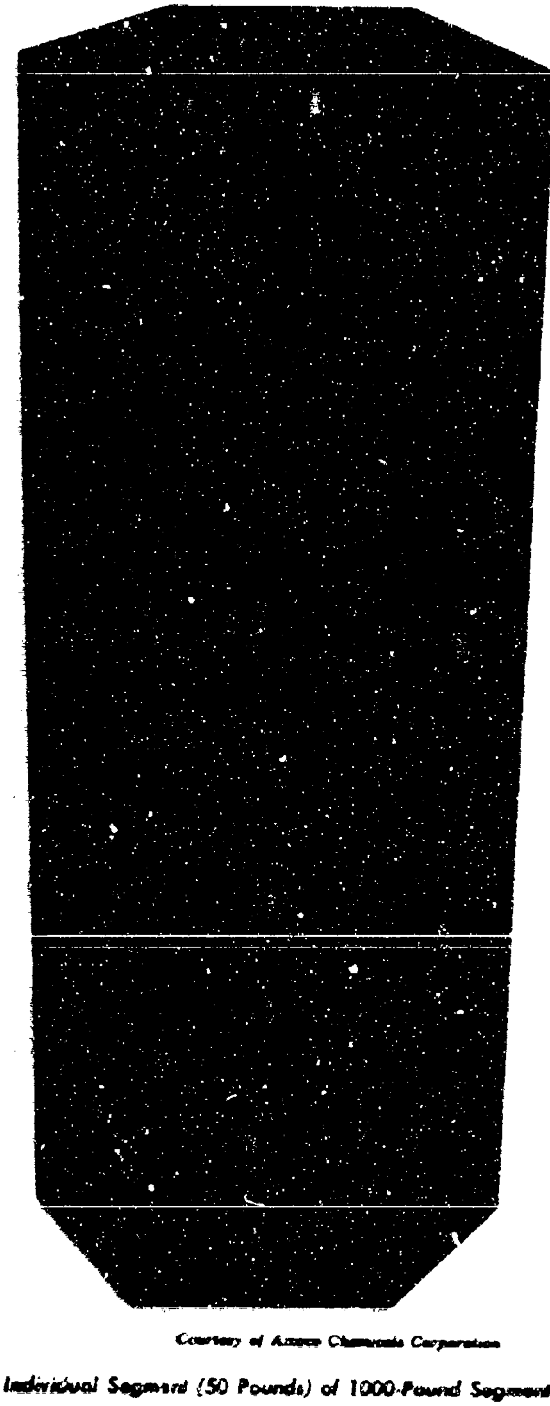
Courtesy of Aerojet General Corporation

Figure 75. Jato Grains



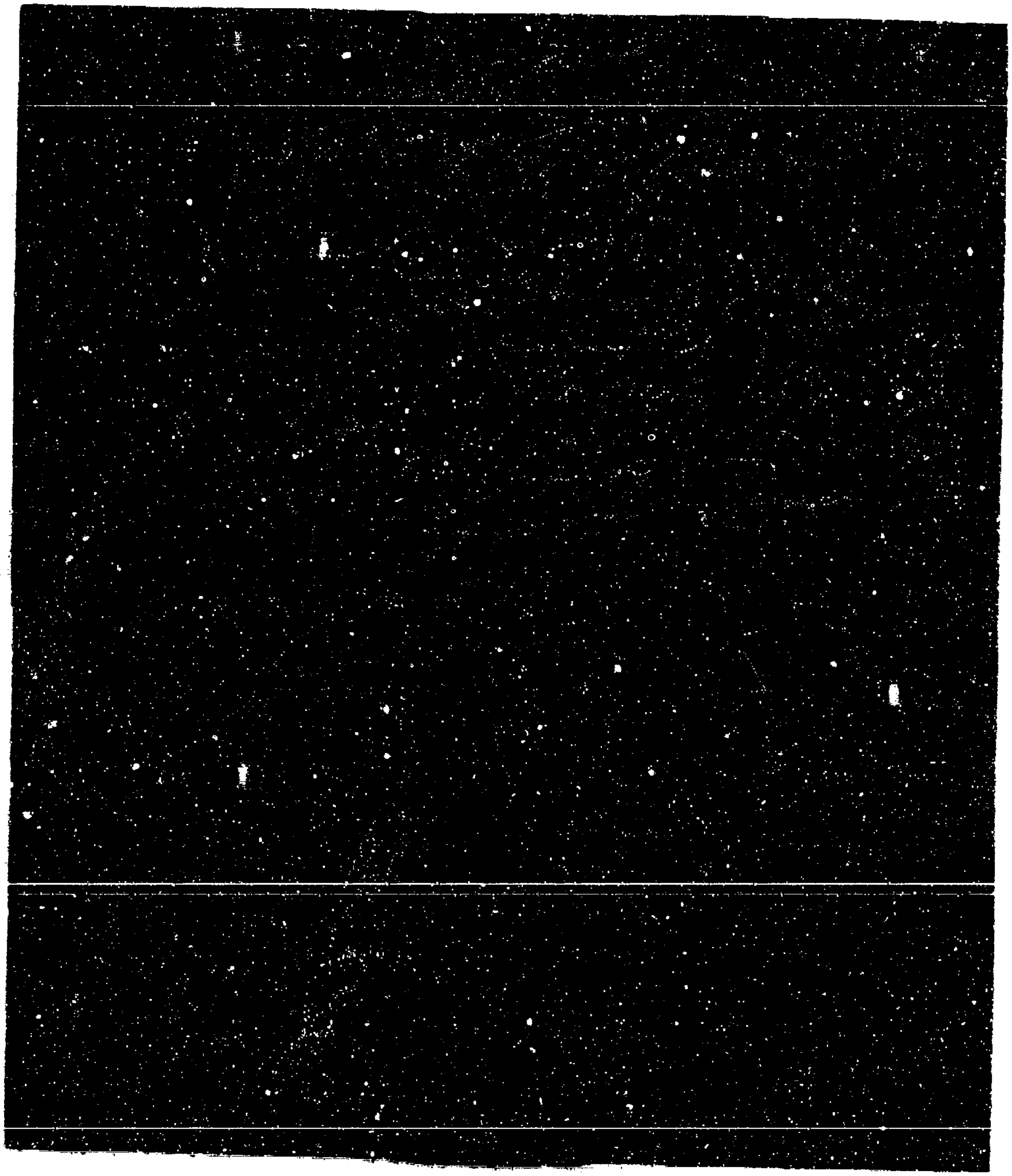
Courtesy of Aerojet-General Corporation

*Figure 76. Finished Jatos*



Courtesy of [illegible] Chemicals Corporation

*Figure 77. Individual Segment (50 Pounds) of 1000-Pound Segmented Grain*



Courtesy of [illegible] Chemicals Corporation

*Figure 78. Segmented Grain (1000 Pounds)*

## REFERENCES


1. R. D. Schultz and A. G. Dekker, "Transition-State Theory of the Linear Rate of Decomposition of Ammonium Perchlorate," *Sixth Symposium (International) on Combustion*, p. 618, Reinhold Publishing Corporation, New York, New York, 1957.
2. M. Summerfield, E. S. Sutherland, M. J. Webb, H. J. Taback and K. P. Hall, *Burning Mechanism of Ammonium Perchlorate Propellants*, paper presented at American Rocket Society 13th Annual Meeting, 17-21 November 1958, New York, New York.
3. R. F. Chaiken and W. H. Anderson, *The Role of Binder in Composite Propellant Combustion*, Aerojet-General Corporation, Report TN-30, AFOSR TN 59-540, July 1959,. Contract AF49(638)-566 (SPIA Abstract No. 19,561).
4. N. A. Laury, *Hydrochloric Acid and Sodium Sulfate*, p. 16, Chemical Catalog Company, Inc., New York, New York, 1927.
5. W. A. Proell, *Development of Ammonium Nitrate Base Solid Propellant*, Standard Oil Company (Indiana), Bimonthly Report No. 3, November 1951, Contract USAF 33(038)27541, CONFIDENTIAL (SPIA Abstract No. 12,468).
6. J. Linsk and R. W. Todd (to Standard Oil Company [Indiana]), U. S. Patent 2,936,225 (1960).
7. Phillips Petroleum Company, *Development of Composite Propellant Into Units*, Final Report on Supplemental Agreement No. 1 (Report 722-3-54RF), 1 July 1954, Contract AF 33(600)6710 (SPIA Abstract No. 14,258).
8. Picatinny Arsenal, *Basic Research on Plastic Rocket Propellants*, MR June-Dec., 1946, Jan.-Dec., 1947, Jan-Dec., 1948, Jan.-May, 1949, CONFIDENTIAL (SPIA Abstract No. 10,073).
9. J. L. Jones, *Progress in the Development of An Ammonium Nitrate Smokeless Solid Propellant*, Jet Propulsion Laboratory, California Institute of Technology, Bulletin of the Fourth Meeting of the Army-Navy Solid Propellant Group, p. 207, CONFIDENTIAL, Solid Propellant Information Agency, Applied Physics Laboratory, The Johns Hopkins University, Silver Spring, Maryland (SPIA Abstract No. 3715).
10. N. J. Bowman, *Development of an Ammonium Nitrate Base Solid Propellant*, Standard Oil Company (Indiana), Quarterly Report No. 29 (Aug.-Oct. 1956), 15 January 1957, Contract 33(038)27541, CONFIDENTIAL (SPIA Abstract No. 17,132).
11. Standard Oil Company (Indiana), private communication.
12. H. W. Ritchey (Thiokol Chemical Corporation), private communication.
13. A. M. Jacobs and J. H. Godsey, *Burning Rate Modification of Double-Base Propellants*, Allegany Ballistics Laboratory, Hercules Powder Company, Bulletin of the Fifteenth Meeting of the Joint Army-Navy-Air Force Solid Propellant Group, Vol. IV, p. 41, CONFIDENTIAL, Solid Propellant Information Agency, Applied Physics Laboratory, The Johns Hopkins University, Silver Spring, Maryland.
14. C. E. Bartley, *A Preliminary Investigation of the Rubber-Base Solid Propellant ORDCIT 21*, Jet Propulsion Laboratory, California Institute of Technology, CIT/JPL PR 4-18, 26 August 1945, CONFIDENTIAL (SPIA Abstract No. 2990).
15. W. C. Aycock, *Design and Internal Ballistic Data for Polysulfide-Perchlorate Propellants*, Thiokol Chemical Corporation, Report No. 24-51, October 1951, CONFIDENTIAL (SPIA Abstract No. 11,287).
16. A. T. Guzzo, *Development of Standard Operating Procedures for Manufacture of Polysulfide Perchlorate Propellants*, Thiokol Chemical Corporation, Report No. 26-51, November 1951, CONFIDENTIAL (SPIA Abstract No. 11,361).
17. C. F. Dougherty, "Processing Rubber-Base Composite Rocket Propellant," *Chem. Eng. Progr.* **53**, 489 (1957).
18. R. S. Dobyns and J. A. McBride, *Production Problems on Solid Propellant Rocket Motors*, paper presented at American Rocket Society Semiannual Meeting, 10-13 June 1957, San Francisco, California.

## CHAPTER 10

# INERT SIMULANTS FOR PROPELLANTS

59. **General.** Propellants are hazardous materials, necessary for functioning in their engines but undesirable for many uses such as display and break-in of manufacturing equipment when functioning is not contemplated. To meet the requirement for materials for such nonfunctioning uses, inert simulants or dummy formulations have been developed to represent propellants. The ideal inert simulant for any propellant should duplicate the propellant in all physical properties—appearance, density, texture, hardness, physical strength, and plasticity over a temperature range—without being a propellant. Considerable compromise with the ideal is permissible and usual to save time and development expense, depending on the use to which the dummy is to be put.

60. **Mock-ups.** Where geometry is the only consideration, as for illustration of the spatial relationship of the propellant to other parts of the engine or for assurance that the engine complete with propellant can be assembled, the dummy may be built of wood and painted the proper color. Coal is an admirable mock-up for black powder.

61. **Simulants to reproduce physical properties.** In order to demonstrate the physical properties of a propellant by the use of an inert simulant, one needs something more closely akin to the propellant than a wood mock-up. Most modern propellants are plastics, and a plastic dummy will look, feel, and handle more like its live counterpart. Most of the physical properties of propellants are traceable to the polymer content. In the case of fuel binder composite propellants the same volume percent of the same binder together with a suitable filler should result in a reasonable duplication of the physical properties. The filler should, if possible, have the same specific gravity and crystal structure as the oxidant used in the live propellant. For example, potassium chloride is a good replacement for ammonium perchlorate. If the specific gravity of the filler cannot be precisely matched and density of the dummy is important, as in locating the center of gravity of the engine, the volume percent of binder can usually be compromised safely. Alternatively, two inert simulants for a propellant may be developed, one to duplicate density and another to duplicate other physical properties required.

The problem is considerably more difficult when the polymer is itself a propellant as is nitrocellulose. In this case an inert polymer should be found, with density and other physical properties duplicating the propellant polymer. This has, in general, not been done. Cellulose acetate is a popular simulant for nitrocellulose, but it is not very good. The difference is appreciable in density, appearance, and feel, even with the best available plasticizers. In order to reproduce density it appears necessary to use crystalline fillers which worsen the match between dummy and live propellant in other properties.

An inert simulant for OIO cast double-base propellant (see SPIA/M2) was formulated as follows.

| | Casting Powder | Casting Solvent |
|---|---|---|
| Cellulose acetate | 0.57 | — |
| Triacetin | 0.10 | 0.962 |
| Graphite | 0.03 | — |
| Red lead | 0.30 | — |
| 2-Nitrodiphenylamine | — | 0.038 |
| | 1.00 | 1.00 |

Comparison of the inert with live OIO:

| | Inert | Live |
|---|---|---|
| Casting Powder | | |
| Density, $\rho$, g/cc | 1.75 | 1.5 |
| Packing density, g/cc | 1.02 | 1.01 |
| Cast Powder | | |
| Density, $\rho$, g/cc | 1.60 | 1.55 |
| Tensile strength, psi | 465 | 900 |
| Elongation, percent | 8 | 49 |
| Volume coefficient of expansion, per degree F | $6.2 \times 10^{-4}$ | — |

62. **Simulants to reproduce manufacturing properties.** In the development of new manufacturing equipment, for checking out extruders and other types of processing machinery after maintenance or prolonged inactivity, and to displace live propellant preparatory to disassembly of processing equipment, it is necessary to have a dummy formulation that behaves like live propellant in process. In general this requires matching mechanical properties not only dry and at ambient temperature but also over a temperature range and

perhaps admixed with volatile solvents. Since it is the polymer which largely determines manufacturing properties as well as product physical properties, substitution of filler is generally adequate in fuel binder composites. It must be verified that the replacement filler will not affect the reaction rate of any chemical changes involved in the manufacture.

There are no good manufacturing dummies for nitrocellulose-base propellants. Wax,[1] with or without sawdust, or similar carbonaceous material and cellulose acetate compositions, respectively, have been used successfully for clean out and to put loads on machinery, but they do not duplicate the operating mechanical loads, nor do they duplicate the dimensional changes in the product during manufacture.

**63. Semilive.** In order to overcome the disadvantages of a completely inert dummy in studying manufacturing problems of nitrocellulose system propellants, semilive simulants have been developed, in which the nitrocellulose is retained as the polymer but all plasticizers used are fuel plasticizers. This results in compositions of low or negative calorific value. If ignited these simulants will burn slowly and incompletely, allowing operating personnel to escape safely but emphatically demonstrating any mechanical situations that could cause destructive damage with live propellant. In formulating a semilive propellant, the concentration of nitrocellulose should be about the same as in the live counterpart and the viscosity of the fuel plasticizer should be as close as possible to the viscosity of the combined plasticizers in the live propellant. With these initial criteria the composition of the semilive propellant can be readily developed empirically.

The composition and physical properties of N-5 and its semilive analog are shown below.

| | N-5 | Semilive |
|---|---|---|
| Nitrocellulose, 12.6% N | 50.00 | 54.19 |
| Nitroglycerin | 34.90 | — |
| Di-n-butyl phthalate | — | 30.97 |
| Di (2-ethyl hexyl) phthalate | — | 10.90 |
| Diethyl phthalate | 10.50 | — |
| 2-Nitrodiphenylamine | 2.00 | 2.11 |
| Lead salts | 2.40 | 2.10 |
| Candelilla wax | 0.20 | 0.21 |
| Specific gravity, ρ | 1.56 | 1.31 |
| Nitrocellulose concentration, g/cc | 0.78 | 0.71 |
| Tensile strength, crosswise, psi | 320 | 210 |
| Tensile strength, lengthwise, psi | 460 | 330 |
| Elongation, percent | 47 | 73 |

The lower tensile strength and greater elongation of the semilive propellant are seen to follow the lower nitrocellulose concentration as predicted. Extrusion pressure with the semilive was also considerably lower than with live N-5. In spite of the fact that the semilive appears to be somewhat deficient in nitrocellulose it has been used successfully to break in extrusion equipment of experimental design.

The measured calorific value, 435 cal/g, is well above the calculated value, demonstrating again the lack of equilibrium in calorimetry of cool propellants discussed in Chapter 2. The burning rate, about 0.07 in/sec at 70°F, 1000 psi, is low enough to prevent destruction of extrusion equipment in case of fire.

## REFERENCE

1. Hercules Powder Company, unpublished data.

# GLOSSARY

The terms below, as used in this Handbook, are Ordnance terms or are used in a specialized sense. Other terms are as defined in AR 320-5, Dictionary of United States Army Terms, *** MIL-STD-444, Nomenclature and Definitions in the Ammunition Area, Merriam-Webster's unabridged dictionary, or common usage.

**ABL.** *(abbr).* Allegany Ballistics Laboratory.

**ARPA.** *(abbr).* Advanced Research Projects Agency.

**bazooka rocket.** Shoulder fired rocket, specifically the 2.36-inch.

**binder.** Continuous phase in which some other material is embedded.

**burning rate, linear.** The rate of burning of a propellant measured normal to the burning surface.

**caliber.** The diameter of a projectile or the diameter of the bore of a gun or launching tube. Axial distance equal to the caliber.

**cannon.** A complete assembly, consisting of a tube and a breech mechanism, firing mechanism or base cap, which is a component of a gun, howitzer, or mortar. May include muzzle appendages. The term is generally limited to calibers greater than 1 inch.

**catapult.** An engine which accelerates a load by means of a piston driven by high pressure gas such as may be generated by the burning of a propellant.

**characteristic velocity.** A figure of merit of a rocket propellant, defined as $\frac{P_c A_t g}{\dot{w}}$.

**composite propellant.** A propellant system comprising a discrete solid phase dispersed in a continuous solid phase.

**covolume.** Volume occupied by a gas when compressed to its limit of compression.

**critical diameter.** Diameter of an explosive column below which detonation will not propagate.

**deflagration.*** Burning process in a solid system comprising both oxidant and fuel in which the reaction front advances at less than sonic velocity and gaseous products if produced move away from unreacted material. A deflagration may, but need not, be an explosion.

**degressivity.** Decrease of weight rate of burning as web is consumed.

**deterrent.** A material added to a propellant composition or applied to the surface of a grain to decrease the flame temperature or rate.

**detonation.** An explosion characterized by propagation of the reaction front within the reacting medium at supersonic velocity and motion of the reaction products in the same direction as the reaction front.

**double-base propellant.** A propellant with two explosive ingredients, such as nitrocellulose and nitroglycerin.

**erosive burning.** Burning at a rate higher than normally associated with existing pressure, due to velocity of combustion products over the burning surface.

**expansion ratio.** The ratio of the nozzle exit section area to the nozzle throat area.

**explosion.** A very rapid chemical reaction or change of state involving generally production of a large volume of gas and resulting in rupture of the container if present and generation of a shock wave in the surrounding medium.

**filler.*** Discrete material dispersed in substantial quantity in the continuous or binder phase of a composite propellant.

**flow, equilibrium.** Condition of continuous chemical equilibrium during expansion in the nozzle.

**flow, frozen.** Condition of no chemical reaction during expansion in the nozzle.

---

*Differs significantly from definition given in MIL-STD-444.

**force.** A figure of merit of a gun propellant, defined as $\frac{R_0 T_v}{M}$

**fuse.** An igniting or explosive device in the form of a cord, consisting of a flexible fabric tube and a core of low or high explosive. Used in blasting and demolition work, and in certain ammunition.

**fuze.** A device with explosive components designed to initiate a train of fire or detonation in an item of ammunition by an action such as hydrostatic pressure, electrical energy, chemical action, impact, mechanical time, or a combination of these. Types of fuzes are distinguished by modifying terms forming part of the item name. (In some cases the explosive components may be simulated or omitted.)

**gas generator.** A device for producing gas, by burning of solid propellant, to pressurize a tank, drive an engine, or actuate a mechanism.

**grain.** A single piece of solid propellant, regardless of size or shape, used in a gun or rocket.

**"green."** Wet with solvent during the manufacturing process.

**grist.** Particle size distribution, especially that produced by grinding.

**gun.** A piece of ordnance consisting essentially of a tube or barrel for throwing projectiles by force, usually the force of an explosive but sometimes that of compressed gas, spring, etc.

**heat of explosion.** Heat evolved in burning (exploding) a sample in a combustion bomb in an inert atmosphere under standardized conditions of pressure and temperature.

**igniter.** A specially arranged charge of a ready burning composition, usually black powder, used to assist in the initiation of a propelling charge.

**impulse.** Product of thrust × time.

**inhibitor.** A material applied to surface(s) of propellant grains to prevent burning on the coated surface(s).

**JANAF.** *(abbr).* Joint Army-Navy-Air Force.

**jato.** *Jet-assist take off*, a rocket motor used to supplement the engines of an aircraft or missile at takeoff.

**M & V.** *(abbr).* Moisture and volatiles.

**mass ratio.** Ratio of the weight of the propellant to the weight of the loaded rocket.

**mesa propellants.** Propellants which show negative values of $n$ over short pressure ranges on a plot of log $r$ versus log $P$ for $r = bP^n$

**monopropellant.*** A single physical phase comprising both oxidizing and fuel elements.

**mortar.** A complete projectile-firing weapon, rifled or smooth bore, characterized by shorter barrel, lower velocity, shorter range, and higher angle of fire than a howitzer or a gun.

**plastisol.** A flowable suspension of a polymer in a plasticizer which the polymer may later imbibe to produce gelation.

**plateau propellant.** Propellant showing a region of markedly reduced slope on a plot of log $r$ versus log $P$ for $r = bP^n$.

**port area.** The area of any opening through which gas moves. Specifically the area of a discharge end of a grain perforation.

**pot life.** Length of time a temporarily fluid system can be held or worked before setting up to a solid.

**primer.** An assembly which ignites a propelling charge, especially in gun ammunition.

**progressivity.** Increase of weight rate of burning as web is consumed.

**resonance rod.** A rod inserted into the perforation of a rocket grain to depress the tendency toward unstable burning.

**rocket motor.** A nonairbreathing reaction propulsion device that consists essentially of a thrust chamber and exhaust nozzle, and that carries its own solid oxidizer-fuel combination from which hot gases are generated by combustion and expanded through a nozzle.

**shelf life.** The storage time during which an item remains serviceable.

**single-base propellant.** Propellant comprising only one explosive ingredient, *e.g.*, nitrocellulose.

**slivers.** Portions of the grain remaining at burn-through.

**small arms.** A gun of small caliber. Within the Ordnance Corps the term is presently applied to guns of caliber up to and including 1 inch. Such hand and shoulder weapons as pistols, carbines, rifles, and shotguns.

* Differs significantly from definition given in MIL-STD-444

## GLOSSARY (Continued)

**smokeless powder.**[*] Solid monopropellant comprising nitrocellulose, with or without oxidizing and/or fuel plasticizers.

**SPIA.** *(abbr)* Solid Propellant Information Agency.

**SPIA/M2.** *Propellant Manual* SPIA/M2, issued by Solid Propellant Information Agency.

**specific impulse.** A figure of merit of a rocket propellant, defined as $\frac{I}{W}$.

[*] Differs significantly from definition given in MIL-STD-444.

**thermochemistry.** The derivation of the composition, temperature, and derived parameters of the combustion products from the composition of the propellant, the heats of formation of the ingredients and the thermodynamic properties of the products.

**triple-base propellant.** Propellant with three explosive ingredients, such as nitrocellulose, nitroglycerin, and nitroguanidine.

**web.** Thickness of propellant wall consumed by burning.

# INDEX

## INDEX (Continued)

U.S. GOVERNMENT PRINTING OFFICE: 1984 - [illegible]