Research paper

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Basic properties of hydroxyl ammonium nitrate (HAN) based monopropellant for thrusters

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Abstract

Basic properties such as toxicity, thermal decomposition temperature, burning rate, and detonability for hydroxyl ammonium nitrate (HAN)/ ammonium nitrate (AN)/ methanol/water mixture solutions are discussed in the paper based on experimental data and qualitative evaluation. From toxicity evaluation, it is expected that HAN based monopropellants have potential as a “Green” propellants, which means we can treat them without self-contained atmospheric protective ensemble (SCAPE) suits. Thermal decomposition temperatures of HAN/AN/methanol/water mixture solutions with various mixture ratios have also been evaluated. Burning rate measurements of combustion waves under pressurized conditions have been taken for many HAN/AN/methanol/water mixture propellants in order to understand the burning rate and process. Then, the contribution of each component of the mixture has become clear. Finally, we found that stoichiometric solution (SHP163) has a low burning rate over a wide range of pressures. From the large scale gap test (LSGT), we found that SHP163 has low sensitivity compared to other high energetic materials.

Keywords : hydroxyl ammonium nitrate, basic properties, thermal decomposition temperature, burning rate, large scale gap test

1. Introduction

Propellant loading onto the reaction control system and the propulsion system for launch vehicles or satellites is one of the more hazardous operations on a launch site because propellants such as hydrazine are toxic. That is why operators must wear SCAPE suits during loading operation. To make this loading operation safer and provide a more efficient propulsion system for launch vehicles and satellites, much research has been conducted about “green propellant” to find alternatives to hydrazine[1)-12)]. There are many kinds of energetic materials having been researched for space propulsion systems ; glycidyl azide polymer (GAP)[13),14)], HAN and ammonium dinitramide (ADN) based mixture solutions. In these energetic materials, Japan Aerospace Exploration Agency (JAXA) has been carrying out research and development for green monopropellant composition : HAN and AN mixture solutions[3)-11)]. They have lower toxicity than hydrazine, and are considered “green propellant”. Therefore, it will not be necessary to wear SCAPE suits. Furthermore, it has approximately 10-20% higher specific impulse, 1.4 times higher density, a lower freezing point, and lower toxicity than hydrazine. From these advantages, a HAN based solution could be an alternative to hydrazine. On the other hand, the burning rate of pure HAN solution is too high to control. So it is important to use it as a mixture with other materials in order to suppress its reactivity. In past studies, combustion characteristics and its mechanism had been studied for some HAN/AN/methanol/water mixture solutions[3)−4)], however, data is not sufficient for controlling and evaluating its safety in practical use. Therefore, we investigated the basic properties of HAN/AN/methanol/water mixture solutions in order to evaluate safety and to find a high performance composition.

2. Experimental and evaluation method

2.1 Risk assessment with respect to toxicity

A qualitative risk assessment has been carried out for green propellant candidates (HAN/AN/methanol/water, HAN/Hydroxyethylhydraziniumnitrate (HEHN)/water, ADN/methanol/ammonia (NH_3)/water) and high purity hydrazine on the basis of a control banding method modified by Japan Industrial Safety & Health Association (JISHA). This assessment was conducted in order to compare the risk level of propellant loading operations to that of hydrazine. The JISHA method[15)] uses control banding method which is basically the same as the controls of substances hazardous to health (COSHH) essentials[16)], except for the introduction of stricter and more quantitative criteria for control banding than those of the COSHH essentials. The COSHH essentials provide advice on controlling the use of chemicals for a range of common tasks[17)]. In the control banding method, risk level is derived from hazard level (HL) and estimated exposure limit (EEL). HL and EEL are ranked considering occupational exposure limit and estimated exposure level respectively[15)]. In the JISHA method, HL is extended to lower concentration level and EEL has more levels by distinguishing local exhaust ventilation type (covered type or uncovered type) compared to COSHH essentials. As a result, the range of HL is from 1 to 5, EEL is from 1 to 7 and risk level is from I to IV (smaller value means safer). This assessment was conducted under conditions where the concentration of the leaked gas or the liquid in the atmosphere are controlled by the local exhaust ventilation system, mixtures with weight percentages of each component are HAN/AN/methanol/water : 57-83/0-12/2-24/balanced, HAN/HEHN/water : 44.5/11/44.5, ADN/methanol/NH_3/water : 60-65/15-30/0-6/balanced and high purity hydrazine.

2.2 Thermal decomposition temperature

To understand the thermal decomposition temperature is important because the heat release from decomposition of HAN is one of the factors to start and sustain its combustion. Thermal decomposition temperatures have been measured for five kinds of HAN/AN/ methanol/water mixtures for SHP163 (Stoichiometric solution of fuel and oxidizer which contains 16.3% weight percent methanol, which is produced by Hosoya Pyro-Engineering Co., Ltd.), H1A3, M2, M3 and M4 in Table 1. The apparatus of thermal decomposition temperature is shown in Figure 1. The sample cell is made of stainless steel and the sample volume is 60 μL. The chamber is filled with nitrogen gas at ambient pressure, 0.6 and 1.0 MPaA. The sample is heated at the rate of 5 degrees Celsius per minute. The thermal decomposition temperature defined in this paper is the temperature at which measured sample cell temperature and chamber pressure increase suddenly because of the exothermal decomposition of sample.

2.3 Burning rate

The measurements of the burning rates of HAN liquid solutions were conducted in a strand burner system for several kinds of HAN/AN/methanol/water mixtures as

Table 1 HAN/AN/Methanol/Water mixtures for burning rate measurement.

Mixture	Weight ratio[−]				Weight percent[%]				Molar ratio	
Name	HAN	AN	Methanol	Water	HAN	AN	Methanol	Water	HNO_3/HAN	Reference
SHP163	95	5	21	8	73.6	3.9	16.3	6.2	1.06	
A2	95	30	21	8	61.7	19.5	13.6	5.2	1.38	
H1A3	60	40	21	8	46.5	31.0	16.3	6.2	1.80	
M0	95	5	0	8	88.0	4.6	0.0	7.4	1.06	ref. 7)
M1	95	5	7	8	82.6	4.3	6.1	7.0	1.06	
M2	95	5	9	8	81.2	4.3	7.7	6.8	1.06	ref. 7)
M3	95	5	29	8	69.3	3.6	21.2	5.8	1.06	ref. 7)
M4	95	5	50	8	60.1	3.2	31.6	5.1	1.06	ref. 7)
A0M4	95	0	50	8	62.1	0.0	32.7	5.2	1.00	
A1M4	95	10	50	8	58.3	6.1	30.7	4.9	1.13	
W1	95	5	20	2	77.9	4.1	16.4	1.6	1.06	
W2	95	5	24	24	64.2	3.4	16.2	16.2	1.06	ref. 7)
W3	95	5	27	39	57.2	3.0	16.3	23.5	1.06	ref. 7)
A0W3	95	0	27	39	59.0	0.0	16.8	24.2	1.00	
A1W3	95	10	27	39	55.6	5.8	15.8	22.8	1.13	

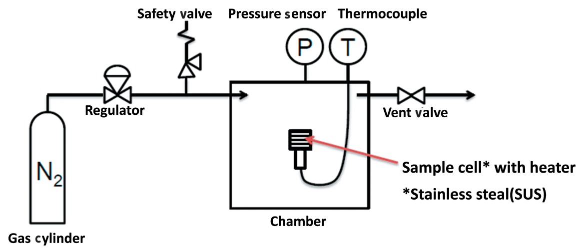

Figure 1 Test apparatus of thermal decomposition temperature measurement.

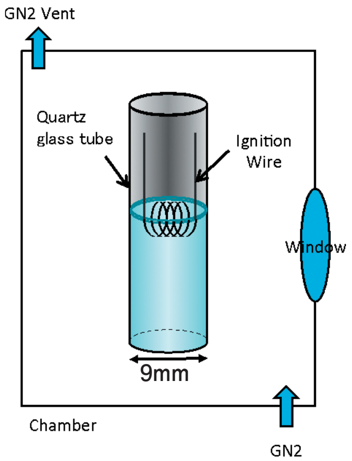

Figure 2 Burning rate measurement apparatus.

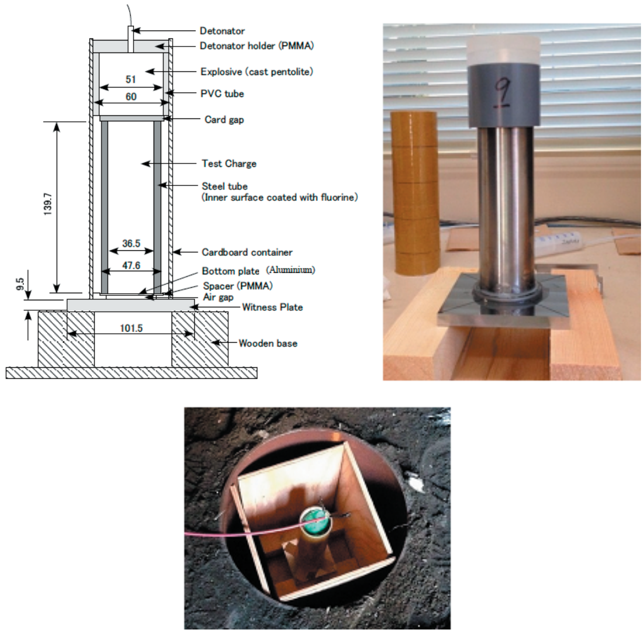

Figure 3 Apparatus of LSGT and pictures of test setup.

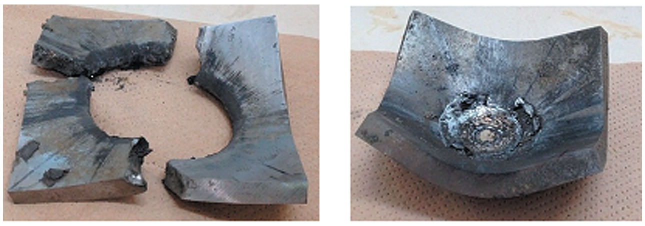

Figure 4 Conditions of witness plate after the test. (Positive result : left, Negative result : right)

shown in Table 1. The apparatus of burning rate measurement is shown in Figure 2. All samples were tested at constant pressure from 1 to 9 MPaA. The Inner diameter of the quartz glass tube is 9 mm. The sample volume is approximately 4 cc and it's initial temperature is room temperature. The power to ignite the monopropellant was heat released from nichrome wire, and the burning process was observed by a high-speed camera at 500 frames per second. The burning rate is calculated by moving images taken with the camera through the window.

2.4 Shock initiation sensitivity

The LSGT test was conducted by reference to MIL-STD-1751A Method 1041 (NOL)[18] in order to evaluate the sensitivity of the propellant for the safety of transportation. Figures 3 and 4 show the apparatus of the test. #8 or #6 blasting cap (detonator) and 50/50 casted pentolite with the density 1.60 ± 0.05 g·cm^{-3} is used for donor charge (explosive). The material used for the steel tube is STKM13A (SAE1018). Polymethylmethacrylate (PMMA) is used for cards. The witness plate is made of mild steel S25C (SAE1025) with the dimension 0.95 cm (thickness) $\times$ 10.15 cm $\times$ 10.15 cm. A witness plate at the base of the test charge provides an indication of whether or not the test charge detonates in each trial. From a series of trials, the card gap thickness that permits 50% of the test charge samples to detonate is estimated[5]. The density for "casted" 50/50 pentolite used in this test is approximately 1.64 g·cm^{-3}, that is larger than that of "pressed" pentolite which is defined in MIL-STD-1751A (1.56 ± 0.01 g·cm^{-3}). For casted pentolite, the density differs from 1.55 to 1.65 g·cm^{-3}, and for pressed pentolite it differs from 1.55 to 1.57 g·cm^{-3}. In order to know the effect of the density, the initial pressure at the end of the "casted" pentolite was calculated by KHT2009 : Analytical program for concentrated high energy materials[19] at the density of donor charge (explosive) 1.55 g·cm^{-3} and 1.64 g·cm^{-3}.

3. Results and discussions

3.1 Risk assessment with respect to toxicity

The result of qualitative risk assessment is shown in Table 2. In the table, level I is defined as "trivial risk", level II is "acceptable risk", level III is "middle risk" and level IV is "large risk". Under preconditions in chapter 2.1, HL and EEL for mixtures No.1~3 in Table 1 are evaluated as HL 1

Table 2 The result of qualitative risk assessment.

	No.1 HAN/AN/Methanol/Water	No.2 HAN/HEHN/Water	No.3 ADN/Methanol/NH_3/Water	No.4 Hydrazine
Minimum OEL content	AN	HEHN	ADN	N_2H_4
Risk level	I	I	I	IV

and EEL 3~4, and for No.4 HL is 5 and EEL is 4~5. As a result, we obtained risk level I for three green propellant candidates (No.1~3 in Table 1). The risk level of hydrazine was evaluated as a reference and it is level IV (large risk). From qualitative evaluation, it became clear that the risk level of HAN/AN/Methanol/Water mixture is same as HAN/HEHN/Water and ADN/Methanol/NH_3/Water. ADN/Methanol/NH_3/Water also are expected no-SCAPE suits operation[12]. Therefore, we can expect no-SCAPE suits operation for HAN/AN/Methanol/Water and HAN/HEHN/Water mixtures. However, the necessity of protective suits or other protective gear depends on regulations which every operator defines. So, in this paper, we only mention the result of risk level.

3.2 Thermal decomposition temperature

The result of thermal decomposition temperature measurements for five kinds of propellant mixtures are shown in Figure 5. Thermal decomposition temperature of tested mixture is approximately no less than 130°C in atmospheric condition in this test condition and it decreases as pressure increases. This tendency that pressure increase causes thermal decomposition temperature decrease is assumed to be from the change of thermal balance or chemical reaction caused by suppressed vaporization of solvent because of the pressure increase as mentioned in reference[9]. H1A3 has the lowest thermal decomposition temperature at each pressure and the minimum thermal decomposition temperature we obtained in this study is around 110°C for H1A3 mixture solution. From this result, we found that the increase of AN with decrease of HAN contributes to a decrease in the thermal decomposition temperature for HAN/AN/methanol/water solution. It was reported that the existence of high concentration ionic iron and increased the molarity ratio of HNO_3/HAN or the molarity of HNO_3 decrease decomposition temperature of HAN mixture solutions and the threshold of decomposition temperature is expressed by the Instability Index[20]. HNO_3 comes from HAN and AN, and the molarity of HNO_3 is near among SHP163, M2, M3 and M4 but H1A3 has higher molar ratio HNO_3/HAN value than others (Table 1). Furthermore, the decomposition temperature tends to decrease as ambient pressure increase. Therefore, we assume that one of the possible factors for the decrease of decomposition temperature in this experiment comes from the increase of the Instability Index cased by the increase of the molar ratio HNO_3/HAN, and another possible factor is high ambient pressure increase. However, further study is necessary for determining its mechanism. Finally, we suggest having an adequate margin toward thermal decomposition temperatures considering surrounding conditions when we treat HAN/AN/Methanol /Water propellant.

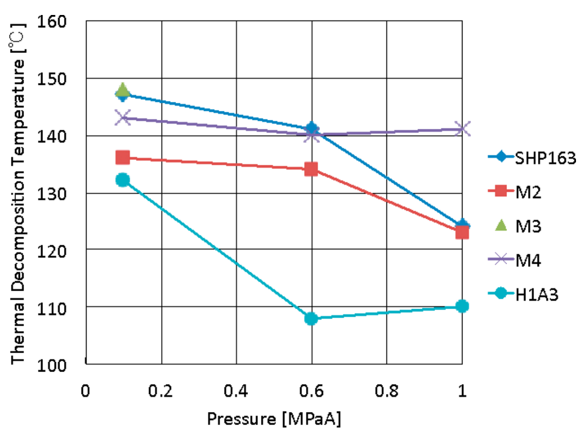

Figure 5 The result of thermal decomposition temperature.

3.3 Burning rate

In this study, the burning rate measurement has been done for HAN/AN/ methanol/water mixtures in Table 1 in order to evaluate the effect of each component to burning rate. Some of the results in Table 1 are from reference[7]. The burning rate of SHP163 shows almost the same value as reported in reference[10]. The effect of AN can be discussed from Figures 6, 7, and 8. From Figure 6, it was found that the burning rate increased over wide range of pressures compared to SHP163 as AN increase and HAN decrease. The effect of methanol is shown in Figure 7 by the comparison among SHP163, M0, M1, M2, M3 and M4. It became clear that SHP163 have relatively low burning rate over wide range of pressures, which means the optimal methanol quantity achieves a low burning rate over wide range of pressures for HAN/AN/methanol/water mixtures[7]. The effect of water is shown

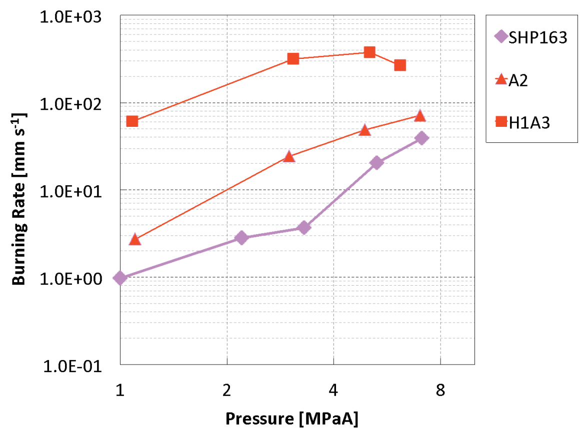

Figure 6 The effect of HAN and AN on burning rate.

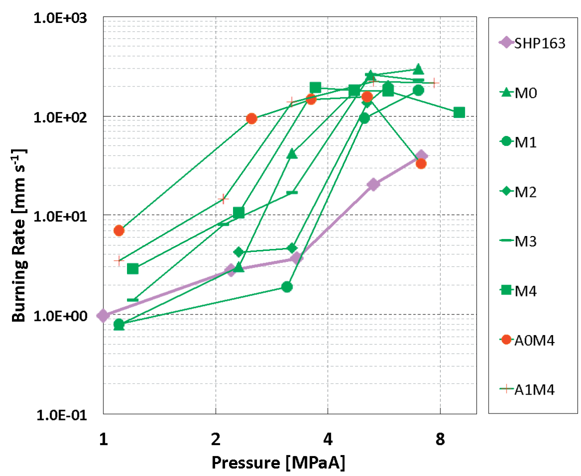

Figure 7 The effect of methanol on burning rate.

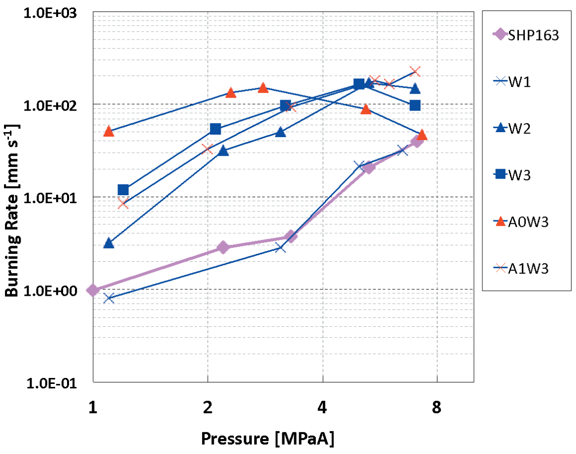

Figure 8 The effect of water on burning rate.

in Figure 8 by the comparison among SHP163, W1, W2, and W3. As the water increased compared to SHP163 the burning rate became higher over a wide range of pressures[7]. Katsumi et al. reported about HAN/AN/methanol/water mixture solutions that the intense boiling of water owing to the rapid bubble formation by superheat is responsible for the high burning rate[10]. Water itself does not included in chemical reaction process, therefore, the burning rate increase when water quantity increase is assumed to be related to superheat mechanism. They also mentioned that methanol reduces the burning rate by decreasing evaporation rate and the hydrodynamic instability is the trigger to jump into the extremely high burning rate region[11]. We confirmed same tendency even for higher methanol concentration mixtures (M3 and M4 in Figure 7) than those of reference 11). Another mechanism that affects to the burning rate is potential chemical reaction rate of propellants. The burning rate of propellants increase when the chemical reaction rate increase, on the other hand, it decrease when the chemical reaction rate decrease. Here, we refer the Instability Indexagain to explain the effect of AN to the burning rate. D. G. Harlow et al. introduced the Instability Index to estimate the decomposition temperature of HAN mixture[20]. It is expressed by the molarity of HNO_3, the molar ratio of HNO_3 and HAN (HNO_3/HAN) and the molarity of ionic iron. The molarity of HNO_3 and the molar ratio HNO_3/HAN plays important role in chemical reaction process of HAN. The molarity of HNO_3 is near among SHP163, A2 and H1A3, and the molar ratio HNO_3/HAN are 1.06, 1.38 and 1.80 respectively. Therefore, the molar ratio HNO_3/HAN governs the Instability Index. When we see Figure 6, the order of burning rate in this pressure region is same as the order of the molar ratio HNO_3/HAN. From the evaluation above, we expect the possibility that the AN affects the chemical reaction rate of HAN, and the Instability Index will help us to explain not only for the decomposition temperature but also for the burning rate. However, the burning rate shows more complex preface when AN is eliminated as in A0M4 in Figure 7 and A0M3 in Figure 8 ; that is, the higher values in low pressure region and lower values in high pressure region compared to those of Figure 6. The burning rate is affected by many other factors such as ratio of contents, pressure, temperature and the instability at boundary face conditions[10], and so on. Therefore, further study is necessary for predicting the burning rate, or obtaining a lower burning rate mixture. Finally, from the comparison of burning rate among all mixtures in Table 1, we found that the burning rate of SHP163 and W1 stays comparatively low over wide range of pressures as shown in Figure 6, 7, and 8. If the ratio among each component changes, physical and chemical properties of mixture solution changes, therefore, we found so far that keeping its ratio near to SHP163 or W1 is preferable in order to keep burning rate low from physical and chemical point of view.

3.4 Shock initiation sensitivity

Table 3 shows the LSGT result for SHP163. #6 blasting cap was used for the first test in the case of number of card 23, 47 and 69, and #8 blasting cap was used from the second test. From this result, the 50% point number of cards for SHP163 is assumed to be between 9 to 11[6] (1 card = 0.01 inch = 0.25 mm). From the calculation by KHT 2009, the pressure at the end of pentolite (explosive in Figure 2) is 20.4 GPa for density 1.55 $g{\cdot}cm^{-3}$, and 23.2 GPa for 1.64 $g{\cdot}cm^{-3}$. The difference of the pressure at the end of pentolite between the density of pentolite 1.55 $g{\cdot}cm^{-3}$ and 1.64 $g{\cdot}cm^{-3}$ is approximately 2.8 GPa. From the calibration data in MIL-STD-1751A Method 1041 (NOL) and results of calculation by KHT2009 we can get the relation between density and 50% number of cards. By using this relation, the difference of initial pressure 2.8 GPa corresponds to the difference in number of cards, approximately 2 cards. This amount of the number of cards should be considered when we compare the result of this study to that of MIL-STD-1751A Method 1041 (NOL) data. The 50 % point number of Composition C-4 is 192, Pentolite 50/50 (Cast) is 301, RDX is 323, TNT (Cast) is from 108 to 198[18]and LMP-103S which is ADN based green propellant[12] is from 18 to 55[5]. Therefore, we found that the sensitivity of SHP163 is relatively low compared to results of LSGT of other high energetic materials and LMP-103S.

4. Conclusion

From risk assessment with respect to toxicity, we can expect no-SCAPE suits operation for HAN/AN/methanol /water mixture, because it has the same risk level as ADN /methanol/NH_3/water, and ADN/methanol/NH_3/water mixture is expected to achieve no-SCAPE suits operation[12]. However, the necessity of protective suits, or other protective gear depends on regulations which every

Table 3 LSGT result for SHP163.

Number of Cards	0	11	23	47	69
Number of Positive result	2	1	–	–	–
Number of Negative result	–	2	3*	2*	2*

* #6 blasting cap is used for one test

Note 1 : Casted 50/50 Pentlite is used for this test

Note 2 : 1 card = 0.01 inch = 0.25 mm

operator defines. So, in this paper, we only mention the result of risk level. From thermal decomposition temperature measurement, we found that the increase of AN contributed to decrease in the thermal decomposition temperature for HAN/AN/methanol/water solution. Also, we suggest having an adequate margin toward thermal decomposition temperatures considering surrounding conditions when we treat HAN/AN/methanol /water propellant. From burning rate measurement, the effect of each component in HAN/AN/methanol/water mixture onto the burning rate became clear. Firstly, the burning rate increase over a wide range of pressures compared to SHP163 as AN increase and HAN decrease. Secondary, the optimal methanol quantity achieves low burning rate over a wide range of pressures. Thirdly, the burning rate became high over a wide range of pressures as the water increased compared to SHP163. Finally, from the comparison of burning rate among several mixtures, we found that the burning rate of SHP163 always stayed comparatively low over a wide range of pressures. From shock initiation sensitivity tests, we found that the sensitivity of SHP163 is low compared to the results of LSGT tests of other high energetic materials.

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