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Design Criteria for Inert or Consumable Polymer Cartridge Materials

by

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Naval Weapons Center
China Lake, California • July 1971

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ABSTRACT

Semiempirical theory is used to provide guidelines for selecting inert or consumable polymer cartridge materials on the basis of chemical, thermal, and mechanical properties for use in existing gun systems. Internal ballistic parameters are obtained using the Le Duc velocity approximation. Resulting energy release, temperature, and transient pressure to the cartridge are then related to rate of degradation, heat transfer, and viscoelasticity in terms of chemical, thermal and mechanical properties using the Arrhenius activation energy theory, and Fourier heat conduction equation, and the Tresca failure criteria. The design criteria are based on simultaneous mechanical failure (powder gas erosive action) and burning/degradative consumption of a filled or unfilled polymeric cartridge material as a function of the time of projectile travel in the gun. The technique for defining the ideal cartridge material property envelope is outlined for any existing gun system. Candidate polymer cartridge materials on one side of the envelope are consumed on firing, whereas those on the other side are inert. The usefulness of the technique is shown for a specific ammunition in a 5-inch 54-caliber Navy gun.

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FOREWORD

This report presents a method by which the operating parameters of the 5-inch 54-caliber gun can be related to the mechanical, thermal, and chemical properties of a cartridge case so that suitable and rational criteria exist to permit the design of a case that will disappear during the combustion of the conventional gun powder and expulsion of the projectile.

The method and criteria developed for this analysis should be generally useful to other caliber guns and to the design of propellants for cartridgeless guns such as liquid guns.

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This report is transmitted for information only and does not represent the official views or final judgment of this Center.

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19 July 1971

Under authority of
HUGH W. HUNTER, Head
Research Department
Design Criteria for Inert or Consumable Polymer Cartridge Materials

Semiempirical theory is used to provide guidelines for selecting inert or consumable polymer cartridge materials on the basis of chemical, thermal, and mechanical properties for use in existing gun systems. Internal ballistic parameters are obtained using the Le Duc velocity approximation. Resulting energy release, temperature and transient pressure to the cartridge are then related to rates of degradation, heat transfer, and viscoelasticity in terms of chemical, thermal and mechanical properties using the Arrhenius activation energy theory, and Fourier heat conduction equation, and the Tresca failure criteria. The design criteria are based on simultaneous mechanical failure (powder gas erosive action, and burning/degradative consumption of a filled or unfilled polymeric cartridge material as a function of the time of projectile travel in the gun. The technique for defining the ideal cartridge material property envelope is outlined for any existing gun system. Candidate polymer cartridge materials on one side of the envelope are consumed on firing, whereas those on the other side are inert. The usefulness of the technique is shown for a specific ammunition in a 5-inch 54-caliber Navy gun.
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NOMENCLATURE

\[ \begin{align*}
    a, b &= \text{Le Duc constants} \\
    A &= \text{gun bore cross section area, in}^2 \\
    B &= \text{Arrhenius equation constant} \\
    c_{P_g} &= \text{powder product gas specific heat at constant pressure at } 2500\,^\circ\text{K, cal/gm}^\circ\text{K} \\
    c_{V_g} &= \text{powder product gas specific heat at constant volume at } 2500\,^\circ\text{K, cal/gm}^\circ\text{K} \\
    c_{V_i} &= \text{powder product gas specific heat of } i^{th} \text{ component of the gas at } 2500\,^\circ\text{K, cal/gm}^\circ\text{K} \\
    D &= \text{gun bore diameter, in.} \\
    D_1 &= \text{outside cartridge diameter, cm} \\
    D_2 &= \text{inside cartridge diameter, cm} \\
    E &= \text{polymer activation energy, kcal/mole} \\
    E_{e_p} &= \text{polymer rubbery extension modulus at } T_p = \text{const, lb/in}^2 \\
    E_{g_p} &= \text{polymer glassy extension modulus at } T_p = \text{const, lb/in}^2 \\
    E_i &= \text{energy release of } i^{th} \text{ component of the powder at } 2500\,^\circ\text{K, cal/gm} \\
    E_r &= \text{polymer relaxation extension modulus at } T_p = \text{const, lb/in}^2 \\
    E_{\text{rel}} &= \text{energy release of powder gas, cal/gm} \\
    f &= \text{powder product gas viscosity proportionality constant} \\
    &= 1.1 \times 10^{-5} \\
    g &= \text{acceleration due to gravity, 32.2 ft/sec}^2 \\
    G_e &= \text{polymer rubbery shear modulus at } T_p = \text{const, lb/in}^2
\end{align*} \]


\[ h_i = \text{powder product gas convective heat transfer coefficient, cal/cm}^2 \text{sec}^0 \text{K} \]

\[ k_s = \text{solid polymer thermal conductivity, cal/sec cm}^0 \text{K} \]

\[ k_l = \text{liquid polymer thermal conductivity, cal/sec cm}^0 \text{K} \]

\[ K_i = \text{dimensionless factor for nonsteady and nonuniform gas flow} \]

\[ K_0 = \text{value of Tobolsky shift factor at inflection point of the transient } E_c, \text{ hr} \]

\[ K_T = \text{polymer degradation rate constant at a given temperature, } \% \text{ volatilized/min} \]

\[ n = \text{Tobolsky power law coefficient} \]

\[ N = \text{weight of powder burned at } t, \text{ gm} \]

\[ p_g = \text{gas pressure, lb/in}^2 \]

\[ p_{g_{\text{max}}} = \text{maximum gas pressure, lb/in}^2 \]

\[ p_L = \text{Le Duc pressure, lb/in}^2 \]

\[ p_{L_{\text{max}}} = \text{maximum Le Duc pressure, lb/in}^2 \]

\[ p_o = \text{gas pressure at instant obturation occurs, } \approx 1,000 \text{ lb/in}^2 \]

\[ q = \text{heat flow into cartridge from powder gas, cal/sec} \]

\[ R = \text{Reynold's number} \]

\[ R_0 = \text{universal gas constant } \approx 1.9865 \times 10^{-3} \text{ kcal/mole}^0 \text{K} \]

\[ S = \text{gun powder chamber volume, in}^3 \]

\[ t = \text{interior ballistic time, sec} \]

\[ t_{\text{m}} = \text{time at which projectile leaves muzzle, sec} \]

\[ T = \text{powder gas temperature, } ^0 \text{K} \]

\[ T_b = \text{polymer brittle temperature, } ^0 \text{K} \]

\[ T_{\text{g}} = \text{polymer glass temperature, } ^0 \text{K} \]
$T_m$ = polymer melting temperature, °K

$T_o$ = adiabatic explosion temperature of powder gas, °K

$T_p$ = temperature at point in polymer, °K

$T_s$ = temperature of gun breech wall, °K

$T_1$ = outer cartridge wall temperature, °K

$T_2$ = inner cartridge wall temperature, °K

$u$ = projectile travel, ft

$u_m$ = projectile travel at maximum cartridge pressure, ft

$u_o$ = projectile displacement at $p_o$, ft

$v$ = projectile velocity, ft/sec

$v_m$ = projectile muzzle velocity, ft/sec

$V$ = average gas velocity parallel to inner cartridge wall, cm/sec

$w$ = projectile weight, lb

$x_i$ = weight fraction of the $i$th component of the powder gas

$z$ = Southerland constant = 120

$\alpha$, $\beta$ = Hicks-Thornhill constants

$\gamma$ = coefficient of expansion, °K$^{-1}$

$\Delta$ = loading density (equals ratio between the charge weight and weight of water required to fill the powder chamber)

$= 27.68 \, \Delta/\gamma$

$u$ = gas viscosity, gm/cm sec

$u_o$ = temperature shift factor at inflection point corresponding to $K_o$

$v$ = Poisson's ratio

$\rho$ = gas density, gm/cm$^3$

$\sigma_1$, $\sigma_3$ = extremal principal stresses at $\phi$, lb/in$^2$
\( \sigma_c \) = circumferential cartridge stress, lb/in^2
\( \sigma_r \) = radial cartridge stress, lb/in^2
\( \sigma_z \) = longitudinal cartridge stress, lb/in^2
\( \tau_{\text{max}} \) = Tresca failure shear stress, lb/in^2
\( \tau_o \) = skin friction shear stress, lb/in^2
\( \langle \tau_{r\theta} \rangle \phi \) = shear stress at \( \phi \), lb/in^2
\( \phi \) = liquid polymer residue layer thickness adjacent to \( D_2 \), cm
\( \chi \) = distance from breech to point in cartridge, cm
\( \dot{\phi}_{\text{max}} \) = maximum shear strain of polymer at \( T_m \), in/in
\( \omega \) = powder weight, lb
INTRODUCTION

The metal ammunition cartridge evolved during the American Civil War where it was first used with the 0.56 Spencer (Ref. 1). In the past 30 years concentrated efforts have been made to reduce the weight (Ref. 2) of the metal cartridge by either substituting a consumable foam plastic material or by using a combustible cartridge. Recent activity has included development of 5.56, 7.62, and 30 mm combustible ammunition (Ref. 3, 4, and 5). Completely new gun-ammunition designs are envisioned (Ref. 6, 7, and 8) once it is demonstrated that the combustible cartridge can meet military specifications.

The analytical aspects of cartridge design are based on pre-World War II semiempirical internal ballistic theory (Ref. 9 through 18). The analytical determinations have been programmed into computer storage tapes to provide tractability (Ref. 19, 20, and 21). The value of this theory has recently been demonstrated for new design concepts (Ref. 22 and 23).

In this report, semiempirical theory is reorganized to define the ideal chemical, thermal, and mechanical properties for candidate polymeric cartridge materials. Design parameters, environmental requirements, and interior ballistics are discussed herein. The material science is organized with a set of engineering assumptions and related to polymer cartridge design. The usefulness of the techniques is shown for a specific ammunition in a 5-inch 54-caliber (5"/54) Navy gun.

DESIGN PARAMETERS

A cartridge obturates gas at the gun breech, houses the ignition primer mechanism and the powder charge, accurately positions the projectile with respect to entry into the gun barrel (fixed ammunition), maximizes strength/weight, and withstands the military environment. Other considerations relate to the cartridge's interaction with the gun. These include the requirement that the cartridge be removed after firing (either mechanically or chemically) and that the cartridge not cause significant gun deterioration because of heat transfer or chemical reaction. It is most important to recognize that the cartridge function
is subordinate to the fundamental requirement that the gun-ammunition system must accurately hit the target within acceptable statistical limits in a military environment.

MILITARY SPECIFICATIONS

The purpose of specifications is to establish a minimum quality assurance such that the end item will perform its function satisfactorily. Aside from manufacturing specifications that are unique to a given design, general purpose ammunition shall satisfy:

1. High and low temperatures (160 to -65°F)
2. Thermal shock cycles between 185 to -40°F
3. Solar radiation (100 to 140 w/ft²) at 113°F in wavelengths below 3,000 angstroms
4. Salt fog test for 48 hours and then shall be cleaned using acceptable methods
5. Fungus growth test.

These test procedures are described in MIL-STD-810B. Other tests (from MIL-STD-331 and MIL-C-13777) include:

1. Two complete 14-day JAN temperature and humidity cycles (cycling nine times between 160°F (95% RH) and -65°F)
2. Transportation vibration at -55, 86, and 160°F
3. Jolting 1,750 times in each axis at a speed of 35 blows per minute
4. Jumble through 3,600 revolutions at a rate of 30 rpm
5. Ten-foot drop test
6. The ozone test which consists of 50 parts of ozone per 100,000,000 (by volume) circulated at 120°F for 7 days.

Other specifications which must be intrinsically satisfied deal with ammunition storage life, raw material availability, ease of manufacturing, safety in handling, stability in storage, uniformity of properties, contributions of heat of explosion via thermal, mechanical, and chemical mechanisms to the gun, ease of charge ignition, corrosion and erosion of rifling, smoke, flash and noise production, hydroscopicity, etc.

The polymeric cartridge that satisfies all the above specifications must also demonstrate that it is more stable and lighter than conventional cartridges. To date, no combustible/consumable cartridge has met all of the stated specifications.
INTERIOR BALLISTICS

The technology used to predict and evaluate the complex chemical, thermal, and mechanical energy conversions between the instant of ignition through the time to projectile expulsion (1 to 30 msec) from the gun barrel is categorized as interior ballistics. The interior ballistics parameters needed for the design criteria for combustible cartridges are the time rate of change of the pressure, temperature, and chemical heat of reaction of the powder within the cartridge.

Gross cartridge behavior is envisioned in the following manner. During the first few milliseconds after primer ignition, the primer housing is forced against the breech block. The powder grain is forced forward against the necked portion of the cartridge case. Emerging gases drive the forward case walls against the chamber prior to pushing on the projectile. The inertia of the projectile eventually being overcome, the projectile moves into the barrel (deforming violently) effecting a gas seal after traveling (perhaps) several inches. The pressure then rises (in a bell shaped pressure time mode) to some 50,000 psi, depending on the propellant charge and gun design. Simultaneously, the forward portion of the case expands, obturating gas to the rear. Friction and chamber support prevents the forward portion of the case from buckling. The relatively stiff aft section of the case does not significantly expand, but serves to hold the cartridge wall in the chamber against the pressure.

An approximate prediction of transient pressure and temperature of the gases within a cartridge can be obtained for existing guns and ammunition. Rigorous approaches may be employed if greater accuracy is required. However, for preliminary design, the approximate theory used below is believed to be adequate for operational weapons. Although each of the equations to be used is well known, certain liberties are taken to relate the equations by means of assumptions derived partly from experimental observations.

The projectile velocity within the gun barrel is calculated from Le Duc's hyperbolic curve assumption

\[ v = \frac{au}{b + v} \]  

Experience suggests that

\[ a = 6823 \left( \frac{\hat{w}}{w} \right)^{0.5} \left( V / 0.0834 \right) \]

(1)
If the position of the projectile \( u_m \) is known at the maximum Le Duc pressure, then

\[ b = 2u_m \]  

(3)

If the maximum Le Duc pressure is known

\[ b = 4.48 \frac{w^2}{27gA} \left( \frac{p_{Lmax}}{A} \right) \]  

(4)

The Le Duc pressure as a function of projectile position is given by

\[ p_L = 1.12 \frac{w^2}{gA} b u \left( b + u \right)^3 \]  

(5)

If it is assumed that the pressure in the cartridge is the Le Duc pressure, then \( \rho g = p_L \) and \( \rho g_{max} = p_{Lmax} \). The time base is obtained by

\[ t = \int \frac{v}{u_0} \, du = a^{-1} \left[ (u - u_0) + b \ln \left( u/u_0 \right) \right] \]  

(6)

\( T \) is obtained by noting that the explosive energy is primarily consumed by kinetic energy of the projectile and the heat transfer (Ref. 9) to the gun, then

\[ 3.0874 Nc_vg (T_o - T) \]

\[ = wv^2/2g + \left[ 0.38D^{1.5} \left( 12u + 4S/\pi D^2 \right) \left( \frac{T_o - T_s}{T_s} \right) \left( \frac{v^2}{v_m^2} \right) \right] \frac{1}{1 + (1.6D^{2.175}/\omega^{0.8375})} \]  

(7)

here (from tables in Ref. 9)

\[ c_{vg} = \sum_{i=1}^{i=1} x_i c_{v_i} \]  

(8)

\[ T_o = 2500 + \left( \sum_{i=1}^{i=1} x_i E_i \right) c_{vg}^{-1} \]  

(9)
The energy released by the explosive gases for temperatures less than 3000°K is approximated by Ref. 24.

\[
E_{\text{rel}} = \left( \frac{1}{\gamma} \times \sum_{i=1}^{n} E_i \right) - (T - 2500) c_v g \tag{10}
\]

It has been shown (Ref. 25) that the energy given up by the powder to the projectile and gun is sensibly linear with gas temperature. Since the heat of explosion of modern powders is of the order of 900 cal/gm, the maximum amount of energy available to degrade/consume a cartridge is of the order of

\[
454(900 - E_{\text{rel}}) \text{ cal at } t_m.
\]

The utility of Eq. 1 through 10 can be demonstrated by predicting the interior ballistics of a Navy 5"/54 gun. The semifixed ammunition used in this example consists of a 70-pound Mk 41 projectile and the Mk 7 Mod 0 cartridge with SPDW 10295 powder. The gun and cartridge parameters are given in Ref. 26 and 27. The nitrocellulose (12.6%N) powder is similar to that of Crow and Grimshaw's N1 (Ref. 11 and 25).

The predictions of pressure, temperature, and density of the propellant gases are given in Fig. 1 together with the projectile displacement and velocity in the barrel as a function of time. Zero time begins at completion of cartridge obturation, which was assumed to occur for \( p_0 = 1,000 \text{ lb/in}^2 \). Projectile displacement at \( t = 0 \) was computed from Eq. 5 and found to be \( u_0 = 0.01 \text{ foot} \). The maximum amount of thermal energy available to consume the cartridge is \( 1.7 \times 10^6 \text{ cal} \).

The accuracy of this proposed method used to compute internal ballistics is believed to be more than adequate for preliminary design material specifications. Pertinent detailed experimental data does not exist. However, state-of-the-art experiments (Ref. 28) have been compared to various theories (Ref. 23) indicating accuracies of approximately 25%. The predictions in Fig. 1 are within 10% of those made using a more complex theory (Ref. 19). The accuracy of the transient temperature prediction is not estimated since the interpretation of temperature during unsteady state heat transfer (Ref. 29) is subjective. The computed \( T \) is assumed to be a mean gas temperature. Unfortunately, appropriate temperature transducers do not exist and only indirect measurements of \( T \) can be obtained to compare theory to experiment.
FIG. 1. Computed $P$, $T$, $v$, $u$, $c$ as a Function of $t$ After Obturation ($P_o = 1,000$ lb/in$^2$) for 5-Inch 54-Caliber Navy Gun, Mk 41 Projectile, and Mk 7 Mod 0 Cartridge with SPDW 10295 Powder.
Only convective heat transfer is important for case analysis since it is well known that conduction and radiation heat transfer are negligible (Ref. 10). Reynolds numbers between $10^5$ to $10^{10}$ are representative domains for gun analysis. An expression for the heat convection coefficient between the gas and cartridge can be estimated from the following equations.

$$h_i = \rho c_{pg} V \left[ a^2 \left( a^{-3} \beta^{-1} (\beta + 2) (\beta + 3) K_i R \right)^2 (\beta + 3)^{-1} - 3a \left( a^{-3} \beta^{-1} (\beta + 2) (\beta + 3) K_i R \right)^{3/2} \right]^{-1}$$

(11)

$$c_{pg} = 1.25 c_{vg} \text{ (at 2500°K)}$$

(12)

$$\rho = 27.68 \omega \left( S + A \int_0^t u dt \right)^{-1}$$

(13)

$$R = 0.0328 \chi_p V u^{-1}$$

(14)

$$K_i = \beta (\beta + 2)^{-1} v^{-1} u (\beta + 2) (3\beta + 4)^{-1}$$

$$\left[ \int_0^t v^2 u (2\beta + 2) (\beta + 2)^{-1} dt \right]$$

(15)

$$u = f T^{1.5} (T + z)^{-1}$$

(16)

A good experimental fit in the range $10^6 < R < 10^9$ is for $\omega = 12.4$ $\omega = 11.3$. Substituting these values together with Eq. 13 into Eq. 11

$$h_i = \left[ 27.68 \omega c_{pg} V (S + A \int_0^t u dt)^{-1} \right]$$

$$\left[ 286 (K_i R)^{0.14} - 50.7 (K_i R)^{0.07} \right]^{-1}$$

(11a)
R (Eq. 14) and $K_1$ (Eq. 15) can also readily be expressed in terms of the gun parameters as

$$R = 0.91 \chi t^{-1} V T^{1.5} \omega (T + z) \left( S + A \int_0^t u dt \right)^{-1} \tag{14a}$$

and

$$K_1 = 0.85 u^{-3.85} (b + u) \left[ \int_0^u \frac{u^2}{u_0^2} \left( b + u \right) \right] \tag{15a}$$

It follows from von Karman's extension of Reynolds' analogy (between the transfer of momentum and heat in turbulent flow) to the Prandtl number that the gas induced skin friction drag per unit area can be expressed by

$$\tau_0 = 1.834 \times 10^{-7} \rho V^2 (\rho K_1)^{-0.14} \tag{16a}$$

This shear stress is available for scrubbing off the liquid polymer residue at the inner surface of the consumable cartridge. It is assumed that $V(t)$ can be taken to be the mirror image of $v(t)$, i.e., $V(0) = v(t_m)$ and $V(t_m) = v(0)$. This assumption together with Fig. 1 allows for the computation of $R$, $h_1$, $K_1$, and $\tau_0$ as a function of interior ballistic time. These results are shown for the Navy gun example in Fig. 2 for $x = 40$ cm (longitudinal center of the cartridge).

**CARTRIDGE CHEMICAL PROPERTIES**

Selected chemical properties of polymers (Ref. 30 and 31) are used to quantify reversible and irreversible behavior. The melting temperature ($T_m$), representing the high end of the melting range, is useful for design since many thermoplastics generally do not chemically degrade below $T_m$. The glass transition temperature ($T_g$) is also useful for design because it represents the polymer state between structural rigidness and leathery-ness. A rough approximation between $T_g$ and $T_m$ is

$$\frac{T_g}{T_m} = 0.6 \tag{17}$$

The decomposition or degrading of a polymer is distinguished by energies of reaction and dissociation. Unfortunately, pyrolytic decomposition of polymers are varied and too complex to render useful generalizations. An important factor determining the rate of a decomposition process is the activation energy ($E$) which is defined from the Arrhenius equation as

$$\kappa_T = B e^{E/R_0 T} \tag{18}$$
FIG. 2. Computed $h_1$, $R$, $\tau_0$, $K_i$ as a Function of $t$ for $l = 40$ cm After Obturation for 5-inch 54-Caliber Navy Gun, Mk 41 Projectile, and Mk 7 Mod 0 Cartridge with SPDW 10295 Powder.
In general, data in the literature are limited to studies of rates of degradation up to 775°C. Typical activation energies range from 18 kcal/mole for phenolic resin to 80 kcal/mole for polytetrafluoroethylene at temperatures around 623°C.

The rate of degradation, \( K_T \), can be obtained by experiment (Ref. 32) over the range \( T_m \leq T \leq T_2 \) and pressures \( P_0 \leq P \leq P_{L\max} \). With these data, together with \( t_m \), a baseline can be established from which to rate candidate polymers. If the cartridge is not consumed by the desired \( t_m \), then the proper cartridge consumption can be tailored in either of two ways. The first way is to introduce oxidizer and/or thermally conductive filler. Since the powder gas is oxidizer poor, self-induced burning of the cartridge requires a tailored oxidizer filler. If degradation is quick enough, e.g., zipper action, then the polymer tailored with thermally conductive filler may be useful. A second way involves the elimination of polymeric liquid and/or residuals on the inner surface of the cartridge by tailoring the mechanical strength of the polymer such that \( T \) will mechanically scrub (erode) these layers at a predicted rate. Obviously optimization may utilize both methods.

If a usable cartridge material is to be consumed, gun erosion due to polymer products must then be considered. One candidate material family (for the Navy gun discussed above) is the aromatic polysulfones (Ref. 33 and 34). The chemical/mechanical stability of polysulfone is excellent for cartridge application. Decomposition products are hydrogen, methane, \( H_2O \), \( CO \), \( H_2S \), \( SO_2 \), benzene and phenol. These materials decompose quickly and completely (Ref. 34) at \( T_2 \approx 1100^\circ K \) if \( O_2 \) is available. Properties pertinent to cartridge design are \( T_g = 463^\circ K \), \( T_b = 173^\circ K \), \( T_m = 713^\circ K \), and \( E = 70 \) kcal/mole. It follows that the energy required to consume polysulfone 0.165 cm thick similar to the Mk 9 Mod 0 case is less than 6 kcal, excluding the cartridge base and any added filler. The consumption of such a small amount of energy obviously will not affect the gas temperature predicted by Eq. 9.

The possible detrimental effects of \( SO_2 \) on the gun should be considered. It appears that at elevated temperatures \( SO_2 \) and \( H_2O \) should not associate and corrosion may not become a problem. Note, however, that alternative polymers such as the "Delrin" type may also be suitable and would not have potential corrosive gases as products. For the purposes here, however, barrel lifetime shall not be considered any further.

The chemical tailoring of the polymer material to be used either as a consumable or nonconsumable cartridge obviously then depends upon adjusting the thermal and mechanical properties of the polymer chemically or with filler in order to control the transient temperatures and stresses within the cartridge wall. If the consumption rate still is not quick enough, 14 msec in the Navy gun example, then oxidizer filler must be introduced in order to cause the case to burn at an appropriate rate.
CARTRIDGE THERMAL PROPERTIES

Temperatures in a cylindrical polymeric cartridge can be estimated for modest temperature gradients using the classical Fourier heat conduction equation (Ref. 35), which assumes that heat transfer is regulated by the conductivity, specific heat, and density of the polymer. Since the internal ballistics occur for such a short period and the specific heat of polymeric materials cannot be readily tailored as a function of heat flux and temperature, it is assumed that only thermal conductivity need be considered for regulating the cartridge temperatures.

The analytical model envisioned for a consumable composite polymeric cartridge consists of two concentric cylinders. The inner ablative cylinder, \( \phi \) thick, consists of liquid polymer residue bounded by \( T_2 \) and \( T_m \). \( q \) entering at \( D_2(t) \) is determined by \( h_i \) and \( (T - T_2) \). The outer cylinder, \( 0.5 \left[ D_1 - (D_2 + 2\phi) \right] \) thick, consists of solid polymer bounded by \( T_m \) and \( T_1 \). \( q \) from the inner cylinder is assumed (no heat sinks/sources) to enter and leave the outer cylinder as would be the case for steady state. The thermal resistance between the outer cylinder and the gun breech is assumed negligible because of the smooth boundaries, high pressures, and the large breech heat sink, hence \( T_1 = T_S \). By assuming an average constant \( k_s \) and \( k_\phi \), the following equation is readily obtained

\[
-k_s \ln \left[ \frac{D_1}{(D_2 + 2\phi)} \right] + k_\phi \ln \left[ \frac{(D_2 + 2\phi)}{D_2} \right] = (T_S - T) \left[ h_i D_2 (T - T_2) \right]^{-1}
\]

In general \( k_s >> k_\phi \) and \( D_2 >> \phi \), then

\[
k_s = (T_S - T) \left[ h_i D_2 (T - T_2) \ln \left( \frac{D_1}{D_2} \right) \right]^{-1}
\]

Equation 20 can be used to estimate \( k_s \) for progressively consumed concentric cylinder layers of a cartridge \( 0.5 \left[ D_1 - (D_2 + 2\phi) \right] \) thick. For the Navy gun example, assume that \( D_2 = 13.71 + 1.8t \) (i.e., complete consumption by \( t_m \)), \( h_i \) (Fig. 2), \( D_1 = 14.04 \), \( T_S = 345^\circ K \), \( T_2 = T_m = 714^\circ K \) (polysulfone), and \( T \) (Fig. 1). Figure 3 shows the resulting \( k_s(t) \) design requirement for an appropriate consumable cartridge. Materials with lower than the predicted \( k_s \) are candidates for an inert cartridge whereas those above are candidates for a consumable cartridge. Note that unfilled polysulfone has a \( k_s \) of the order of 0.008 cal/sec cm \(^\circ K\) which is much too low for a consumable cartridge. However, graphite or aluminum filler, with \( k_s \approx 400 \) cal/sec cm \(^\circ K\), could be used for tailoring \( k_s \) through the cartridge thickness to that given in Fig. 3.
FIG. 3. Design Criteria for $k_s$ When $T_2 = 714^\circ K$. 

NOTE: 

- $k_s$ POLYSULFONE $\approx 0.008$ CAL/SEC CM$^*K$
- $k_s$ GRAPHITE OR ALUMINUM FILLER $\approx 400$ CAL/SEC CM$^*K$
The critical mechanical behavior of a cartridge is defined by the stress-strain/strain rate response of the cartridge during the interior ballistics phase. If the cartridge is to be inert and, therefore, maintain its integrity, sufficient structural strength must be available to extract it from the gun after firing. If the cartridge is to be consumed, its strength should significantly deteriorate after maximum pressure is attained.

The strength of a cartridge can be estimated by its stress state, which is a function of temperature and strain. Mechanical moduli are defined by approximate constitutive equations. In order to estimate desired mechanical properties, it is common practice to utilize the theory of linear elasticity or viscoelasticity with appropriate safety factors. Rate and thermal effects are approximated on a quasistatic basis. A general requirement for a cartridge material is that it be elastic, i.e., $T_g > 345^\circ \text{K}$, and not brittle, i.e., $T_b < 219^\circ \text{K}$, for handling-in-the-field induced stresses, and viscoelastic (Ref. 36 and 37) during the internal ballistics phase, i.e., exhibit stress relaxation. If the cartridge is not to be consumed, sufficient elasticity must be available to break the chamber seal prior to cartridge removal.

A failure criterion is necessary to establish a material reference baseline as well as for estimating cartridge reliability. A specific failure criterion can readily be empirically obtained for cartridge materials for a given loading path. The loading path events envisioned for the cartridge are as follows:

1. Relatively rigid (elastic) cartridge is positioned in gun. $T_1$ rises to $T_g$. Positive thermal expansion initiates obturation.

2. Powder is ignited. Initial pressure rise in case completes obturation (mechanical failure must not occur). $T_2$ rises to $T_m$.

3. The subsequential rise of $p$ in the case is largely reacted by the rigid (assumed) gun breech. The case experiences an increasing hydrostatic stress state. $T_p$ increases depending on $k_g$. Powder decomposition gases induced shearing stresses $\tau_0$ act on $D_2$ and are reacted on $D_1$. A portion of the case inner wall ($\tau$) may be consumed due to chemical degradation and/or $\tau_0$. 

Cartridge mechanical design is predicated upon gun design. In general, a cartridge redesign requires specific gun design modifications. In this report it is assumed that the gun will not be modified. This requirement of no gun design change may involve subsequent trade-offs since the current gun is already a well optimized system.
4. \( p \) and \( P_0 \) significantly drop. \( T_p \) continues to rise. \( D_2 \) increases until the last layer \( \phi \) of the consumable cartridge is either chemically consumed forming gaseous products and/or is mechanically broken up/swept away by both polymer degradation gas products and \( T_0 \) by the time the projectile leaves the muzzle.

5. Residual hot gases flush the gun barrel of most residual materials.

Failure criteria for phases 1 through 3 are the same as now used to verify military environment requirements. In general, such criteria are not analytical, but are based on the survival of prototype cartridges after environmental and material testing. However, for phase 4, it is desirable to have an analytical reference to compare candidate cartridge materials. The Tresca failure criterion (Ref. 38) mechanism is suggested because \( T_0 \) is envisioned as removing the liquid polymer residue layer \( \phi \) by a scrubbing action. It remains then, to define the ideal moduli as a function of stresses for the polymer in terms of the Tresca failure criterion.

The Tresca criterion for failure stress is reasonable for a consumable cartridge because it assumes that a plastic/viscous state \((E_r \rightarrow \infty)\) is created when the maximum shearing stress just reaches the value of the inner (molecular) resistance of the material against shear. It is here postulated that this will occur at \( \phi \), at which location the polymer begins to melt.

If \( k_s \) is tailored as discussed above, then concentric isotherms are envisioned in the cartridge case during the interior ballistics time. The outer concentric isotherm of the cartridge is assumed to remain at \( T_0 \) because the gun breech is an excellent heat source and the interior ballistic time is short. The inner concentric isotherm at \( \phi \) is assumed to be \( T_m \) for the polymer. Then for a point on any physical concentric circle, the temperature will rise from the cartridge storage temperature \( T_p \) to \( T_m \) before \( t = t_m \). During the rise in temperature, the polymer will experience viscoelastic stress relaxation, which is a function of the \( t \) and \( T_p \), at each radial point.

The stresses in the cartridge are due to \( T_0, P_g \) and thermally induced stresses (Ref. 39). These stresses are approximated at \( \phi \), assuming \( D_2 >> \phi \), an incompressible polymer, a rigid gun breech, and steady state heat flow by

\[
(\sigma_p)_{\phi} = -P_g
\]
This stress state will cause failure if $E_e$ is tailored (chemically or by utilizing filler) in such a manner to satisfy a failure criterion, e.g., Tresca's. (It should be pointed out that failure could also occur at $D_1$ because of a mechanism closer to Griffin's failure criteria, but it is assumed that the tailoring of the mechanical and thermal properties can readily avoid or include this type of failure at $D_1$.)

The isothermal Tresca criterion at $\phi$ relates the maximum principal stresses to a constant, or

$$0.5 (\sigma_1 - \sigma_2) = (\tau_{\text{max}}) = \text{constant} \quad (22)$$

By definition let

$$(\tau_{\text{max}}) = (\psi_{\text{max}} E_e) \approx \left( \frac{\psi_{\text{max}} E_e}{3} \right)$$

$$(\sigma_1 - \sigma_2)$$ is readily obtained from Eq. 21. Therefore, it remains only to tailor a polymer such that $(\psi_{\text{max}} E_e / 3) \hat{\phi}$ satisfies Eq. 23. Recall that the failure mechanism is that $\tau_0$ scrubs off the concentric cylinder layer $\phi$, whose strength is determined by Eq. 22.
$E_e$ is represented (Ref. 40) by the rubbery plateau (which may be quite short) common to many polymers. Ideally, the magnitude of the relaxation modulus $E_r$ should drop instantly from the glassy modulus $E_g$ to $E_e$ at the specified relaxation time and $T_m$. For polymers the relaxation transition time is finite, but can be much less than a millisecond. An approximate characterization of the $E_r$ transition phase was proposed by Tobolsky (Ref. 41) as

$$E_r = E_e + \frac{(E_g - E_e)}{(1 - \mu_o t)^n} \tag{24}$$

where

$$\mu_o = \frac{1}{K_0} \left(\frac{E_g}{E_e}\right)^{2n} \tag{25}$$

and

$$(E_r)_o = \sqrt{E_g E_e} \tag{26}$$

Equations 24 through 26 can only be considered approximate since they are based on unique assumptions which are not representative of polymers in general (Ref. 41). Assuming that the accuracy is still suitable for engineering preliminary design, these isothermal equations can be used as a baseline for mechanical property specifications for consumable cartridges.

Equations 24 through 26 are approximately valid for an isothermal relaxation experiment. To relate $E_r$ at different temperatures, experimental observations and theoretical predictions suggest that multiplication by the ratio of the respective absolute temperatures is a fair approximation,

i.e., $E_r(T_p) = \frac{T_p}{T_r} E_r(T_g)$.

The design goal proposed for mechanical failure is for the tailored polymer to relax at $T_m$ so that $E_r$ goes from $E_g + E_e$ (apparent or real) rapidly enough for $\tau_o$ to completely scrub the concentric residue cylinder layers ($\phi$) by $T_m$. The cartridge specifications for the polymer can thus be expressed in terms of Eq. 24, subject to $k_g$.

At $t = 0$, $E_r \equiv E_g$. The cartridge modulus must be large enough to satisfy rigidity requirements for handling operation and positioning in the gun breech. $E_g (345^\circ K)$ should be at least equal to $10^5$ lb/in$^2$. $E_g (T_p)$ is obtained from Eq. 21 through 23 (here the correspondence principal (Ref. 42) is applied to elastic structural theory (Ref. 39)).
for a given gun-ammunition system. The physical time is simply the interior ballistic time, \( t \). The utilization of the proposed technique can next be demonstrated using the Navy gun as an example.

Assume that at \( t = 0 \), \( (T_p)_p = (T_m)_m \). Equation 24 is then used at \( \phi \) for \( T_m \). Since obturation has occurred at \( t = 0 \), it is desirable that the relaxation time be much less than a millisecond. Rules of thumb suggest that for a filled polymer, \( \log \left( \frac{E_g}{E_e} \right) \approx 2 \) and \( n \approx 0.5 \) as compared to an unfilled polymer, where \( \log \left( \frac{E_g}{E_e} \right) \approx 3 \) and \( n \approx 0.7 \). By choosing a relaxation time of \( 10^{-8} \) hour, \( K_0 = 10^{-8} \) hour. For a filled polymer, Eq. 25 predicts \( \nu_0 = 10^{-10} \). From Eq. 21 through 23, \( E_e \left( T_m \right) = 6.7 \times 10^4 \) lb/in\(^2\) for \( \nu_{\text{max}} = 1.0 \) in/in. (Another approximate material requirement trade off between \( E_e \) and \( \nu_{\text{max}} \) can be made satisfying Eq. 21 through 23, i.e., \( E_e \nu_{\text{max}} = \text{constant} \).) Since \( E_g \approx 6.7 \times 10^6 \) lb/in\(^2\), Eq. 24 for the Navy gun becomes at \( T_m \),

\[
E_r = 6.7 \times 10^4 + \frac{6.7 \times 10^6}{\left[ 1 - 10^{-10} \left( \frac{t}{\text{hour}} \right)^{0.5} \right]} \tag{27}
\]

If \( T_m = 714^\circ \text{K} \), and \( E_g \) is given at \( T_p = 273^\circ \text{K} \), then \( E_r \left( 273^\circ \text{K} \right) \approx \left( 273/714 \right) E_r \left( 714^\circ \text{K} \right) = 0.38 E_r \left( 714^\circ \text{K} \right) \). Figure 4 is a plot of Eq. 27 at \( T_p = 714^\circ \text{K} \).

Polymers, for which \( E_r \) is above and to the right from that given in Fig. 4, are candidates for an inert cartridge whereas those below and to the left from that given in Fig. 4 are candidates for a consumable cartridge. It appears that polysulfone may be a consumable cartridge candidate. Unfortunately, appropriate relaxation data have not been found for the various polysulfones and, therefore, its potential utility cannot yet be ascertained. The accuracy of the baseline for \( E_r \) is only approximate. It is probable that the \( E_r \) will be greater than the predicted values for short relaxation times and high temperatures. Also note that the consumption of the case may be faster than the relaxation times obtained from state-of-the-art experiment because of the relaxation occurring at points between \( \phi \) and \( D_l \) due to the rise of \( T_p \). A more accurate analysis would integrate the relaxation effect using transient thermo-elasticity theory. However, this extra effort is not deemed warranted for preliminary design since a significant number of assumptions have already been incorporated and would tend to make greater sophistication meaningless.
FIG. 4. Design Criteria for 
$E_r$ at $T_p = 714^\circ K$.

DISCUSSION

The material design guidelines for $k_g$ and $E_r$ are approximate and suitable for preliminary design. A number of factors have been excluded or assumed negligible such as coupling between relaxation time and viscous flow activation energy and the neglect of cartridge vibration. The objective of this report has been to show, for short times, the interactions between chemical degradation, mechanical properties and failure, and thermal properties of polymers. The magnitudes and rates of these chemical, mechanical, and thermal properties were obtained using a simplified interior ballistics approach which gives reasonable results for a given gun-ammunition system.
A method has been developed for specifying the chemical, thermal, and mechanical properties of the polymer in order to tailor a polymer for use as either an inert or consumable cartridge in the 5-inch Navy gun. The method is generally applicable to other gun systems.
REFERENCES


