Research and Development on Thrusters with HAN (Hydroxyl Ammonium Nitrate) Based Monopropellant

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Abstract

This paper introduces HAN-based monopropellant research results performed in JAXA such as large scale card gap test, BAM (Bundesanstalt für Material-forschung und -prüfung: The Federal Institute for Materials Research and Testing) friction test, BAM fall hammer test, material compatibility test…etc. Test results showed that HAN/AN/Methanol solution is a hopeful candidate of green propellant from the viewpoint of safety and performance (Isp). Firing tests using 20 N class research thruster have been conducted to obtain design data of thruster and catalyst, and the effect of each design parameters have been evaluated.

1. Introduction

Propellant loading onto reaction control system (RCS) and propulsion system for launch vehicles or satellites is one of the hazardous operations on launch site because propellant like hydrazine is toxic. That is why operators must wear Self Contained Atmospheric Protective Ensemble (SCAPE) suits during loading operation. To improve loading operation safety and provide higher performance than hydrazine, several developing programs of "Green Propellant" are being conducted in the world [1,2]. JAXA also has been carrying out research and development about new monopropellant composition: HAN-based solution. It has lower toxicity than hydrazine, and is called as one of the "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, and lower freezing point and lower toxicity than hydrazine (Isp of hydrazine is approximately 220 s). From these advantages, HAN based solution could be an alternative to hydrazine. On the other hand, pure HAN solution is an explosive, so it is important to use it as a mixture with other materials in order to suppress its reactivity.

In Japan, HAN-based liquid propellant has been studied [3–5] because of its promising characteristics of lower toxicity and higher performance than hydrazine, and also because there is domestic HAN manufacturing technique. From the past researches, we have two propellant candidates that explosibility or detonability is suppressed by adding some kinds of solvent into HAN-based solution. One is HAN/AN/Methanol/H_2O mixed solution (which is called SHP) and another is HAN/HN (Hydrazine Nitrate)/TEAN (TriEthanol Ammonium Nitrate) /H_2O mixed solution. In this paper, we introduce the HAN mixture selection and thruster research status.

2. HAN-Based Monopropellant Mixture and Safety Evaluation

2.1 HAN Based Monopropellant Mixture

(1)Toxicity

LD_{50}rat (orally) of SHP163 (stoichiometric solution ratio for HAN, AN and methanol, which means the highest Isp) was measured in accordance with a OECD guideline (Guideline for Testing of Chemicals, Updating Guideline #420)[6]. Three numbers after “SHP” express the wt.% of methanol, for example SHP163 contains 16.3 wt.% methanol. Table 1 shows the result of LD_{50}rat (orally) measurement for SHP163 and its comparison to hydrazine. When GHS (Globally Harmonized System of Classification and Labelling of Chemicals) criteria for LD_{50} is applied to this result, SHP163 and ADN are categorized in category 4 (Harmful if swallowed) and hydrazine is in category 3 (Toxic if swallowed).

Table 1: LD_{50} of SHP163 and comparison with other monopropellants (ADN, Hydrazine) and NaCl

	LD_{50}rat (mg/kg)
SHP163	300 ~ 2000
ADN	832
Hydrazine	60
NaCl	3750

Ames test was carried out for HAN 46 % aqueous solution according to GLP (Good Laboratory Practice)[6]. Table 2 shows the result of Ames test for HAN 46 % aqueous solution, AN and methanol. AN and methanol are widely used, and some database such as IUCLID (International Uniform ChemicaL Information Database) or EHC (Environmental Health Criteria) show the results of Ames test for those substances as negative.

Table 2: Results of Ames test

HAN46% aqueous solution	Negative
AN	Negative
Methanol	Negative

(2)Detonability

Steel tube tests were conducted for evaluating potential detonability of HAN/AN/Methanol/H_2O mixed solutions [5]. Schematics of a test tube are shown in Fig.1. Detonability of the propellant was evaluated from the fragmented states of the tube. Detonability is classified into three categories “(a) No Detonation, (b) Partial Reaction, (c) Detonation” depending on fragmented states. Fig.2 shows the detonability map (ternary diagram) with respect to weight ratio of HAN/AN, methanol, H_2O. Isp (calculated) contour is also presented in the map. From this map, we can find that this solution have potential to be higher Isp than hydrazine (Isp of hydrazine is approximately 235s) even in No Detonation region because No Detonation region almost corresponds to Isp less than 260 s.

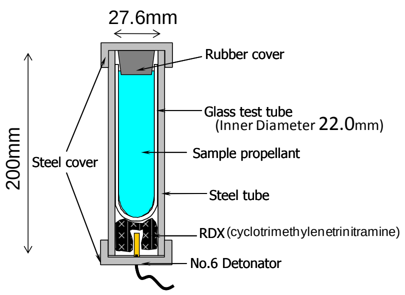

Fig. 1: Schematics of a test tube

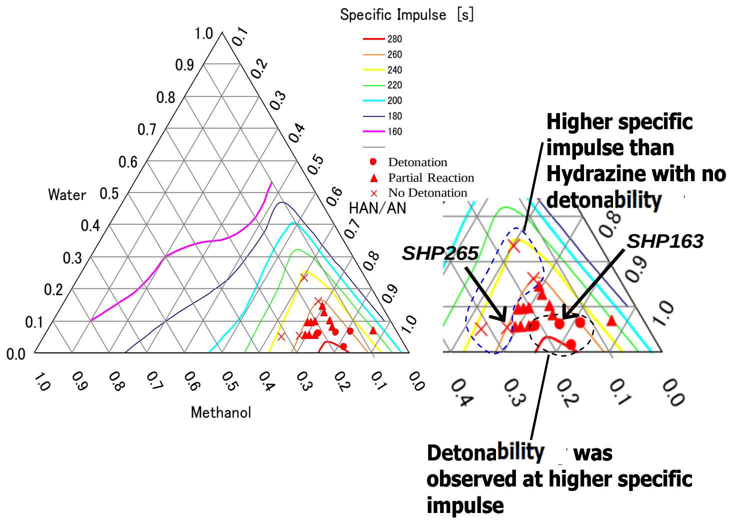

Fig. 2: Detonability map with respect to weight ratio of each solute and specific impulse contour

Critical diameter test was conducted to find the minimum diameter that can sustain a detonation in a tube.
Table 3 presents the result of these tests. From this table, we obtained that the critical diameter of SHP163 is between 10 mm to 27.6 mm and detonation is no longer created in tube with its inner diameter less than 6.7 mm with any weight percent of methanol in HAN/AN/Methanol/H_2O mixture.

Table 3: Result of Critical Diameter Test

Tube Inner Diameter [mm]	Weight Percent of Methanol in HAN/AN/Methanol/H2O mixture								
	31.6	26.5	25.0	23.9	22.3	21.2	16.3	12.2	6.1
27.6	×	×	▲	▲	▲	●	●	●	▲
10	-	×	-	-	-	▲	▲	▲	×
7.8	-		-	-	-	-	▲	-	-
6.7	-	×	-	-	-	-	×	-	×

× : No Detonation / ▲ : Partial Reaction / ● : Detonation

From the viewpoint of performance and toxicity potential trade-off, we consider HAN/AN/Methanol/H_2O mixed solution as a primary candidate for green propellant.

2.2 Safety Evaluation Testing

(1)UN Transportation Tests

Following tests were conducted for SHP163 according to United Nations Recommendations on the Transport of Dangerous Goods known as the “Orange Book”.
The BAMFallhammer Test is used to determine the sensitivity of a given solid and liquids to drop-weight impact.

Table 4: Results of BAM Fallhammer Test

Drop Height [cm]	Impact Energy [J]	Results of Test						Firing Rate (Probability of Ignition or Explosion)
		1	2	3	4	5	6	
5	2.5	×	-	-	-	-	-	0 / 1
10	4.9	×	-	-	-	-	-	0 / 1
15	7.4	×	-	-	-	-	-	0 / 1
30	14.7	×	-	-	-	-	-	0 / 1
40	19.6	×	×	×	×	×	×	0 / 6
50	24.5	×	×	×	×	×	×	0 / 6

× : No Ignition or Explosion / ● : Ignition or Explosion

The BAM Friction Test is used to determine friction sensitivity of explosives, propellants, pyrotechnics…etc. The obtained results indicate that SHP163 is insensitive at friction load at 353 [N] (> 80 [N]: safety criteria of this test).

Table 5: Results of BAM Friction Test

Load [N]	Results of Test						Firing Rate (Probability of Ignition or Explosion)
	1	2	3	4	5	6	
79	×	-	-	-	-	-	0 / 1
157	×	×	×	×	×	×	0 / 6
353	×	×	×	×	×	×	0 / 6

×: No Ignition or Explosion / ● : Ignition or Explosion

Thermal stability was examined at 75 degC with 48 h as time duration. Fig. 3 shows the test apparatus. No ignition or explosion was observed in this test.

Fig. 3: Apparatus of Thermal Stability Test

The small-scale burning test is used to determine the response of a substance to fire. Fig. 4 shows the apparatus and picture of this testing. Two tests for a 10 g of sample size and two tests for a 100 g of sample size were performed. No explosion was observed in these tests.

Fig. 4: Apparatus and Testing of Small-Scale Burning Test

From the above results [6], SHP163 is categorized as “PROVISIONALLY ACCEPT INTO CLASS1” so far. Further safety evaluations are being planned.

Large scale gap test (LSGT) was conducted by reference to MIL-STD-1751A Method 1041 (NOL). Fig.5 shows the apparatus of the test. Substance considered being Division 1.3 (low explosive) in Orange Book if sensitivity is less than 70 cards. #8 or #6 blasting cap is used for detonator and 50/50 pentolite (Cast) with the density 1.6 ± 0.05[g/cm^3] is used for booster. The material used for 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) × 10.15 cm × 10.15 cm. A witness plate at the base of the test charge provide an indication of whether or not the test charge detonates in each trial. From a series of trials, the thickness of card gap that permits 50 % of the test charge samples to detonate is estimated. Table 6 shows the results of this test. From this testing, the 50% point number of cards is varying from 0 to 11 (1 card = 0.01 inch = 0.25 mm).

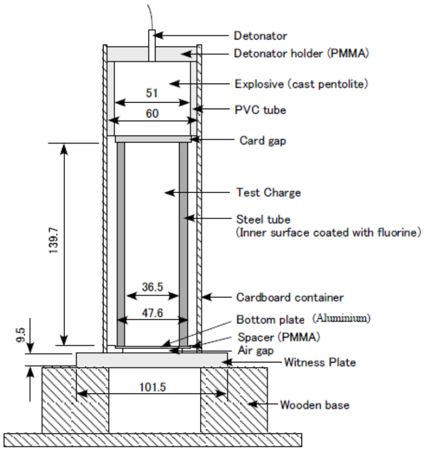

Fig. 5: Apparatus of LSGT

Fig. 6: Pictures of test setup

Fig. 7: Conditions of witness plate after the tests
(Positive result: left, Negative result: right)

Table 6: Result of the LSGT

Number of Cards	0	11	23	47	69
Number of Positive result (Detonation)	2	1	-	-	-
Number of Negative result (No Detonation)	-	2	3*	2*	2*

* #6 blasting cap is used for one test.

(2)Material Compatibility Test

Material compatibility tests were conducted with various materials [7]. Stainless Steels (SUS304/SUS316/SUS430), Titanium, Ti-6Al-4V, Teflon, EPDM, O-rings were soaked into SHP163 for 90 days. No big change of weight was observed, however, a minute amount of Fe ion elution from metals was observed. Therefore, more detail and long term compatibility tests will be necessary.

(3)Other Basic Property

Auto-ignition temperature under various conditions and mixtures are evaluated by TG-DTA (ThermoGravimetry-Differential Thermal Analysis) [8]. In this test, the effect of ions to auto-ignition temperature was examined. Fe, Al, Ni, Cr ion was doped into HAN solution respectively (max 30 ml/L doping) under 0 ～ 0.9 MPaG conditions and it is found that 95 degC is the minimum auto-ignition temperature in this test conditions.

3. Thruster Development Program

Firing tests using 20 N class research thruster have been conducted to obtain design data of thruster and catalyst development. Fig. 9 shows the basic concept of research thruster and Fig.10 shows the picture of the thruster in vacuum chamber. The catalyst bed is pre-heated before firing. In these tests, the effect of each design parameters such as catalyst initial temperature and propellant mass flow to thruster performance have been evaluated [6].

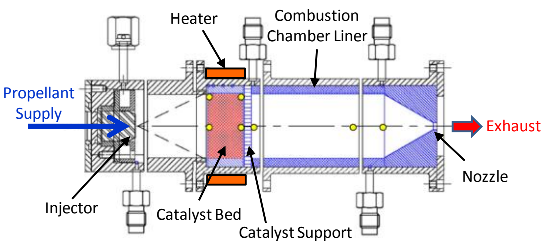

Fig. 9: Basic Concept of Research Thruster

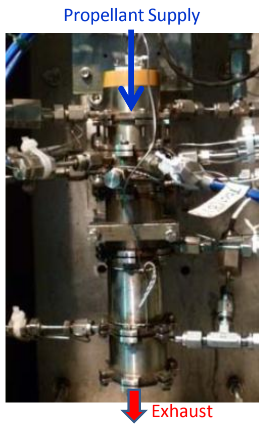

Fig. 10: Research Thruster in Vacuum Chamber

4. Conclusion

Several kinds of tests about HAN monopropellant have been conducted to ensure the safety. For example, LSGT was conducted for SHP163 and found that the 50% point number of cards is varying from 0 to 11 which means SHP163 considered being Division 1.3 (low explosive). Results from several kinds of tests shows that HAN/AN/Methanol solution is hopeful candidate of green propellant from the viewpoint of safety and performance (Isp). Thruster and catalyst development is also in progress in JAXA.

Acknowledgement

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