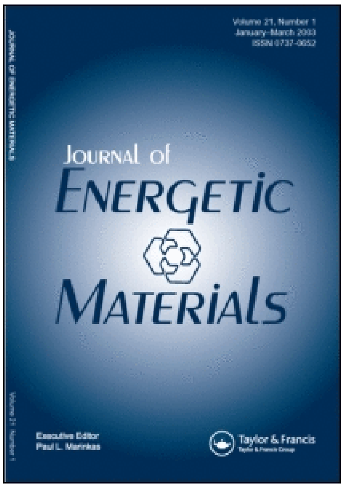

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STUDIES ON EFFECT OF INCORPORATION OF BDNPF/A ON BURNING RATES OF RDX/AP/Al FILLED CMDB PROPELLANTS

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ABSTRACT

This paper reports the effect of replacement of non -energetic plasticizer diethyl phthalate (DEP) by nitroplasticizer [1:1 mixture of bis (2,2 dinitro propyl) formal (BDNPF) and bis (2,2 dinitro propyl) acetal (BDNPA)] on burning rates and Isp of nitramine (RDX) / ammonium perchlorate (AP) based composite modified double base (CMDB) propellants. Addition of BDNPF/A led to overall 9 - 46% increase in burning rates, as well as gain in Isp to the order of 5-10 s in both the systems. Inclusion of copper chromite (C.C.) led to further improvement in burning rates. A typical aluminized (17.5%)- ecofriendly RDX (12.5%)-CMDB formulation gave burning rates of the order of 8- 22 mm/s in the pressure range of 2.9-10.8 MPa with Isp (theoretical) of 264 s. Aluminized AP–CMDB propellant with low pressure combustion limit of 1.9 MPa and burning rates of 15-31 mm/s was also realized during this work. Superior oxygen balance and heat of formation of BDNPF/A compared to DEP appear to play contributory role in this regard. Heat feed back from intensified combustion near the deflagrating propellant surface may be facilitating the decomposition of condensed phase. This is clearly brought out from estimated activation energy values for BDNPF/A plasticized RDX propellants.

Key words : nitroplasticizers BDNPF/A

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INTRODUCTION

Energetic *gem* dinitro aliphatic compounds are emerging as potential propellant /explosive additives. Eutectic mixture of bis (2,2 dinitro propyl) formal (BDNPF) & bis (2,2 dinitro propyl) acetal (BDNPA) is finding application as plasticizer in advanced propellants/ explosive formulations[1]. Replacement of currently used plasticizer (phthalate esters) by energetic nitroplasticizers is evincing interest all over the globe as it can result in burning rate enhancements & Isp improvement of double base and composite modified double base (CMDB) propellants, without adverse effect on sensitivity characteristics. Such compounds can also offer a means to overcome inherent combustion problems encountered in nitramine based systems. BDNPF/A is being manufactured on commercial scale by Aerojet Strategic Propulsion Company (USA) and Thiockol corporation (USA)[1]. Ter-meer[2] reaction is being widely used to prepare precursors of BDNPF/A. Recent trends are to adopt eco-friendly process avoiding use of chlorine[3]. Reed & Chan[4] have reported nitroplasticizer containing energetic explosives having detonation velocity of 8400m/s & C-J. pressure of 309 kbar. Rothenstem & Goldhagen[5] have reported BDNPF/A plasticized explosive formulations with the VOD of about 8370 m/s. Klager & Winkler[6] observed an increase in Isp of double base propellant by about 15 s on replacement of triacetine by BDNPF/A. Authors have also found these compounds of interest[7]. In recent times such nitrocompounds are also emerging as plasticizer for GAP based propellants[8].

During this work, BDNPF/A was synthesized and characterized in the laboratory. 1:1 eutectic mixture of BDNPF/A was incorporated as potent plasticizer and its effect on burning rates of AP/RDX-CMDB propellant was determined. Selected formulations were evaluated in miniature rocket motor to obtain confirmatory trends. DSC data was generated to get an insight of the prevailing combustion processes

EXPERIMENTAL

1. Synthesis and Characterization of BDNPF/A

BDNPF and BDNPA were synthesized on the line of the methods reported by Shipp et. al.[9] and Michel et.al.[10] These synthesized compounds were characterized by FTIR (Perkin-Elmer Model – 1605) and NMR (Bruker - 90 MHz), UV Visible – NIR Spectrophotometer (Hitachi Model – 340 - C) and Elemental analyzer (Carlo Erba-EA 1110). The data obtained is summarized below.

UV : λ_{max} 280 nm

FTIR : C-NO_2 (1576, 1330 cm^{-1}), C-O-C (1100, 1000 cm^{-1})

Elemental analysis :

BDNPF	C 29.4	H 4.29	N17.17	(Theoretical)
	C 29.3	H 4.02	N 17.01	(as obtained)
BDNPA	C 26.92	H 3.84	N17.17	(Theoretical)
	C 26.3	H 3.02	N 17.01	(as obtained)

2. Processing of Propellant

Nitrocellulose (12.2% nitrogen content) was used as binder component in the form of dense spheroids (DNC) of 25-45 μ size. DNC comprised NC:90 NG:7 centralite : 3%. SNC was processed with nitroglycerine (80%) desensitized with

18% non energetic plasticizer (diethyl phthalate - DEP) or energetic plasticizer (BDNPF/A). 2 nitrodiphenyl amine (2N-DPA) was added as stabilizer (2 %) to desensitize NG. Solid ingredients, AP (5 & 10±1 μ)/RDX(25± 2μ) and Al (16 μ) were incorporated to the matrix. In ballistically modified composition, 2 parts of copper chromite was added along with AP/Al. All the mixing operations were carried out in planetary mixture. The slurry was cast in the mould evacuated to 10mm of Hg and cured at 60±2 °C. Compositional details are given in Table 1. All the solid ingredients were dried to the moisture level of < 0.5% before processing and desensitized nitroglycerine (DNG) was deaerated under vacuum of 10 mm of Hg to the moisture level of < 0.2%. Cured propellant samples were cut into strands of dimensions 6 x 6 x 10 mm for evaluation in acoustic strand burner. Propellant pieces were also obtained for thermal studies. Propellant grains of 70mm OD, 20mm ID & 100mm L were subjected to static evaluation in miniature rocket motor.

3. Evaluation

Strand burner test

The burning rates of the propellant samples were measured in pressurized (1.8-10.8 MPa) strand burner by sensing acoustic signals from deflagrating samples. The signals were transmitted through water medium and sensed by piezoelectric transducer (resonance frequency 200 KHz)[11]

Thermal analysis

Thermal decomposition patterns of BDNPF/A & propellants were studied under N_2 at the heating rate of 5°C/min to 25°C/min at a increment of 5°C/min using DSC of

Perkin Elmer make. Activation energy (E) was computed by applying ASTM mehod[12] using kissinger relation

$$\ln\left(\frac{\beta}{T_m^2}\right) = \ln\left(\frac{ZR}{E}\right) - \frac{E}{RT_m}$$

β - Heating rate in deg/min
T_m - Peak temperature
Z - Prexponential factor
E is calculated from the slope of curve using

$$\text{Slope} = \left[d - \ln\left(\frac{\beta}{T_m^2}\right) / d\left(\frac{1}{T_m}\right)\right]$$

RESULTS AND DISCUSSION

I) Burning Rates

AP - CMDB

DEP plasticized AP (30%) based CMDB propellants gave stable combustion in the pressure range of 1.9 –10.8 MPa (Table 2 & Fig.1). The burning rates obtained were 9.5 – 20 mm/s. Replacement of DEP by BDNPF/A resulted in 28 – 46% burning rate enhancement. Addition of 2 parts of copper chromite (C.C.) led to further improvement in burning rate to the extent of 7 to 38%. Aluminized AP based CMDB compositions also exhibited more or less similar trends of burn rate enhancement on replacement of DEP by BDNPF/A. AP-Al-BDNPF/A formulation containing 2 parts copper- chromite (C.C.) gave burning rates of 15 to 31 mm/s in the pressure range of 1.9–10.8 MPa. The supporting data on burning rate pattern was obtained by statically evaluating the cast propellants in miniature rocket motors (Fig 2). The burning rates obtained in static firing were relatively higher (21 – 31 mm/s in the pressure range of 4.9 – 8.8 MPa).This trend is generally attributed to the difference in combustion environment in strand burner(N_2) and rocket motor (high temperature combustion gases). Theoretical Isp of the composition as computed from NASA 273 code was 262 s.

RDX-CMDB

DEP plasticized RDX based CMDB formulation did not undergo stable combustion upto 4.9 MPa (Table 3 & Fig 3).Burning rates realized for the composition in the pressure range of 6.8 to 10.8MPa were 6.4 to 10.3 mm/s. Incorporation of BDNPF/A and copper chromite (C.C.) was found effective in burning rate increase to the extent of 8 to 10 % and 20 to 64% respectively, in the pressure range of 6.8 – 10.8 MPa.

Aluminized RDX-CMDB formulation plasticized with BDNPF/A, and containing copper chromite along with (5μ) AP as additive exhibited low pressure combustion limit (LPCL) of 2.9 MPa. The composition gave burning rate of 8.6 to 22.2 mm/s, in the pressure range of 2.9 – 10.8 MPa. In miniature rocket motor burning rates (Fig. 4) obtained were 12.7 – 19.3 mm/s in 4.9-8.8 MPa region. The theoretical Isp of the composition computed using NASA 273 code was found to be 264 s for RDX – Al – CMDB composition.

II) Thermal Decomposition Studies

30 % AP and RDX based formulations were subjected to DSC studies (Table 4). It was observed that DSC of AP-CMDB propellant gives one major exotherm around 185 °C - 188 °C at the heating rate of 10 °C/min. (Fig. 5 & 6). DSC experiments conducted at different heating rates also confirm the same pattern.

Activation energy obtained from these experiments is 102 ± 2 kJ/mole for both AP/DEP and AP/BDNPF/A propellants (Fig.7 & 8).

In case of RDX-CMDB formulation, two exotherms were observed with T_m at around 208°C and 240°C at the heating rate of 10 °C/min. (Fig.9 & 10). These temperatures are close to the decomposition temperatures of double base matrix and RDX. As CMDB propellants with less amount of RDX exhibit one exotherm at 190°C [13], the first exotherm may be resulting from combined decomposition of double base matrix and part of RDX. Residual nitramine may be decomposing at higher temperature. Activation energy corresponding to first decomposition stage for the composition plasticized with DEP was 171.2kJ/mol while that for RDX/BDNPF/A propellant was 137.2 kJ/mol (Fig.11 & 12).

III) Mechanistic Aspects

High burning rates and performance parameters obtained during this work for BDNPF/A plasticized formulations compared to DEP based compositions may be correlated to their relative heat of formation and oxygen balance. Both, BDNPF and BDNPA are much superior [ΔH_f ; – 457 & - 484 cal/g and oxygen balance –51 & -63%] to DEP [ΔH_f -806 cal/g & oxygen balance –200%] in these regards. The burning rate patterns suggest that the superior oxygen balance and heat of formation influence the stiochiometry and heat output of combustion reactions near- surface gas- phase reactions.

Thermal decomposition pattern of AP/RDX based propellants brings out that the replacement of DEP by BDNPF/A does not have much effect on decomposition temperature of propellant suggesting compatibility of BDNPF/A with propellant ingredients in both the cases. Overall DSC pattern for AP based propellant is different from that of AP alone. As reported by Kubota et.al. [14] it may be due to intensive interaction between oxygen rich AP and fuel rich double base matrix. In case of RDX-CMDB, part of RDX tends to melt on the surface and forms a mixture with double base matrix. However, both decompose without mutual interaction as RDX is oxygen deficient (oxygen balance–22%) unlike AP (oxygen balance+35%).

As regards activation energy, replacement of DEP by BDNPF/A did not have any appreciable effect in case of AP-CMDB propellants. However, it brought down the activation energy appreciably for RDX-CMDB propellant. This trend may be an outcome of the fact that interactions between oxygen rich AP and fuel rich DB matrix or their products are remarkably intensive and E_a is already on lower side than that of even RDX-BDNPF/A propellant. In contrast, RDX acts as an overall diluent. Thus, the effect of increased feed back from the near surface gas phase reactions on global kinetics appears to be more evident in this system.

CONCLUSION

The work carried out during this research program clearly establishes the potential of BDNPF/A as plasticizer for CMDB propellants designed to realize improved burning rate and performance levels. Global kinetics of the BDNPF/A plasticized propellants suggest that BDNPF/A catalyzes near surface combustion process of CMDB system.

ACKNOWLEDGEMENT

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TABLE 1 :Compositional details of AP/RDX CMDB formulations

Comp. No.	DNC	NG	DEP	BDNPF/A	2NDPA	AP	Al	RDX	*C.C. in parts
1	29.5	32	8	-	1	29.5	-	-	-
2	29.5	32	2	6	1	29.5	-	-	-
3	29.5	32	2	6	1	29.5	-	-	2
4	29	28	7	-	1	17.5	17.5	-	2
5	29	28	2	5	1	17.5	17.5	-	2
6	29.5	32	8	-	1	-	-	29.5	-
7	29.5	32	2	6	1	-	-	29.5	-
8	29.5	32	2	6	1	-	-	29.5	2
9	29	28	7	-	1	5	17.5	12.5	2
10	29	28	2	5	1	5	17.5	12.5	2

*C.C. - Copper Chromite

TABLE 2 : Burning rate results of AP-CMDB propellants

Comp. No.	Components	Pressure (MPa)						Isp (s)
		1.9	2.9	4.9	6.8	8.8	10.8	
		Burning rate (mm/s)						
1	AP / DEP	9.5	11.3	14.7	16.8	18.4	19.8	248
2	AP/ BDNPF/A	12.2	14.1	19.7	20.6	26.9	29.2	254
3	AP/ BDNPF/A / CC	13.5	19.5	23.9	26.6	29	31.2	253
4	AP / Al /DEP / CC	9.9	13.5	17.1	19.6	22.1	27.6	257
5	AP / Al / BDNPF/A / CC	14.9	17.0	19.2	22.9	28.4	31.0	262

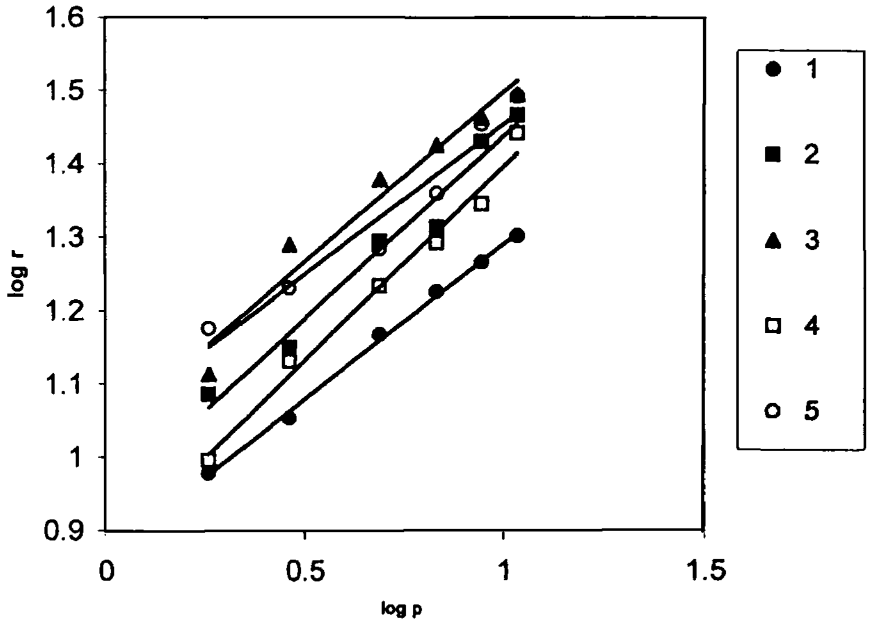
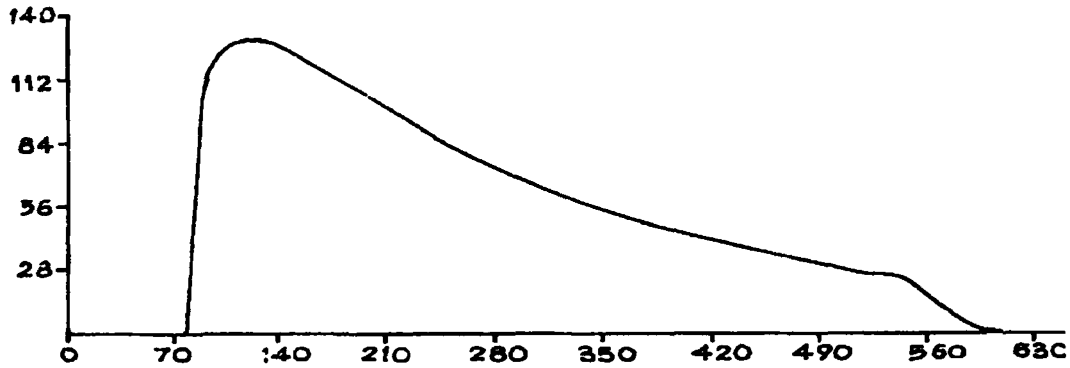


Fig1. Burn rate vs Pressure for AP-CMDB Propellant



↑ PRESSURE (kg/cm^2) – TIME (s) →

Fig. 2 Static Evaluation out put of BDNPF/A plasticized AP/Al/CMDB (comp.no. 5)

ź$_{50}$ – 21, ź$_{70}$ – 26.2, ź$_{90}$ – 30.8 mm/s

TABLE 3: Burning rate results of RDX-CMDB propellants

Comp. No.	Components	Pressure (MPa)					Isp (s)
		2.9	4.9	6.8	8.8	10.8	
		Burn rate (mm/s)					
6	RDX /DEP	-	-	6.4	8.7	10.3	244
7	RDX/BDNPF/A	-	-	7	9.5	11.2	254
8	RDX / BDNPF/A / CC	-	-	10.5	11.6	12.3	253
9	RDX / Al / AP / DEP / CC	-	9.0	11.8	14.3	17.7	259
10	RDX /Al / AP / BDNPF/A / CC	8.6	10.4	13.6	18.6	22.2	264

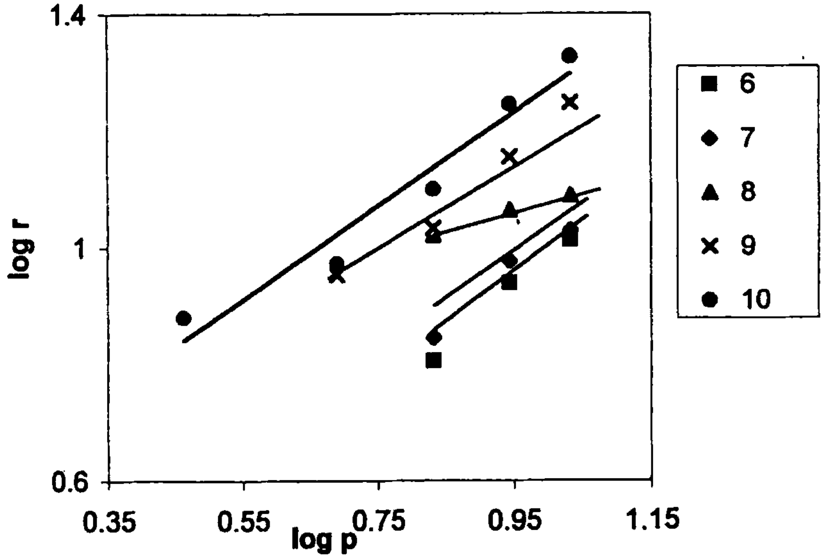
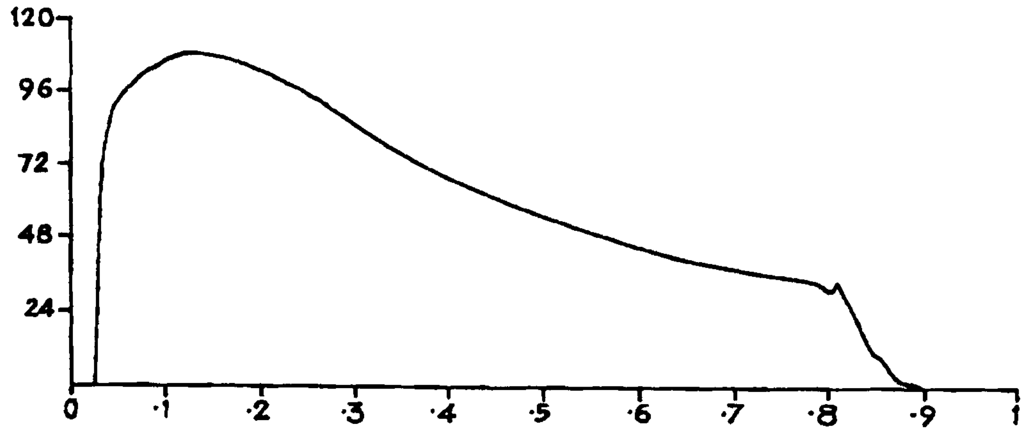


Fig3. Burn rate vs Pressure for RDX -CMDB propellant



↑ PRESSURE (kg/cm^2) – TIME (s) →

Fig. 4 Static Evaluation out put of BDNPF/A plasticized RDX/CMDB (comp.no.10)

$\hat{r}_{50}$ – 12.7, $\hat{r}_{70}$ – 16.1, $\hat{r}_{90}$ – 19.3 mm/s

TABLE 4 : DSC results on RDX/AP Propellants

Heating Rate (^0C/min)	RDX-DEP (comp.no.6)		RDX-A/F (comp.no.7)		AP-DEP (comp.no.1)	AP-A/F (comp.no.2)
	T_1	T_2	T_1	T_2	T_1	T_1
5	199.6	226.4	196.6	228.8	179.0	174
10	205.1	237.2	207.7	238.0	188.5	184.3
15	209.7	243.2	211.9	243.1	195.2	192.84
20	212.8	246.1	215.3	248.5	201.3	195.97
25	216.9	250.1	217.7	253.4	205.2	199.4
	* Ea 171.2		* Ea 137.2		* Ea 104	* Ea 102

*Ea - Activation energy in kJ/mol

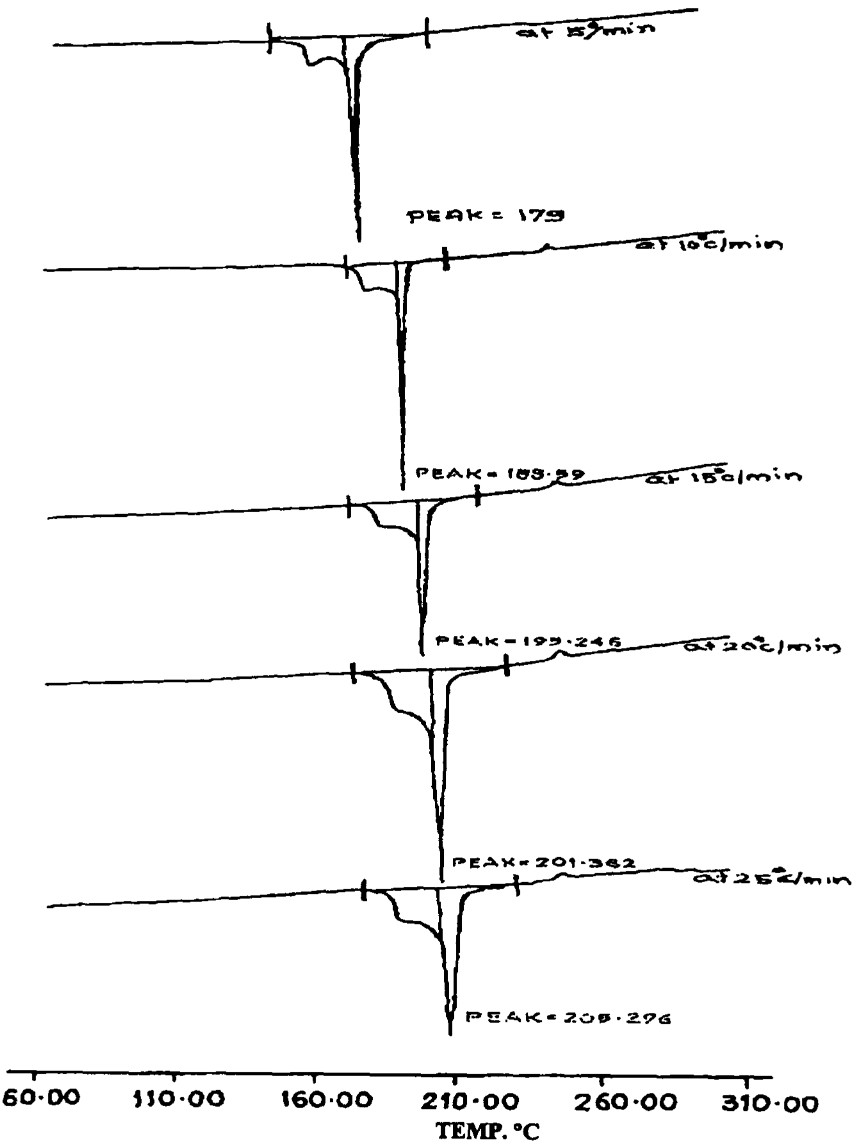


Fig. 5 DSC Curves for DEP plasticized AP-CMDB (comp.1)

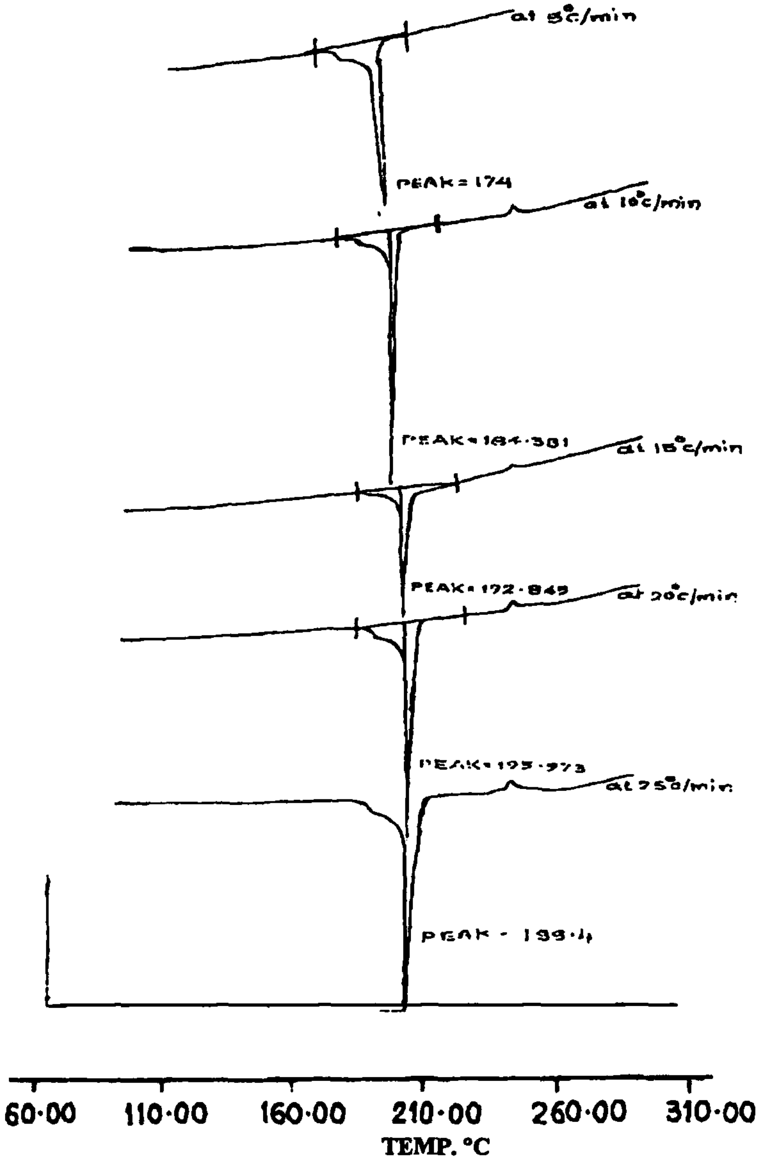


Fig. 6 DSC Curves for BDNPF/A plasticized AP-CMDB (comp.2)

KISSINGER KINETIC GRAPHS.

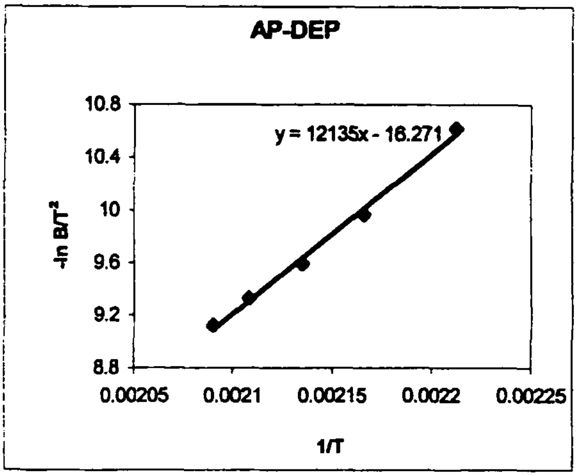


Fig 7: Kissinger kinetic plot for composion no.1

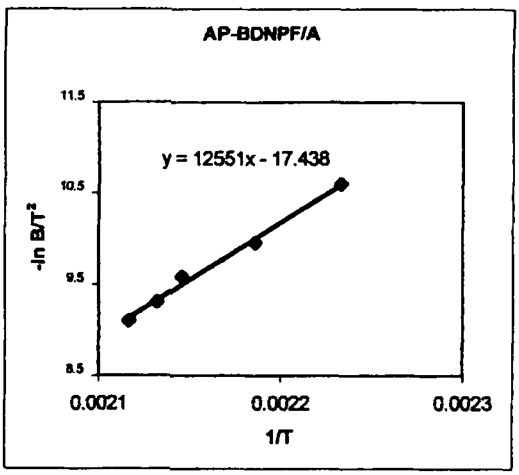


Fig 8 : Kissinger kinetic plot for composion no.2

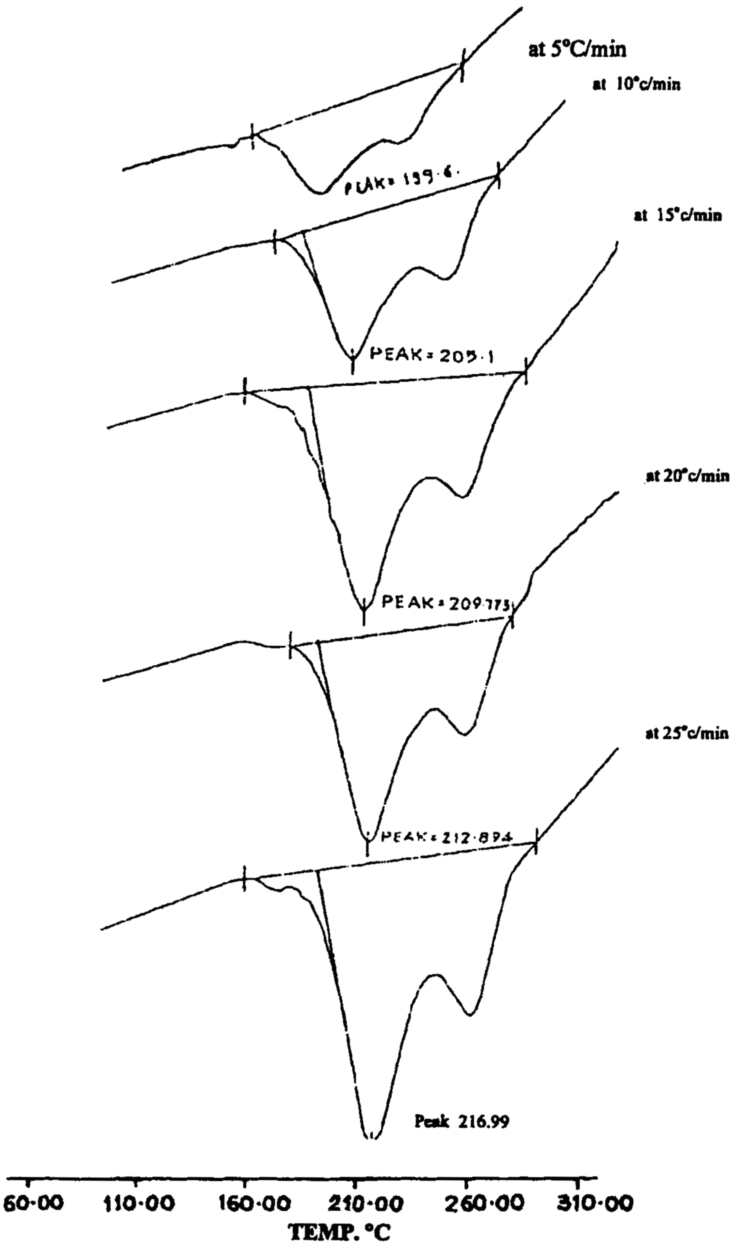


Fig.9 DSC Curves for DEP plasticized RDX-CMDB (comp.6)

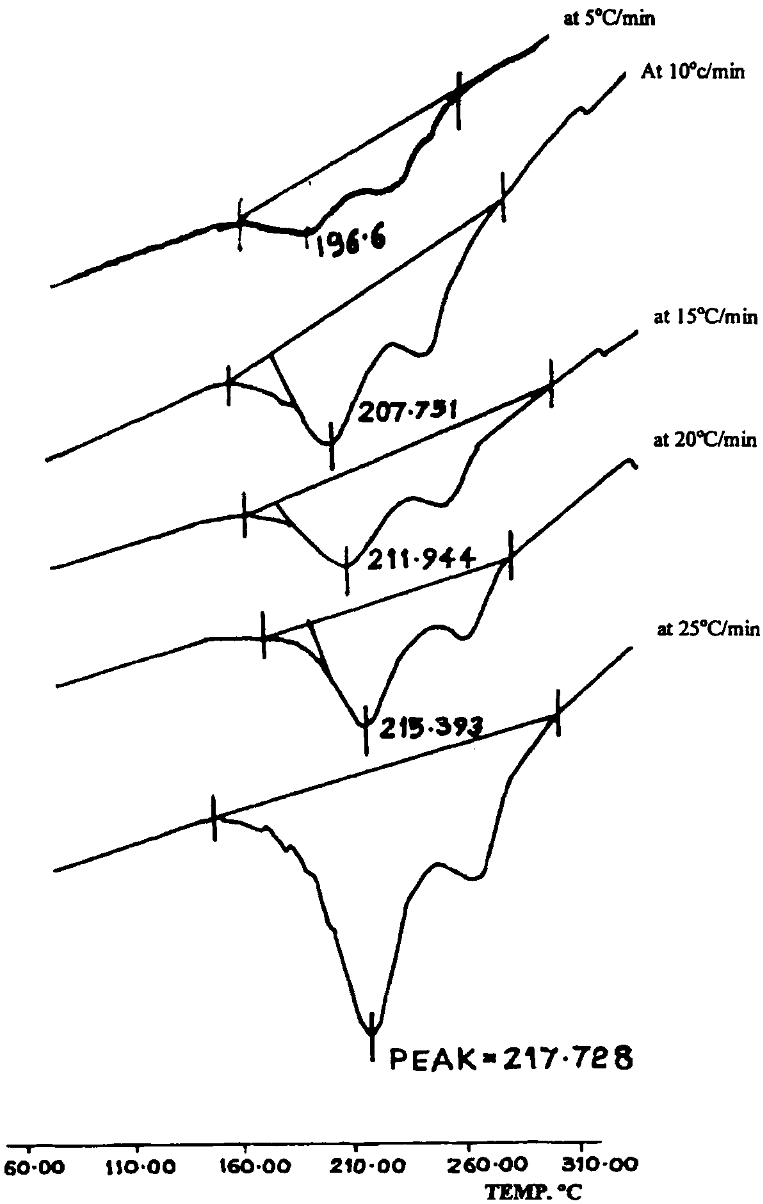


Fig. 10 DSC Curves for BDNPF/A plasticized RDX-CMDB (comp.7)

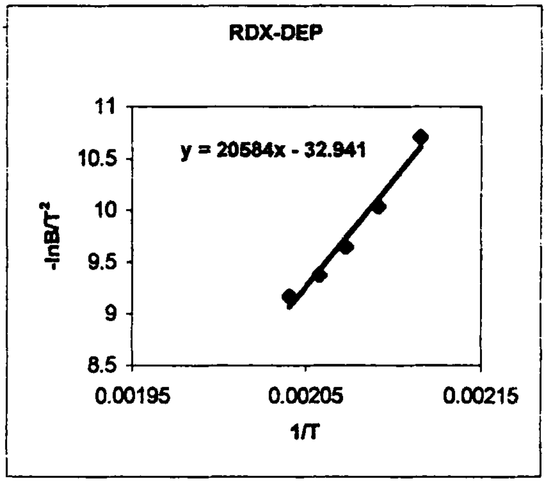


Fig 11: Kissinger kinetic plot for compositon no.6

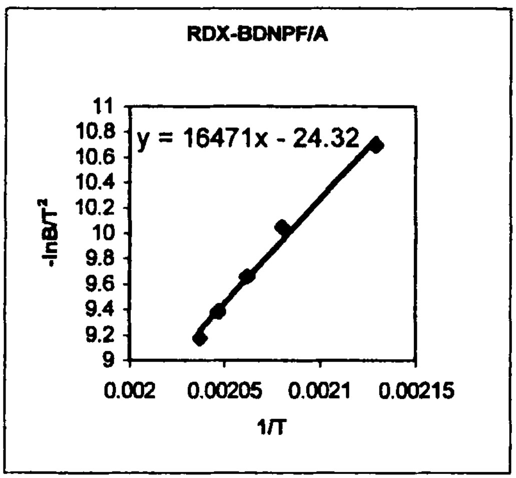


Fig 12: Kissinger kinetic plot for composion no. 7