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Chemical stability, thermal behavior, and shelf life assessment of extruded modified double-base propellants

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ABSTRACT

Double base propellant suffers from lack of chemical stability; this could result in self ignition during storing. Modified double base (MDB) propellant based on stoichiometric binary mixture of oxidizer-metal fuel (Ammonium perchlorate/Aluminum), and energetic nitramines (HMX) offered enhanced thrust as well as combustion characteristics. This study is devoted to evaluate the impact of such energetic additives on thermal behavior, chemical stability, and shelf life. Extruded MDB formulations were manufactured by extrusion process. Artificial aging at 80 °C for 28 days was conducted. Shelf life assessment was performed using Van't Hoff's equation. Quantification of evolved NO_x gases with aging time was performed using quantitative stability tests. MDB formulation based on HMX demonstrated extended service life of 16 years compared with (AP/Al)-MDB which demonstrated 9 years. This finding was ascribed to the reactivity of AP with nitroglycerin with the formation of perchloric acid. Thermal behavior of aged MDB, exhibited an increase in heat released with time; this was ascribed to the autocatalytic thermal degradation during artificial aging. The increase in released heat by 31% was found to be equivalent to evolved NOx gases of 6.2 cm^3/5 g and 2.5 cm^3/1 g for Bergmann-Junk test, and Vacuum stability test respectively. This manuscript shaded the light on a novel approach to quantify evolved NOx gases to heat released with aging time. MDB based on HMX offered balanced ballistic performance, chemical stability, and service life.

1. Introduction

Modified double base (MDB) propellants have found wide applications in modern military and space rocketry, in view of their superior performance [1,2]. It is well known that MDB propellants are evolved from double-base by integrating energetic fillers such as HMX or RDX. There is also another trend to integrate potential oxidizers such as ammonium perchlorate (AP), as well as active metal fuels such as aluminum, magnesium, and boron [3–6]. This is why MDB propellants have recently been used in booster, sustainer, and dual thrust rocket motors [7–9].

MDB can exhibit a wide range of burning rate up to 40 mm/s; specific impulse can also be varied from 220 to 270 s [9–12]. It has been reported that integration of stoichometric binary mixture of oxidizer-metal fuel (AP/Al), and energetic nitramine such as HMX offered a higher specific impulse (Fig. 1) [9,13–15].

MDB based on binary mixture of AP/Al and HMX offered higher specific impulse by 10% and 9% respectively compared with reference formulation [9]. Stoichometric binary mixture of AP/Al had a dual effect by increasing the average operating pressure and burning rate [9]. This action was ascribed to the gaseous decomposition nature of AP (Equation (1)), and the exothermic oxidation of Al metal fuel which could enhance the heat of combustion, and flame temperature [1,2,7,16].

$$10NH_4ClO_4 \rightarrow 2.5\,Cl_2 + 2N_2O + 2.5NOCl + HClO_4 + 1.5HCl + 18.75H_2O + 1.75N_2 + 6.38O_2 \quad (1)$$

Aluminum metal fuel, with high exothermic heat of combustion (7.4 kcal/g) and excellent thermal conductivity values, tended to increase the burning rate [7,17,18]. Aluminum particles are able to react not only with free oxygen resulted from oxidizer decomposition; but also it is able to react with inert decomposition gaseous products and add much more heat to the combustion process

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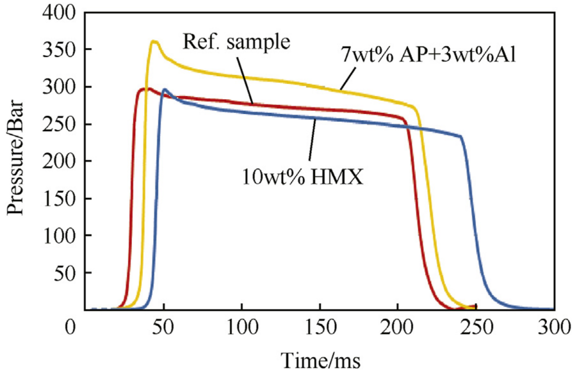

Fig. 1. Practical measurements of pressure-time curves of developed MDB using small-scale ballistic evaluation test motor [9].

[18–20].

The great impact of HMX on ballistic performance was attributed to the positive heat of formation (+353.8 kJ/kg). HMX is a highly effective explosive material with heat of explosion 6197 kJ/kg and gaseous product of 902 L/kg [13]. HMX also has a slightly negative oxygen balance which means decomposition products of low molecular weight [13,21]. Much research has been directed toward the development of MDB propellants with enhanced combustion characteristics and high specific impulse [22–25]. However less attention has been directed to investigate the impact of different energetic additives on chemical stability, thermal behavior, and shelf life [26].

1.1. Chemical stability of MDB propellants

The nitrate esters (nitrocellulose & nitroglycerine), the main constituents of double-base propellant, are molecules that aren't chemically stable. Their decomposition is slow in ambient conditions of temperature, pressure, and humidity. In severe environments, the chemical decomposition becomes autocatalytic [11]. There are many mechanisms through which chemical decomposition can occur; these mechanisms include:

1.1.1. Chain reactions

Chain reactions start with the homolytic breaking of the weak O-NO_2 bond, forming nitrogen dioxide and the corresponding alkoxyl radical [27–29]. These reactive free radicals immediately undergo consecutive reactions with nearby nitrate ester molecules [29].

$$R - O - NO_2 \rightarrow R - \dot{O} + \dot{N}O_2 \tag{2}$$

1.1.2. Saponification (hydrolysis)

Another main decomposition pathway is the neutral to acid hydrolysis of the nitrate esters [28]. This reaction is catalyzed by moisture and residual acids (which weren't fully removed after nitrate ester synthesis), or by water, or by acids formed during decomposition (Equation (3)).

$$R - O - NO_2 + 2H_2O \xrightarrow{H^+} R - OH + HNO_3 \tag{3}$$

A further decomposition reaction is the “enhanced hydrolysis”. This reaction was found to have low activation energy of 71 kJ/mol. Therefore it can be a dominant decomposition reaction at lower temperatures [30].

1.1.3. Auto-catalytic reactions

Decomposition products of reactions (2) can further transformed in presence of moisture and oxygen as follow:

$$2\dot{N}O + O_2 \rightarrow 2\dot{N}O_2 \leftrightarrow N_2O_4 \tag{4}$$

$$\dot{N}O + \dot{N}O_2 + H_2O \rightarrow 2HNO_2 \tag{5}$$

$$3\dot{N}O_2 + H_2O \rightarrow 2HNO_3 + \dot{N}O \tag{6}$$

Whereas the primary homolytic reaction (2) can't be suppressed, the consecutive reactions (3–6) can be slowed down nearly to zero by binding or elimination of acids, nitric oxides, and water from the system. This fact was employed for the stabilization of double-base propellants by integrating stabilizing agents [30,31]. Stabilizers fulfill their purpose by reacting with the nitrogen oxides and neutralize the decomposition products [32]. Conventional double-base propellants, with proper percentage of stabilizer, can offer a safe chemical life of at least 20 years [33]. For modified systems containing energetic solid additives similar shelf life should be secured [34]. A number of studies have been carried out on the thermal stability of MDB propellants [35–38]. Complete information regarding the influence of high energy ingredients including (in organic oxidizers/high explosives) on MDB propellant stability and shelf life is vital in regards of their handling, processing, transportation, and storage.

1.2. Impact of different energetic additives on chemical stability

AP has a great impact on the degradation of propellants containing nitrate esters. Many researchers have studied the rate of stabilizer depletion and the time to ignition of such propellants [39]. Asthana, Divekar et al. investigated the stability, auto ignition, and stabilizer depletion of MDB propellants containing NG and AP [40]. It was noted that the inclusion of AP increased the auto-catalytic behavior of MDB propellants over time [41]. MDB based on AP demonstrated ease of ignition suggesting faster decomposition kinetics [42]. AP-MDB propellants possess shorter shelf life than their conventional counterparts [40,43]. Further research showed that MDB containing AP and NG exhibited less stability than conventional double-base [44]. However, nitramine double-base propellants exhibited relatively good thermal stability [45–49]. This paper is devoted to investigate the effect of binary mixture of oxidizer/metal fuel (AP/Al) and energetic nitramine (HMX) on DB chemical stability, thermal behavior, as well as shelf life assessment. MDB formulation based on HMX demonstrated extended service life of 16 years compared to (AP/Al)-MDB which demonstrated 9 years. DSC outcomes demonstrated an increase in heat released with aging time. The released heat was increased by 31, 41, and 25% for reference, (AP/Al)-MDB, and HMX-MDB formulations respectively. This thermal behavior was ascribed to the auto-catalytic thermal degradation over artificial aging. Correlation between the increase in heat released and the evolved nitrogen oxides was conducted.

2. Experimental

2.1. Manufacture of MDB formulations

Screw extrusion technique emphasizes mixing of different ingredients to ensure good homogenization, high density, and dimensional stability. This technique included many stages such as blending, followed by rolling, grinding, granulation, and finally

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