

Studies on Combustion of Metallized RDX-Based Composite Modified Double-Base Propellants

C. N. Divekar,* S. N. Asthana,[†] and Haridwar Singh[‡]
High Energy Materials Research Laboratory, Pune 411 021, India

This paper reports the results obtained during research work carried out on metallized cyclo trimethylene trinitramine (RDX)-composite modified double-base (CMDB) propellants with the aim of realizing superior burning rates as well as performance. Nickel (Ni) and titanium (Ti)-based formulations exhibited burning-rate characteristics superior to those for aluminized (Al) compositions, whereas zirconium (Zr)-based formulations gave the best results. An attempt has been made to explain the burning-rate pattern observed on the basis of combustion characteristics of metals. Among selected ballistic modifiers, basic lead salicylate (BLS) + Cu₂O + carbon black (C-black) combination and copper chromite (Cu-chromite) gave catalytic effect superior to that of ferric oxide (Fe₂O₃) and ferric acetyl acetonate (FeAA). Incorporation of 5% ammonium perchlorate (AP) of 5 μ size augmented the catalytic effect of ballistic modifiers remarkably. Thus, RDX (12.5%)-Zr (17.5%) CMDB formulation with 5% AP (5 μ) and two-parts Cu-chromite gave burning rates of the order of 4–21 mm/s in the pressure range of 1–10.8 MPa and pressure index value of 0.66 with Isp (theoretical) of the order of 241 s. To take advantage of pyrophoric nature of Zr and superior heat of combustion of Al, a combination of both the metals was evaluated. Composition containing 13% Al and 4.5% Zr along with 12.5% RDX in a double-base matrix with 5% AP and two parts of Cu-chromite as additives gave stable combustion in the pressure range of 1–10.8 MPa (burning rates 4–18 mm/s) and Isp (theoretical) of 259 s. Kinetic parameters obtained for RDX-CMDB formulations during differential thermal analysis studies (Ea 48 kcal/mole and A 7.2×10^{19}) established that the RDX decomposition is the rate-controlling step. Addition of Al did not have a remarkable effect on the kinetic parameters of thermal decomposition. However, Ni/Ti/Zr brought down Ea and A values drastically, suggesting that heat feedback caused by efficient combustion near the deflagrating propellant surface influences subglobal kinetics and facilitates the decomposition of condensed phase. Thermogravimetric and differential scanning calorimetry (DSC) results bring out that Fe₂O₃ and BLS + Cu₂O + C-black do not play a catalytic role in condensed-phase decomposition, whereas Cu-chromite and FeAA appear to catalyze both gas- as well as condensed-phase reactions.

Introduction

NITRAMINE-BASED propellants occupy a position of eminence in view of their dual advantage of higher performance and clean burning characteristics.¹ Third-generation antitank missiles entering in the world market in the 21st century are reported to be powered by nitramine-based propellants instead of conventional double-base propellants, the work-horse propellants of first- and second-generation antitank missiles.² This changeover is attributed to higher energy requirements of future missiles. Moreover, nitramine-based propellants with marginally superior energetics than ammonium perchlorate (AP)-composite/composite modified double-base (CMDB) propellants have tremendous potential to replace later, posing pollution hazards. In case of AP-CMDB propellants, additional problems arise because of the catalytic effect of AP on decomposition of nitroglycerine (NG) resulting in acceleration of autocatalysis.³ Although ammonium dinitramide like hydrazinium nitro formate appears to be superior to cyclo trimethylene trinitramine (RDX)/cyclo tetramethylene tetranitramine (HMX) as propellant oxidizer,⁴ production technology of RDX/HMX has been well established resulting in their easy availability at relatively low cost.

Generally, nitramine-based CMDB propellants offer better energetics than nitramine composites with inert polybutadiene binder system caused by the energetic nature of nitrocellulose (NC)-NG binder. However, in the case of nitramine-based CMDB propellants, gas-phase reaction rate in fizz zone decreases with an increase in

nitramine content resulting in a decrease in heat feedback to the burning surface as compared to that in a double-base system. In addition, nitramines tend to melt on the surface prior to decomposition, thereby robbing the energy released in condensed phase.^{5,6} Brill⁷ opined that exothermic secondary reactions occur in gas-phase far away from the surface and, thereby do not contribute to the condensed-phase temperature profile. This phenomenon leads to an overall decrease in burning rates. Thus, nitramines act as a diluent on the propellant surface. Moreover, this class of propellants resists ballistic modification because most of the catalysts do not have much effect on the rate-controlling step of their combustion. Combustion problem becomes more severe on addition of metal fuel, generally aluminum (Al), (to realize superior performance) because of the presence of a protective metal oxide layer.^{8,9} Metals produce primary smoke unlike AP which produces secondary smoke with chlorine-containing compounds. Intensive research is ongoing all over the globe to overcome these problems of nitramine-based formulations. Ronald¹⁰ has recommended the incorporation of Al, zirconium (Zr), tantalum, magnesium (Mg), silver, copper (Cu), and titanium (Ti) staples in AP/RDX-based CMDB propellants to achieve improvement in burning-rate characteristics. During the present work, slurry-cast metallized nitramine-based CMDB propellants were investigated in detail with the aim of arriving at formulations with superior burning rates. Another aim of this study was to examine formulations for stable combustion at low pressure. Metals selected were Zr and Ti in view of their pyrophoric nature^{8,9,11} and nickel (Ni) because of its reported¹² catalytic effect on dark-zone reactions of double-base matrix. Aluminized formulations were studied for generating comparative data.

Experimental

Propellant Formulations and Processing Method

Basic formulation studied during this work was spheroidal NC (SNC) (NC:90, NG:7, Sym-diethyl diphenyl urea:3) 31.5%,

Presented as Paper 98-3389 at the AIAA/ASME/SAE/ASEE 34th Joint Propulsion Conference and Exhibit, Cleveland, OH, 12–15 July 1998; received 16 October 1998; revision received 1 July 1999; accepted for publication 24 January 2000. Copyright © 2000 by the American Institute of Aeronautics and Astronautics, Inc. All rights reserved.

*Senior Technical Assistant, HEMRL, Pune.

[†]Scientist 'E', HEMRL, Pune.

[‡]Director, HEMRL, Pune. Member AIAA.

desensitized NG (NG:80, diethyl phthalate:18, 2-nitro diphenyl amine: 2) 38.5%, RDX (25 μ) 30%. In metallized formulations, RDX was replaced by 2.5–17.5% metal fuels (98% pure) namely, Al (16 \pm 2 μ), Zr (7 \pm 2 μ), Ti (10 \pm 2 μ), and Ni (17 \pm 2 μ) in the increment of 2.5%. The compositions were prepared by adopting slurry-cast technique.¹³ The SNC was mixed with desensitized NG in a planetary mixer. Oxidizer (RDX) and metals were added step by step in separate installments to the double-base matrix in the mixer. In ballistically modified compositions ballistic modifiers (two-parts), namely copper chromite (Cu-chromite)/ferric acetyl acetate (FeAA)/ferric oxide (Fe₂O₃)/basic lead salicylate (BLS) + Cu₂O + carbon black (C-black) were added in the last step. Mixing was continued for 15 min without vacuum and 45 min under vacuum at 25°C. The slurry obtained was cast in an evacuated mold and curing was carried out at 50°C for 10 days.

Studies Conducted

Strand burning rates were determined in the pressure range of 1–10.8 MPa by employing the acoustic emission technique.¹⁴ The methodology involved combustion of strands (6 \times 6 \times 100 mm) in the nitrogen-pressurized steel bomb. Acoustic signals generated by the deflagrating sample were unidirectionally transmitted through the water medium and sensed by the piezo-electric transducer of resonance frequency of 200 kHz. For differential thermal analysis (DTA) studies, indigenously fabricated equipment with platinum (Pt)/Pt-rhodium (13%) thermocouple was used. Selected heating rates were 5, 10, 15, and 20°C/min. The experiments were carried out in air atmosphere. Thermogravimetric (TG) analysis was carried out on simultaneous TG analyzer (Perkin-Elmer, Norwalk, CT, USA) under nitrogen atmosphere at the heating rate of 10°C/min. Differential scanning calorimetry (DSC) was undertaken with Perkin-Elmer equipment under N₂ atmosphere at the heating rate of 10°C/min.

Results and Discussions

Nitramine-Based CMDB Compositions with Al/Ni/Ti/Zr Metals

During this study, composition containing 30% RDX in 70% double-base matrix was taken as control. It did not undergo stable combustion after initial ignition at chamber pressure below 6.8 MPa. The burning rates obtained in the pressure range of 6.8–10.8 MPa were 6.4–10.3 mm/s. On incorporation of 2.5–7.5% Al at the cost of RDX, a marginal increase in burning rates (1–12%) was observed consistently (Table 1, Fig. 1). Increase in Al content to 10–12.5% level resulted in a drop in burning rates to the level of that of the control propellant. Compositions containing 15–17.5% Al did not undergo stable burning even at 6.8 MPa chamber pressure, whereas burning rates in the pressure range of 8.8–10.8 MPa were comparable to those for compositions containing 10–12.5% Al. The pressure-index values for aluminized formulations (0.90 \pm 0.1) were close to that for control propellant (\sim 1). In case of Ni-based formulations, incorporation of 2.5–7.5% Ni did not have any appreciable effect on burning rates with respect to control. An interesting feature was that an increase in nickel from 10 to 17.5% level resulted in a consistent decrease in burning rates in the pressure range of 8.8–10.8 MPa (10–20%), whereas burning rates at 6.8 MPa pressure remained unaffected and unlike corresponding aluminized formu-

Table 1 Burning rates of aluminized RDX-CMDB propellants

Metal content	Burn rates at MPa, mm/s			Pressure index, η
	6.8	8.8	10.8	
Control	6.4	8.7	10.3	1.02
2.5% Al	6.8	8.8	10.2	0.88
5% Al	6.9	9.1	10.7	0.95
7.5% Al	7.1	9	10.8	0.91
10% Al	6.9	8.4	10.6	0.92
12.5% Al	6.8	8.2	10.4	0.91
15% Al	—	8.1	10.2	1.06
17.5% Al	—	8	10.1	1.14

Basic composition (%): SNC 31.5, desensitized NG 38.5, RDX 30–12.5, Al 0–17.5.

Table 2 Burning rates of RDX-CMDB propellants with Ni

Metal content	Burn rates at MPa, mm/s			Pressure index, η
	6.8	8.8	10.8	
Control	6.4	8.7	10.3	1.02
2.5% Ni	6.3	8.9	10.5	1.11
5% Ni	6.3	8.9	10.4	1.09
7.5% Ni	6.5	8.9	10.1	0.96
10% Ni	6.6	7.9	8.9	0.65
12.5% Ni	6.6	7.1	8.2	0.46
15% Ni	6.4	7.2	8.1	0.51
17.5% Ni	6.4	7.0	8.0	0.47

Basic composition (%): SNC 31.5, desensitized NG 38.5, RDX 30–12.5, Ni 0–17.5.

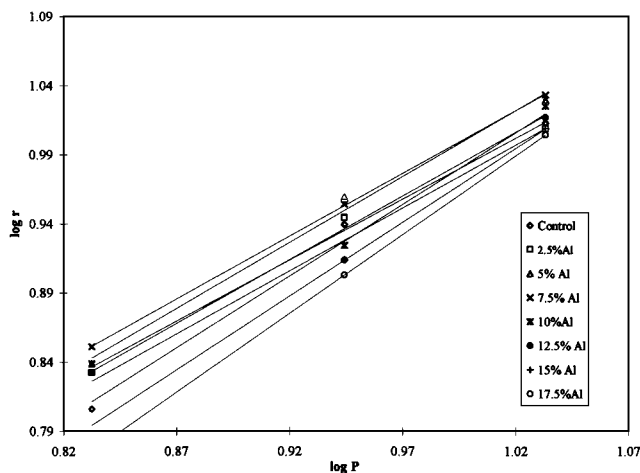


Fig. 1 Pressure-burn-rate (log-log) relationship for RDX-Al CMDB propellant systems.

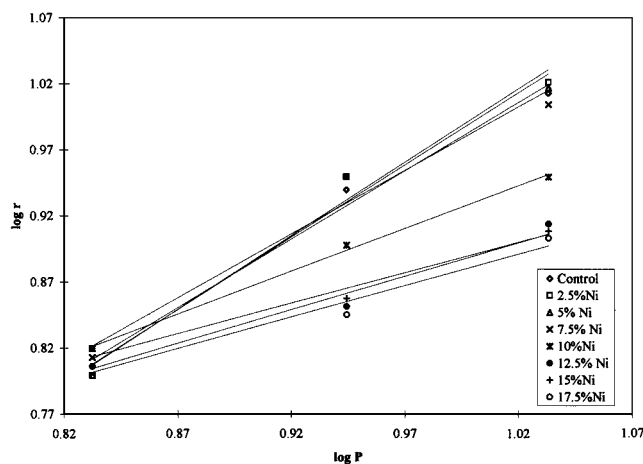


Fig. 2 Pressure-burn-rate (log-log) relationship for RDX-Ni CMDB propellant systems.

lations; propellant compositions containing even 15–17.5% Ni gave stable combustion at this pressure level (Table 2, Fig. 2). Regarding Ti, incorporation of 2.5% metal at the cost of RDX did not have any appreciable effect on burning rates. Increase in metal content to the level of 5–10% resulted in about 14–20% burning-rate enhancement at 6.8 MPa, whereas in the pressure range of 8.8–10.8 MPa increase was of the order of 2–7%. Increase in Ti content beyond 10% led to a marginal drop in burning rates at 6.8 MPa and a remarkable decrease in burning rates (to the level of control) in the pressure range of 8.8–10.8 MPa. Consequently, pressure-index value for these compositions was of the order of 0.7–0.8 (Table 3, Fig. 3). Unlike Al/Ni/Ti-based formulations, Zr-based RDX-CMDB compositions exhibited stable combustion even at a lower pressure level of 4.9 MPa. Moreover, there was a consistent increase in burning rates on an increase in Zr content from 2.5–17.5% level. The effect was more pronounced beyond 12.5% Zr content (burning-rate enhancement 1–15% upto 10% Zr and 15–35% beyond 10% Zr content). Thus, a composition

Table 3 Burning rates of RDX-CMDB propellants with Ti

Metal content	Burn rates at MPa, mm/s			Pressure index, η
	6.8	8.8	10.8	
Control	6.4	8.7	10.3	1.02
2.5% Ti	6.3	8.7	10.3	1.07
5% Ti	7.3	9.1	10.5	0.79
7.5% Ti	7.3	9.3	10.9	0.87
10% Ti	7.7	9.3	10.9	0.75
12.5% Ti	7.6	9.5	10.7	0.74
15% Ti	7.4	8.9	10.3	0.71
17.5% Ti	7.3	8.4	10	0.67

Basic composition (%): SNC 31.5, desensitized NG 38.5, RDX 30-12.5, Ti 0-17.5.

Table 4 Burning rates of RDX-CMDB propellants with Zr

Metal content	Burn rates at MPa, mm/s				Pressure index, η
	4.9	6.8	8.8	10.8	
Control	—	6.4	8.7	10.3	1.02
2.5% Zr	5.3	6.3	8.6	9.8	0.81
5% Zr	5.7	6.7	8.9	11.5	0.89
7.5% Zr	6.1	6.9	9.0	11.4	0.79
10% Zr	5.6	7.4	8.9	11.5	0.88
12.5% Zr	6.4	8.4	9.7	12.2	0.78
15% Zr	6.5	8.4	10.2	12.8	0.84
17.5% Zr	6.7	8.9	10.3	13.6	0.85

Basic composition (%): SNC 31.5, desensitized NG 38.5, RDX 30-12.5, Zr 0-17.5.

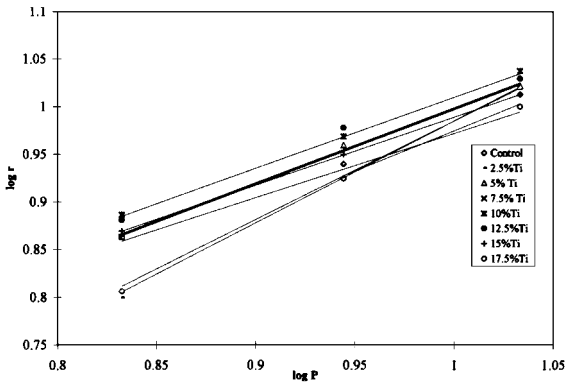


Fig. 3 Pressure-burn-rate (log-log) relationship for RDX-Ti CMDB propellant systems.

containing 12.5% RDX along with 17.5% Zr in a double-base matrix gave the best result as compared to other compositions studied during this work as revealed by burning rates of the order of 7–14 mm/s in the pressure range of 4.9–10.8 MPa (Table 4, Fig. 4). In view of its superior combustion characteristics, the formulation was chosen for further studies carried out to evaluate the effect of selected ballistic modifiers.

Ballistic Modification of RDX-Zr Formulation

Addition of Fe₂O₃ to selected RDX-Zr formulation resulted in a 1–7% increase in burning rates in the pressure range of 4.9–8.8 MPa while the burning rate at 10.8 MPa remained unaffected. Incorporation of FeAA led to a 7–14% increase in burning rates not only in the pressure range of 4.9–8.8 MPa but also at 10.8 MPa. Copper-chromite was more effective in the lower pressure range of 4.9–8.8 MPa (burning-rate enhancement 10–30%), whereas its catalytic effect was comparable to that of FeAA at 10.8 MPa. Thus, pressure-index value obtained for copper-chromite-based composition was 0.68 as compared to the value of 0.78 for FeAA-based composition. BLS + Cu₂O + C-black ballistic modifier system exhibited typical burning-rate behavior as revealed by extension of combustion to lower pressure region (up to 2.9 MPa). Its incorporation resulted in increase in burning rates by 7–13% in the pressure region of 4.9–

Table 5 Effect of ballistic modifiers on burning rates of RDX/Zr CMDB propellants

Ballistic modifiers two parts	Burn rates at MPa, mm/s					Pressure index, η
	2.9	4.9	6.8	8.8	10.8	
Basic composition	—	6.7	8.9	10.3	13.6	0.85
Fe ₂ O ₃	—	7.2	9.0	11.7	13.3	0.80
BLS + Cu ₂ O + C/black	5.7	7.6	9.5	11.0	12.1	0.58
FeAA	—	7.9	9.5	11.4	15.0	0.78
Cu-chromite	—	8.7	9.8	12.1	14.9	0.68

Basic composition (%): SNC 31.5, desensitized NG 38.5, RDX 12.5, Zr 17.5.

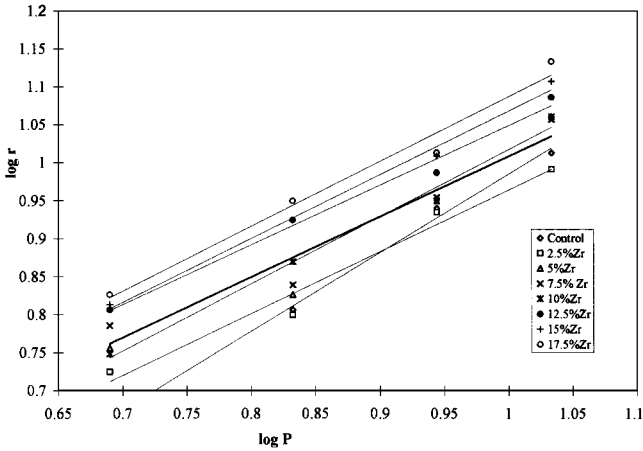


Fig. 4 Pressure-burn-rate (log-log) relationship for RDX-Zr CMDB propellant systems.

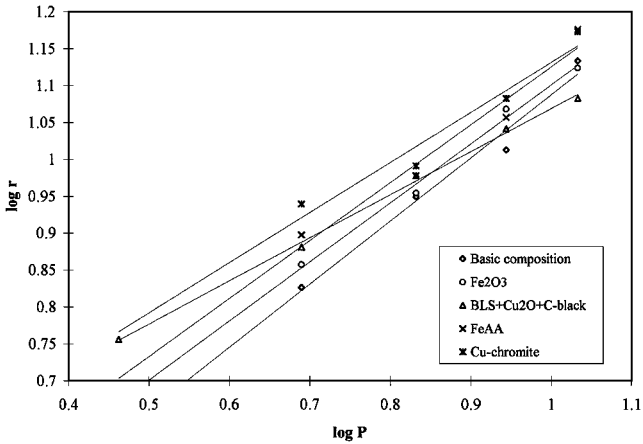


Fig. 5 Pressure-burn-rate (log-log) relationship for ballistically modified RDX-Zr CMDB propellant.

8.8 MPa and decrease in burning rate by 11% at 10.8 MPa leading to a reduction in pressure-index value to the level of 0.58 (Table 5, Fig. 5). In view of these results, Cu-chromite and BLS + Cu₂O + C-black based compositions were selected for the next set of experiments in which 5% AP of 5 μ size was incorporated at the cost of double-base matrix to achieve further improvement in ballistics.

AP as Additive in RDX-Zr Based Formulations

Inclusion of AP as an additive led to a remarkable improvement in burning-rate pattern as brought out by extension of region of stable combustion to the still lower pressure level (1 MPa). Moreover, 5% AP-based formulation (Table 6, Fig. 6) with BLS + Cu₂O + C-black and copper-chromite gave 50–75% higher burning rates than those for the control, respectively. Thus, composition containing 12.5% RDX, 17.5% Zr, 5% AP, and 65% double-base matrix with two parts copper-chromite gave burning rates of 4–21 mm/s in the pressure range of 1–10.8 MPa.

Table 6 Combined effect of AP (5 μ) and ballistic modifiers on burning rates of RDX /Zr CMDB propellants

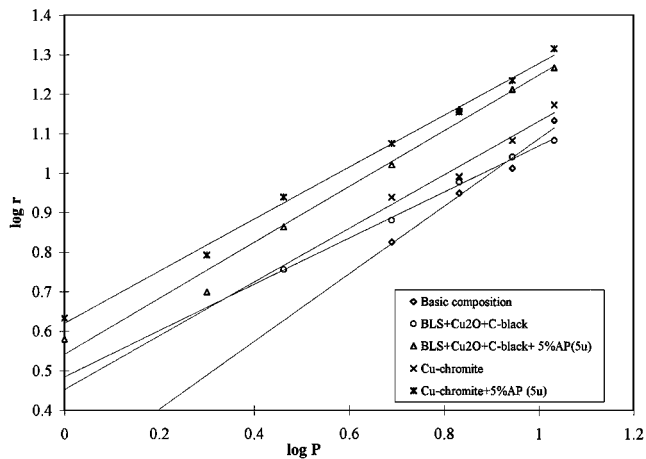
Ballistic modifiers, two parts	Burn rates at MPa, mm/s							Pressure index, η
	1	2	2.9	4.9	6.8	8.8	10.8	
Basic composition	—	—	—	6.7	8.9	10.3	13.6	0.85
BLS + Cu ₂ O + C/black	—	—	5.7	7.6	9.5	11.0	12.1	0.58
BLS + Cu ₂ O + C/black + AP [5 μ] 5%	3.8	5.0	7.3	10.5	14.5	16.3	18.5	0.70
Cu-chromite	—	—	—	8.7	9.8	12.1	14.9	0.68
Cu-chromite + AP [5 μ] 5%	4.3	6.2	8.7	11.9	14.3	17.2	20.7	0.66

Basic composition (%): SNC 31.5, desensitized NG 38.5, RDX 12.5, Zr 17.5 (5% AP in place of 2.5% each of SNC and desensitized NG).

Table 7 Theoretical Isp and flame temperature (T_f) at 6.8 MPa of RDX-CMDB propellants with various metal fuels

Metals	% of metals at the cost of RDX							
	0	2.5	5	7.5	10	12.5	15	17.5
Al								
Isp, s	223	229	235	240	245	249	252	253
T_f , K	2275	2413	2550	2686	2819	2947	3002	3436
Ti								
Isp, s	223	224	225	226	227	228	229	236
T_f , K	2275	2334	2395	2457	2520	2584	2650	3073
Zr								
Isp, s	223	223	223	224	224	225	225	233
T_f , K	2275	2330	2387	2447	2509	2572	2638	3082

Basic composition (%): SNC 31.5, desensitized NG 38.5, RDX 30-12.5, Metals 0-17.5 (Increase in metal content >17.5% results in drop in Isp).

**Fig. 6** Pressure-burn-rate (log-log) relationship for ballistically modified RDX-Zr CMDB propellant with 5% AP (5 μ).

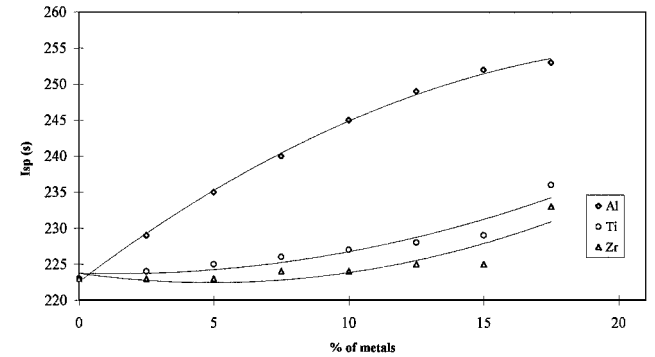
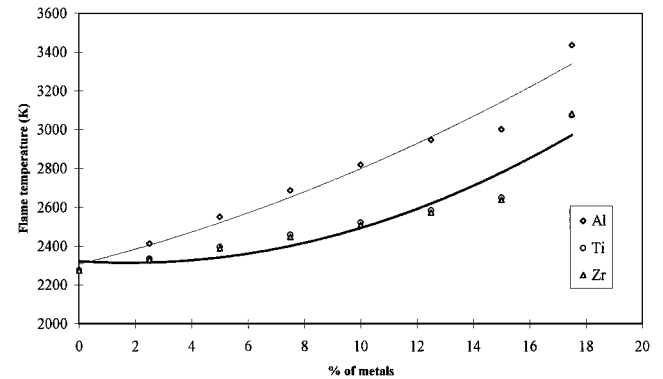
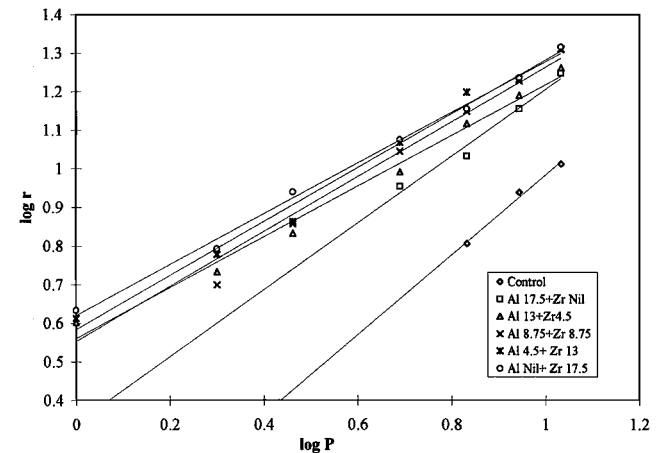
Al-Zr Combination

Regarding Isp (theoretical), 2.5–17.5% Zr-based RDX-CMDB compositions gave values of 224–233 s, whereas Al-based formulations gave Isp of 229–253 s (Table 7, Fig. 7a). Higher performance levels of aluminized formulations can be attributed to their higher flame temperature (Fig. 7b) resulting from the higher heat of formation of Al_2O_3 than that for TiO_2 and ZrO_2 (Ref. 9). Moreover, aluminized formulations are also expected to give relatively lower mean molecular weight of combustion products than Zr-based and Ti-based formulations caused by the significant difference in their atomic weight. Incorporation of AP (5 μ) resulted in increase in Isp by 8–10 s, which can be attributed to its potential as oxidizer. In view of these observations, a combination of Zr and Al was evaluated to realize superior burning rate as well as Isp (Table 8, Fig. 8). A composition containing 13% Al and 4.5% Zr with 12.5% RDX and 5% AP in 65% double-base matrix with two parts of Cu-chromite

Table 8 Burning rate results of Al:Zr containing RDX-CMDB propellants

Pressure, MPa	Control	Al 17.5 Zr Nil	Al 13 Zr 4.5	Al 8.75 Zr 8.75	Al 4.5 Zr 13	Al Nil Zr 17.5
1	—	—	4	4.1	4.1	4.3
2	—	—	5.4	5	6	6.2
2.9	—	—	6.8	7.2	7.3	8.7
4.9	—	9	9.8	11.1	11.7	11.9
6.8	6.4	10.8	13.1	14.1	15.8	14.3
8.8	8.7	14.3	15.5	16.9	17.1	17.2
10.8	10.3	17.7	18.3	20.4	20.5	20.7
Isp, s	223	263	259	251	246	241
@ 6.8 MPa, η	1.02	0.91	0.66	0.71	0.70	0.66

Basic composition (%): SNC 29, desensitized NG 36, RDX 12.5, Al : Zr 17.5, AP (5 μ) 5, Cu-chromite 2.

**Fig. 7a** Empirical relationship between Isp and percent of metals for metallized RDX-CMDB propellant system.**Fig. 7b** Empirical relationship between the flame temperature (K) and percent of metals for the metallized RDX-CMDB propellant system.**Fig. 8** Pressure-burn-rate (log-log) relationship for the ballistically modified RDX-Al/Zr CMDB propellant with 5% AP (5 μ).

as ballistic modifier was found to be superior in this regard (burning rate 4–18 mm/s in the pressure range of 1–10.8 MPa and Isp of 259 s). Propellant grains were cast in this promising composition and subjected to static tests in a ballistic evaluation motor at various temperatures. Burning rates obtained were in close agreement with the values obtained in the strand burner, and the temperature sensitivity of the burning rate was about 0.02%/°C in the temperature range of –40 to +55°C.

Mechanism

Brewster and Hardt¹⁵ carried out quench collection during burning-rate studies on Al-based composite propellants and reported that metal needed to be heated to higher temperature up to the ignition point, resulting in a heat-sink effect. However, a compensating heat feedback is produced from metal combustion. Ishihara et al.¹⁶ have theoretically predicted the radiative heat flux of 3000–4000 kW/cm² at 3.5–6.8 MPa, whereas conductive heat feedback from gas-phase ranges between 1500–2000 kW/cm² in the pressure range of 0.1 to 1 MPa for aluminized formulations. However, conductive feedback largely depends upon agglomeration pattern. As the metal content increases, heat-sink effect and size of the agglomeration increase, resulting in overall reduction in burning rates. The increase in burning rates up to 7.5% Al level and, subsequent decrease in burning rates on increase in Al content observed during the present study can be explained on the basis of these reasonings. The combustion inefficiency problem of aluminized RDX-based propellants is more serious because melting of RDX facilitates adhering of Al on the deflagrating surface resulting in increased agglomeration.¹⁷

Kubota¹² has reported that addition of Ni does not influence burning rate and pressure-index values. A similar trend was observed on the incorporation of 2.5–7.5% Ni in nitramine-based compositions studied during the present work. A drop in burning rates on further increase in Ni content can be explained on the basis of increase in heat-sink effect because of its higher melting and boiling points (1728 and 3039 K, respectively). However, unlike aluminized compositions, Ni-based formulations exhibited superior burning-rate characteristics in a lower pressure range (6.8 MPa). This can also be explained on the basis of Kubota's¹² findings. He has reported a decrease in the standoff distance between luminous flame and burning surface on addition of Ni as well as a decrease in the pressure limit of stable flame burning. He has also established that Ni does not influence the temperature gradient in the fizz zone. However, it increases the dark zone temperature leading to its eventual elimination and appearance of luminous flame next to the fizz zone.

As regards Ti, its oxide is soluble in molten metal. Thereby, metal can diffuse out of the oxide layer and undergo combustion at a relatively lower temperature than Al.^{8,9,11} As a consequence, combustion of Ti takes place relatively near to the deflagrating propellant surface resulting in increased heat feedback in comparison to that in the case of Al, which undergoes combustion away from the surface (luminous zone). These reasonings explain a remarkable increase in the burning rates of Ti-based formulations, particularly in a lower pressure range, up to 10% metal content. However, increase in Ti content beyond this level resulted in a drop in burning rates, which can be attributed to heat-sink effect caused by its high melting point (1950 K).

Zr gave the best results as compared to other metals studied during this work. Superior burning rates of Zr-based formulations can be explained on the basis of the fact that its oxide is soluble in metal as in the case of Ti. The major advantage of Zr is that it undergoes ignition at about 1100°C in an oxidizing environment.^{8,9} Pyrophoric nature of Zr like Mg appears to overcome the combustion problems of Al leading to its combustion near the propellant surface in formulations containing the Al-Zr combination.

AP is expected to provide oxidizer-rich decomposition products in the vicinity of the burning surface, which interact exothermically with fuel-rich decomposition products of binder leading to enhanced reaction in the fizz zone and, thereby, an increase in heat feedback to the condensed phase. Heat generated during an exothermic interaction is also expected to provide a conducive thermal environment for metal combustion near the deflagrating surface resulting in an

additional release in energy. Cohen-Nir¹⁸ has reported that the effect is more pronounced with 5μ AP, which is used during this study.

Thermal Decomposition

Nonmetallized RDX-CMDB composition gave a peak decomposition temperature of 205°C in DTA with activation energy (*E_a*) of the order of 47.9 kcal/mol and frequency factor *A* of the order of 7.2×10^{20} . These values are in close agreement with the values reported for RDX, suggesting that its decomposition is the rate-controlling step during the thermal decomposition of these propellant systems.¹⁹ Incorporation of Al did not have a remarkable effect on the decomposition pattern. However, addition of Ni, Ti, and Zr brought down both *E_a* and *A* values drastically to the order of 23–28 kcal/mol and 10^{11} – 10^{13} , respectively. This suggests that heat feedback caused by efficient combustion of Ti/Zr near the surface and catalytic effect of Ni on fizz-zone reactions influence subglobal kinetics facilitating the decomposition of the condensed phase.

Addition of ballistic modifiers did not influence peak decomposition temperature but resulted in a change in kinetic parameters suggesting their influence on overall condensed-phase processes. Incorporation of AP (5μ) brought down the peak decomposition temperature drastically (by about 25°C), suggesting its remarkable influence on decomposition pattern of the condensed phase (Table 9, Figs. 9a and 9b).

In DSC, nonmetallized control composition gave ΔH of 1385 J/g. Incorporation of metals resulted in an ΔH value of the order of 845–954 J/g (Ti < Al < Ni < Zr). This trend can be attributed to an overall heat-sink effect of metals. Relatively higher values of ΔH for Zr-based formulation among metallized compositions can be explained on the basis of comparatively greater compensating heat feedback caused by combustion of Zr near the surface. Incorporation of Fe₂O₃ in RDX-Zr based formulation resulted in a drop in ΔH value, which can be attributed to the fact that Fe₂O₃ needs to be heated to an elevated temperature and, probably converted into fine α-Fe₂O₃ particles before being effective as a ballistic modifier.²⁰ These results are in line with those of Wang et al.,²¹ who have reported a decrease in surface temperature of propellants on incorporation of Fe₂O₃. Kishore and Gayathri²⁰ have reviewed the effect of catalysts on combustion behavior of an AP-based propellant and reported that most of the researchers are of the view that the site of action of Fe₂O₃ is the gas-phase combustion process, whereas some of the researchers are of the opinion that Fe₂O₃ catalyzes both the condensed- and gas-phase reactions. As regarding BLS + Cu₂O + C-black combination, it brought down the ΔH value, suggesting that lead (Pb) and Cu compounds undergo an endothermic process, probably involving decomposition of Pb salt to Pb. It is reported²² that the temperature of Pb salt needs to be increased to the level of about 700°C for

Table 9 DTA results of metallized RDX-CMDB propellants

Compositions, %	DTA					
	Peak temperature, °C, at heating rate, °C/min				<i>E_a</i> , kcal/mol	<i>A</i>
	5	10	15	20		
Reference	200	205	210	212	47.9	7.2×10^{19}
RDX 12.5 + Al 17.5	197	205	208	210	44.5	2.27×10^{20}
RDX 12.5 + Ti 17.5	185	200	204	210	23.1	2.53×10^{11}
RDX 12.5 + Ni 17.5	189	200	205	210	28.0	1.58×10^{13}
RDX 12.5 + Zr 17.5	190	202	208	212	26.4	1.13×10^{12}
RDX 12.5 + Zr 17.5	192	202	207	212	29.8	2.25×10^{13}
Fe ₂ O ₃ two parts						
RDX 12.5 + Zr 17.5	185	195	202	207	26.0	7.03×10^{11}
FeAA two parts						
RDX 12.5 + Zr 17.5	190	200	203	205	36.9	1.94×10^{16}
BLS + Cu ₂ O + C-black two parts						
RDX 12.5 + Zr 17.5	198	205	210	212	41.6	6.80×10^{20}
Cu-chromite two parts						
[with AP (5μ)]	[174]	[180]	[182]	[185]	[49.5]	$[1.88 \times 10^{20}]$

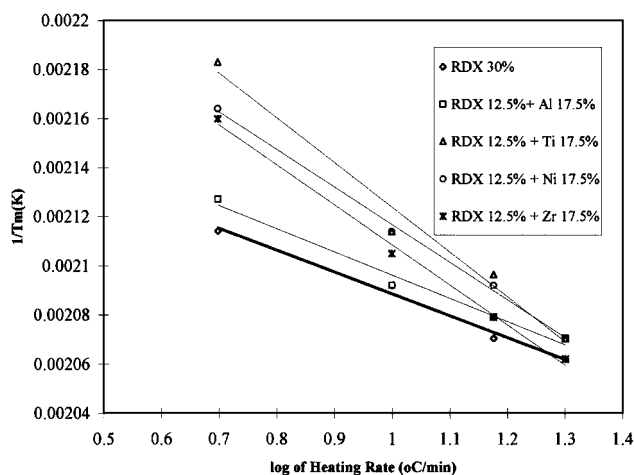


Fig. 9a Arrhenius plot of inverse of T_m (K) vs log of heating rate ($^{\circ}\text{C}/\text{min}$) for metallized RDX-CMDB propellants.

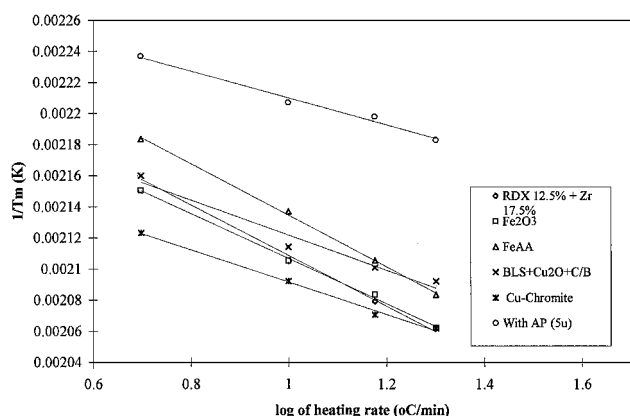


Fig. 9b Arrhenius plot of inverse of T_m (K) vs log of heating rate ($^{\circ}\text{C}/\text{min}$) for ballistically metallized RDX-CMDB propellant and with 5% AP (5μ).

decomposition to occur. These findings suggest that the active form of the Pb-salt (PbO) is obtained only above the surface, where it is trapped in the carbon residue. Lengelle et al.²² have opined that super-burning-rate-producing lead additives in a double-base matrix do not take part in the condensed phase and more likely the site of their action is gas phase. Youfang²³ has explained in detail the basic chemical reactions operating during catalysis of double-base matrix by lead salicylate. They have suggested that PbO formed on the decomposition of lead salicylate reacts with decomposition products of the double-base matrix [HCHO , CHO , and $(\text{CHO}_4)_2$], producing carbon nuclei resulting in the formation of a char layer. This char deposits on the burning surface and shifts the reducing site of NO near the burning surface from the luminous zone leading to an enhancement of the temperature gradient. As the luminous flame approaches the surface on an increase in pressure, the char thickness reduces because of the interaction with adsorbed oxidizing moieties, resulting in an overall decrease in the catalyzed burning rate in the condensed phase. FeAA and Cu-chromite incorporation led to a marginal increase in the ΔH value during this work. An increase in ΔH was relatively less for Cu-chromite, despite the fact that it enhanced the burning-rates to a greater extent suggesting that it catalyzes both condensed- and gas-phase reactions with a major contribution to the latter. In the case of Cu-chromite, Boggs²⁴ has proposed that an exothermic redox cycle between $\text{CuO}/\text{Cu}_2\text{O}/\text{Cu}$ is established at a higher temperature leading to heat release on the surface of the propellant resulting in burning-rate enhancement. Incorporation of AP brought down the peak temperature as in case of DTA and led to an increase in the ΔH value by about 128–163 J/g, confirming its remarkable effect on the overall condensed-phase decomposition process (Table 10).

Table 10 TGA and DSC results of metallized RDX-CMDB propellants

Compositions, %	TGA		DSC	
	Temp. range, $^{\circ}\text{C}$	Wt. loss, %	ΔH , J/g	Peak temp., $^{\circ}\text{C}$
Reference	80–310	94	1385	205.6
RDX 12.5 + Al 17.5	95–287	73	867	205.9
RDX 12.5 + Ti 17.5	75–430	76	845	206.3
RDX 12.5 + Ni 17.5	67–260	79	923	203.6
RDX 12.5 + Zr 17.5	90–340	70	954	203.7
RDX 12.5 + Zr 17.5 Fe_2O_3 two parts	68–375	71	864	205.9
RDX 12.5 + Zr 17.5 FeAA two parts	82–285	86	1009	206.2
RDX 12.5 + Zr 17.5 BLS + Cu_2O + C-black two parts	110–370	68	698	206.2
RDX 12.5 + Zr 17.5 Cu-chromite two parts [with AP (5μ)]	60–395 [70–202]	75 [88]	968 [1105]	206.2 [184.9]

TGA of the control propellant revealed single-stage weight loss amounting to 94%, suggesting that RDX and double-base matrix decompose as a homogeneous mass. Incorporation of metals resulted in a decrease in weight loss corresponding to the metal content, indicating that metals do not influence the basic condensed-phase decomposition process of nitramine-based CMDB propellants. Incorporation of BLS + Cu_2O + C-black combination and Fe_2O_3 did not have much effect on the weight loss pattern, suggesting that they do not influence condensed-phase reactions significantly. FeAA incorporation resulted in a remarkable increase in weight loss, whereas Cu-chromite, which was found to be the best ballistic modifier, gave intermediate values. These results further confirm that Cu-chromite catalyzes both condensed- as well as gas-phase reactions. AP brought down temperature range of decomposition and resulted in an increase in weight loss to the 88% level, which further establishes its involvement in catalyzing condensed-phase reactions (Table 10).

Conclusions

Ni-based and Ti-based RDX-CMDB formulations, unlike Al containing composition with 15–17.5% metal content, exhibit stable combustion even at 6.8 MPa. Incorporation of Zr extends the stable combustion limit of RDX-CMDB systems to 4.9 MPa chamber pressure.

BLS + Cu_2O + C-black combination and copper-chromite are more effective ballistic modifiers for RDX-Zr CMDB formulations than Fe_2O_3 and FeAA. Incorporation of ballistic modifiers in combination with AP (5μ) results in further improvement in burning-rate behavior and leads to an extension of the stable combustion limit to 1 MPa.

CMDB composition containing 12.5% RDX along with 13% Al and 4.5% Zr with 5% AP and two parts of Cu-chromite gave superior burning-rate behavior (burning rate 4–18 mm/s in the pressure range of 1–10.8 MPa) with Isp of 259 s. DTA/TG/DSC studies suggest that metals play an important role in gas-phase reactions, whereas AP contributes significantly toward facilitating condensed-phase decomposition. The data obtained establish that the site of action of BLS + Cu_2O + C-black system is in the gas-phase, whereas Cu-chromite catalyzes both condensed- and gas-phase combustion reactions.

References

- Kubota, N., Masamoto, T., and Hazama, M., "Combustion of HMX Composite Propellants," *Proceedings of Twelfth International Symposium on Space Technology and Science*, AGNE Publishing, Inc., Tokyo, 1977, pp. 507–512.
- Iyer, N. R., "Recent Advances in Antitank Guided Missile System," *Defence Science Journal*, Vol. 45, No. 3, 1995, pp. 187–197.
- Asthana, S. N., Deshpande, B. Y., and Singh, H., "Evaluation of Various Stabilizers for Stability and Increased Life of CMDB Propellants,"

Propellants, Explosives, Pyrotechnics, Schubert, H., (Fraunhofer-ICT-Germany), VCH Verlagsgesellschaft mbH, Weinheim, Vol. 14, No. 4, 1989, pp. 170–175.

⁴Schoyer, H. F. R., Schnorhk, A. J., Korting, P. A. O. G., van Lit, P. J., Mul, J. M., Gadiot, G. M. J. L., and Meulenbrugge, J. J., “High-Performance Propellants Based on Hydrazinium Nitroformate,” *Journal of Propulsion and Power*, Vol. 11, No. 4, 1995, pp. 856–869.

⁵Kubota, N., and Masamoto, T., “Flame Structure and Burning Rate Characteristics of CMDB Propellants,” *Sixteenth International Symposium on Combustion*, Combustion Inst., Pittsburgh, PA, 1976, pp. 1201–1209.

⁶Kubota, N., “Survey of Rocket Propellants and Their Combustion Characteristics,” *Fundamentals of Solid Propellants Combustion*, edited by K. K. Kuo and M. Summerfield, Vol. 90, Progress in Astronautics and Aeronautics, AIAA, New York, 1984, pp. 1–52.

⁷Brill, T. B., “Multiphase Chemistry Considerations of the Surface of Burning Nitramine Monopropellants,” *Journal of Propulsion and Power*, Vol. 11, No. 4, 1995, pp. 740–751.

⁸Rastogi, R. P., and Deepak, D., “Combustion of Metallized Propellants,” *Journal of Scientific and Industrial Research*, Vol. 36, 1997, pp. 470–490.

⁹Athawale, B. K., Asthana, S. N., and Haridwar Singh, “Metallized Fuel-Rich Propellants for Solid Rockets—A Review,” *Defence Science Journal*, Vol. 44, No. 4, 1994, pp. 269–278.

¹⁰Ronald, L., “Random Orientation of Staple in Slurry Cast Propellants,” U.S. Patent 3,813,458, 28 May 1974.

¹¹Mama, H. P., “Solid Rocket Propellants. The European Scene,” *International Defense Review*, Vol. 21, No. 3, 1988, pp. 291–295.

¹²Kubota, N., “Role of Additive in Combustion Waves and Effect on Stable Combustion Limit of Double Base Propellants,” *Propellants and Explosives*, Vol. 3, No. 6, 1978, pp. 163–168.

¹³Bhat, V. K., Singh, H., and Rao, K. R. K., “Processing of High Energy Crosslinked Composite Modified Double Base Propellants,” *Eighteenth International Jahrestag Fraunhofer Institute Treib Explosivst*, Karlsruhe, Fraunhofer Inst. Chemisch Technologie, Germany, 1987, pp. 18/1–18/10.

¹⁴Rindorf, H. J., “Acoustic Emission Source Location in Theory and in Practice,” *Technical Review to Advanced Techniques in Acoustical, Electrical and Mechanical Measurements*, Bruel and Kjaer, DK-2850 NAERUM, Denmark, Vol. 2, 1981, pp. 3–32.

¹⁵Brewster, M. Q., and Hardt, B. E., “Influence of Metal Agglomeration and Heat Feedback on Composite Propellants Burning Rate,” *Journal of Propulsion*, Vol. 7, No. 6, 1991, pp. 1076–1078.

¹⁶Ishihara, A., Brewster, M. Q., Sheridon, T. A., and Krier, H., “The Influence of Radiative Heat Feedback on Burning Rate in Aluminized Propellants,” *Combustion and Flame*, Vol. 84, Nos. 1–2, 1991, pp. 141–153.

¹⁷Liu, T., Perng, H., Luh, S., and Liu, F., “Aluminum Agglomeration in AP/RDX/Al/HTPB Propellant Combustion,” *Journal of Propulsion and Power*, Vol. 8, No. 6, 1992, pp. 1177–1184.

¹⁸Cohen-Nir, E., “Combustion Characteristics of Advanced Nitramine Based Propellants,” *Eighteenth International Symposium on Combustion*, Combustion Inst., Pittsburgh, PA, 1981, pp. 195–206.

¹⁹Oyumi, Y., “Melt Phase Decomposition of RDX and Two Nitrosamine Derivatives,” *Propellants, Explosives, Pyrotechnics*, Schubert, H., (Fraunhofer-ICT-Germany), VCH Verlagsgesellschaft mbH, Weinheim, Vol. 13, No. 1, 1988, pp. 42–47.

²⁰Kishore, K., and Gayathri, V., “Chemistry of Ignition and Combustion of Ammonium Perchlorate Based Propellants,” *Fundamentals of Solid Propellants Combustion*, edited by K. K. Kuo and M. Summerfield, Vol. 90, Progress in Astronautics and Aeronautics, AIAA, New York, 1984, pp. 53–119.

²¹Wang, S. Y., Wang, S. S., Liu, F., and Chiu, H. S., “An Investigation of Catalysis in the Combustion of Iron Catalyzed Composite Propellants,” *Proceedings of the 19th International Annual Conference of ICT*, Karlsruhe, Fraunhofer Institute Chemische Technologie, Germany, 1988, pp. 8–1–8–14.

²²Lengelle, G., Bizot, A., Duterque, J., and Trubert, J. F., “Steady State Burning of Homogeneous Propellants,” *Fundamentals of Solid Propellants Combustion*, edited by K. K. Kuo and M. Summerfield, Vol. 90, Progress in Astronautics and Aeronautics, AIAA, New York, 1984, pp. 361–407.

²³Youfang, C., “Combustion Mechanism of Double-Base Propellants with Lead Burning,” *Propellants, Explosives, Pyrotechnics*, Schubert, H., (Fraunhofer-ICT-Germany), VCH Verlagsgesellschaft mbH, Weinheim, Vol. 12, No. 6, 1987, pp. 209–214.

²⁴Boggs, T. L., “The Thermal Behavior of Cyclotrimethylenetrinitramine (RDX) and Cyclotetramethylenetetramine (HMX),” *Fundamentals of Solid Propellants Combustion*, edited by K. K. Kuo and M. Summerfield, Vol. 90, Progress in Astronautics and Aeronautics, AIAA, New York, 1984, pp. 121–175.