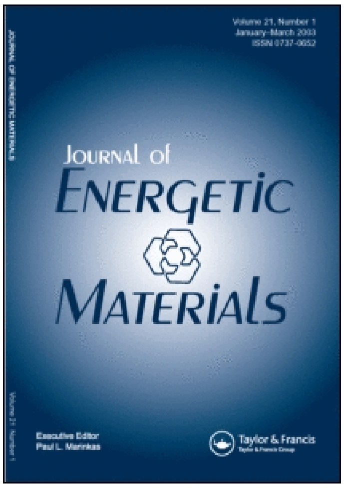

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INFLUENCE OF 1,4-DINITROPIPERAZINE (DNP) ON THE PRESSURE INDEX OF RDX CONTAINING EXTRUDED DOUBLE BASE PROPELLANTS

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ABSTRACT

Effect of 1,4-dinitropiperazine (DNP) in bringing down the pressure index (n) in RDX - containing extruded double base propellants has been studied. Experiments have been conducted on two sets of formulations based on controls of low calorimetric value (870 cal/g) and high calorimetric value (1070 cal/g). RDX content was varied between 10 and 20% and DNP content from 2 to 6 parts per 100 parts of the base composition. DNP alone does not bring down n appreciably; however, in

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conjuction with Basic Lead Salicylate, a well known ballistic modifier (2 parts), it brings down the n in the 70 - 105 kg/cm^2 pressure range significantly. The effect is more pronounced in the low calorimetric value compositions and a plateau effect has been observed. Addition of dinitropiperazine does not adversely affect the thermal and chemical stability of the formulations nor their mechanical properties. The temperature sensitivity of burn rate of DNP containing formulations was reduced to 0.21% / °C as compared to that of the control having of 0.32% / °C.

INTRODUCTION

Remarkable enhancement of energetics[1], thermal stability and smokelessness[2] of double base (DB) propellants is achieved by the incorporation of nitramines like RDX or HMX in DB matrix. However, this innovation suffers from a major drawback of higher pressure exponent (n)[3], which is undesirable from the view points of consistent ballistics and hardware safety. Ballistic modifiers have been used[4-6] to modify the burn rate - pressure relationship such that n (as in $r = aP_c^n$ where r = burn rate,

P_c = chamber pressure and a and n are constants whose value depends on propellant formulations), is significantly reduced over a useful pressure range. Use of the energetic additive, 1,4-dinitropiperazine (DNP)[7,8] in some RDX containing DB formulations has been reported to decrease the n value appreciably. These reports mainly concentrated on the effect of DNP on the burn rate characteristics of RDX-containing DB propellants by partially or fully replacing RDX by DNP. In the present study, we report the results of experiments conducted on two series of extruded RDX-containing DB propellants having (i) low calorimetric value of 870 cal/g and (ii) high calorimetric value of 1070 cal/g. Nitrocellulose (NC) in both the formulations was replaced by RDX to the extent of 10, 15 and 20%. The effect of addition of 2 to 6 parts of DNP per 100 parts of base mix on the burning characteristics of these formulations is discussed.

EXPERIMENTAL

Method of Synthesis of DNP[9]

DNP was synthesized on a laboratory scale from piperazine in three steps. In the first step, piperazine (200 g) was added to cold concentrated HCl (200 g) taken in a beaker with continuous stirring. After complete addition, the solution was stirred for one more hour and the piperazine dihydrochloride was precipitated by adding excess alcohol. The product was filtered and dried. The yield was 65%. In the second step, piperazine dihydrochloride (150 g) was added in half an hour to a mixture of 98% HNO_3 (400 ml), acetic anhydride (500 ml) and glacial acetic acid (262.5 ml) under nitrogen atmosphere maintaining the temperature between -5 and +5°C. The contents of the flask were brought to room temperature and stirring was continued for 72 hours. The contents were then washed with water, filtered and dried. In the third step, the residue (55 g) recrystallized from glacial acetic acid was treated with ammonium persulphate (210 g) dissolved in 98% HNO_3 (300 ml) at 0°C, stirred for 3 - 5 hours, poured on to ice and filtered. The product was washed successively with dilute $NaHCO_3$, water and alcohol, and recrystallized from ethyl acetate in 70% yield.

<u>Propellant Formulation : Processing and Evaluation</u>

RDX - double base formulations based on two types, viz. low and high calorimetric value compositions, replacing 10 to 20% NC by RDX were processed by standard solventless extrusion technique[10]. Incorporation was carried out for 3 hours. After drying the propellant paste in a steam heated oven maintained at 50°C for 6 - 8 hours was passed through steam heated rollers maintained at 80°C. A minimum of 30 passes were required to obtain a good gelatinized sheet. Discs were punched out of these propellant sheets and were then loaded in the press basket, which was also maintained at 80°C by steam heating. The propellant was extruded in the form of strands (3 x 150 mm) at an extrusion pressure of 50 kg/cm^2). RDX, basic lead salicylate (BLS) and DNP were added during the kneading stage. The details of the formulations are presented in Table 1.

Methods

Elemental analysis was done on a Perkin Elmer instrument model 240 C. X-ray diffraction patterns were obtained on a Philips X-ray diffractometer model PW 1730/10 with a vertical goniometer. CuK$_\alpha$ radiations were employed. Analytical parameters employed were, a = 40 kV, b = 20 mA. The sample was in finely powdered form.

TABLE 1

Compositional Details of the Formulations

Ingredient	LCC	LCC 1	HCC	HCC 1	HCC 2	HCC 3
Nitrocellulose (NC)	59.5	49.5	58	48	43	38
Nitroglycerine	30.5	30.5	37	37	37	37
Diethyl-phthalate	7	7	--	--	--	--
Carbon black	3	3	2	2	2	2
Calcium carbonate	--	--	3	3	3	3
RDX	--	10	--	10	15	20

LCC - Low Calorimetric Value Control

HCC - High Calorimetric Value Control

Burn rates were measured using a Crawford Bomb[11], in nitrogen atmosphere in the pressure range 35 - 105 kg/cm^2. Chemical stability of the formulations was determined by B & J Test at 120°C using 5 g sample[12]. The calorimetric values (cal.val.) of the propellant formulations were determined by a Parr adiabatic bomb calorimeter using 1 g sample in air. Impact sensitivity was measured on a fall hammer (2.0 kg weight) type assembly fabricated in-house. Friction sensitivity was determined on a Julius Peter apparatus.

Static evaluation of the low cal.val. propellant grains containing 10% RDX with and without DNP was conducted in a Ballistic Evaluation Motor (BEM) with propellant grains of dimension 40 (OD) x 20 (ID) x 50 (L) mm and conditioned at -20 and +50°C. From the pressure-time (P-t) profile obtained, ballistic parameters were calculated.

RESULTS AND DISCUSSION

The structural and thermal analysis data of the DNP used are given in Table 2. The results are in close agreement with the reported ones, indicating that pure DNP in 70% yield has been obtained following the three-step method.

Sensitivity

Data on friction, impact and spark sensitivities (Table 3) show that presence of DNP in the RDX formulation does not adversely affect the sensitivities and the formulations are quite safe for processing.

TABLE 2

Data on DNP Characterization

	Experimental	Reported
Density, g/cc(25°C)	1.62	1.63
Melting point, (°C)	214	214 - 216
pH	6.72	--
DTA (°C) (endotherm)	214*	216
Elemental analysis		
% Carbon	27.39	27.27
% Hydrogen	4.61	4.54
% Nitrogen	31.31	31.81
X-ray diffraction pattern I/Io		
0	5.467	5.564
8	3.790	3.795
7	3.235	3.795
3	3.097	3.116
2	3.040	3.053
1	1.992	1.986
Particle size, µm	50	------
Impact sensitivity, cm	145	------
Friction sensitivity, kg (insensitive upto)	>36	------

TABLE 3

Data on Sensitivity Tests of DNP Containing Formulations

Propellant	Friction Sensitivity (kg)	Impact Sensitivity ($h_{50\%}$, cm)	Spark Sensitivity (J)
LCC 1	24	44	5
LCC 1 + 2BLS	24	46	5
LCC 1+2BLS+4DNP	21.6	44	5
LCC 1+2BLS+6DNP	21.6	44	5
HCC 1	25.2	32.5	5
HCC 1 + 2BLS	25.2	31.0	5
HCC 1+2BLS+4DNP	28.8	32.5	5
HCC 1+2BLS+6 DNP	28.8	33.0	5
HCC 2	24	27.0	5
HCC 2 + 2BLS	25.2	28.5	5
HCC 2 +2BLS+4DNP	25.2	27.5	5
HCC 2+2BLS+6 DNP	28.8	29.0	5
HCC 3	21.6	24.0	5
HCC 3 + 2BLS	21.6	25.5	5
HCC 3+2BLS+4DNP	21.6	27.5	5

TABLE 4

Effect of DNP on the Burn Rates of LCC1 Based Formulations

Composition	Burn rate mm/s at pressure kg/cm^2					n value over pressure range kg/cm^2			
	35	50	70	90	105	35-50	50-70	70-90	90-105
LCC1	4.1	5.2	6.6	8.1	9.0	0.66	0.71	0.81	0.68
LCC1+ 2DNP	4.0	5.0	6.4	7.7	8.4	0.62	0.73	0.73	0.56
LCC1+ 4DNP	4.1	5.2	6.3	7.3	8.1	0.66	0.57	0.58	0.67
LCC1+ 6DNP	3.8	5.0	6.0	7.0	7.7	0.77	0.54	0.61	0.62
LCC1+ 8DNP	3.6	4.8	5.8	6.7	7.4	0.81	0.56	0.57	0.64
LCC2	3.7	4.7	6.0	7.3	8.2	0.67	0.72	0.78	0.75

Burn Rate

The results of burn rate measurements (Table 4) of LCC-1 formulations indicate that with the addition of 2 parts DNP, the burn rates are lowered in the entire pressure range studied, with a marginal decrease in the n value. Subsesquent increase in the concentration of DNP to 4 and 6 parts shows that the trend observed is more or less the same. Further, on 50% replacement of RDX by DNP in the LCC1 formulation (this formulation is designated LCC2 in Table 4), there was hardly any influence on the n value.

In the presence of BLS, however, the LCC1 composition containing DNP showed a significant effect on n value as seen from the results presented in Table 5. Thus, a composition containing 2 parts each of DNP and BLS produced drastic reduction in n value in the pressure range 70 - 105 kg/cm^2 (0.13 to 0.25 as against 0.68 to 0.81 for the control). Further increase in the concentration of DNP to 4 and 6 parts without altering the BLS concentration, lowered n value in the entire pressure range; but a more pronounced effect was observed in the pressure range 70 - 105 kg/cm^2. In fact, a plateau region was observed in the pressure range 90 - 105 kg/cm^2 (Table 5). These results indicate that DNP alone is not so effective in bringing down the n value of the nitramine - containing propellant; however, in conjunction with BLS, DNP has great influence on the pressure exponent in the pressure range 90 - 105 kg/cm^2.

Table 5

Effect of DNP on the Burn Rates of LCC1 Formulations in Presence of BLS

Composition	Burn rate mm/s at pressure kg/cm^2					n value over pressure range kg/cm^2			
	35	50	70	90	105	35-50	50-70	70-90	90-105
LCC1	4.1	5.2	6.6	8.1	9.0	0.66	0.71	0.81	0.68
LCC1+ 2BLS	7.0	8.0	9.3	10	10.4	0.38	0.44	0.28	0.25
LCC1+ 2BLS+ 2DNP	7.1	8.2	9.1	9.7	9.9	0.4	0.31	0.25	0.13
LCC1+ 2BLS+ 4DNP	6.8	8.2	9.1	9.4	9.5	0.52	0.31	0.13	0.07
LCC1+ 2BLS+ 6DNP	6.5	7.7	8.6	9.0	9.0	0.48	0.33	0.18	0
LCC1+ 2BLS+ 8DNP	6.4	7.5	8.2	8.7	8.7	0.44	0.27	0.24	0

With a view to investigate the role of DNP in influencing the pressure exponent value of HCC formulations containing RDX, another set of experiments was carried out. The RDX concentration used was 10, 15 and 20 (HCC1, HCC2and HCC3 based formulations respectively). The results of burn rates presented in Tables 6 - 8 reveal that in case of these compositions, the addition of DNP in presence of BLS tend to reduce pressure index significantly in the pressure range 90 - 105 kg/cm^2. With 6 parts DNP in presence of 2 parts BLS, the n value is of the order 0.26 to 0.34 as against 0.53 to 0.59 for the respective control. The plateau effect observed in LCC1 formulation, however, was apparently missing in the HCC series. The effect of concentration of DNP on the pressure index at different pressures is shown in Figure 1.

The overall data on burn rate on low and high Cal. Val. nitramine-containing formulations indicate that in presence of DNP, the burn rates of nitramine propellant are lowered. These results are in agreement with the findings reported earlier[8]. According to Kubota's findings[9], the flame structure and temperature profile of fizz and dark zone of double base propellant are not altered by the addition of nitramines. DNP decomposes after melting at 214 - 216°C for which the heat energy is derived from the burning surfaces. The highly fuel rich nature, negative oxygen balance (-72.7%)

TABLE 6

Effect of DNP on the Burn Rates of HCC1 Formulations in Presence of BLS

Composition	Burn rate mm/s at pressure kg/cm²					n value over pressure range kg/cm²			
	35	50	70	90	105	35-50	50-70	70-90	90-105
HCC1	8.6	11.2	13.2	15.3	16.6	0.74	0.6	0.59	0.53
HCC1+ 2BLS	10.1	12.2	14.4	15.8	16.8	0.53	0.45	0.37	0.39
HCC1+ 2BLS+ 4DNP	9.6	11.7	14.0	15.5	16.2	0.49	0.46	0.40	0.29
HCC1+ 2BLS+ 6DNP	9.4	11.2	13.5	14.9	15.4	0.49	0.35	0.38	0.21

TABLE 7

Effect of DNP on the Burn Rate of HCC2 Formulations in Presence of BLS

Composition	Burn rate mm/s at pressure kg/cm²					n value over pressure range kg/cm²			
	35	50	70	90	105	35-50	50-70	70-90	90-105
HCC2	8.3	10.3	12.8	15.0	16.4	0.6	0.64	0.63	0.58
HCC2+ 2BLS	10.7	12.3	14.1	15.7	16.7	0.39	0.40	0.43	0.40
HCC2+ 2BLS+ 4DNP	10.2	11.6	13.3	15.0	15.8	0.36	0.41	0.48	0.33
HCC2+ 2BLS+ 6DNP	9.6	11	12.8	14.4	15.0	0.38	0.45	0.46	0.26

TABLE 8

Effect of DNP on the Burn Rate of HCC3 Formulations in Presence BLS

Composition	Burn rate mm/s at pressure kg/cm^2					n value over pressure range kg/cm^2			
	35	50	70	90	105	35-50	50-70	70-90	90-105
HCC3	7.9	9.8	12.6	14.6	16	0.6	0.74	0.58	0.59
HCC3+ 2BLS	9.7	11.2	13.9	15.5	16.6	0.4	0.64	0.43	0.37
HCC3+ 2BLS+ 4DNP	9.4	10.9	13.4	14.8	15.6	0.41	0.61	0.40	0.34

and higher nitrogen content (31.8%) of DNP introduces a cooling effect on the burning surface. Thus DNP + BLS combination appears to be highly effective to obtain lower n value or a plateau effect for RDX based extruded DB formulations. The results of B & J test (Table 9) show that the stability is not adversely affected by the incorporation of DNP and it is compatible with the DB matrix.

The calorimetric values obtained in respect of the propellant composition studied (Table 9) reveal that the cal. val. decreases by the addition of DNP. The descending trend in cal.val. in presence of DNP may be attributed to the less energetic nature of DNP as compared to RDX.

Ballistic Evaluation

The predicted performance of the experimental compositions in terms of characteristic velocity (C*) and energy (Isp) values shows marginal reduction only, over the control, in spite of adding upto 6 parts of DNP.

P-t Profile

P-t profiles of low cal.val formulations clearly indicate that there is no combustion instability in the pressure range 50 - 100 kg/cm^2 with and without DNP. A typical P-t profile of the DNP (6 parts) containing LCC1 formulation is shown in Figure 2.

Temperature Sensitivity of Burn Rates

Table 10 gives the burn rates of the propellant at -20°C, ambient and +50°C. Temperature sensitivity of burn rate, $(\Pi r)p$, is 0.21%/°C against 0.32%/°C for RDX based control composition. This means DNP plays an important role to make the formulation burn rate less sensitive to temperature.

TABLE 9

Data on Thermal and Chemical Stability of DNP Based Nitramine Propellant

Composition	Calorimentric value (cal/g)	Stability (B&J) (min)
LCC	870	2.2
LCC 1	904	1.9
LCC 1 + 2 BLS	876	2.0
LCC 1 + 2BLS + 4 DNP	868	1.9
LCC 1 + 2BLS + 6 DNP	866	2.2
HCC	1060	1.9
HCC 1	1116	1.8
HCC 1 + 2 BLS	1088	2.0
HCC 1 + 2 BLS + 4 DNP	1076	2.0
HCC 1 + 2 BLS + 6 DNP	1065	2.0
HCC2	1163	1.9
HCC 2 + 2 BLS	1125	2.2
HCC 2 + 2 BLS + 4 DNP	1097	2.2
HCC 2 + 2BLS + 6DNP	1100	2.0
HCC 3	1181	2.0
HCC 3 + 2 BLS	1144	2.0
HCC 3 + 2 BLS + 4 DNP	1144	2.0

TABLE 10

Temperature Sensitivity of Burn Rate (BEM Firing)
Formulation : LCC1 + 2 BLS + 6 DNP
Grain dimensions : 40(OD)x 20(ID) x 50(L) mm

Temperature (°C)	Burn rate (at 70 kg/cm^2 pressure)	(Π r)p (%/°C)
Ambient	9.0	0.32
+ 50	9.5	--
- 20	8.2	0.21

Mechanical Properties

Ultimate Tensile Strength (UTS) and % elongation of the samples conditioned at -20°C, ambient and +50°C do not show any adverse effect of the addition of DNP.

CONCLUSIONS

From the data generated, the following broad conclusions may be drawn.

i) DNP alone does not bring down the pressure index in nitramine (RDX) containing double base propellants appreciably; however, in conjunction with BLS, DNP brings down the pressure index in the pressure range 70 - 105 kg/cm^2 significantly.

ii) The plateau effect is more pronounced in low cal. val. formulations; n value to the extent of zero was obtained as compared to high cal.val. formulations.

iii) By adding DNP, the energetics of the formulations is only marginally decreased and stability remains unaffected.

iv) In presence of DNP the temperature sensitivity of burn rate of the formulations studied is lowered considerably.

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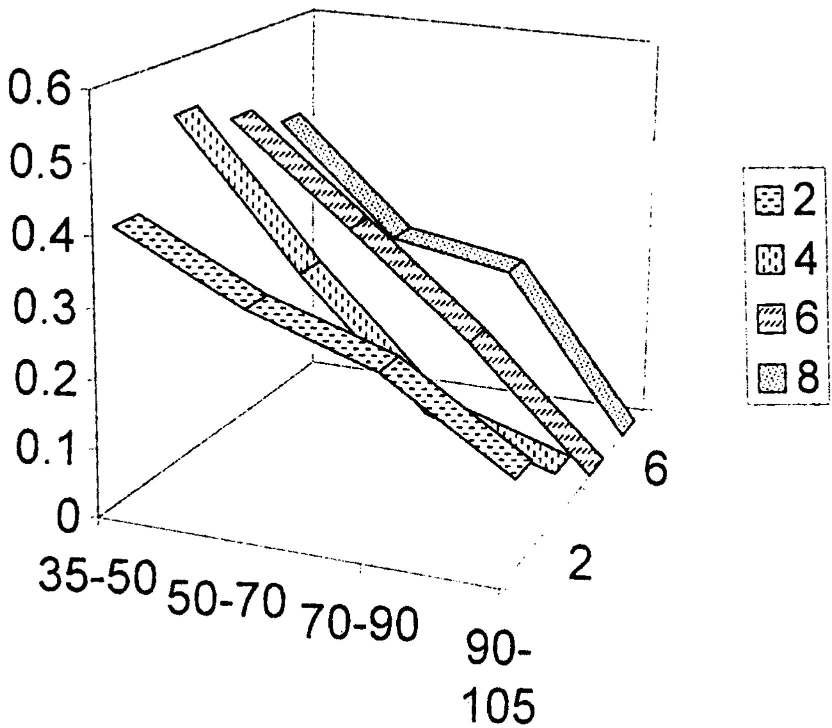

FIGURE 1

Effect of DNP Concentration on Pressure Index

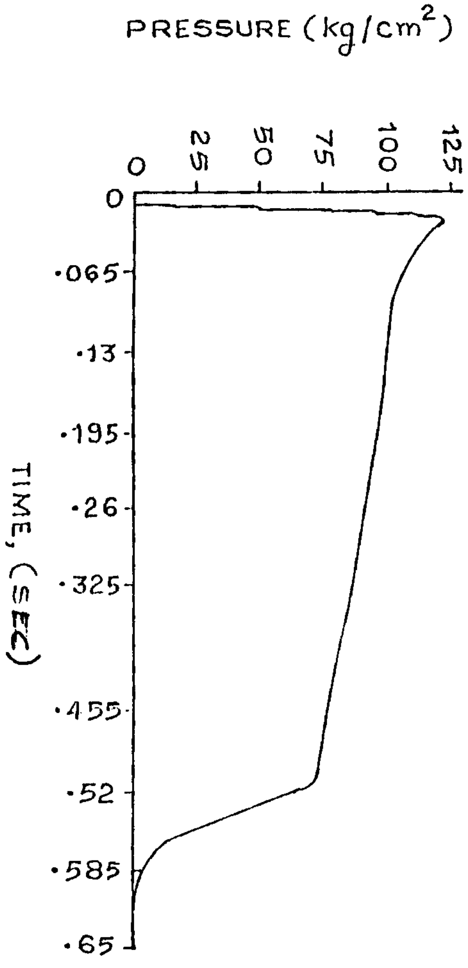

FIGURE 2

P-t Profile of DNP (6 parts) Containing LCC1 Formulation