



Effect of Some Inorganic Nitrate Salts on the Ignition Delay Time of DMAZ-IRFNA and DMAZ-WFNA Bi-propellants

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Abstract: Dimethylaminoethyl azide (DMAZ) is a good replacement for the hydrazine group in the space industry. However, it has a relatively long ignition delay time with the liquid oxidizer, white fuming nitric acid (WFNA), and is nonhypergolic with inhibited red fuming nitric acid (IRFNA). In this article, the ignition delay times of DMAZ-WFNA and DMAZ-IRFNA bi-propellants were reduced by the addition of some inorganic nitrate salts, such as NH_4NO_3 , KNO_3 , NaNO_3 , AgNO_3 and LiNO_3 , to the liquid oxidizers. The results showed that WFNA containing 0.1 wt.%, 0.3 wt.% and 0.5 wt.% of LiNO_3 reduced the ignition delay time of DMAZ-WFNA from 88 ms to 18 ms, 14 ms and 8 ms, respectively. The same percentages of LiNO_3 caused the nonhypergolic DMAZ-IRFNA bi-propellant to have ignition delay times of 42 ms, 34 ms and 22 ms, respectively. Moreover, calculations indicated that the addition of LiNO_3 to both oxidizers did not have a significant affect on the specific impulse of the bi-propellants. Consequently LiNO_3 could be an appropriate additive for the reduction of the ignition delay times of DMAZ-WFNA and DMAZ-IRFNA bi-propellants.

Keywords: DMAZ, liquid oxidizers, ignition delay time, inorganic nitrate salts, specific impulse

1 Introduction

Hydrazine and its derivatives, such as monomethylhydrazine (MMH) and unsymmetrical dimethylhydrazine (UDMH), have been widely used in the space industries since 1959 [1, 2]. They have good performance and physicochemical properties. However, they are carcinogenic [3].

Scientists and engineers are searching for good alternative liquid fuels [4]. The US space agency has introduced dimethylaminoethyl azide (DMAZ) as a safe candidate. It is not carcinogenic and has properties comparable with those of the hydrazine family [5, 6].

For the selection of a good liquid oxidizer for DMAZ in a liquid bi-propellant system, two main basic parameters should be considered: specific impulse (I_{sp}) and ignition delay time (ID time) [7]. Specific impulse is defined as the produced thrust per weight flow rate of a propellant. It is proportional to the square root of the combustion temperature per molecular weight of exit gases and may be calculated by computer codes or measured by experimental technics [2]. The ID time is defined as the time interval between contact of the oxidizer and fuel and the presence of flame [8, 9]. The estimation or prediction of an ID time for a liquid propellant is difficult. Therefore, it is measured experimentally [10]. The ID time is dependent on the measurement method [10-12]. On a laboratory scale, the cup test or drop test method is used for the measurement of the ID time [10, 11]. In order to have smooth combustion, the ID time should be low [8]. Various upper limits for ID times have been reported. It should be less than 25 ms for a hypergolic liquid bi-propellant for space programs [13-15].

Based on the physicochemical properties of liquid oxidizers (such as boiling point, corrosiveness, toxicity, the process of production and the final cost), liquid oxidizers white fuming nitric acid (WFNA) and inhibited red fuming nitric acid (IRFNA) have been commonly used in space programs [2, 3, 16]. The performance of DMAZ with both oxidizers was assessed [7]. It was founded that DMAZ-WFNA bi-propellant had an ID time of 88 ms. Moreover, DMAZ-IRFNA bi-propellant was demonstrated to be non-hypergolic [7]. Therefore, it is necessary to reduce the ID time of DMAZ with the liquid oxidizers WFNA or IRFNA.

DMAZ is a novel liquid fuel and there is no information available for the reduction of its ID time. However, some researches have been reviewed for other liquid bi-propellants [17]. One way of reducing the ID time is the use of chemical additives which are generally added to the liquid fuel. However, there is scarce information for the use of additives in liquid oxidizers. It is important that the amount of additive in a bi-propellant system should be low, preferably 0.1 wt.% to 5 wt.% based on the non-hypergolic liquid fuel or oxidizer [18], because small amounts lead to small changes in the physicochemical properties of the propellant.

The reaction mechanism between an amine (such as DMAZ) and an acid (such as WFNA or IRFNA) is complex. It may be neutralization, oxidation or nitration [15, 19-21]. The roll of neutralization in an ignition reaction is generally

known [19, 21]. On the basis of literature surveys [22-24], inorganic nitrate salts are sources of oxygen and readily available. Therefore, addition of these salts to liquid oxidizers may give more oxygen to a hypergolic reaction. Also, dissolution of nitrates in both oxidizers and thence nitronium ion formation may accelerate the nitration reaction of DMAZ.

In the present research, the effect of some inorganic nitrate salts on the reduction of the ID time for DMAZ-WFNA and DMAZ-IRFNA bi-propellants will be studied. In other words, the type of mechanism for initiation of the ignition reaction will be identified. Moreover, the effect of the best salt additive on I_{sp} for both bi-propellants will be investigated.

2 Materials and Methods

2.1 Chemicals

DMAZ was synthesized by reaction between 2-dimethylaminoethyl chloride and sodium azide, and concentrated in a vacuum distillation column (at $P=40$ kPa) to a purity of 99.93 wt.% [25]. WFNA (> 99 wt.% purity, from Merck Co., Darmstadt, Germany) and IRFNA (type IIIB with HNO_3 , 82.9 wt.%; NO_2 , 13.87 wt.%; H_2O , 2.5 wt.%; nitrate solids, 0.03 wt.%; HF inhibitor, 0.7 wt.% and density of 1550 kg/m³ from DLA Co., Wheat Ridge Co, USA) were purchased.

The inorganic nitrate salts NH_4NO_3 , KNO_3 , $NaNO_3$, $AgNO_3$ and $LiNO_3$ (powder form with purity > 98 wt.%) were purchased from Merck Company.

2.2 Measurement of ID times

The ignition delay time was measured with the open cup test method. In this method, a certain mass of liquid oxidizer was poured into a cup vessel equipped with a temperature controller at 25 °C. A given mass of liquid fuel at 25 °C was then dropped onto the cup from a height of 25 cm using a syringe connected to a motor with 3 rpm rotation. The ID time was measured and recorded *via* a high speed camera (1000 frames per second, model CASIO EXLIM FX-X1 [CASIO Co., Tokyo, Japan]).

2.3 Calculation of I_{sp} values

NASA-CEC-71 software (NASA Lewis research Center, Cleveland, USA) [26] was used to calculate I_{sp} values. It uses the assumptions of adiabatic, reversible and one-dimensional flow in all calculations on the basis of minimizing the Gibbs free energy. DMAZ was introduced to the software as a liquid fuel. WFNA and IRFNA (type IIIB) were presented as liquid oxidizers. Moreover, the inorganic

nitrate salts were introduced to the software as additives. For the calculation of an I_{sp} , the following conventional conditions were applied [2]:

- (i) The pressure in the combustion chamber was taken as 1000 psi or 68 atm;
- (ii) The ratio of the nozzle diameter to the throat diameter was taken as 10;
- (iii) The exit pressure from the nozzle was chosen as 1 atm (at sea level).

3 Results and Discussion

3.1 Effect of inorganic nitrate salts on the ID times of DMAZ-IRFNA and DMAZ-WFNA bi-propellants

The ID time variations for different percentage weights of the nitrate additives to the oxidizer WFNA in contact with the liquid fuel DMAZ are demonstrated in Figure 1. In a similar way, Figure 2 represents the ID time variations for DMAZ with IRFNA. The experiments were carried out at room temperature (approx. 25 °C) and the mean ID time was determined from at least six runs.

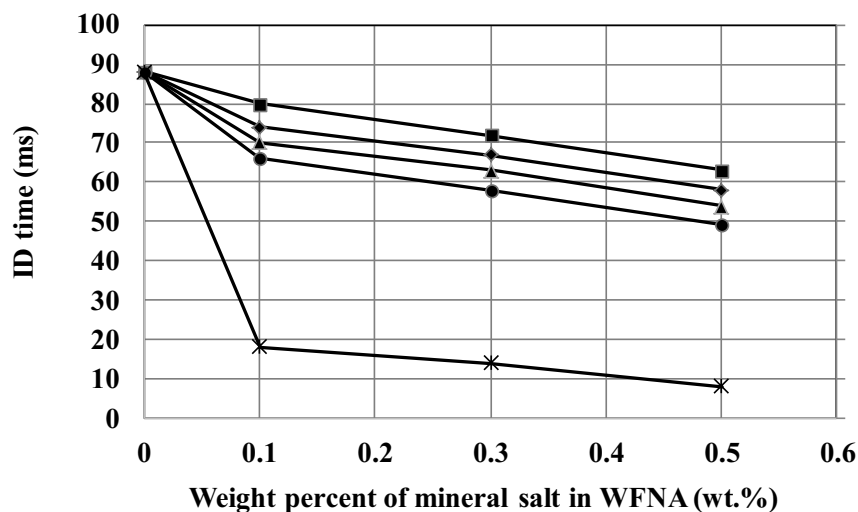


Figure 1. ID time variations for DMAZ with WFNA containing different weight percentages of nitrate(V) salts at $O/F=2.5$ (NH_4NO_3 -■-; KNO_3 -◆-; NaNO_3 -▲-; AgNO_3 -●-; LiNO_3 -✱-)

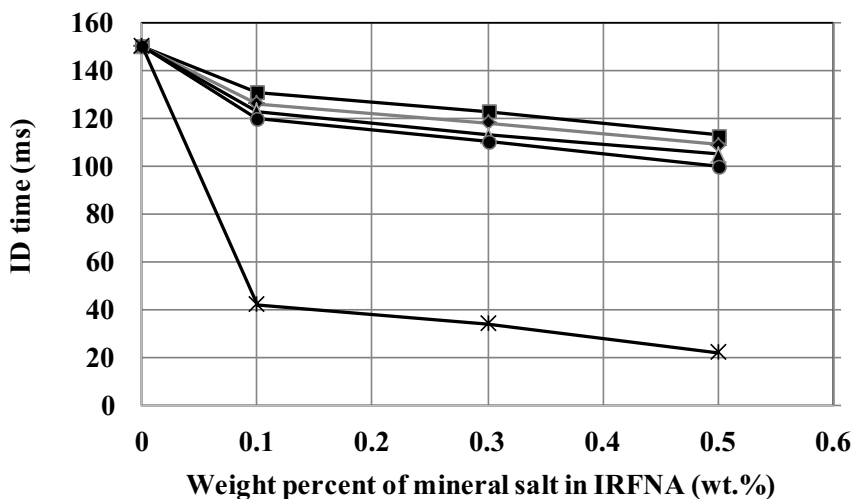
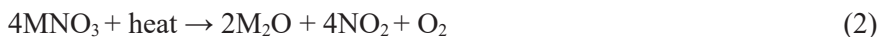


Figure 2. ID time variations for DMAZ with IRFNA containing different weight percentages of nitrate(V) salts at O/F=2.5 (NH₄NO₃ -■-; KNO₃ -◆-; NaNO₃ -▲-; AgNO₃ -●-; LiNO₃ -*-)

The reaction of DMAZ with WFNA or IRFNA is an exothermic reaction [27]. The heat released may lead to thermal decomposition of the inorganic nitrate(V) salts and produce oxygen as indicated in the general equations below [28-32]:



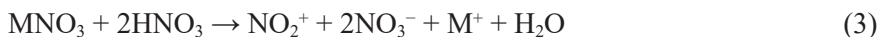
or



in which M is the cation, such as K, Ag, Na, NH₄ and Li.

The oxygen release rate by the thermal decomposition of the inorganic nitrate(V) salts is not high and is generally accelerated by catalysts [28-32]. In other words, the nitrate(V) salts cannot initiate the ignition of DMAZ with WFNA or IRFNA by the oxygen release mechanism. Thus, the oxidation mechanism is not prevalent in the initiation of ignition with the nitrate(V) salts.

Nitrate salts react with WFNA or anhydrous nitric acid (Equation 3) [33] according to the general equation below:



in which M is the cation, such as K, Ag, Na, NH₄ and Li. The reaction of DMAZ (as a base) with WFNA (as an acid) is an acid-base neutralization. On the other hand, the nitronium cation (NO₂⁺) from Equation 3 acts as a nitrating agent. The rate of the nitration reaction is usually greater than the rate of the acid-base neutralization [33] and thus initiates the ignition reaction. Thus, the nitration reaction appears to be the prevalent initiation mechanism. To confirm this, as is shown in Figures 1 and 2, a larger concentration of NO₂⁺ (or larger concentration of nitrate salt) leads to a higher rate of the nitration reaction or a decrease in ID time.

The nitration reaction rate depends on the type of cation involved. Among the cations NH₄⁺, K⁺, Na⁺, Ag⁺ and Li⁺, the lithium cation or lithium nitrate (LiNO₃) acts the most rapidly because of the atomic size of lithium [33-35]:



The size of NH₄⁺, K⁺, Na⁺, Ag⁺ and Li⁺ ions in picometers (pm) is 175, 152, 116, 114, and 90, respectively [36-38].

It is also shown that the ID time is proportional to the weight percent of the inorganic nitrate(V) salt. In other words, there is a relation between the ID time and weight percent of the inorganic nitrate(V) salt. This may be correlated as:

$$ID(ms) = ID_o(ms) \times e^{-k \times \text{wt.}\%} \quad (4)$$

where *ID* (in ms) is the ignition delay time between DMAZ and the liquid oxidizer containing the inorganic nitrate(V) additive; *ID*_o (in ms) is the ignition delay time between DMAZ and the liquid oxidizer without an inorganic nitrate(V) additive; wt.% is the weight percent of the inorganic nitrate(V) additive or weight concentration of the additive; *k* is the proportionality constant (in 1/wt.%).

The value of *k* for each inorganic nitrate(V) salt in WFNA and IRFNA is given in Table 1. It may be supposed that the *k* value is equivalent or similar to the nitration reaction constant. Table 1 shows that the nitration reaction is faster for LiNO₃ than the other inorganic nitrate(V) salts both for WFNA and IRFNA. As was already mentioned, this is due to the small size of the Li⁺ cation.

Since the concentration of nitric acid in IRFNA (82.9 wt.%) is lower than that in WFNA (>99.5 wt.%), it was expected that the reaction rate for IRFNA would be slower than for WFNA. In other words, the ID time in DMAZ-IRFNA would be longer than in DMAZ-WFNA for the same weight percent of each nitrate(V) salt. It should be considered that among the nitrate(V) salts, the addition of LiNO₃ to the nonhypergolic DMAZ-IRFNA bi-propellant causes it

to become hypergolic. Moreover, it has a significant and the largest reduction in ID time for both of the liquid oxidizers.

Table 1. Value of k for inorganic nitrate(V) salts in WFNA and IRFNA with DMAZ

Inorganic nitrate(V) salt	Value of k for each inorganic nitrate(V) salt in liquid oxidizers in reaction with DMAZ	
	WFNA	IRFNA
NH ₄ NO ₃	0.644	0.514
KNO ₃	0.769	0.570
NaNO ₃	0.886	0.641
AgNO ₃	1.060	0.725
LiNO ₃	4.060	3.255

The ignition steps or sequences for various contents of LiNO₃ in WFNA with DMAZ are given in Figure 3, where $t=0$ ms is the time at which the liquid fuel droplet makes contact with the liquid oxidizer. In a similar way, Figure 4 shows ignition for IRFNA. As is shown in Figure 3, the ID times for DMAZ with WFNA containing 0.1 wt.%, 0.3 wt.% and 0.5 wt.% were 18 ms, 14 ms and 8 ms, respectively. From Figure 4, the ID times for DMAZ with IRFNA containing 0.1 wt.%, 0.3 wt.% and 0.5 wt.% were 42 ms, 34 ms and 22 ms, respectively.

3.2 Effect of LiNO₃ on the I_{sp} of DMAZ-WFNA and DMAZ-IRFNA bi-propellants

The specific impulses for DMAZ-WFNA and DMAZ-IRFNA bi-propellants were calculated, *via* the CEC software, for the range of O/F ratios 1.5 to 3.5 [7]. The effect of LiNO₃, as a proper inorganic nitrate(V) salt, on the I_{sp} values at the optimum O/F ratio is given for both bi-propellants in Table 2.

Table 2. Effect of LiNO₃ on the I_{sp} value at the optimum O/F ratio of 2.5 for DMAZ-WFNA and DMAZ-IRFNA propellants

LiNO ₃ content in oxidizer [wt.%]	I_{sp} [s]	
	DMAZ-WFNA	DMAZ-IRFNA
0	270.6	272.6
0.1	270.6	272.6
0.3	270.6	272.6
0.5	270.6	272.6

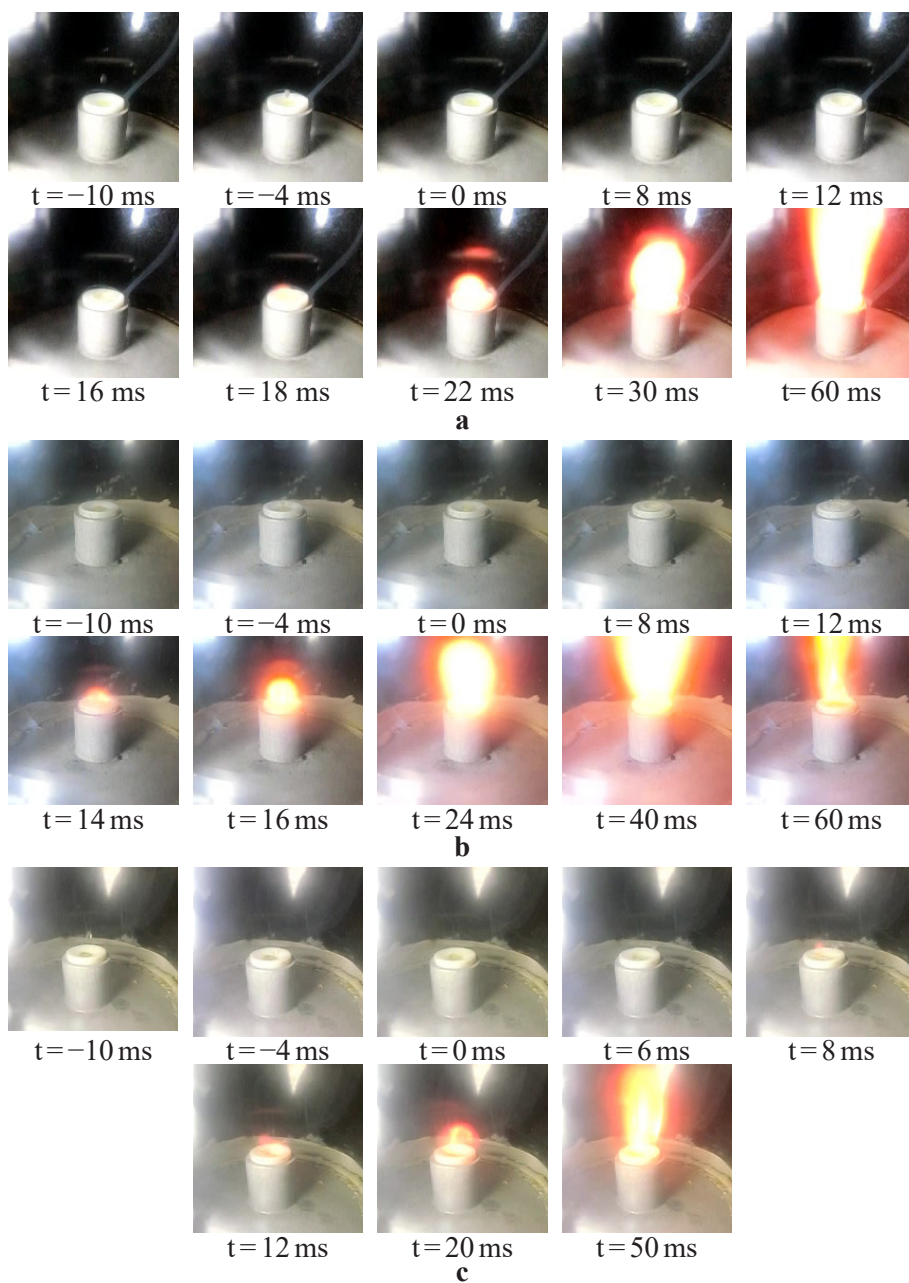


Figure 3. Images of the ID times for various contents of LiNO_3 in WFNA with DMAZ. a) 0.1 wt.% of LiNO_3 in WFNA, b) 0.3 wt.% of LiNO_3 in WFNA, c) 0.5 wt.% of LiNO_3 in WFNA

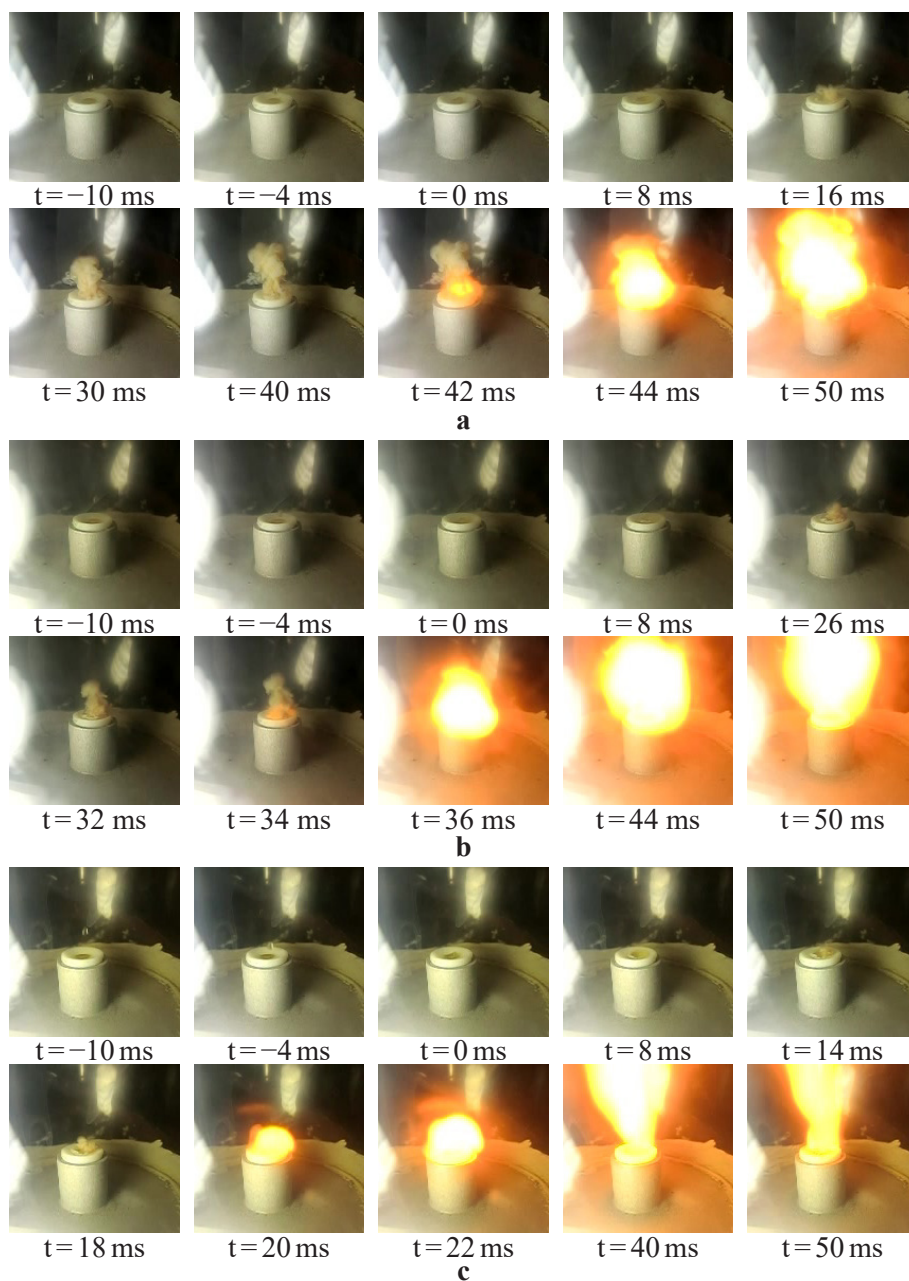


Figure 4. Images of the ID times for various contents of LiNO_3 in IRFNA with DMAZ. a) 0.1 wt.% of LiNO_3 in IRFNA, b) 0.3 wt.% of LiNO_3 in IRFNA, c) 0.5 wt.% of LiNO_3 in IRFNA

As is demonstrated in Table 2, the addition of 0.1 wt.%, 0.3 wt.% and 0.5 wt.% of LiNO_3 to both oxidizers does not change the maximum I_{sp} . This may be due to the very small amounts of the additive.

Since the no precipitation was observed in both liquid oxidizers during the addition of LiNO_3 , it seems that the use of LiNO_3 would cause no problems in rocket engines, such as in the injectors, pumps *etc.* Therefore, LiNO_3 may be an appropriate additive for liquid oxidizers WFNA and IRFNA for enhancing the hypergolicity of DMAZ-WFNA and DMAZ-IRFNA bi-propellants in space programs.

4 Conclusions

Dimethylaminoethyl azide (DMAZ) is a good replacement for the hydrazine family in space programs because of its good performance and physicochemical properties. However, it suffers from relatively long ignition delay times with the liquid oxidizers WFNA and IRFNA. In this research, the effect of some inorganic nitrate(V) additives, such as NH_4NO_3 , KNO_3 , NaNO_3 , AgNO_3 and LiNO_3 , on the ID times of DMAZ-WFNA and DMAZ-IRFNA bi-propellants was studied. The results showed that WFNA and IRFNA containing 0.1 wt.%, 0.3 wt.% and 0.5 wt.% of the nitrate(V) additives reduced the ID times of both bi-propellants. Also, LiNO_3 gave the most significant reduction in the ID times of both bi-propellants. According to the three weight percentages of LiNO_3 , the ID times for DMAZ-WFNA bi-propellant was reduced from 88 ms to 18 ms, 14 ms and 8 ms, respectively. The use of the liquid oxidizer IRFNA with the same contents of LiNO_3 caused the nonhypergolic DMAZ-IRFNA to have ID times of 42 ms, 34 ms and 22 ms, respectively. The I_{sp} calculations, *via* CEC software, indicated that no change occurred in the I_{sp} values for both bi-propellants with the different contents of the LiNO_3 additive. Therefore, LiNO_3 could be an appropriate additive for the reduction of the ID times for DMAZ-WFNA and DMAZ-IRFNA bi-propellants.

Abbreviations and symbols

DMAZ Dimethylaminoethyl azide ($\text{C}_4\text{H}_{10}\text{N}_4$)

IRFNA Inhibited red fuming nitric(V) acid

WFNA White fuming nitric(V) acid or anhydrous nitric(V) acid

ID time Ignition delay time (ms)

ID_o time Ignition delay time between DMAZ and a liquid oxidizer without an inorganic nitrate(V) additive (ms)

- wt.% Weight percent of the inorganic nitrate(V) additive or weight concentration of the additive
- k Proportionality constant (in 1/wt.%)

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