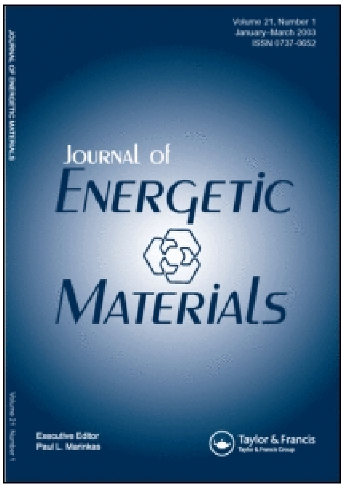
This article was downloaded by:
On: *16 January 2011*
Access details: *Access Details: Free Access*
Publisher *Taylor & Francis*
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Journal of Energetic Materials

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713770432

A Study on Gun Propellants Based on Butyl-NENA

T. K. Chakraborthy; K. C. Raha; B. Omprakash; Amarjit Singh

Online publication date: 24 June 2010

To cite this Article Chakraborthy, T. K. , Raha, K. C. , Omprakash, B. and Singh, Amarjit(2004) 'A Study on Gun Propellants Based on Butyl-NENA', Journal of Energetic Materials, 22: 1, 41 — 53
To link to this Article: DOI: 10.1080/07370650490438293
URL: http://dx.doi.org/10.1080/07370650490438293

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.informaworld.com/terms-and-conditions-of-access.pdf

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Energetic Materials, 21: 41–53, 2004

ISSN: 0737-0652 print
DOI: 10.1080/07370650490438293

A Study on Gun Propellants Based on Butyl-NENA

T. K. CHAKRABORTHY
K. C. RAHA
B. OMPRAKASH
AMARJIT SINGH

High Energy Materials Research Laboratory,
Pune, India

Researchers have sought to improve performance of gun propellants by incorporating various additives in the propellant matrix. Energetic plasticizers were primarily introduced in the formulation to improve the energy content of the propellant with the possible fallout in the form of improvement in the mechanical property. Butyl-NENA is widely reported to play the dual role of better energetics with an improved mechanical property. In the present paper butyl-NENA has been introduced in typical single, double, and triple base propellant formulations. Introduction of butyl-NENA in a single base propellant has resulted in significant improvement in energetics, while in double base and triple base propellants, it has contributed to enhancing insensitivity and improving mechanical properties.

Keywords: butyl-NENA, plasticizer, propellant

Address correspondence to T. K. Chakraborthy, High Energetic Materials Research Laboratory, Pune 411-021, India. E-mail: hemrl@yahoo.co.in

Introduction

Tremendous development is taking place in the field of gun propellant formulation with the introduction of specific additives in the propellant matrix to produce properties like low vulnerability, higher energy, better mechanical properties, thermal stability, and environmental friendly nature. On the one hand, energy content of the propellant formulation is being increased by introducing solid energetic compounds like 1,3,5-trinitro-1,3,5-triazacyclohexane (RDX), triamino guanidine azide (TAGAZ), and 2,4,6,8,10,12-hexanitrohexaaza-tetracyclododecane (CL-20) in the nitrocellulose matrix. On the other hand, energetic plasticizers like 1,5-diazido-3-nitrazapentane (DANPE) and N-n-butyl-N-(2-nitroxy-ethyl) nitramine (Bu-NENA) have increasingly taken over the twin role of increasing the energy as well as plasticization to give better mechanical properties [1–7].

Since its synthesis by Blomquist and Fiedorik [8, 9] butyl-NENA has been at the center of intense research. Volatility of butyl-NENA vis-à-vis nitroglycerine and other energetic compounds was studied by Cartwright [10]. Randal and Mallay studied its stability and performance characteristics [11], and kinetic study on the thermal decomposition was carried out by Bohn [12]. The use of butyl-NENA encompasses the whole ambit of explosive formulations. It has been used in solid rockets, single-, double-, and triple-base gun propellants, and insensitive high-energy propellant formulations [13,14]. However, most of the work is in the form of patents, and very little work has been reported in publicly available literature. Hence, a need was felt to carry out an exhaustive study by incorporating butyl-NENA in single-, double-, and triple-base formulations to study their ballistic behavior, friction, and impact sensitivity and evaluate them with respect to their thermal stability and mechanical properties

Experimental

Butyl-NENA was synthesized following the method of Chen et al. [15]. Thereafter it was purified, and characterized by FTIR, HPLC, and DSC techniques. The batch size was gradually raised from 100 g (two batches) to 200 g (31 batches) to

300 g (four batches). The reported physico-chemical properties of the compound along with our own observations are given in Table 1. The THERM program developed at HEMRL was employed for the computation of thermo-chemical properties of the Bu-NENA-based gun formulations. Bu-NENA was introduced in the single-base formulations, sequentially, replacing dinitrotoluene (DNT) and dibutyl phthalate (DBP) in the propellant matrix. The energetic plasticizer nitroglycerine (NG) as well as the inert plasticizer DBP have been replaced sequentially in double-base formulations. Partial replacement of NG has been attempted in the triple-base formulations to study the effect on energy content, thermal properties, mechanical behavior, and sensitivity aspects.

All the gun propellant formulations were processed with a solvent technique. The ether:alcohol solvent mix (60:40 ratio) was employed in the processing of single-base propellant

Table 1
n-butyl-NENA characteristics

Sr.No.	Test	Reported	Observed
1	Appearance	Pale yellow liquid	Pale yellow liquid
2	Elemental analysis		
	%C	Theo. 34.78%	34.41–35.69%
	%N	Theo. 20.29%	19.06–20.29%
	%H	Theo. 6.28%	6.18–6.60%
3	Purity by HPLC	97–98%	94–96%
4	FTIR spectra	—	Matches with reported peaks
5	Density,g/cc@27°C	1.21	1.21
6	Viscosity@27°C, cS	—	12.67
7	Exothermic peak temp., °C	211.8	211.9
8	Refractive index, @27°C	—	1.474
9	Yield	85%	85%

where solvent quantity was optimized to 75% of the batch size. Similarly the solvent mix of composition, acetone:alcohol in a 80:20 ratio, was used for the double-base propellant dough processing, where solvent quantity employed was 20% of the batch size. Well-established solvent composition CD solvent containing acetone and water in a 92.5:7.5 ratio was employed in the processing of triple-base compositions at 16% of the batch size. Ingredients were mixed in a 1.5 l sigma mixer for a duration of 5–6 hr to produce a satisfactory dough. Propellant dough was then extruded into cord-shaped strands having a diameter of 3 mm using a 60 tonne hydraulic press. After overnight predrying at ambient temperature, the propellant strands were dried for 40 hr in a drying oven maintained at a temperature of 40°C by blowing hot air. Evaluation of the propellant formulations was accomplished by determining calorimetric value with a Julius Peters adiabatic bomb calorimeter, stability with the Abel heat test and methyl violet test, impact sensitivity by a Bruceton method, mechanical properties with a Hounsfield H25KS instrument, and, finally, ballistic parameters, viz., force constant, pressure exponent, and burning rate coefficients, via closed-vessel firings conducted in a vessel of 700 cc capacity at a loading density of 0.2 g/cc.

Results and Discussions

Thermo-chemical data for single-, double-, and triple-base compositions under investigation are given in Tables 2–4. The THERM program developed at HEMRL was employed to furnish the salient features [16]. In single-base formulations (Table 2), gradual replacement of DNT by Butyl-NENA leads to an increase in the force constant and flame temperature. Significantly, the specific heat ratio (γ) shows a downward trend, thus exhibiting a beneficial effect on specific energy. The high point of the compositions is reached when both DBP and DNT are totally replaced by Bu-NENA in composition 4, thus causing an increase in the force constant by 100 units and flame temperature by about 316 K. The specific heat ratio is lowest while mean molecular weight moderately increases in

Table 2

Theoretical and experimental thermochemical data for single-base propellant

	Composition				
Ingredient	1	2	3	4	5
NC (GB) (%$N = 13.15$)	83	83	83	83	83
DPA	1	1	1	1	1
K_2SO_4	1	1	1	1	1
DBP	5	5	5	0	0
DNT	10	5	0	0	10
Bu-NENA	0	5	10	15	5
Force constant (J/g)	913	924	936	1013	991
Flame temperature (K)	2469	2480	2490	2785	2772
Pressure of explosion, Pm (MPa)	228	231	233	251	246
No. of moles of gas formed (n)(mole/g)	0.04448	0.04484	0.04520	0.04473	0.04301
Specific heat (cal/g/c)	0.3387	0.3436	0.3485	0.3474	0.3382
Co. volume (cc/g)	0.9942	0.9916	0.9888	0.9678	0.9733
Specific heat ratio (γ)	1.2609	1.2593	1.2577	1.2498	1.2527
Calorimetric value (Q) (cal/g)	706	723	740	855	821
Mean molecular weight of gases (g/mole)	22.48	22.30	22.12	22.87	23.25
Gas volume (V), (cc/g)	996	1004	1012	980	963
Closed vessel firing results					
Force constant (J/g)	900	915	925	987	958
Linear burning coefficient (β_1) (cm/s/Mpa)	0.0913	0.0855	0.0829	0.0998	0.1051
Pressure exponent (α)	0.7368	0.7043	0.6781	0.7237	0.7406

Table 3
Theoretical and experimental thermochemical data for double-base propellant

	Composition					
Ingredient	1	2	3	4	5	6
NC(B), (%$N = 12.95$)	54	54	54	54	54	54
NG	28	28	28	28	23	23
Carbamite	2	2	2	2	2	2
DEP	16	11	6	0	16	11
Bu-NENA	0	5	10	16	5	10
Force constant (J/g)	912	989	1061	1141	862	945
Flame temperature (K)	2395	2469	2901	3198	2178	2434
Pressure of explosion, Pm (MPa)	201	217	263	249	191	209
No. of moles of gas formed (n) (mole/g)	0.0455	0.0449	0.0440	0.0429	0.0476	0.0467
Specific heat (cal/g/c)	0.3479	0.3491	0.3505	0.3523	0.3525	0.3537
Co. volume (cc/g)	1.0222	1.0048	0.9892	0.9720	1.0488	1.0282
Specific heat ratio (γ)	1.2616	1.2555	1.2494	1.2421	1.2685	1.2626
Calorimetric value (Q) (cal/g)	698	801	904	1027	621	721
Mean molecular weight of gases (g/mole)	21.84	22.27	22.73	23.30	21.00	21.40
Gas volume (V), (cc/g)	1026	1006	986	961	1067	1047
	Closed vessel firing results					
Force constant (J/g)	885	966	1042	1116	872	945
Linear burning coefficient (β_1) (cm/s/Mpa)	0.0786	0.0826	0.1093	0.1319	0.0753	0.0832
Pressure exponent (α)	0.7858	0.7941	0.8211	0.8484	0.8143	0.8064

Table 4
Theoretical and experimental thermochemical data for triple-base propellant

	Composition			
Ingredient	1	2	3	4
NC(B), (%$N = 12.95$)	20.8	20.8	20.8	20.8
NG	20.6	17.10	13.60	10.10
Picrite	55.0	55.0	55.0	55.0
Carbamite	3.60	3.60	3.60	3.60
K_2SO_4	0.30	0.30	0.30	0.30
Bu-NENA	0	3.50	7.0	10.5
Force constant, (J/g)	1032	1009	982	953
Flame temperature (K)	2771	2643	2503	2365
Pressure of explosion, Pm(Mpa)	255	251	245	239
No. of moles of gas formed (n) (mole/g)	0.04476	0.04592	0.0472	0.04848
Specific heat (cal/g/c)	0.3535	0.3566	0.3599	0.3633
Co. volume (cc/g)	0.9578	0.9722	0.9903	1.0101
Specific heat ratio (γ)	1.2516	1.2559	1.2606	1.2652
Calorimetric value (Q) (cal/g)	870	825	774	722
Mean molecular weight of gases (g/mole)	22.34	21.78	21.19	20.63
Gas volume (V) (cc/g)	1003	1028	1057	1086
	Closed vessel firing results			
Force constant (J/g)	1034	991	981	936
Linear burning coefficient (β_1), (cm/s/Mpa)	0.1402	0.1123	0.1028	0.0950
Pressure exponent (α)	0.7664	0.8255	0.8405	0.9077

this formulation (composition 4). The force constants realized in CV firings are in close agreement with the theoretical values. Note that induction of Bu-NENA at the cost of DNT lowers the pressure exponent (α) from 0.7368 (composition 1) to 0.6781 (composition 3) and linear burning rate values (β_1) from 0.0913 cm/s/MPa (composition 1) to 0.0829 cm/s/MPa (composition 3). β_1 values rise to 0.0998 and 0.105 cm/s/MPa and α values to 0.7237 and 0.7406 in compositions 4 and 5, respectively, where flame temperature and force constant also exhibit a substantial increase.

Thermo-chemical data for double-base compositions are computed and shown in Table 3. In compositions 1–4, where gradual replacement of diethyl phthalate (DEP) by butyl-NENA has taken place, gradual improvement in the force constant from 912 J/g (composition 1) to 1141 J/g (composition 4) with a steady increase in flame temperature from 2395 K (composition 1) to 3198 K (composition 4) is observed. Replacement of NG in composition 1 with Bu-NENA by 5% brings down the force constant from 912 J/g (composition 1) to 862 J/g (composition 5) and flame temperature from 2395 K (composition 1) to 2178 K (composition 5). However, the simultaneous replacement of NG and DEP by Bu-NENA causes an increase in the force constant from 912 J/g (composition 1) to 945 J/g (composition 6) with marginal increase in flame temperature from 2395 K to 2434 K (composition 6). The specific heat ratio (γ) shows a downward trend from composition 1 to 4, while in compositions 5 and 6 just the opposite trend is observed. This trend is reversed when the mean molecular weight of gases is taken into consideration.

The experimental values of the force constant achieved are in close agreement with theoretical values. Note that as the Bu-NENA constituent increases in formulations 1–4 at the cost of DEP, the linear burning rate coefficient increases from 0.0786 to 0.1319 cm/s/MPa and the pressure exponent from 0.7858 to 0.8484. Partial replacement of NG by Bu-NENA in composition 5 leads to a decline in the force constant and flame temperature. The pressure exponent α shows an increase to 0.8143, and linear burning coefficient β_1 a decrease to

0.0753 cm/s/MPa. On simultaneous replacement of NG and DEP by Bu-NENA in composition 6, α_1 and β values increase to 0.8064 and 0.0832 cm/s/MPa, respectively.

The thermo-chemical calculations for the triple-base formulations are shown in Table 4. Bu-NENA has replaced NG in compositions 1–4, gradually. Note that this process leads to a deline in the force constant from 1032 J/g (composition 1) to 953 J/g (composition 4). Flame temperature is reduced significantly from 2771 K (composition 1) to 2365 K (composition 4). Although mean molecular weight decreases from 22.34 (composition 1) to 20.63 (composition 4), the specific heat ratio (γ) increases from 1.2516 (composition 1) to 1.2652 (composition 4). In CV firings the linear burning rate coefficient decreases from 0.1402 (composition 1) to 0.095 cm/s/MPa (composition 4), while the pressure exponent increases from 0.7664 (composition 1) to 0.9077 (composition 4).

Friction and impact sensitivity of all the formulations are shown in Table 5. The introduction of Butyl-NENA as a substitute for DNT or DBP in a single-base propellant composition does not cause any rise in sensitivity. In fact, compositions 4 and 5 having the maximum energy content exhibit enhanced insensitivity as friction insensitivity increases from 24 (composition 1) to more than 36 kg (in compositions 4 and 5). Compared to single-base propellants, double-base gun propellant formulations show somewhat enhanced values of FOI while they remain insensitive to friction up to above 36 kg. In triple-base formulations the friction insensitivity increases from 16 kg (composition 1) to over 36 g (composition 4), while FOI increases from 28 (in composition 1) to 45 (in composition 4). This may be ascribed to the replacement of more sensitive nitroglycerine containing three $-O-NO_2$ groups by less sensitive butyl-NENA containing one $-O-NO_2$ and $=N-NO_2$ group. Thus, it can be concluded that the introduction of *n*-Bu-NENA in triple-base propellant formulations leads to a decrease in sensitivity.

Mechanical properties of the formulation are shown in Table 6. Introduction of butyl-NENA at the cost of DEP in double-base formulations leads to an increase in compressive strength

Table 5
Friction and impact sensitivity data

Sr. No.	Propellant	Composition						Figure of insensitivity	Friction sensitivity, (kg)
	Single Base	NC	DNT	DPA	K_2SO_4	DBP	Bu-NENA		
1		83%	10%	1%	1%	5%	0%	26	24
2		83	5	1	1	5	5	32	19
3		83	0	1	1	5	10	28	24
4		83	0	1	1	0	15	26	>36
5		83	10	1	1	0	5	26	>36
	Double base	NC	NG	DEP	Bu-NENA		Carb.		
1		54%	28%	16%	0%		2%	64	>36
2		54	28	11	5		2	42	-do-
3		54	28	6	10		2	44	do-
4		54	28	0	16		2	39	-do-
5		54	23	16	5		2	48	-do-
6		54	23	11	10		2	42	-do-
	Triple base	NC	NG	Picrite	K_2SO_4	Carb.	Bu-NENA		
1		20.8%	20.6%	55%	0.3%	3.6%	0%	28	16
2		20.8	17.1	55	0.3	3.6	3.5	38	>36
3		20.8	13.6	55	0.3	3.6	7.0	42	-do-
4		20.8	10.1	55	0.3	3.6	10.5	45	-do-

Table 6
Mechanical properties and heat test data

Sr. No.	Propellant	Composition						Compression strength (kg/cm ^{2})	Percentage compression	Heat test value, min.
	Single base	NC (GB)	DNT	DPA	K_2SO_4	DBP	Bu-NENA			
1		83%	10%	1%	1%	5%	0%	*	*	15
2		83	5	1	1	5	5			15
3		83	0	1	1	5	10			15
4		83	0	1	1	0	15			15
5		83	10	1	1	0	5			20
	Double base	NC (B)	NG	DEP	Bu-NENA		Carb.			M.V. test, min.
1		54%	28%	16%	0%		2%	293	55.3%	70
2		54	28	11	5		2	362	62.2	70
3		54	28	6	10		2	331	64.5	80
4		54	28	0	16		2	404	65.4	80
5		54	23	16	5		2	297	62.3	80
6		54	23	11	10		2	351	63.6	80
	Triple base	NC (B)	NG	Picrite	K_2SO_4	Carb.	Bu-NENA			M.V.test, min.
1		20.8%	20.6%	55%	0.3%	3.6%	0%	370	9.0	55
2		20.8	17.1	55	0.3	3.6	3.5	365	10.0	55
3		20.8	13.6	55	0.3	3.6	7.0	370	9.8	55
4		20.8	10.1	55	0.3	3.6	10.5	370	12.2	55

*Mechanical property of the single-base compositions could not be determined as the samples were prone to develop fissures during drying.

significantly, while NG substitution leads to marginal improvement only, presumably due to the higher specific volume of the compositions containing Bu-NENA owing to the existence of a long butyl chain. In triple-base formulations the replacement of NG by Bu-NENA does not result in significant improvement in compressive strength, while percentage compression shows marginal improvement.

Conclusions

Bu-NENA gun propellant formulations present an enticing array of compositions having a higher force constant, reduced sensitivity, and better mechanical properties. In single-base propellant formulations the introduction of butyl-NENA has effected a significant gain in energy without adversely affecting the linear burning rate coefficient. The introduction of butyl-NENA at the cost of diethyl phthalate in double-base propellant formulations has resulted in appreciable gain in energy as well as compressive strength, while in triple-base propellant formulations it has caused an appreciable fall in sensitivity with some improvement in mechanical properties. Thus, the introduction of Bu-NENA-based gun propellant formulations would allow a better and mechanically improved, energetically enhanced, and less sensitive gun propellant.

Acknowledgement

We are thankful to the director of HEMRL for his active interest and constant encouragement in this work.

References

[1] Volk, F. and H. Helmut. 1997. *Propellant, Explosives, Pyrotechnics*, 22: 120.
[2] Simmons, R. L. and C. M. Walsh. 2001. 32nd International Annual Conference of ICT, 43/1.
[3] Brown, L. 1998. U.S. patent, US 116744 (16 July).
[4] Jeck-Prosch, U., U. Seffner-Lehner, and P. Lang. 2000. Eur. Pat. Appl. EP 103548 Al 30 (August).

[5] Lu Aufang and Liao Xia. 1993. 24th International Annual Conference of ICT, Karlsruhe, Germany, 86/1.

[6] Silver, P. A. and N. F. Stanley. 1981. JANNAF Propulsion Meeting, New Orleans, LA, 2: 515.

[7] Lu, A., Q. Shen, X. Liao, and G. Bao. 1996. 7th International Annual Conference of ICT, 51/1.

[8] Blomquist, A. T. and F. D. Fiedorik. 1954. U.S. patent 2,678,946 (18 May).

[9] Blomquist, A. T., and F. D. Fiedorik. 1949. U.S. patent 2,485,855 (25 October).

[10] Cartwright, R. V. 1995. *Propellants, Explosives, Pyrotechnics*, 2: 51.

[11] Randal, A., and J. J. Mallay. 1992. *Proceedings of the American Defence Preparedness Association, Energetic Materials Technology*, p. 116.

[12] Bohn, M. A. 1999. *Thermochimica Acta*, 337:121.

[13] Hatch, R. L., et al. 1995. CA, 123, 87608j (21 August).

[14] Schmitt, D., P. Eyerer, and P. Elsner. 1997. *Propellants, Explosives, Pyrotechnics*, 22: 109.

[15] Chen Qiong Hua et al. 1996. 27th International Annual Conference of ICT, Karlsruhe, 133/1.

[16] Karir, J. S. 2001. Calculation of Thermochemical Constants of Gun Propellant by Computer Programme THERM, HEMRL, Pune, India.