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INVESTIGATING THE IMPACT OF MAGNESIUM ADDITION ON IGNITION DELAY TIME OF SOLID HYPERGOLIC FUELS WITH ROCKET-GRADE HYDROGEN PEROXIDE

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Abstract

This research innovates a novel metalized solid fuel formulated with paraffin wax, sodium borohydride enhanced with magnesium being hypergolic with Concentrated H2O2 (90wt%). Ignition delay times (IDTs) of the metalized fuel were investigated using a professional drop test apparatus with High speed camera. A lower IDT expresses relatively enhanced reactivity of the reactants preferred for faster actuation of space vehicles. The test result outputs ignition delay time variation from 8.7±1.4ms to 1.4±0.36ms. The trend shows a decrease in IDT with increased wt% Mg in fuel. These IDTs are comparable to those of hypergolic liquids (table 2) and pre-existing Hypergolic Aluminized fuels (HAF[1]), indicating the potential of this fuel to serve as a viable replacement for existing hypergolic liquids and HAF.

1. Introduction

Hybrid rockets are recognized for their simplicity, safety, and ease of handling. This propulsion system comprises a solid fuel and a liquid/gaseous oxidizer. However, an ignition system is required to initiate combustion. In liquid rocket propulsion, many hypergolic propellants exist. Hypergolicity is the ability of an oxidizer and fuel to react and ignite spontaneously upon contact with each other, eliminating the need for an ignition system to initiate the combustion. Hypergolic propellants are preferred in upper-stage launch vehicles requiring multiple restarts and in satellite applications requiring attitude control systems with minimal ignition delay time for precise operation. Hypergols can also be used as ignitors for rocket engines.[2] Combinations of currently existing hypergolic propellants include:- (table 1)

Table 1: Common hypergolic propellant examples.[3]

Category	Examples
Hydrazine Derivatives	Hydrazine (N_2H_4), UDMH, MMH
Amine-Based Fuels	Triethylamine (TEA), TMEDA, TAEA
Ionic Liquids	[EMIM][C_2N_3], [DMIM][C_2N_3]
Borohydride-Based Fuels	Ammonia Borane (AB), [EMIM][BH_4]
Unsaturated Hydrocarbons with Additives	1-octene + BDMS
Azides	Cyanogen Azide
Nitrogen Oxides (Oxidizers)	N_2O_4, MON-3, MON-10
Nitric Acid Derivatives (Oxidizers)	RFNA, IRFNA, WFNA
High-Concentration Hydrogen Peroxide	95-98% H_2O_2

Typically, liquids have been used as hypergolic propellants, complicating the system with the requirement of separate high structural requirements. Hypergolic liquids produce good I_{sp} but a lower density I_{sp} as compared to solid hypergolic fuels due to the lower density of liquids. It has been reported that most used liquid hypergolic propellants like $N_2O_4 - MMH$ possess toxic fumes release,[4] which can cause health issues if exposed to combustion fumes. This affects the environment, which raises urgent requirement of development of a sustainable, safe hypergolic propulsion system eliminating toxic fumes responsible for depleting the environment. A list of liquid hypergolic propellants, their ignition delay time, and their toxicity is presented in the Table 2.

Fuel	Oxidizer	IDT (ms)	Toxicity	Reference
UDMH (Unsymmetrical Dimethylhydrazine)	NTO (Nitrogen Tetroxide)	1-10	Carcinogenic; high vapor pressure increases inhalation risk	[3]
TMEDA + TAEA (mixture)	Not specified	8-9	TMEDA is less toxic and non-mutagenic compared to hydrazine derivatives	[5]
TMEDA (alone)	Not specified	14	LD_{50} in mice: 268 mg/kg; considered relatively safe	[5]
TAEA (alone)	Not specified	43	Specific toxicity data not available; caution advised due to azide group	[5]
[DMIM][C_2N_3] + AMPZ	WFNA	20	Ionic liquids generally have lower volatility and toxicity; specific data not available	[6]
[DMIM][C_2N_3] (alone)	WFNA	35	Same as above	[6]
[EMIM][C_2N_3] (alone)	WFNA	52	Same as above	[6]
1-hexyl-1-methylpyrrolidinium cyanotrihydroborate	WFNA	5	Specific toxicity data not available; caution advised due to borohydride group	[7]
Ammonia Borane (AB)	95% H_2O_2	8.1	Lower toxicity compared to hydrazine; still requires careful handling	[8]
[EMIM][BH_4]	95% H_2O_2	18.5	Ionic liquid with borohydride; lower volatility; specific toxicity data not available	[8]
[EMIM][BH_4] + MIMB (1:1 w/w)	95% H_2O_2	35	Same as above	[8]
1-butyl-3-methylimidazolium dicyanamide	WFNA	31-47	Ionic liquid; lower volatility; specific toxicity data not available	[9]
Allyl-methylimidazolium dicyanamide	WFNA	43	Same as above	[9]
Propargyl-methylimidazolium dicyanamide	WFNA	15	Same as above	[9]

Table 2: Toxicity Information and Ignition Delay Time (IDT) for Various Hypergolic Propellants

1.1 Disadvantages of liquid hypergolic propellant system

Referring to the citations from Table 2, it can be shown that most of the currently existing hypergolic propellants are highly toxic and volatile, including ionic liquids and borohydride-based fuels, which are relatively new formulations demanding stringent handling precautions. This toxicity from the above-cited propellants poses risks to personnel and hikes the operational costs due to the need for specialized storage, transportation, and emergency systems.

The fuel and the oxidizer, are stored in liquid state, so their densities are relatively low as compared to solids, which require a larger storage tanks than solids to accommodate the same amount of usable energy.

Since the fuel and the oxidizer are liquid and hypergolic, they must be stored separately. Hence, a dual-feed system is required to inject fuel and oxidizer into the chamber, which requires separate pumps for turbo-pump configuration, two valves, two injectors, etc. This indulges complexity in the system, increasing the modes of failure.

1.2 Advantages of Solid Hypergolic Fuels

A solid hypergolic fuel consists of a binder, a reductant hypergolic with oxidizer, and an additive to enhance combustion. Compared to conventional liquid propellants, these solid hypergolic formulations exhibit higher density, enabling more energy storage in a low volume. This compactness is preferred in aerospace applications.

As fuel exists in the solid state, it does not require an injection system, which reduces the complication and, thus, the mode of failure by half.

1.3 Application of Solid Hypergolic Fuels in Attitude control system (ACS) Thrusters

Typically, ACS thrusters require fast response characteristics for immediate attitude control.[10] A short ignition delay time (IDT less than 10ms), the most significant parameter of hypergolic fuel, is required to apply ACS.

1.4 History and Advantages of using H_2O_2 as an oxidizer

Hydrogen peroxide is a chemical compound consisting of hydrogen and oxygen elements, which has been widely used for over 100 years for various applications[4] . Ventura et al[11] presented the use of H2O2 in aerospace applications until

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the 21st century. Hellmuth used 80% H_2O_2 for the first time in history for hypergolic rocket application[11] . Hydrogen peroxide is a good choice for hypergolic rocket applications, including hypergolic hybrids and liquids[12, 13] .

1.5 Hypergolicity and ignition delay time

An important factor determining the extent of hypergolicity is the ignition time delay.The lower the ignition delay time, the higher the extent of hypergolicity. Among liquid hypergolic propellants, the combination of NTO and UDMH exhibits the lowest ignition delay times, typically in the range of 1.5 to 5 ms.[10] To serve as a viable replacement for NTO UDMH hypergolic propellant, alternative hypergolic propellant must possess a comparable ignition delay time. **The current study focuses on developing a metalized solid fuel with ignition delay time in the range of 1 to 8 ms.**

2. Development of metallic solid hypergolic fuel

Early work in developing hypergolic solid fuels includes work from Desain et al., who developed fuel with LiAlH4 using paraffin wax as a binder and nitric acid as an oxidizer, which could not exhibit a sustainable and stable ignition.[14] Santos et al. highlighted the application of Sodium borohydride as a fuel additive[15] while Rang et al. experimented the hypergolicity of hydrogen peroxide with many fuels.[4] Jeong et al. Experimented with Hypergolic fuel derived from ammonia borane (AB). Davis et al. experimented with the hypergolicity of Tri-ethylaluminium with N_2O.[16] Most of these hypergolic solid fuels (HSF) consist of hazardous metal additives that cause harm to the environment. Hence, there is a need to develop a green propellant that doesn't poison nature. This research bridges the gap by formulating a green, environment-friendly solid hypergolic propellant. Sahul and Ramakrishna developed a hypergolic aluminized fuel (HAF) offering a sustainable ignition and low ignition delay time of 8.7 to 3.2ms.[1] Motivation in this research is to develop a green environment friendly solid hypergolic with IDT comparable to that of NTO UDMH hypergol and HAF.[1] The fuel consists of Paraffin wax, magnesium powder and sodium borohydride. Chemistry of exothermic reaction goes as follows:-

Sodium Borohydride shows exothermic redox reaction with hydrogen peroxide where hydrogen peroxide acts as oxidizer and sodium borohydride acts as reductant forming Di-sodium metaborate and water. Addition of magnesium to this fuel increases the exothermicity of the reaction as magnesium reacts with hydrogen peroxide exothermically to form MgO and H_2O. Mg Also reacts with water formed as a residual product of $NaBH_4$ - H_2O_2 reaction to form $Mg(OH)_2$ and releases hydrogen gas. Due to elevated temperatures, water disassociates releasing energy. Paraffin was is added as a binder to the system which being a hydrocarbon undergoes combustion with oxygen released from dissociation of hydrogen peroxide and residual oxygen formed as a reaction between Mg and H_2O_2 to release CO_2 and H_2O_2.

Ignition delay time of the solid fuel has been estimated through experiments by keeping the sodium borohydride concentration as fixed at 10% and by varying Mg and paraffin content in the fuel.

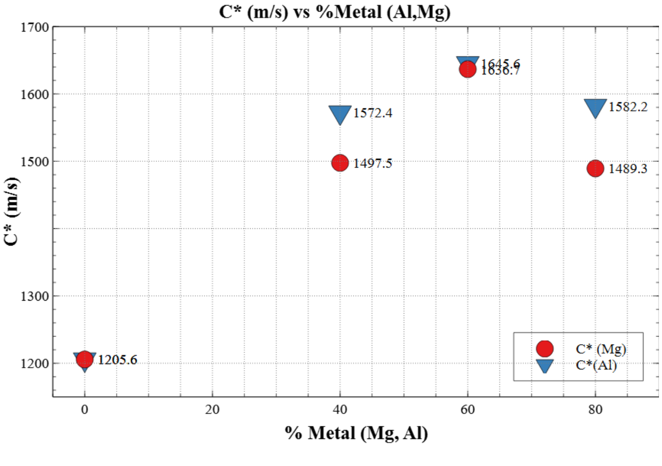

Figure 1: Comparing Characteristic Velocities of HSF used in this research and HAF[1] (NASA CEA)

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3. Experimental Section

3.1 Materials

Magnesium powder, Sodium borohydride from merck sigma aldrich and paraffin was Mahatha Petroleum Pvt. Ltd were selected as fuel ingredients for HSF. In this investigation, Sodium borohydride had a critical role by introducing hypergolicity upon contact with oxidizer. Paraffin acts like a binder and Magnesium enhance the hypergolicity of the reaction decreasing the IDT.

Hypergolicity of this fuel was studied with 90wt% rocket grade hydrogen peroxide obtained from Vikram Sarabhai Space Centre, Thiruvananthapuram. Thermophysical properties of the fuel can be observed in table 3.

Description	**Reductant** Sodium borohydride	**Additive** Magnesium	**Binder** Paraffin wax
Chemical Formulae	$NaBH_4$	Mg	$C_{26}H_{54}$
Density (kg/m^3)	1070	1738	900
Enthalpy of formation (kJ/mol)	-191.8	0	-587.6
Physical state	Powder	Powder	Pellets

Table 3: Properties of the reductant, additive and binder materials

3.2 Experimental Setup

A Drop test apparatus was used to estimate the ignition delay time of the hypergolic reaction where solid fuel was kept on a test plate and hydrogen peroxide droplet was dropped with the help of a dropper as shown in Figure 2. As the droplet falls on the surface of the fuel, it spontaneously ignites. There was a delay from the time when H_2O_2 touches the fuel surface to the observation of first visible flame. A high speed camera was used to capture the phenomenon. The experimental setup consists of:- a solid fuel with 10% $NaBH_4$ (this concentration was fixed in all fuel configurations), Mg (0%, 40%, 60% and 80%) and the remaining being paraffin wax, 90% concentrated rocket grade hydrogen peroxide, a dropper to drop the droplets of oxidizer onto the fuel surface, a stand to hold the dropper, photron high speed camera to capture the combustion phenomenon which was used to calculate ignition delay time, data acquisition software (photron), a fan to prevent high speed camera from overheating, thermal and electrical safety equipments to conduct experiment safely.

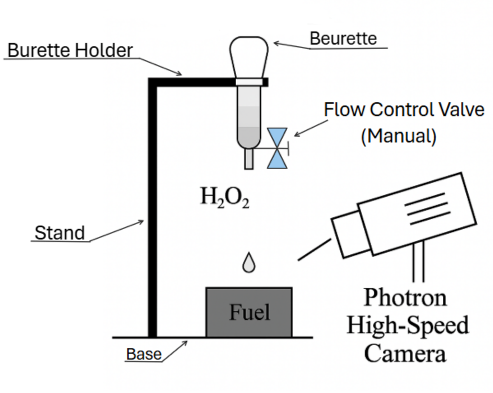

Figure 2: Schematics of Experimental Setup

3.3 Fuel Preparation

There are 2 methods for fuel preparation viz molding method and pressing method.[4] Fuel prepared using molding method exhibits poor ignition performance or no ignition[4] and hence pressing method was opted for casting fuel for this study.

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Fuel Casting Procedure:- Fuel was prepared using pressing method.[4] Oil bath was utilized to maintain constant temperature of 85 deg c which is slightly over melting point of paraffin wax and an additional thermocouple was inserted in the oil surface as a backup for temperature measurement. aluminium vessel was kept in oil bath until temperature of vessel equilibrates with oil bath temperature. As temperature of Al vessel reached 85 deg c, paraffin wax crystals were scattered in the vessel and allowed to melt. Once the wax melted, Reductant i.e sodium borohydride was added to the vessel and stirred gently to make a uniform mixture. As the mixture became uniform, Magnesium powder was slowly poured into the mixture stirring it continuously. After adding Magnesium, the composition was stirred continuously till the mixture appears uniform. The fuel mixture was taken to the Temperature and humidity control room where temperature was maintained at $24°c$ and relative humidity was maintained at 40-45%. Custom design and fabricated cylindrical mold of diameter 1.3cm and length 3cm was used to cast fuel by applying a maximum pressure of 10 bar to avoid shear loads while ensuring good mechanical properties in the resulting fuel. Fuel was stored in dessicators under vacuum condition to avoid degradation of the fuel. table 4 reflects the different composition of HSF used for this research study.

Fuel	**$NaBH_4$ (%)**	**Mg (%)**	**Paraffin wax (%)**
HSF(1)	10	0	90
HSF(2)	10	40	50
HSF(3)	10	60	30
HSF(4)	10	80	10

Table 4: Composition of different HSF blends with magnesium additive

3.4 Experimental Procedure

Experiments were conducted at the Rockets and Missiles lab, Indian Institute of Technology Madras which is a dedicated facility for the research on rocket propulsion ensuring safety as a major priority. Fuel once cured was dimensioned to length of 1-2cm and is attached to the base of drop test stand with the aid of epoxy hardener (5 min for hardening) which restricts the movement of fuel during drop test. Concentrated Hydrogen peroxide (90 wt%) was filled in the burette and the burette was aligned such that the bottom most tip of the burette being at a distance of 1 foot or 12 inches from the exposed surface of the fuel. A constant height of 1 foot was maintained during all drop tests. High speed camera was aligned at a distance of 3 feet from the fuel surface to ensure safety of camera from hot gases and flame produced during the experiment. A resolution of 3600 fps have been used for high speed imaging for these experiments. Data acquisition was conducted using photron software by connecting camera to the device with the software. A fan was used to cool down the camera during operation during operation due to operational temperature limit of camera. Author used thermally insulated apron, arm cover, helmet and leather shoes to ensure safety during operation. Manual valve was opened and before first drop falls over the fresh fuel surface, high speed camera was triggered to record the phenomenon and ignition delay times were calculated using these images. Experiments were repeated multiple times with different samples of same composition to ensure repeatability of the reaction and mean IDT along with standard deviation from all experiments have been presented in the result section of this research. Experiments were repeated with HSF 2, HSF 3 and HSF 4 and result trend have been validated from the NASA CEA outputs.

4. Results and Discussion

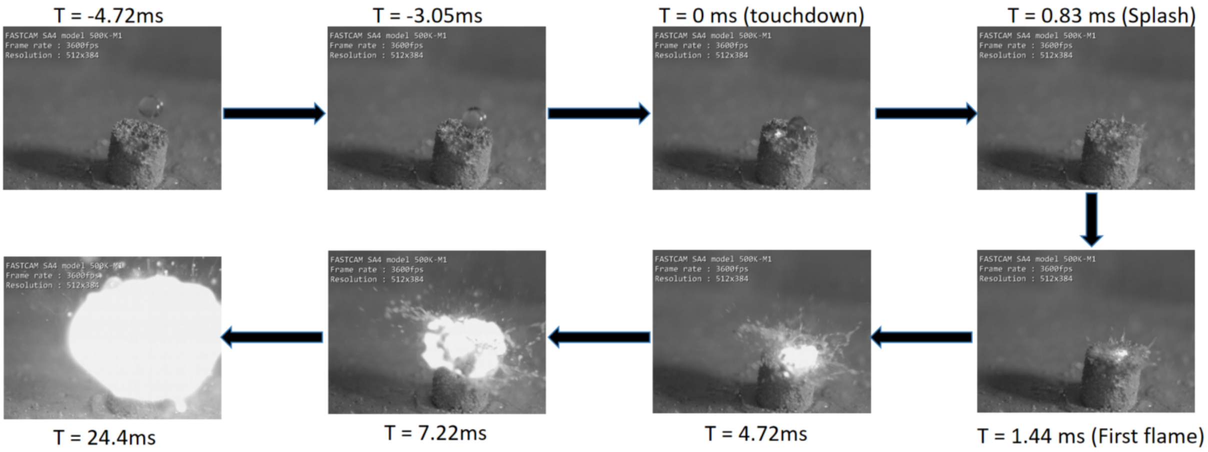

Figure 3: High speed camera captures for 60% Mg fuel

Fuel	IDT mean (ms)	IDT standard deviation (ms)
HSF 1	8.7	0.74
HSF 2	2.5	0.99
HSF 3	1.44	0.37
HSF 4	2.3	0.45

Table 5: Ignition Delay Times (IDT) for different HSF fuels

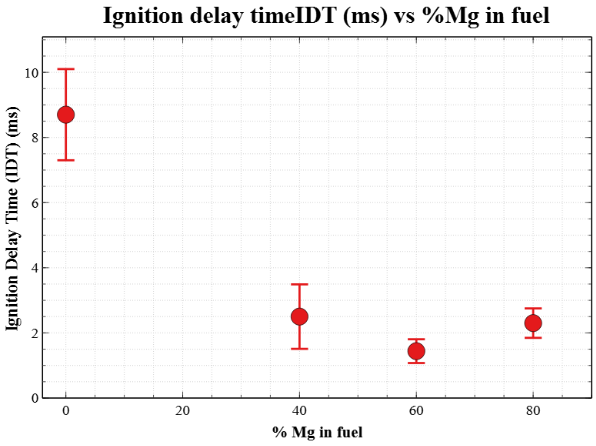

Figure 4: Ignition Delay Time (IDT) vs %Mg fuel

This section provides a detailed data analysis of the ignition delay time (IDT) measured using photron high speed camera of 4 different fuel compositions used in this research viz. HSF1 to HSF4. Each composition of fuel has same concentration of sodium borohydride and the concentration of Mg/paraffin is varied across different fuel composition. All fuel surfaces are sanded before experiment

4.1 Ignition Delay Time (IDT) of HSF3 And Sequence of Events

HSF 3 consists of 60wt% Mg, 10wt%$NaBH_4$ and 30wt% paraffin wax. Result can be seen in Table 5 and figure 4. HSF3 resulted in a minimum ignition delay time from experiments and provided highest characteristic velocity in

NASA CEA output (Figure 1). HSF 3 resulted in an ignition delay time of 1.44ms. At t = -4.72ms, hydrogen peroxide droplet is visible in the frame. The time at which hydrogen peroxide droplet touches the fuel surface is labelled as t = 0. At t = 0.83ms, a splashdown is observed in the image (4). splashdown time is the time after touchdown of the oxidizer on the fuel in which there is no reaction and the droplet is splashed across the cross section of the fuel. Liquid phase reaction begins post t = 0.83ms and is followed by the visibility of the first flame at t = 1.44ms. The flame was accompanied by an explosive sound and developed over time till 24.4ms and started to diminish post 24.4ms.
After the flame is extinct, the surface becomes eroded due to the highly exothermic and aggressive chemical reactions.

4.2 Comparison of IDT Values Across HSF Compositions

Figure 4 depicts the average IDT and standard deviation over mean IDT for all 4 compositions. 4 drop tests were conducted with each fuel composition and average IDT along wih standard deviation were extracted through the experiments. Drop test of HSF1 resulted in IDT from 7.96ms to 9.44ms with standard deviation of 0.74ms, HSF2 resulted in IDT from 1.51ms to 3.49ms with standard deviation of 0.99ms, HSF3 resulted in IDT from 1.07ms to 1.81ms with standard deviation of 0.37ms, HSF4 resulted in IDT from 1.85ms to 2.75ms with standard deviation of 0.45ms. Highest IDT in HSF1 is due to large binder content masking the reductant exposed to the oxidizer. HSF2 has lower IDT in comparison to HSF1 and HSF3 in comparison to HSF1 AND HSF2 due to decrease in binder content decreasing the masking of reductant. This gives us a good point to optimise binder content and increase metal content, however there is a limit to decrease binder content as seen from experiments that reducing binder content and increasing metal content over a particular limit increases IDT as seen in Table 5 and Fig 4.

4.3 Impact of High Metal Loading In The IDT Of The Reaction

At low to moderate concentrations, magnesium serves as a highly reactive metallic additive that significantly lowers ignition delay time. This reduction occurs primarily because magnesium accelerates the decomposition of hydrogen peroxide into reactive radical species such as OH and O, thereby promoting rapid combustion. Additionally, the presence of magnesium increases local flame temperatures and improves the overall reactivity of the fuel oxidizer mixture through enhanced gas-phase ignition characteristics. These effects collectively contribute to a sharp reduction in IDT as magnesium is initially added to the fuel mixture.

However, as the magnesium content is increased beyond an optimal threshold, a reversal in this trend is observed, and the IDT begins to increase. This increase is attributed to several limiting physical and chemical phenomena. One of the most prominent issues is agglomeration, where fine magnesium particles cluster together to form larger masses. These agglomerates have reduced surface area available for reaction, thereby diminishing their effectiveness. Another contributing factor is the formation of oxide or hydroxide layers on the surface of magnesium particles, especially in the presence of moisture or hydrogen peroxide. These layers act as passivation barriers that hinder ignition. Together, these factors explain the increase in IDT beyond a critical magnesium concentration.

5. Conclusion

This investigation successfully developed and characterized a solid hypergolic fuel formulation comprising sodium borohydride and varying concentrations of paraffin wax and magnesium. Key conclusions from the research work are:- Ignition delay time decreased significantly with increasing magnesium concentration, reaching a minimum at 60% Mg by weight. Further increase beyond 60% resulted in increased ignition delay times, indicating an optimal range for magnesium addition. NASA CEA predictions for characteristic velocity supported experimental trends thus highlighting the consistency between theoretical performance and practical ignition behavior. The formation of MgO as a combustion product at higher magnesium loadings contributed to reduced exothermicity and ignition reactivity. This, along with particle agglomeration and passivation effects, led to an increase in ignition delay time beyond a certain Mg concentration, indicating that the optimal magnesium content lies below this critical threshold for practical operation. Overall, This study demonstrated that controlled addition of magnesium to solid hypergolic fuel compositions can improve ignition performance with rocket-grade hydrogen peroxide, making it a viable candidate for satellite attitude control systems (ACS) and other propulsion applications requiring reliable, fast-response hypergolic ignition.

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