Short Communication

Propellants,
Explosives,
Pyrotechnics

Preparation of Fine Ammonium Perchlorate by Employing Dual-Sonic Premixer: Freeze-Drying Method

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Abstract: Ammonium perchlorate (AP)-based composite propellant is the most widely used solid propellant. Fine AP is required to obtain a propellant with a high burning rate. To prepare fine AP, an emulsion was prepared by emulsifying toluene and the AP solution. The emulsion was frozen rapidly with liquid nitrogen and then freeze-dried. Fine AP was prepared by this freeze-drying method. In this study, the emulsion was prepared with the premixer adopted dual-sonic technology and an attempt was made to prepare finer AP. By using a dual-sonic premixer, the emulsion was efficiently prepared, and therefore, a fine AP sample was obtained, compared with the homogenizer that is commonly used. It was found that the AP sample could be used as a propellant oxidizer according to its impact and thermal sensitivities.

1 Introduction

A high-burning-rate composite propellant is required to operate high-performance rocket motors. Ammonium perchlorate (AP)-based composite propellants are the most widely used composite propellants, and it is generally known that the burning rate of AP propellants increases with decreasing particle size of AP. Therefore, fine AP is required to obtain a high-burning-rate propellant. It is difficult to prepare fine AP particles safely by grinding because fine AP ignites and explodes easily due to impact and friction. Therefore, special equipment is required to safely manufacture fine AP samples. Several safe methods of preparing fine AP particles have been developed [1–8].

One such preparation method is the freeze-drying method described below [2]. The oil-in-water emulsion was prepared by emulsifying with 10 cm^3-toluene as the dispersed phase and 200 cm^3-aqueous AP solution as the dispersion medium for 8 min. The emulsion was frozen rapidly with liquid nitrogen, and the frozen emulsion was freeze-dried. The fine AP prepared by this freeze-drying method was designated as FDAP. The photograph of FDAP is shown in Figure 1. The surface-weighted mean diameter (D) of FDAP was approximately 3 μm. The preparation of emulsions is an important process in this method. The emulsions were prepared using an ultrasonic homogenizer (US-300T, NISSEI Corp.) in a previous study [2].

Since then, a new technique for the preparation of emulsions has been developed. If toluene could be effectively dispersed into the AP solution using the latest dispersion method, it is expected that finer AP particles would be prepared, compared to FDAP. Dual-sonic technology is an excellent technique for emulsion preparation and is a patented method [9]. A premixer (PR-1, THINKY Corp.) is a
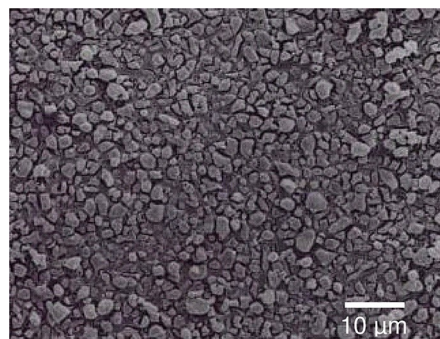

Figure 1. Photograph of FDAP.

homogenizer/mixer that adopts dual-sonic technology. Figure 2 shows the schematic diagram of PR-1. And Table 1 lists the main product specifications. An ultrasonic wave irradiates the sample in the container from the bottom and sides of the ultrasonic bath. In addition, this mixer is designed to rotate the container. Rotating the container at an angle of 45 degrees causes convection in the materials, and thus ultrasonic irradiates the entire sample.

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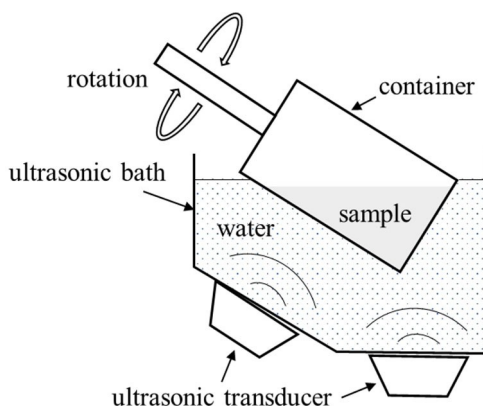*Kanagawa 239-8686, JAPAN*
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Figure 2. Schematic diagram of PR-1.

Table 1. Main product specifications of PR-1.

Dispersion method		Dual-sonic
Ultrasonic wave	Transducer output	70 W×2 transducers
	Modulation mode	Frequency-modulation
	Rotation speed	40 kHz
Rotation speed		Max. 600 rpm

2 Experimental Section

2.1 Preparation of AP

In a previous study [2], the emulsion was emulsified with 10 cm³-toluene and 200 cm³-aqueous AP solution for 8 min. In this study, the 13 wt%-AP solution was used in the same manner as in the previous study [2], but the amount of AP solution was 150 cm³ because this is the maximum amount that can be put into the container of PR-1. Table 2 shows the conditions used to prepare the emulsions. The amounts of toluene used were 5 and 10 cm³, and the emulsifying periods were 1.5, 3, 5, 7, and 10 min. The AP samples prepared with 5 cm³ and 10 cm³ toluene were designated as samples A and B, respectively. The rotation speed was constant at 80 rpm. The emulsion was frozen with liquid nitrogen, and the frozen emulsion was freeze-dried with a freeze dryer (CA801, Yamato Scientific Co., Ltd.).

Table 2. Symbols of preparation conditions.

Amount of toluene [cm³]	Emulsifying period [min]				
	1.5	3	5	7	10
5	A1	A2	A3	A4	A5
10	B1	B2	B3	B4	B5

2.2 Analytical Methods

Scanning electron microscopy (SEM; NeoScope JCM-500, JEOL Ltd.) was used to obtain external views of the sample. The specific surface area (S_w) of the sample was measured using the BET method (BELSORP-max, MicrotracBEL Corp.) and the air-permeability method (SS-100, Shimadzu Corp.). The S_w measured by the BET method and the air-permeability method were designated as S_{wb} and S_{wp}, respectively.

The thermal decomposition behavior of the samples was investigated by thermogravimetric and differential thermal analysis (TG-DTA; Thermoplus TG8120, Rigaku Corp.). The equipment used was operated under flowing nitrogen of 0.5 dm³/min at atmospheric pressure. The sample weight for TG-DTA was ~1 mg and the heating rate was 20 K/min.

The ignition temperature test was performed to investigate the temperature sensitivity. These tests were performed according to the Explosives Society Standards-11. A Krupp ignition-point test rig consisting of a steel cylinder was heated in an electric furnace to a temperature of ~870 K. Thereafter, the temperature of the rig was adjusted to decrease at a rate of less than 2 K/min. Samples of ~20 mg were placed in the rig and the ignition delay times were measured for each 2 K decrease in the temperature.

The sensitivity to impact was investigated by a drop hammer test based on the Japanese Industrial Standard K4810. The drop hammer test involved dropping a 5 kg iron hammer onto the test sample gripped between two cylindrical rollers placed on the anvil of the test rig, and sensitivity was investigated from the relationship between the height from which the hammer was dropped and whether or not there was an explosion.

3 Results and Discussion

3.1 Particle Properties

It is necessary to investigate the homogeneous emulations prepared with the conditions shown in Table 2. All the emulsions were homogeneously white, and the magnitude of color was constantly based on visual observation. A thin toluene layer was observed on the emulsions. The result indicated that a homogeneous emulsion could be obtained by emulsifying with 5 cm³-toluene and 150 cm³-AP solutions even at the low emulsifying period of 1.5 min.

The emulsion flowed into liquid nitrogen, and then, it was immediately frozen. The frozen emulsion was freeze-dried with the freeze dryer. Figure 3 shows SEM image of sample A3. The shape of sample A3 was almost spherical, and the other samples had a shape similar to that of sample A3. The particle size was measured using the Feret diameter (Figure 4) from the SEM photographs with a vernier caliper. The diameter was defined as the distance between
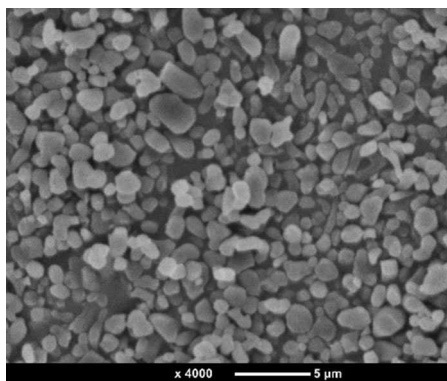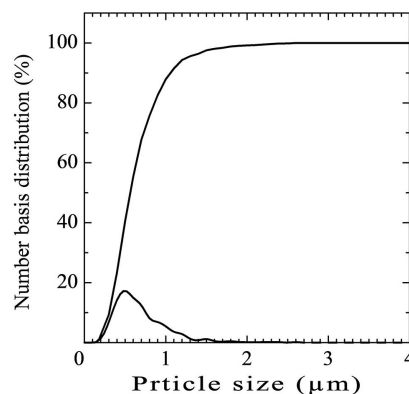
Figure 3. SEM image of sample A3.

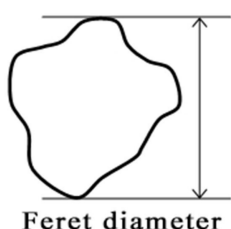**Figure 5.** Particle size distribution of sample A3.

Figure 4. Feret diameter.

Figure 6. Relationship between D and emulsifying period.

the two parallel lines restricting the particle perpendicular to horizontal direction.

Figure 5 shows the particle size distribution of sample A3. The size distribution was less than 4 μm, and approximately 97 % of particles were below 2 μm. The distribution was unimodal and its peak was 0.5 μm. The particle distributions of the other samples were almost identical to that of sample A3. D was calculated based on the particle distribution. The standard deviation of D was less than 0.68. Figure 6 shows the relationship between D and the emulsifying period. The variation of D was narrow: the value of D ranged from 1.3 to 2.2 μm. The shape and D of the sample were independent of both the amount of toluene and the emulsifying period.

Figure 7 shows the relationship between the emulsifying period and (a) S_{wb} and (b) S_{wp}. The standard deviations of S_{wb} and S_{wp} were less than 0.36 and 0.18, respectively. The dependence of the emulsifying period on S_{wb} and S_{wp} for sample A was almost the same as that for sample B, but the S_{wb} value for sample A was slightly higher than that for sample B for the same emulsifying period. The S_{wb} was almost constant below 5 min, and above that decreased with increasing emulsifying time. On the other hand, S_{wp} slightly increased with increasing emulsifying time below 5 min, and above that, it was almost constant. The emulsifying time dependence of S_{wb} did not depend on that of S_{wp} because of the difference in the measurement principle.

Fine AP has a large S_w, and a high-burning-rate propellant is also manufactured using AP with a larger S_w [10]. The AP
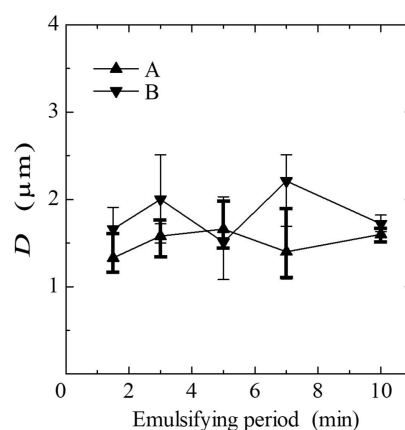
sample prepared with 5 cm³-toluene and at the emulsifying period of 5 min, that is, sample A3 had maximum values for both S_{wb} and S_{wp}. Therefore, sample A3 was the most preferable sample in this study. Sample A3 was designated as FAP and will be used in the following experiments.

D, S_{wb}, and S_{wp} of FAP were 1.7 μm, 1.76 m²/g, and 0.95 m²/g, respectively. On the other hand, D, S_{wb}, and S_{wp} of FDAP were 3 μm, 1.40 m²/g, and 0.61 m²/g [2]. FAP is finer than FDAP and the S_w of FAP is larger than that of FDAP. Furthermore, on comparison with the preparation method reported in a previous study, fine AP prepared using PR-1 needs a smaller amount of toluene and a shorter emulsifying period.

3.2 Thermal Decomposition Behaviors

For the typical TG-DTA thermogram [11], the endothermic peak of the crystal transformation of AP from orthorhombic to cubic structure is observed at approximately 516 K. Subsequently, there are two exothermic decompositions, namely, low-temperature decomposition and high-temperature decomposition. A slight consumption of AP starts at the onset
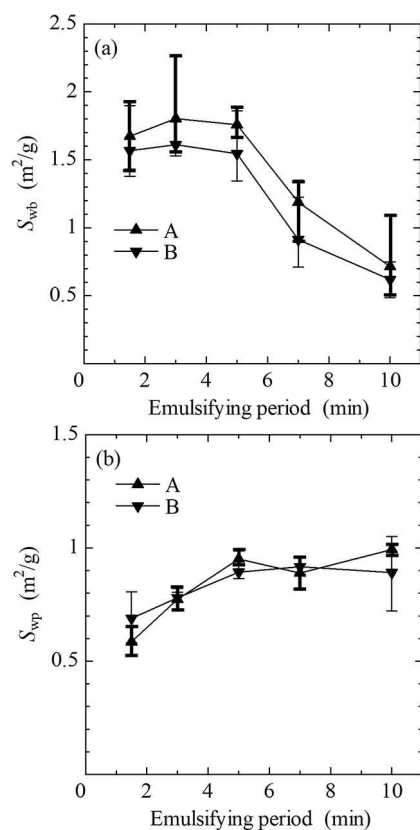
Figure 7. Relationship between emulsifying period and (a) S_{wb} and (b) S_{wp}.

temperature of low-temperature decomposition. Consumption at low-temperature decomposition is small and does not affect the consumption of AP during high-temperature decomposition. At the high-temperature decomposition, rapid consumption of AP occurs and it is consumed completely.

Figure 8 shows the TG-DTA curve of FAP. The DTA curve shows the endothermic peak of crystal transformation of AP at 518 K. A small exothermic decomposition peak due to low-temperature decomposition is observed at 617 K and a
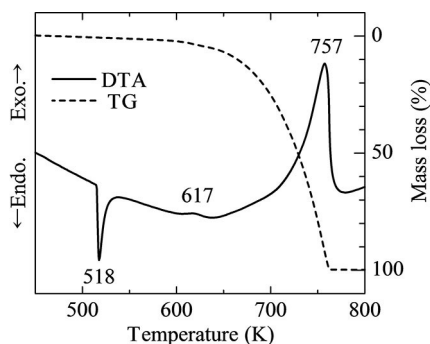
Figure 8. TG-DTA curve of FAP.

remarkable exothermic decomposition peak at 757 K is attributed to high-temperature decomposition. The TG curve shows minor consumption during low-temperature decomposition. The main consumption occurs during high-temperature decomposition, and FAP is completely consumed at approximately 760 K.

From the TG-DTA curve of FDAP [12], low-temperature and high-temperature decompositions were observed at 607 K and 766 K. The consumption of FDAP at low-temperature decomposition was slight, and a rapid and complete consumption occurred during high-temperature decomposition. It was found that the thermal decomposition behavior of FAP was almost identical to that of FDAP.

3.3 Sensitivities

As AP is an excellent oxidizer, it easily ignites with heating and explodes upon impact. An ignition test is conducted to evaluate the temperature sensitivity, and the impact safety is estimated by a drop hammer test. Explosives Society Standard-11 defines the ignition point as the temperature required to achieve ignition at 4 s. The ignition point of FAP was 713 K, while that of FDAP was 759 K [12]: the ignition point of FAP is 46 K lower than FDAP. The impact sensitivity class of FAP was 4th and that of FDAP was 5th. [12]. These results indicate that the temperature and impact sensitivities of FAP were higher than those of FDAP, indicating that FAP is a finer AP particle than FDAP.

Explosive materials such as RDX and HMX are added to solid propellants for high-performance purposes [13]. The ignition points of RDX and HMX are 530 and 580 K, and the impact sensitivity classes are 2nd and 1st, respectively [14]. The sensitivity of FAP is thus considerably lower than those of RDX and HMX. FAP can be used as an oxidizer in a composite propellant, provided that sufficient care is taken to avoid impact.

4 Conclusions

The toluene/AP solution emulsion was frozen rapidly with liquid nitrogen, and the frozen emulsion was freeze-dried. This freeze-drying method allows the preparation of fine AP particles. In this study, the emulsion was prepared using a mixer-adopted dual-sonic technology, which is a patented technique for emulsification, and an attempt was made to prepare finer AP particles. The mean particle diameter and the specific surface areas measured by the BET method and the air-permeability method were 1.7 μm, 1.76 m²/g, and 0.95 m²/g, respectively. Fine AP could be prepared using the premixer even with a smaller amount of toluene and a shorter emulsifying period, compared with the preparation reported in a previous study.

The temperature and impact sensitivities of the AP particles prepared in this study were high, but it was found that this fine AP can be used as an oxidizer in a composite

propellant, provided that sufficient care is taken to avoid impacts.

It is expected that high-performance composite propellants would be manufactured with this fine AP sample. This preparation would be useful not only to obtain the fine AP but also to develop the preparations of the various types of fine particles.

Data Availability Statement

No Data available.

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