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Burn Rate Studies on AN-Based Propellants: Effect of *N-N* Bonded Binders

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ABSTRACT

New epoxy resins having *N-N* bonds in their structures have been employed as binders for ammonium nitrate (AN)-based propellants. The resins have been characterized by various analytical techniques. The effect of the new binders on the burn rates of AN-based compositions including the metallized systems has been examined. The overall enhancement in the burn rate, as compared to that observed with conventional binders, has been explained in terms of the combustion reactivity of the *N-N* bond with the oxidizing species produced during combustion. Further increase in burn rate can be achieved by inclusion of magnesium metal or ammonium perchlorate into these compositions.

1. INTRODUCTION

The increased concern for environmental hazards, of late, has led to a renewed interest in clean burning propellants. A major flaw of the commonly used solid propellants based on ammonium perchlorate (AP) is that they produce hazardous combustion products such as, HCl, chlorine and its oxides. To overcome this, attempts have been made in recent years to develop chlorine free, minimum smoke, clean burning propellants[1,2]. Various viable methods tried out in this direction include, usage of HMX and RDX instead of AP, inclusion of Mg in AP propellants, use of AP/AN mixtures with metallic alloys like Mg-Al which can scavenge HCl, use of new polymers like GAP with AN, application of new oxidizers like ammonium dinitramide, etc. Many of the reported attempts are based on ammonium nitrate (AN)-based compositions. The innocuous nature of the combustion products of AN, its low cost and easy availability, makes it an attractive oxidizer. However, although AN based systems have several positive features, they are not free from drawbacks. Major problems involved in the use of AN, till a few years back, were its room temperature phase transformation involving a volume expansion, hygroscopicity and low burn rate. Of these, the first two problems have been overcome in recent times. Inclusion of potassium nitrate in AN has now been established as a phase stabilization technique. The hygroscopicity problem can be managed by coating the particles with hydrocarbon/polymers. However, the major technical problem in the use of AN as a substitute to AP in solid propellants is the low burn rate (BR). Attempts made to increase the burn rate include the use of catalysts such as ammonium dichromate, copper chromate, chromium and iron oxides[3,4]. Some enhancement in the propellant burn rate is observed in AN/PPG propellants when magnesium is included in the composition. The chemical nature of the binder is yet another important consideration in enhancing the burn rate. It is reported that highly oxygenated binders produce higher burn rate[5].

Energetic compounds having *N-N* bonds have long been used in propellant formulations. The extreme reactivity of hydrazine and its derivatives with liquid oxidizers has been made use of in hypergolic biliquid propellants. Solid derivatives of hydrazine and polymeric resins based on these hydrazones have been reported to have extreme reactivity to oxidizers like

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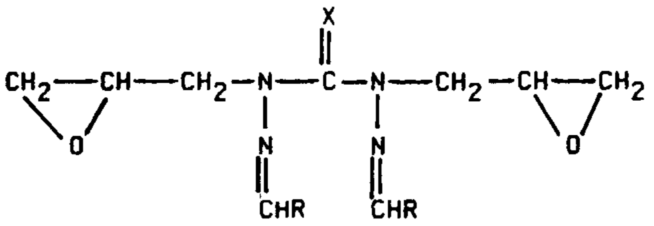
nitric acid[6]. A series of resinous prepolymers with *N-N* bond in their backbone, based on carbono- and thiocarbono hydrazones, have been synthesized for use in hybrid propellants[7], and are also reported to significantly enhance the burn rate when used in AP-based powder compositions[8]. It was envisaged that a similar modification in the burn rate could result when AN is used in place of AP. In view of these considerations, a few of the *N-N* bonded resins, based on carbono- and thiocarbono-hydrazones with epoxide as end groups, have been synthesized by an improved method. The effect of these resins, when used as binders in AN propellants, on the burn rate, is examined in this investigation.

2. EXPERIMENTAL DETAILS

2.1 Structure & Preparation of Resins

The following four diglycidyl amine-epoxy resins based on bis-carbono- and thiocarbono-hydrazones, were prepared, by adopting a procedure similar to that described earlier[9]. The general structure of the resins could be described as follows.



where,

1) $X = O$, $R = -C_6H_5$; Diepoxide of bisbenzaldehyde carbonohydrazone (BCHR)

2) $R = -C_5H_4O$; Diepoxide of bisfurfuraldehyde carbonohydrazone (FCHR)

3) $X = S$, $R = -C_6H_5$; Diepoxide of bisbenzaldelhyde thiocarbonohydrazone (BTCHR)

4) $R = -C_5H_4O$; Diepoxide of bisfurfuraldehyde thiocarbonohydrazone (FTCHR)

The present synthetic route optimizes some of the reaction parameters and ensures better epoxidation which has an eventual bearing on the viscosity of the final product. The epoxidation of the hydrazones, was carried out by refluxing the hydrazones with excess epichlorohydrin at 120 °C. The duration of refluxing to ensure the completion of reaction, varied with the substituents in the hydrazone. The reaction mixture was subsequently treated with a calculated amount of 40 per cent sodium hydroxide solution for a period of three hr at room temperature. After the removal of the precipitated salt, the resin was washed several times with water. The excess epichlorhydrin was then removed under reduced pressure at 90 °C.

2.2 Characterisation of the Resins

The resins were characterized by their epoxy content, IR, ^1H NMR and ^{13}C NMR spectra. Thermal characterization of these resins and the propellants were carried out using a simultaneous DTA-TG unit (Schimadzu DT-40) in flowing nitrogen employing a heating rate of 10 °C/min. Viscosity measurements at different temperatures were made on an AIMIL rheometer.

2.3 Propellant Processing

Propellant samples based on the four resins as binders, with 80 per cent solid loading were processed

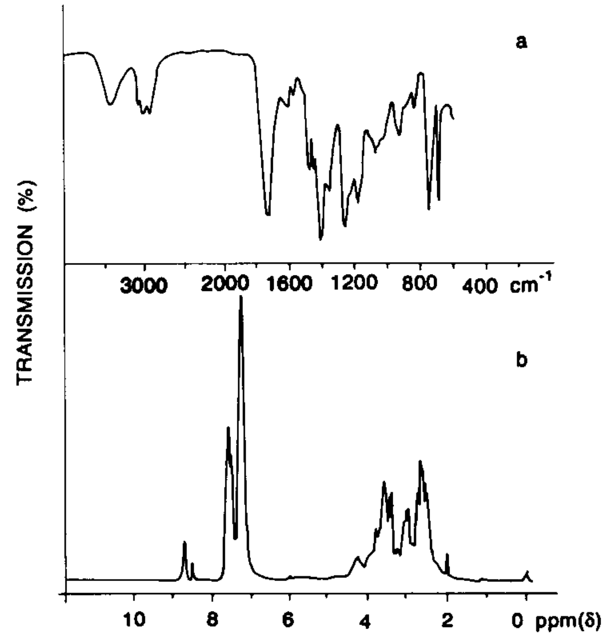


Figure 1. (a) IR and (b) ^1H NMR spectra of BTCHR resin.

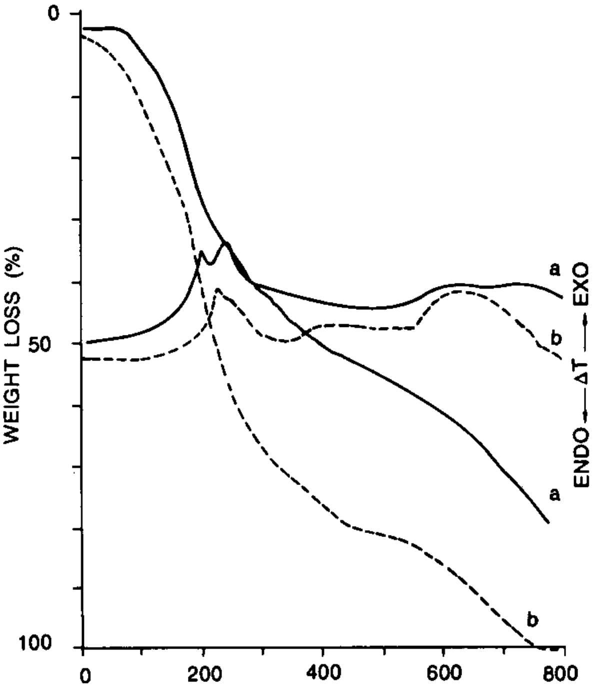


Figure 2. Simultaneous DTA-TG of (a) FCHR and (b) BCHR resins.

under identical conditions. Ammonium dichromate, because of its property of inducing an exothermic decomposition in AN, was used as a catalyst (2 per cent by weight of the oxidizer) in all the compositions. Diaminodiphenylmethane (DDM) dissolved in a plasticizer dimethyl sebacate (DMS) was used to cure the epoxy binder. Particle sizes of AN, AP, magnesium powder and ammonium dichromate, were maintained same in all the formulations. The propellant mix was cast into moulds, and cured at 80 °C for different durations depending upon the binder employed. Burning rate measurements were made in nitrogen atmosphere using a strand burner. A fuse wire technique employing thin tin/lead alloy wire was used to determine the burn rate. Strands for the control propellant, with CTPB binder were also made under identical conditions.

3. RESULTS & DISCUSSION

The spectral data of the resins clearly show the N-epoxidation of the NH protons of bis-carbonyl and thiocarbonyl hydrazones. The IR and ^1H NMR spectra of a typical resin shown in Fig. 1, give all the expected signals. The spectra have better resolution than those reported earlier[9]. Besides, ^{13}C spectra of the resins, recorded for the first time complement the structural assignments carried out using other analytical techniques.

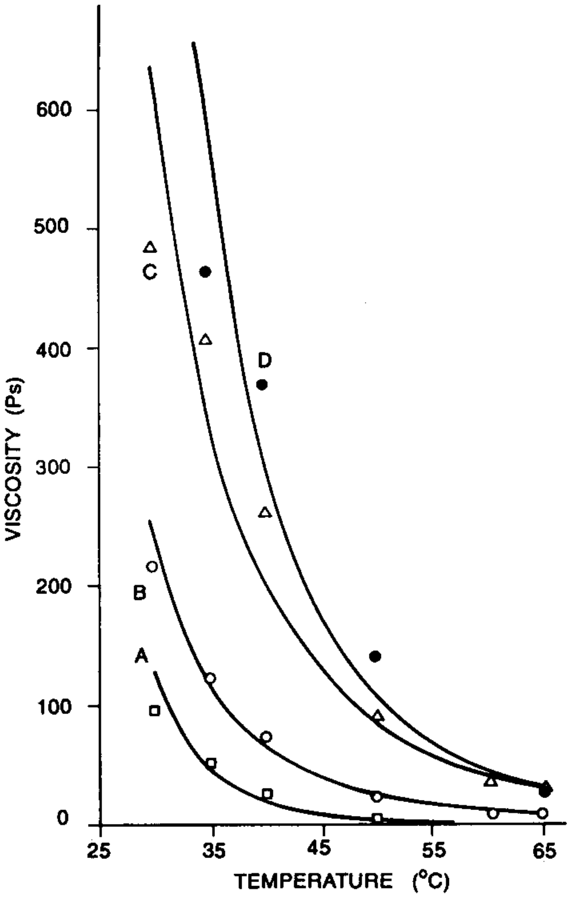


Figure 3. Effect of temperature on the viscosity of resin (A) BTCHR (B) BCHR (C) FCHR (D) FTCHR.

Table 1. Thermogravimetric data for *N-N* bonded resins

Temperature (°C)	Weight loss (%)			
	FCHR	FTCHR	BTCHR	BCHR
100	0	0	2	7
200	19	10	13	33
300	39	35	50	65
400	48	46	69	75
500	54	53	73	81
600	60	60	77	85
700	68	72	90	94
800	80	86	98	100

In the simultaneous DTA-TG analysis, the DTA show almost similar exothermic decomposition pattern for all the resins (Fig. 2). One prominent exotherm around 250 °C and another broad exotherm around 600 °C are a common feature for all the resins. The thermogravimetric data given in Table 1, show that the

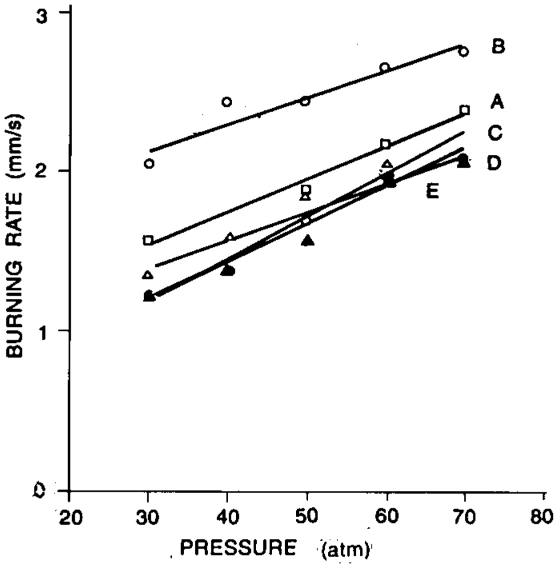


Figure 4. Variation of burning rate with pressure of systems (A) FTCHR-AN (B) FCHR-AN (C) CTPB-AN (D) BTCHR-AN (E) BCHR-AN.

change of carbono-to thio-group does not affect the weight loss behaviour significantly. The TG curves (Fig. 2), in general, show continuous weight loss starting around 120 °C. The TG curves show a sharp drop in the weight around the first exotherm (DTA), and a slow continuous weight loss thereafter. The small weight loss observed at low temperatures could be due to the presence of low boiling solvents or by-products of epoxidation.

The variation of viscosity with temperature of the resins shown in Fig. 3, shows a steep fall in viscosity with increase in temperature. The viscosity of these resins ranges from 50 to 470 poise at 35 °C. It can be seen that the resins based on benzaldehyde have lower viscosity than those based on furfuraldehyde. Both the carbono-and thiocarbono-resins with the same substituent have similar viscosities.

A notable feature of the combustion behaviour of propellants based on different binders and AN, is that they burn with virtually no residue. The burning rate (BR) data of various propellant formulations based on four different epoxy binders and conventional hydrocarbon binder processed, for combustion studies have been divided into three groups. (a) Samples based on AN (80 per cent) , (b) Samples with 80 per cent solid loading inclusive of 5 per cent magnesium metal powder, and (c) Samples having mixed oxidizer, AN and AP in wt ratio 3:1 are given in Table 2.

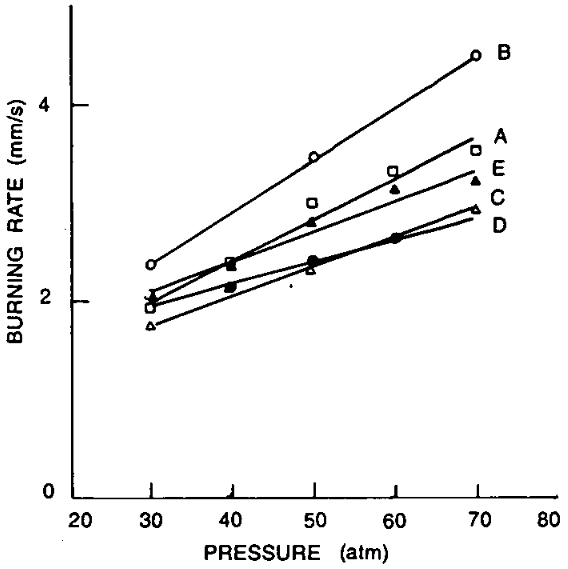


Figure 5· Variation of burning rate with pressure of systems (A) FTCHR-AN-*Mg* (B) FCHR-AN-*Mg* (C) CTPB-AN-*Mg* (D) BTCHR-AN-*Mg*

Table 2. Combustion characteristics of AN-based propellant formulations.

Propellant Composition Wt ratio	BR at 70 atm. mm/s	Pressure index *n*
FTCHR-AN (20/80)	2.4	0.4889
FCHR-AN (20/80)	2.78	0.3334
BTCHR-AN (20/80)	2.1	0.6836
BCHR-AN (20/80)	2.2	0.5739
CTPB-AN (20/80)	2.11	0.6788
FTCHR-AN-MG (20/75/5)	3.5	0.7482
FCHR-AN-MG (20/75/5)	4.46	0.7494
BTCHR-AN-MG (20/75/5)	2.9	0.4086
BCHR-AN-MG (20/75/5)	3.19	0.5675
CTPB-AN-MG (20/75/5)	2.9	0.6225
FTCHR-AN-AP (20/60/20)	4.8	0.7776
FCHR-AN-AP (20/60/20)	5.26	0.5417
BTCHR-AN-AP (20/60/20)	3.54	0.7634
BCHR-AN-AP (20/60/20)	3.9	0.5503
CTPB-AN-AP (20/60/20)	2.4	0.3896

It is seen that the samples having carbonohydrazone based resins give higher BR than those based on thiocarbonohydrazones (Fig. 4) . Interestingly this trend is observed in all the other compositions as shown in

Figs. 5 and 6. Another common feature observed is the higher BR of furfuraldehyde based resin as compared to those based on benzaldehyde, which have a BR not very different from those based on CTPB systems.

Addition of *Mg* increases the BR of AN-based systems significantly (Fig. 5). The effect is more pronounced in *N-N* bonded resin systems than conventional binders. Introduction of 5 per cent magnesium metal powder results in an enhancement of almost 50 per cent in the BR values in all the resins. It may be recalled that the addition of magnesium to AN changes its thermal characteristics significantly[10]. The effect is so drastic that AN which usually decomposes around 270 °C undergoes almost explosive decomposition at 130 °C itself. Combustion studies carried out on ternary AN-*Mg*-hydrazone mixtures show significant alteration in the combustion properties of hydrazones in the presence of *Mg* and AN.

Propellant compositions based on *N-N* bonded resins having 80 per cent AP loading are reported to have 3 to 4 fold higher BR than those based on conventional hydrocarbon binders[8]. It was, therfore, felt that systems with mixed oxidizers (AN and AP) would burn relatively faster. Similar attempts to increase the BR of AN propellants have been reported[11,12] where the concentration and particle size of AP were used to regulate the BR. Results of the BR studies carried out at various pressures on different propellant formulations with mixed oxidizers, shown in Fig. 6, indicate considerable increase in the BR for the systems based on *N-N* bonded resins as binders. Furfuraldehyde based systems show a BR, almost double to that of the CTPB based similar system. Here again, carbonohydrazone systems are found to have higher BR than corresponding thiocarbonohydrazone systems. The comparatively lower BR of benzaldehyde carbonohydrazone based resin systems is in conformity with the results of similar studies carried out on AP based systems where benzaldehyde carbonohydrazone based systems were found to have a lower burn rate than that of composition with furfuraldehyde carbonohydrazone based resin systems. It has been shown earlier that while the effect of these binders on the BR of AP based systems is remarkable, no such effect is seen on potassium perchlorate (KP)-based systems[8]. The enhancement in the BR could be attributed to the reactivity of *N-N* bonded resins to the acidic species generated from the combustion of AN and AP. As cited earlier, *N-N* bonded compounds react with extreme rapidity with acids resulting in ignition[6].

Attempts to explain the difference in BR of benzaldehyde and furfuraldehyde carbonohydrazone resin-based systems through DTA studies lead to some interesting observations. The BCHR-AN composition although starts to decompose immediately after the melting of AN at 169 °C, a sharp exotherm indicating ignition is observed only around 250 °C (Fig. 7). The FCHR-AN composition, on the other hand, ignites around 180 °C itself. Similar observations have been made on mixed oxidizer systems . While the FCHR-AN-AP system, which has got the highest burn rate (Table 2), ignites around 190 °C, CTPB-AN-AP system undergoes exothermic decompostition only above 230 °C. The BCHR-AN-AP systems, which have intermediate BRs, interestingly decompose in two steps, showing two exotherms , one at 170 °C and other at 230 °C. Thermal studies of metallized propellants also gave similar results (Fig. 8). While CTPB based system ignites only above 200 °C, the exothermic decomposition of FCHR and BCHR based metallized systems, is initiated at 169 °C itself. The thermally sensitized systems, thus, have higher burn rates.

From BR plots, the pressure exponents *n* were calculated for all the propellants (Table 2). In general, it can be concluded that all non-metallized propellants with thiocarbonohydrazone-based resins have higher *n* value than those based on carbonohydrazone group, having the same substituents. In metallized systems, however, the substituent effect dominates. Furfuraldehyde thiocarbono- and carbonohydrazone

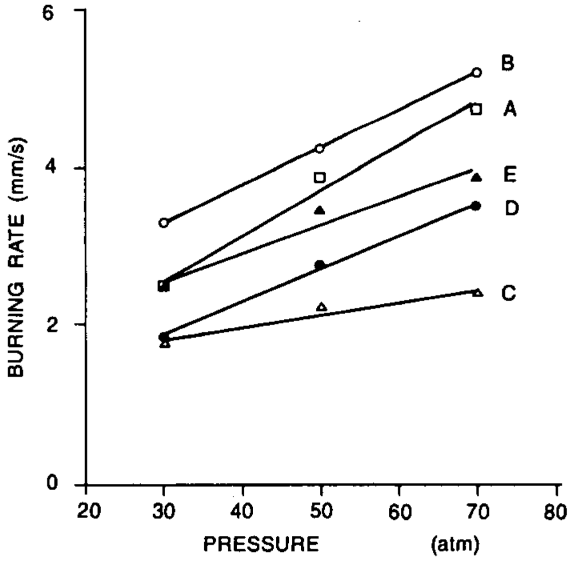


Figure 6. Variation of burning rate with pressure of systems (A) FTCHR-AN-AP (B) FCHR-AN-AP (C) CTPB-AN-AP (D) BTCHR-AN-AP

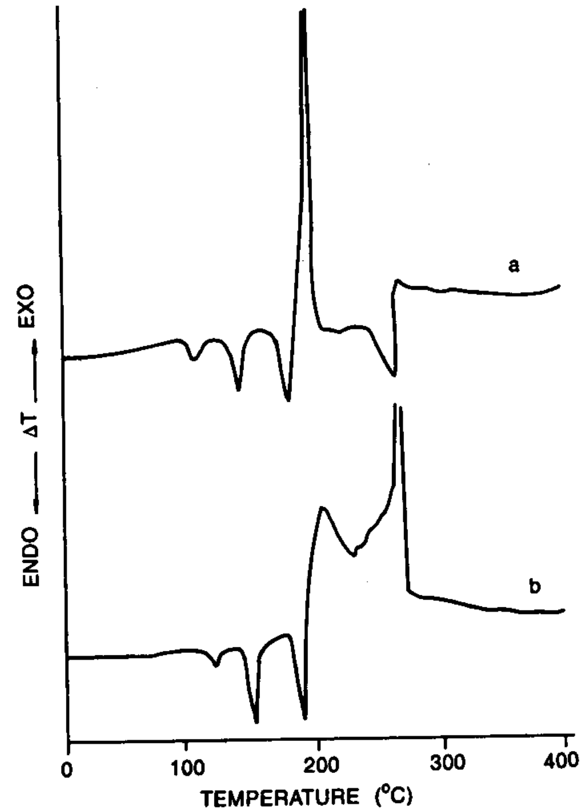


Figure 7. DTA of propellant samples (a) FCHR-AN (b) BCHR-AN.

resin-based metallized systems, have close *n* values, which are higher than the corresponding benzaldehyde carbono- or thiocarbonohydrazone based resin systems. It can also be seen that the *n* values of AN-AP based systems are higher compared to those based on AN systems, having the same binders.

4. CONCLUSION

The use of *N-N* bonded resins based on carbono- and thiocarbonohydrazones as binders in AN-based propellants results in enhancement of the burn rate. Further increase in the burn rate could be achieved by inclusion of magnesium metal or ammonium perchlorate into these systems.

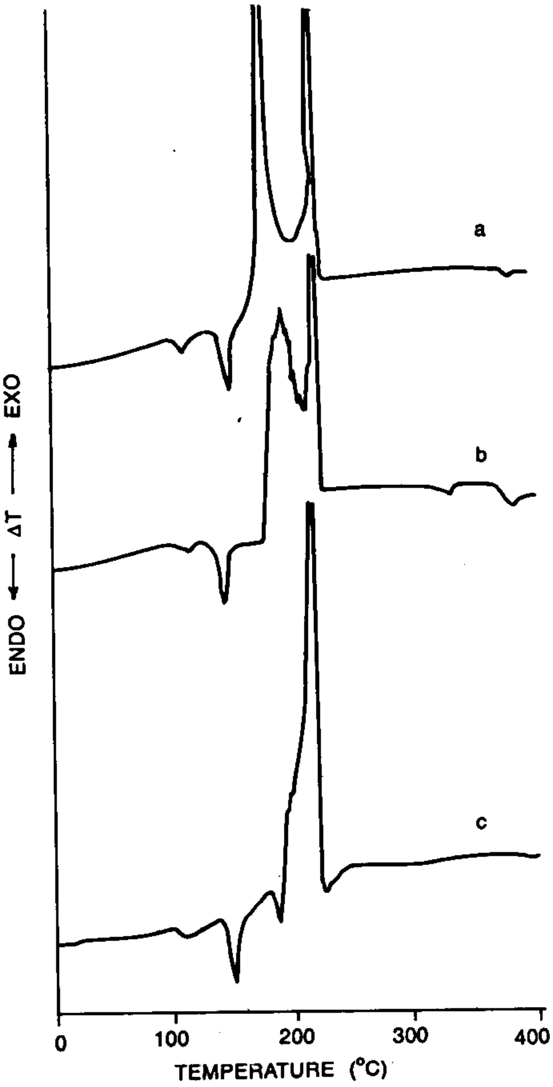


Figure 8. DTA of propellant samples (a) FCHR-AN-*Mg* (b) BCHR-AN-*Mg* (c) CTPB-AN-*Mg*.

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