Engineering Notes

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Lead Aliphatic Mono- and Dicarboxylates as Ballistic Modifiers

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Introduction

THE application of lead salts to render burning rates of double-base rocket propellants independent of chamber pressure has been investigated by a number of research workers.[1-4] In the series of lead aliphatic salts, Preckel[2] reported the effect of lead stearate and lead 2-ethyl hexoate on both single- and double-base propellants. Camp and Crescenzo[3] patented the use of combinations of lead and copper salts of aliphatic and aromatic acids to produce mesa characteristics. Costa and Lantz[4] claimed good plateau ballistics with lead stearate and lead tartrate. These studies, however, cover the effect of lead salts over a very limited pressure range. Furthermore, much of the information is either classified or patented. Therefore, a systematic study was undertaken to investigate the influence of a series of lead salts of mono- and dicarboxylic acids.

Experiments

The basic propellant composition contained 52% nitrocellulose (NC), 36% nitroglycerine (NG), 3% carbamite, 3.5% dinitrotoluene (DNT), and 5.5% dibutyl phthalate (DBP). Modified propellant compositions contained 2 parts of lead salts and 0.5 part of carbon black per 100 parts of basic composition. Lead salts of lauric, palmitic, stearic, oleic, adipic, succinic, oxalic, sebacic, and tartaric acids were made by the precipitation method.[5]

Propellant compositions were made by the solventless extrusion technique.[6,7] Burning rates at different pressures were determined by using indigenously fabricated strand burner equipment.

Results and Discussions

Lead acetate (Fig. 1) increased burning rates in the entire pressure range studied, except between 65-105 kg/cm^2, and produced a plateau effect in the pressure range 35-70 kg/cm^2. Lead laurate raised burning rates in the regions between 35-60 and 140-175 kg/cm^2. It lowered the pressure exponent (n) value only in the pressure range 35-70 kg/cm^2. Lead palmitate enhanced burning rates almost throughout and its catalytic activity (catalyzed burning rate/uncatalyzed burning rate) was better than that of lead laurate between 50-105 kg/cm^2. It reduced the n value to 0.35 in the 70-105 kg/cm^2 pressure region. Lead stearate also gave higher burning rates and reduced the n value to 0.25 (70-105 kg/cm^2). Lead oleate (lead salt of an unsaturated acid) gave a marginally higher catalytic effect than lead stearate.

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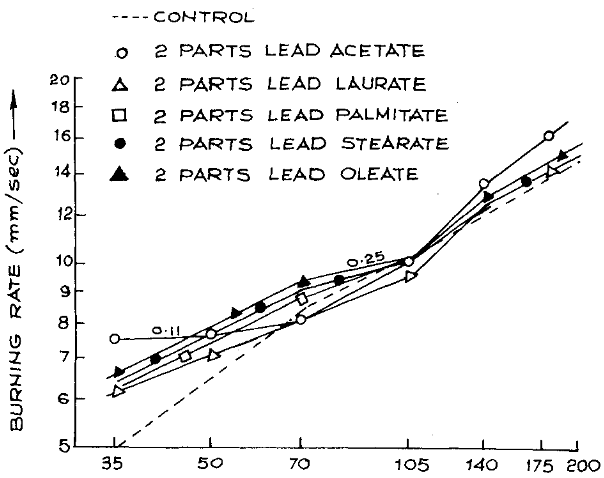

Fig. 1 Effect of lead aliphatic monocarboxylates on the burning rates of double-base propellants.

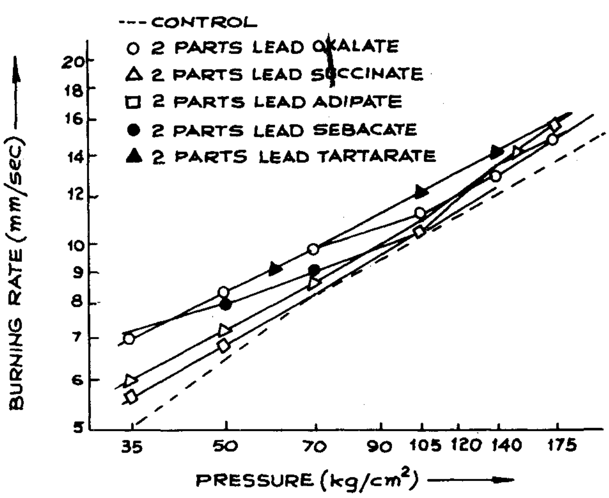

Fig. 2 Effect of aliphatic lead dicarboxylates on the burning rates of double-base propellants.

Thus, the catalytic activity of lead monocarboxylates was confined to the lower pressure region. Beyond 50 kg/cm^2, the effect was not significant. Pressure exponent values were lowered by all these salts up to 105 kg/cm^2. Results obtained indicate that the catalytic effect increases with increasing carbon chain length of the lead salts and the shift in plateau effect/significant reduction of the n values is obtained with an increase of carbon chain length of the acids.

Although Lantz[8] has claimed that thorium succinate and adipate produce plateau ballistic properties in double-base propellants, no other lead dicarboxylate, except lead tartrate, is reported to affect burning rate-pressure relationship. Hence the influence of lead dicarboxylates was studied (Fig. 2).

Lead oxalate increased burning rates throughout and lowered the n value to 0.36 (70-105 kg/cm^2). Lead succinate also gave higher burning rates. Lead adipate produced

Table 1 Decomposition temperatures of lead salts and propellants

A. Rate of heating			B. Maximum temperature	
i) Lead salts 10°C/min			i) Lead salts 1000°C	
ii) Propellants 3°C/min			ii) Propellants 500°C	

Lead salts/propellants	Exothermic decomposition temperature, °C — Inception temperature, *Ti*	Final temperature, Tf	Peak temperature, *Tm*,	Endotherm, C
Lead acetate	130	384	372	80
Lead stearate	336	530	502	11,428
Lead palmitate	287	540	520	112
Lead oxalate	375	414	391	
Lead succinate	325	391	360	
Propellant (control)	150	179	174	
Control plus lead acetate	147	166	162	
Control plus lead palmitate	145	162	157	
Control plus lead sebacate plus carbon black	146	162	155	
Control plus lead oleate plus carbon black	147	164	156	

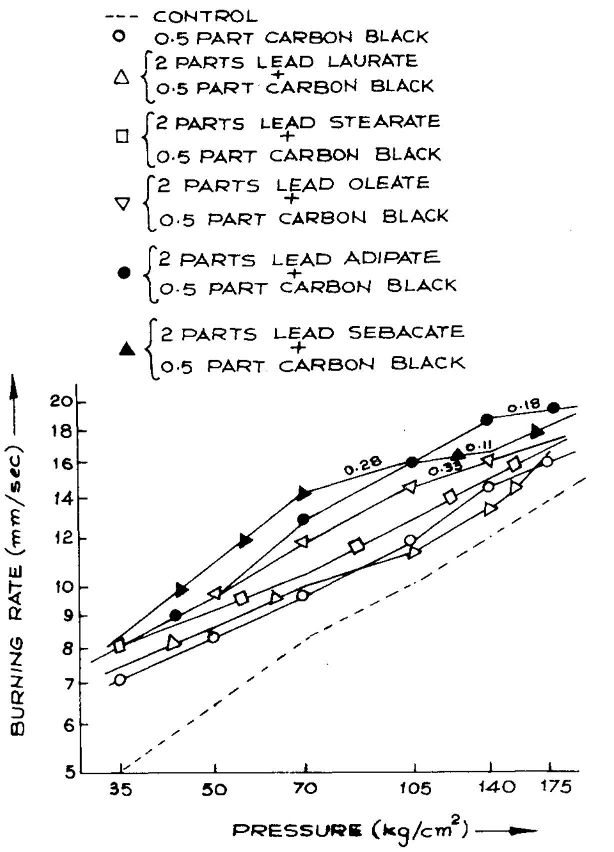

Fig. 3 **Effect of carbon black on the burning rates of double-base propellants.**

enhanced burning rates without any marked influence on the *n* values. On the other hand, lead sebacate, besides giving higher burning rates, lowered the *n* value from 0.73 to 0.30 (35-70 kg/cm^2). Lead tartrate (lead salt of a dihydroxy dicarboxylic acid) increased the burning rate by about 80% at lower pressures.

Preckel[9] has reported that the inclusion of carbon black along with lead salts further enhances the burning rates and shifts the plateau to the higher-pressure side. Hence, the effect of carbon black was studied with a few lead mono- and dicarboxylates (Fig. 3).

Inclusion of carbon black with lead monocarboxylates gave higher burning rates with reduction of the *n* values up to 140 kg/cm^2 pressure. A similar behavior was observed with lead dicarboxylates and carbon black combinations. Thus, carbon black-lead salt combinations, in general, lowered the pressure exponent and shifted the plateau to the higher-pressure regions.

A number of attempts have been made to explain the role of lead salts in the combustion of double-base propellants.[10-14] Most of the researchers feel that lead salts affect the reactions in the surface and fizz zones, with very little or no effect on the reactions of the luminous flame zone. In order to find the role of lead salts in the combustion of double-base propellants, differential thermal analyses (DTA) of a few lead salts as well as propellants were carried out (Table 1). Lead mono- and dicarboxylates decomposed in an exothermic mode in the temperature range of 300-500°C. These temperatures are very close to the temperatures of the surface and fizz zones. Hence, exothermic decomposition of lead salts may affect the reactions in the surface and fizz zones. DTA results of propellants reveal that the propellants containing lead salt and carbon black decomposed at lower temperatures than the control. Hence, lower decomposition temperatures of modified propellants may be responsible for their catalytic effect.

With regard to the mechanism of platonization, the results of the present study do not lend support to any of the existing theories. However, the fact that inclusion of carbon black with lead salts not only produced enhanced burning rates, but shifted the plateau effect to a higher-pressure range, indicates that extra carbon affects burning by the continuation of exothermic reactions between carbon and decomposition products of nitric esters (mainly NO) in the fizz zone. These observations support the combustion model of Hewkin et al.[13] in an indirect way.

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Hovering Motion of a Friction-Driven Gyroscopic Mass

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Nomenclature

A	= minor moment of inertia (about axis perpendicular to hole)
M	= applied torque due to friction
λ	= expression of inertial imbalance; $\lambda+1$ = major moment of inertia divided by minor moment of inertia
ϕ,θ,ψ	= Euler angles (see Fig. 1)
ω_c	= angular velocity of cavity
ω_r	= angular velocity of ball relative to cavity

REFERENCE 1 is a theoretical and experimental treatment of the motion which occurs when a ball is mounted within a spinning spherical cavity. The configuration is one in which a gyroscopic mass (the ball) is driven by means of friction between itself and the spinning cavity. The ball in this case is endowed with a major and minor axis of inertia by the simple means of a hole bored symmetrically through its center. The gyroscopic motion is such that the ball eventually aligns its major axis of inertia (axis through the hole) with the axis of spin of the spherical cavity. A specific application of this phenomenon is described in Ref. 2, where the ball is used as an automatically opening plug in a spinning tubular projectile. In both of these previous works it has been noted that under certain conditions the ball will "hover" about its initial orientation with the result that the alignment of the hole axis with the cavity spin axis is significantly delayed. In this Note, the equations of motion are shown to predict the existence of the hovering mode and this leads to a simple guideline by which the hovering behavior (which is normally undesirable) may be avoided.

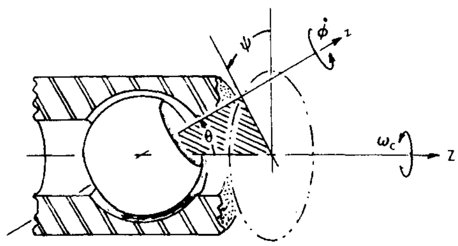

Fig. 1 Sketch defining components of ball motion within the spinning cavity.

Figure 1 illustrates the coordinate systems used in the analysis. The equation governing the angle of tilt (nutation angle) of the ball axis relative to the cavity spin axis is[1]

$$\ddot{\theta} = -(M/A\omega_r)\dot{\theta} - \dot{\psi}\sin\theta[(\lambda+1)\dot{\phi} + \lambda\dot{\psi}\cos\theta] \qquad (1)$$

The initial conditions governing the motion are

$$\theta(0) = \theta_0 \qquad \dot{\theta}(0) = 0 \qquad \dot{\psi}(0) = \omega_c \qquad \dot{\phi}(0) = 0$$

and in the initial instants of motion Eq. (1) may be approximately written as

$$\ddot{\theta}_0 = -(M/A\omega_r)\dot{\theta}_0 - (\lambda/2)\omega_c^2\sin 2\theta_0$$

Here we have retained the term involving $\dot{\theta}_0$ because even though $\dot{\theta}_0$ itself is initially at zero, a large applied moment M may give significance to this term. In addition, in the initial instants of motion, the relative angular velocity ω_r is essentially due to this nutation rate so that $\dot{\theta}_0 \simeq -\omega_r$ and the initial acceleration is given by

$$\ddot{\theta}_0 = M/A + \omega_c^2 D$$

where, as in Ref. 1, $D = (\lambda/2)\sin 2\theta_0$. In situations where hovering occurs, this initial angular acceleration is approximately zero so that if $M \simeq -A\omega_c^2 D$ the condition for hovering is met. For smaller values of M the angular acceleration will be negative and non-zero and the hovering behavior may thereby be avoided by design. A general design guideline may be formulated as follows:

$$H \equiv (M/A\omega_c^2 |D|) \leq 1 \qquad (2)$$

for the avoidance of hovering.

Further explicit formulation of the value of H requires the expression of the torque term M in terms of the design parameters. Such expressions are given in Refs. 1 and 2. It may be noted, however, that from the definition of D hovering is unavoidable when $\lambda \to 0$ or when $\theta_0 \to \pi/2$ (the case $\theta_0 = 0$ is the trivial case when the motion begins with the ball hole aligned with the spin axis). The first case ($\lambda \to 0$) represents the situation when the hole in the ball is vanishingly small and there is no inertial imbalance to drive the motion. In the second case ($\theta_0 \to \pi/2$) the ball hole is initially aligned normal to the spin axis and the system is in a metastable state of equilibrium which will persist in the absence of an external disturbance. Both cases are in consonance with physical intuition. The criterion in Eq. 2 is further substantiated by comparison with the experimental results reported in Ref. 1.

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