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Influence of Lead Inorganic Compounds on Combustion Rate of Double Base Rocket Propellants

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Abstract. The influence of lead nitrate, red lead, lead chromate, lead fluoride and lead carbonate on the combustion behaviour of double base propellants in the pressure range–35-140 kg/cm^2 was studied. While all these compounds increased burning rates in lower pressure range (35–60 kg/cm^2) and higher pressure range (120–140 kg/cm^2), only lead chromate and lead fluoride were effective in the intermediate pressure range of 60–105 kg/cm^2. None of these compounds were effective as platonizer, except lead fluoride, which lowered n value to 0.34 in the lower pressure range. Addition of carbon black along with lead compounds raised burning rates further and reduced n values significantly in the higher pressure regions. A probable mechanism on the role of lead compounds studied has been suggested based on burning rate and DTA results.

1. Introduction

Inclusion of lead salts is reported to affect the burning rate-pressure relationship of double base propellants[1,2,3]. Preckel[1,2] reported that lead oxides (PbO, PbO_2, Pb_3O_4) produce catalytic and plateau effects in double base propellants and addition of carbon black increases burning rates further and shifts plateau effect to higher pressure region. Hewkin *et al.*[4] found that oxides of iron, cobalt and zinc etc give only enhanced burning rates, whereas litharge produces mesa behaviour. However, Kubota & co-workers[5] observed that litharge works only as a burning rate catalyst without any plateau or mesa characteristic. Thus, although limited studies have been carried out on the effect of a few lead inorganic compounds, detailed information on their influence are not available in the open literature. Furthermore, most of the data reported are confined to a limited pressure range. Hence, a systematic study was undertaken to study the influence of certain lead compounds on the burning rates, calorimetric value (calval) and stability of double base propellants. This paper reports the results on the influence of lead nitrate, red lead, lead chromate, lead fluoride and lead carbonate in the pressure range 35–140 kg/cm^2. The effect of carbon black was also studied along with a few selected lead compounds.

2. Experimental

Nitrocellulose (NC) of 12.2% nitrogen content made from cotton linters, nitroglycerine (NG), carbamite (symm-diethyl diphenylurea) and dinitro-toluene (DNT) received from Ordnance factories were used. Lead compounds and dibutyl phthalate (DBP) were procured from trade and their purity was checked before use. Carbon black of Royal Ordnance Factory (UK) origin was used.

Propellants in the form of strands were made by solventless extrusion method[6,7]. To 100 parts of basic mix containing NC, NG, carbamite, DNT, and DBP, 2 parts of lead compounds passing through 200 BSS were added and incorporation was carried out in a 1 kg mixer for 5 hrs. Mix was then dried and rolled through even speed rollers. About 30 passes were given to each composition. Rolled sheets were cut into suitable discs and strands were extruded through an extrusion block, having 3 holes of 3.2 mm diameter. Extruded propellants were cut into pieces of 150 mm length.

Burning rates at different pressures were determined by Crawford bomb method[8], using nitrogen as inert gas. Minimum 5 strands were fired at each pressure. The standard deviation of burning rates was of the order of ± 0.05 mm/sec.

The heat of explosion of propellants was determined at atmospheric conditions, at a loading density of 0.016 g/cc. The deviation was of the order of ±3 cal/g. Heat test values were determined as per Abel's heat test method[9].

Differential thermal analysis (DTA) of lead compounds and propellants was studied with the help of DTA apparatus of M/s Stanton Red Croft (UK). Alumina was used as a reference sample. Rate of heating of 10°C/min and 4°C/min was used for lead compounds and propellants respectively.

3. Results and Discussion

Results on the influence of lead nitrate, red lead, lead chromate, lead fluoride and lead carbonate on burning rates are given in Table 1 and shown in Fig 1.

Table 1. Effect of lead inorganic compounds on the burning rate-pressure relationship of double base propellants

(NC-51, NG-37, Carbamite-3.0, DNT-3.5, DBP-5.5)

Additives (2 parts/ 100 parts)	cal val (cal/g)	Heat test at 160°F (min)	Burning rates (mm/sec) at pressures (kg/cm²)					Pressure index over pressure range (kg/cm²)		
			35	50	70	105	140	35–70	70–105	105–140
NIL	912	12	4.6	6.1	7.9	10.4	11.9	0.78	0.68	0.47
Lead nitrate ($Pb(NO_3)_2$)	898	11	5.3	6.3	7.4	9.7	12.4	0.48	0.67	0.85
Red lead (Pb_3O_4)	894	13	5.2	6.2	7.3	10.2	12.6	0.49	0.82	0.73
Lead chromate ($PbCrO_4$)	900	13	5.3	6.8	8.5	11.2	13.6	0.68	0.68	0.67
Lead fluoride (PbF_2)	880	13	6.3	7.1	8.0	10.0	12.2	0.34	0.55	0.69
Lead carbonate ($PbCO_3$)	894	14	5.0	6.2	7.6	10.6	12.8	0.60	0.82	0.60

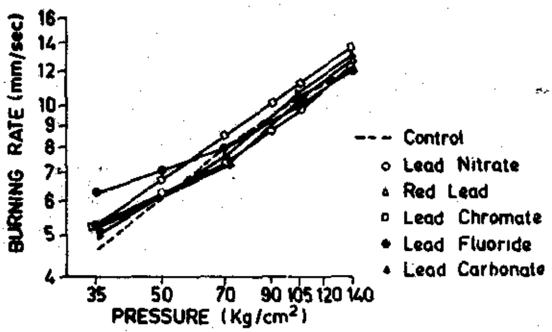

Figure 1. Effect of lead inorganic compounds on the burning rates of double base propellants.

It is found that inclusion of 2 parts of lead nitrate increased burning rates in the pressure range 35–60 kg/cm^2 and 130–140 kg/cm^2. It reduced pressure index *n* values from 0.78 to 0.48 only in the pressure range 35–70 kg/cm^2. *n* value remained the same (0.67) as that of control in the pressure range 70–105 kg/cm^2, and was raised from 0.47 to 0.85 in 105–140 kg/cm^2 range.

In the case of red lead, burning rates were higher at 35 and 140 kg/cm^2 pressures. At remaining pressures burning rates were either same as those of control or marginally lower. Red lead brought down *n* value from 0.78 to 0.49 in the pressure range 35–70 kg/cm^2 and raised it to 0.82 from 0.68 and to 0.73 from 0.47 in the pressure regions 70–105 kg/cm^2 and 105–140 kg/cm^2 respectively.

Lead chromate gave enhanced burning rates throughout, without any significant reduction of *n* values in any of the pressure regions studied. However, it maintained an uniform *n* value of 0.68 in the whole pressure range studied.

Lead fluoride, on the other hand, increased burning rates in the whole pressure range studied, except at 105 kg/cm^2, where burning rate was reduced marginally. It lowerd *n* values from 0.78 to 0.34 in 35–70 kg/cm^2 region and from 0.68 to 0.55 in 70–105 kg/cm^2 region. In 105–140 kg/cm^2 region, *n* value was raised from 0.47 to 0.69.

These results indicate that while lead nitrate and red lead showed comparatively higher burning rates than control at low and high pressures along with the reduction of *n* values to 0.48 level only in the low pressure region, lead chromate and lead fluoride produced increased burning rates almost throughout and lead fluoride reduced *n* value to 0.34 in 35–70 kg/cm^2 region. Lead carbonate did not show any significant catalytic or plateau effect. Thus, lead fluoride seems to be a better ballistic modifier than other lead compounds studied and lead chromate appears to be a better catalyst than others in 70–140 kg/cm^2 region.

Addition of lead compounds lowered heat of explosion by 14 to 30 cal/g, without affecting the stability of propellants, as seen from heat test values of 11 to 14 min. as against 12 min. for control.

The results on the effect of carbon black with and without red lead and lead nitrate on burning rates are given in Table 2 and shown in Fig 2.

Addition of carbon black alone raised burning rates throughout and reduced *n* values in the pressure range 35–105 kg/cm^2. In combination with red lead, carbon black

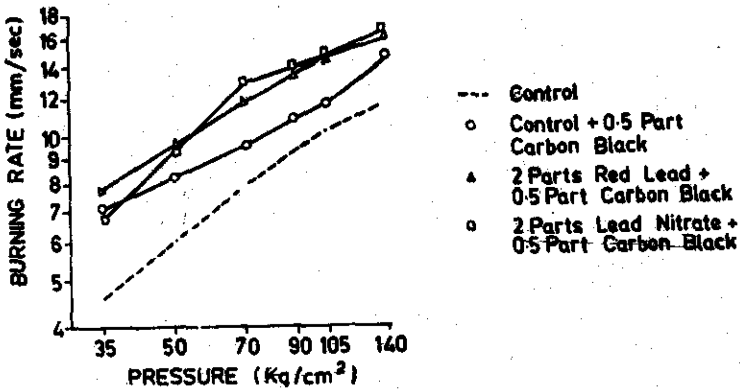

Figure 2. Effect of carbon black on the burning rates of double base propellants containing lead compounds.

Table 2. Effect of carbon black on the burning rates of double base propellants

(NC-51.0, NG-37.0, Carbamite-3.0, DNT-3.5, DBP-5.5)

Additives	cal val (cal/g)	Heat test at 160°F (min)	Burning rates (mm/sec) at pressures (kg/cm²)					Pressure index over pressure range (kg/cm²)		
			35	50	70	105	140	35–70	70–105	105–140
Nil	912	12	4.6	6.1	7.9	10.4	11.9	0.78	0.68	0.47
Control + Carbon black (0.5 parts)	890	12	7.1	8.3	9.7	11.8	14.7	0.45	0.49	0.75
Red lead (2 parts) + carbon black (0.5 parts)	875	11	7.8	9.7	12.0	14.6	16.0	0.62	0.48	0.32
Lead nitrate (2 parts) + carbon black (0.5 parts)	888	11	6.9	9.5	12.9	14.6	16.5	0.90	0.30	0.42

enhanced burning rates in the entire pressure range studied. *n* value was raised to 0.62 from 0.45 (35–70 kg/cm²), remained the same (0.48) in 70–105 kg/cm² region and was lowered to 0.32 from 0.75 in 105–140 kg/cm² region.

With lead nitrate also carbon black increased burning rates throughout, except at 35 kg/cm². As observed in the case of red lead, carbon black along with lead nitrate reduced *n* values in the higher pressure range and raised it in the lower pressure range.

These results suggest that carbon black alone raises burning rates, but in presence of lead compounds burning rates are enhanced further and plateau effect shifts to higher pressure side. These findings are in agreement with the results of Preckel[2].

The primary process in the combustion of double base propellants is the decomposition of organic nitrates, $RO—NO_2$, with an activation energy of about 40 KCal/mole. The breaking of $O-N$ bond gives a free radical and NO_2. This primary reaction is followed by subsequent reactions between NO_2 and other decomposition products to ultimately lead to final products namely, CO_2, H_2,H_2O, N_2 etc.

During the steady state of combustion, four reaction zones namely, foam or sub surface reaction, fizz, dark and luminous zones have been identified[10]. Lead salts found effective as catalyst and platonizer can, therefore, affect the reactions in one or all of the above zones.

In order to understand the probable role of lead compounds studied, DTA of lead compound was studied. Results are given in Table 3 and shown in Fig 3.

Results obtained show that lead nitrate, lead chromate and lead carbonate decomposed in an endothermic way in the temperature range 260–600°C. These temperatures are very close to the temperature of surface and fizz zones[11]. Hence, decomposition of lead compounds studied are likely to affect the reactions taking place in foam and fizz zones. The reactions in the flame zone are likely to be least affected, in view of lower heat of explosion of modified propellants (cal-val is proportional to flame temperature).

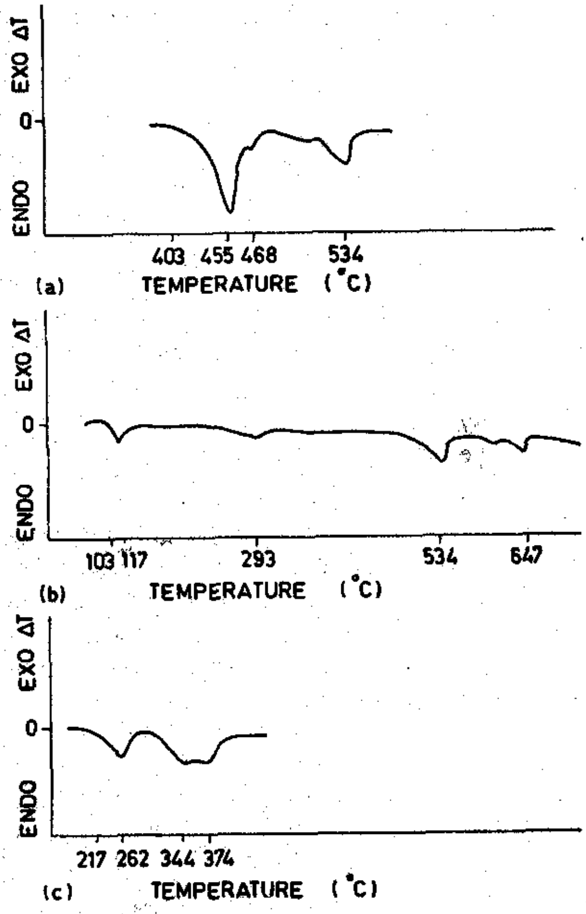

Figure 3. Decomposition temperature of lead compounds: (i) DTA trace of lead nitrate decomposition. (ii) DTA trace of lead chromate decomposition. (iii) DTA trace of lead carbonate decomposition.

Table 3. Thermal decomposition temperatures of lead compounds and propellants

1. Rate of heating:
   (a) Lead compounds—10°C/min, (b) Propellants—4°C/min

2. Maximum temperature:
   (a) Lead compounds—900°C, (b) Propellants—500°C

Composition	Decomposition temperature (°C)			
	Endotherm		Exotherm	
	Inception	Peaks	Inception	Peaks
Lead nitrate	403	455 I 468 II 534 III		
Lead carbonate	217	262 I 344 II 374 III		
Lead chromate	103	117 I 293 II 534 III 647 IV		
Propellant (control)			150	174
Control + lead nitrate			142	169
Control + lead carbonate			146	170
Control + lead chromate			147	166

A number of mechanisms mainly in the form of hypothesis have been proposed from time to time to explain the role of lead salts in the combustion of double base propellants[10,11]. They can be broadly classified as (1) photo-chemical mechanism (2) free radical theory (3) π-complex theory and (4) carbon or carbonaceous matter formation theory. None of these mechanisms can explain all the observed facts satisfactorily. The results of present study do not support or contradict any of the existing theories directly. However, results on the influence of carbon black in the presence and absence of lead salts support carbon or carbonaceous matter formation theory. According to which the burning process of double base propellant involves the formation of a limited amount of carbon in the condensed phase and in the presence of ballistic modifiers the amount of carbon or carbonaceous matter is increased. In the plateau region carbon is removed away due to oxidation by *NO*, as fast as it is produced and carbon is not available as catalyst or catalyst carrier in the post plateau region.

The results obtained in the present study (Table 2) show that inclusion of carbon black not only increased the burning rates significantly, but also reduced *n* values considerably in the higher pressure regions. These results suggest that shift in plateau effect to higher pressures in the presence of carbon black may be due to availability

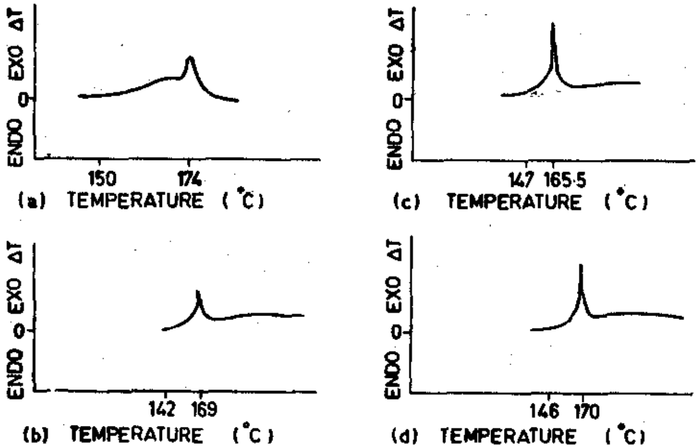

Figure 4. Decomposition temperature of propellant: (i) DTA trace of control propellant. (ii) DTA trace of propellant containing lead chromate. (iii) DTA trace of propellant containing lead nitrate. (iv) DTA trace of propellant containing lead carbonate.

of extra carbon, resulting in continuation of super rate to higher pressure regions. It is also possible that during the course of combustion lead salts may catalyse the reactions between carbon and combustion products of propellants.

To understand the role of lead salts during combustion of propellants, DTA of both modified as well as unmodified propellants was carried out and results are given in Table 3 and shown in Fig 4. Results obtained indicate that modified propellants decompose at lower temperatures than control in an exothermic mode. Hence, lower decomposition temperature (inception and peak) and probably higher heat of reaction may be responsible for increased burning rates.

From the above, it can be concluded that lead inorganic compounds studied affect the reactions in foam and fizz zones and formation and availability of carbon or carbonaceous matter controls the super rate burning and plateau effect.

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