Article

Critical thickness for detonation propagation in tri-n-butyl phosphate and fuming nitric acid (TBP/FNA) mixtures

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Tri-n-butyl phosphate (TBP) and nitric acid, which is commonly used in the PUREX method for reprocessing spent-nuclear fuel, is known to be detonable under extreme condition when fuming nitric acid (FNA) is employed and ignited by an explosive. The chemical properties of the TBP/FNA mixtures along with the elapsed time were evaluated by FT-Raman spectroscopy. Raman spectrum of the TBP/FNA mixtures after the first 2 hours showed no significant chemical change. The critical thickness of detonation propagation in the TBP/FNA mixtures within the first two hours was evaluated by the wedge method. Nitromethane (NM) was used as a comparison. The critical thickness of the TBP/FNA mixtures were very small, determined as 0.5-0.6 mm, and independent of the mixture ratio. Dark waves, a common phenomenon in liquid explosive, were observed from the trace on the recording plate just short of the failure point. The detonation propagation in the wedge charge was confirmed by framing camera photography. The average detonation velocity was 6.24±0.24 km/s.

1. Introduction

A mixture of tri-n-butyl phosphate (TBP) and nitric acid is commonly used in the PUREX method for reprocessing spent-nuclear fuel. The mixture when heated for a prolonged period can form 'red oil', which is a highly dense, energetic, organic based material. If it is heated at an elevated temperature (more than 135°C as the thermal restriction value in Japan), it can lead to an exothermic reaction of explosive violence. Therefore, it has caused some explosion accidents in the past, such at Tomsk-7 (Russia, 1993), Savannah River and Hanford (United States, 1953 and 1975). At present, the TBP/nitric acid mixture is used at ambient temperature without heating the TBP and has performed safely[1,2].

However, even at the ambient temperature, and without the red oil being generated, the mixture can be detonable under extreme conditions when employing fuming nitric acid (FNA) and ignited by an explosive. As a consequence, recently, the detonation performance of the TBP/FNA mixture has been evaluated. In a polyvinyl chloride (PVC) cylindrical charge with 20 mm i.d., experiments have shown that the mixture detonated when the TBP/FNA mixture ratio was 13/87 - 36/64 wt.%. The detonation velocity of the stoichiometric TBP/FNA (22/78 wt.%) mixture was 6.45 km/s, and the detonation pressure was approximately 14 GPa[3].

In safety evaluations of the detonation hazard, the failure condition of detonation propagation is usually examined. The failure condition of detonation propagation is usually defined as critical diameter or critical thickness. The critical diameter or critical thickness is the smallest diameter or thickness at which the explosive would propagate the detonation. However, no experimental data are

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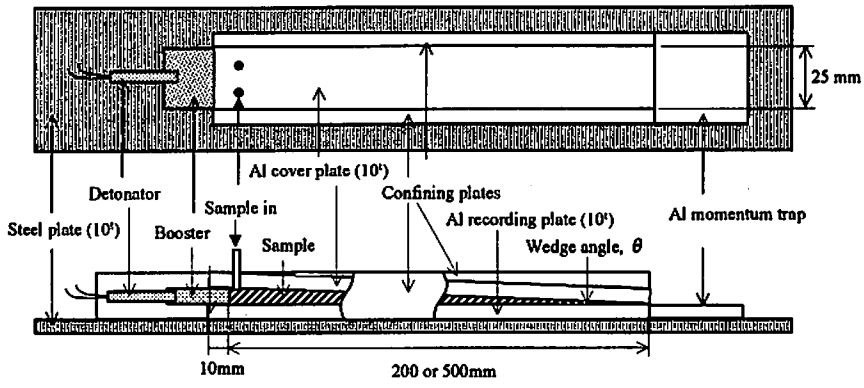

Fig. 1 Assembly of critical thickness measurement by the wedge method

available on the critical diameter or critical thickness of the TBP/FNA mixture.

There are several methods to examine the critical diameter or the critical thickness. Cylindrical charge[1] and conical charge[5] are used to determine the critical diameter. Wedge charge[6-8] and prism charge[9] are used to determine the critical thickness. The value of critical diameter is predicted to be several times that of the critical thickness[6,9]. The common method of determining critical diameter is to prepare cylindrical charges of various diameters. Unfortunately, the critical diameter of the TBP/FNA mixture was considered to be equal to that of liquid explosives, which is very small[4], and FNA has high toxicity and high corrosive oxidation. For this reason, a wedge method[6-8] was adopted to determine the critical thickness of the TBP/FNA mixture, which is relatively simple compared to the other methods.

The purpose of this study is to determine the critical thickness of the TBP/FNA mixture and its correlation with the mixture ratio. To examine the existence of the chemical reaction along with the elapsed time in the TBP/ FNA mixture, first FT-Raman spectroscopy is analyzed. In order to observe the detonation propagation in the wedge charge and determine the detonation velocity, framing camera photography is then employed.

2. Experimental

2.1 Raman spectroscopic analysis

TBP ($CH_3(CH_2)_3O)_3PO$, extra pure reagent), FNA (nitric acid conc.94wt.%, guaranteed reagent) and nitromethane (NM, guaranteed reagent) were obtained from Nacalai Tesque, Japan and used as received.

Raman spectra were measured with an InGaAs of Spectrum GX NIR FT-Raman (Perkin-Elmer). A Nd-YAG laser (1064 nm) was used as the excitation source. The spectra were measured with 1-150 scans, with a laser power of 100-200 mW.

The samples were inserted into the capillary cell and sealed up with an adhesive. Measurements of the samples were performed along with the elapsed time (2 hours-14 days) after being mixed at room temperature.

2.2 Critical thickness measurement

Fig. 1 shows the assembly of the explosive wedge used in the present study. The wedge was assembled by gluing together two pieces of Al alloy (JIS H4000 A5052P, Al 95%, tensile strength >235 N/mm^2, proof stress >175 N/mm^2, Brinell hardness 68HB) plate 210 mm long, 25 mm wide and 10 mm thick into a wedge shape with two side plates confining it. The wedge angle was set at 1.1°-4.3°. The bottom plate was used as the recording plate for recording the traces of detonation propagation. To evaluate the resulting trace of the detonation failure, the same Al alloy plate with a length of 510 mm and a pure Al (JIS H4000 A1050P, Al 99.5%, tensile strength 95-125 N/mm^2, proof stress >75 N/mm^2, Brinell hardness 20HB) plate were also used as the recording plate. Since FNA is corrosive, the inside of the assembly was covered by 80μm-thick resin adhesive tape (Nitto Denko, No.903UL). The mixture was ignited with a booster (Pentaerythritol tetranitrate, PETN/silicon rubber, SR=75/25 wt.%, 2-34 g) and an exploding bridge wire (EBW) detonator (PETN 0.8 g, Nippon

Kayaku) at ambient temperature (7-25°C). The detonation propagated through the explosive wedge, and failure occurred at a thickness critical value.

The failure point was determined from the dent in the recording plate recovered after firing. The failure point was defined as the end center of the dent at which the thickness of the recording plate changed most rapidly. The critical thickness was defined as the thickness of the wedge at the failure point.

As a preliminary experiment, NM was used to evaluate the effects of the wedge angle, the material and the thickness of side plates, and the booster mass.

2.3 Framing camera photography

The photography of the detonation propagation in the wedge of the TBP/FNA mixture was performed by an ultra high-speed framing camera (Imacon200, DRS Hadland camera, 16 fully independent frames, 100-200,000 frames/s). A strobe (PE560MGN National, G.N. 56, flash time 1/750s) was used as a back light source. The photography was conducted from the side view with a 2μs frame interval. To observe the inside of the wedge, 5 mm-thick glass plates were used as the confining plates.

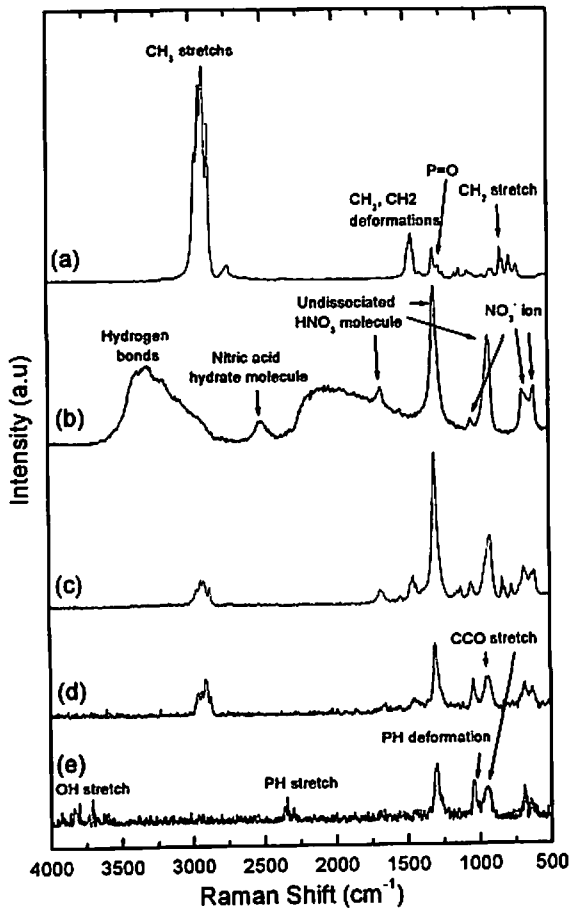

Fig. 2 Raman spectra of (a) neat TBP, (b) neat FNA, and TBP/FNA (22/78 wt.%) mixtures in the first (c) 2 hours, (d) 8 days and (e) 14 days after being mixed

3. Results and discussions

3.1 Raman spectroscopic analysis

The Raman spectra and their assignments[10-12] of neat TBP, neat FNA and the first 2 hours, 8 days and 14 days after mixing of the TBP/FNA (22/78 wt.%) mixture are shown in Fig. 2. The spectrum of the first 2 hours showed the sum of the spectrum of neat TBP and neat FNA, but there were extinguishments of bands at ~2200 cm^{-1}, ~2500 cm^{-1} (belong to nitric acid hydrate molecule), and ~3400 cm^{-1}(belong to nitric acid molecules linked by hydrogen bond)[11,12]. We can't assign the band at ~2200 cm^{-1}, but it is considered to be an effect of impurities or fluorescence of the sample.

Along with the elapsed time, the background noise increased and some changes in the spectrum were detected. The spectrum of the first 8 days showed a new peak at 953 cm^{-1} (probably belonging to the symmetric C-C-O stretching of alcohol).

The spectrum of the first 14 days showed decomposition of TBP and the formation of some new materials. The extinguishments of typical peaks of alkyl at 2970-2870 cm^{-1} and the generation of some new peaks, such as at 1033 cm^{-1}, 2346 cm^{-1} (probably belonging to PH bending and PH stretching of phosphonate ester, respectively) and 3707 cm^{-1} (probably belonging to the OH stretching of alcohol) were detected. It was difficult to make definitive statements about the chemical reaction pathway. Other chemical analytical approaches should be conducted for further investigation.

Therefore, for the measurement of critical thickness, the mixture within the first 2 hours was chosen, because there was no significant chemical reaction detected.

3.2 Critical thickness measurement

Fig. 3(a) shows the photograph of the recording plate after the firing of NM. The results of the

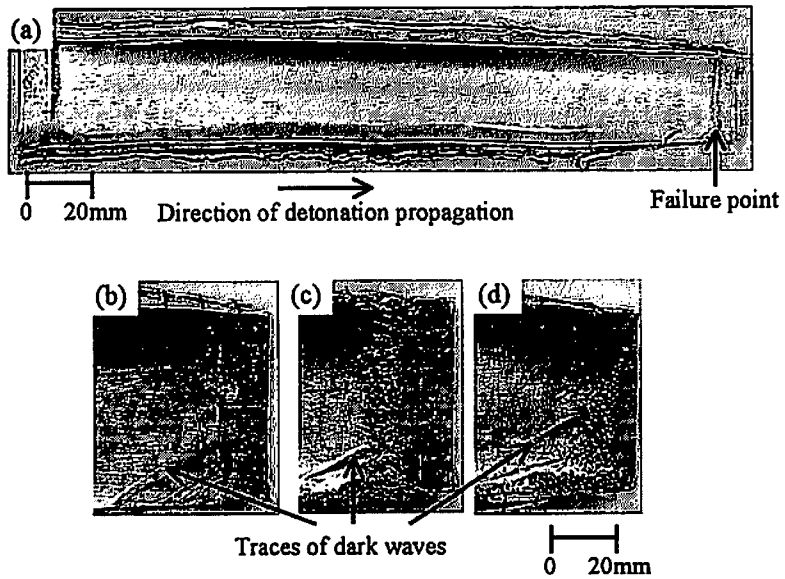

Fig. 3 Photograph of (a) the recording plate after firing of NM, and the failure area on the recording plates; (b) for NM, (c) and (d) for TBP/FNA mixtures (22/78 wt.%)

Table 1 Critical thickness of NM and TBP/FNA mixtures with various measurement conditions

Sample	Mixture ratio (wt.%)	Wedge angle(°)	Confining plate		Booster (g)	Recording plate		Critical thickness, T_{cr} (mm)
			Material	Thickness (mm)		Material	Length (mm)	
NM	–	1.4	Al	10	17	Al alloy	210	No detonation
NM	–	2.9	Al	10	32	Al alloy	210	03
NM	–	4.3	Al	10	40	Al alloy	210	Detonation
NM	–	2.9	PMMA	3	34	Al alloy	210	No detonation
NM	–	2.9	Al	3	34	Al alloy	210	0.2
NM	–	2.9	Al	6	34	Al alloy	210	0.3
NM	–	2.9	Al	10	2	Al alloy	210	No detonation
NM	–	2.9	Al	10	5	Al alloy	210	0.3
NM	–	2.9	Al	10	10	Al alloy	210	0.3
NM	–	2.9	Al	10	20	Al alloy	210	0.2
TBP/FNA*1	13/87-32/68	2.9	Al	10	34	Al alloy	210	0.5-0.6
TBP/FNA	22/78	1.1	Al	10	34	Al alloy	210	0.6
TBP/FNA	22/78	2.9	Al	10	34	Pure Al	210	0.5

*) The details are shown at Fig. 5

NM : Nitromethane, TBP : Tri-n-butyl phosphate, FNA : Fuming nitric acid

critical thickness measurement of NM with various measurement conditions are summarized in Table 1. The critical thickness (T_{cr}) was obtained using following formula:

$$T_{cr} = L \cdot \tan \theta \qquad (1)$$

where L is distance from the wedge toe to the failure point, and θ is angle of the wedge.

The critical thickness of NM seems unchanged with the change in the thickness of the Al confining plate (3-10 mm) and booster mass (5-34 g), which was determined as 0.2-0.3 mm. But the distance between the failure point at the center and that at the periphery of the recoding plate decreased with the increase of the confinement or the booster mass. Al confining plate with thickness more than 3 mm seems has sufficient confinement to evaluate the critical thickness of NM, because the critical thickness is independent of the confining plate with the thickness more than 3 mm. A booster mass of more than 5 g was considered to have sufficient

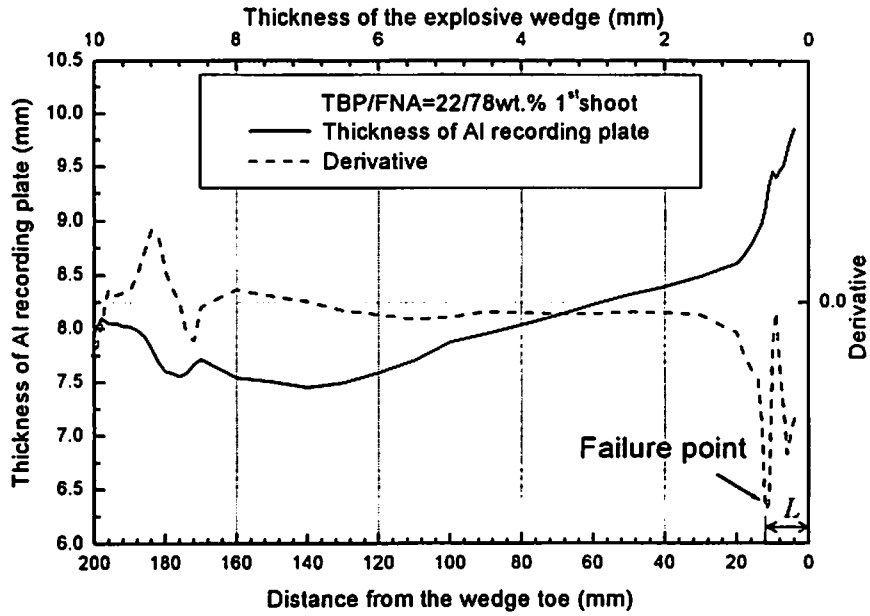

Fig. 4 Procedure for defined failure point in the TBP/FNA mixture.

energy (approximately more than 1.13 kJ) to ignite NM.

From the preliminary experiment, for critical thickness measurement of the TBP/FNA mixture, the confining plate used was a 10 mm-thick Al plate, the wedge angle was set at 2.9°and the mixture was ignited with 34 g of booster mass at ambient temperature.

The photograph of the failure point after firing of the NM and TBP/FNA mixture (2 shots), are shown in Fig. 3 (b), (c) and (d) respectively. The failure point of the TBP/FNA mixture is unclear compared to that of NM. To determine the failure point more accurately in the TBP/FNA mixture, the thickness of the center part of the recording plate was measured by micrometer (resolution 0.001 mm) and the first derivative (Fig. 4) was computed. The failure point was determined to be the drastic change of the slope (the first derivative value).

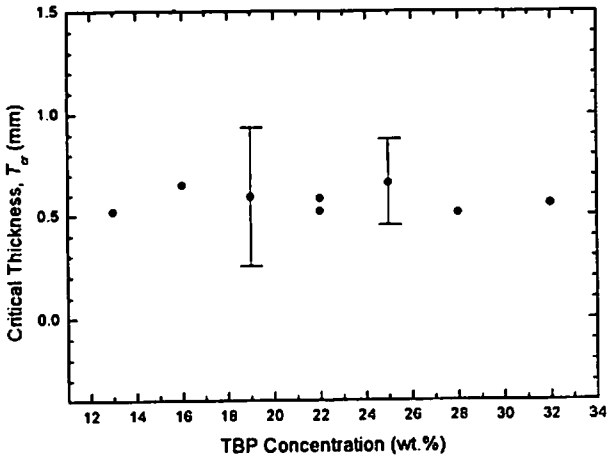

Fig. 5 Critical thickness of TBP/FNA mixture and its correlation with the mixture ratio

Fig. 5 shows the critical thickness of TBP/FNA and correlation with the mixture ratio. Critical thicknesses of TBP/FNA were determined as 0.5-0.6 mm, but the critical thicknesses of TBP/FNA at 19/81 and 25/75 wt.% were shown as error bars. The critical thickness appears to be independent of the mixture ratio.

For the recording plate, a longer Al alloy plate (wedge angle was set at 1.1°) and a pure Al plate (wedge angle was set at 2.9°) were employed (bottom of Table 1). The result showed that the determination of the failure point was slightly easier, due to the distance of the failure point being further from the wedge toe when a long plate was employed, and the resulting dent being deeper when a pure Al plate was employed. But the critical thickness of the TBP/FNA mixture appears independent of the length and the purity of the Al recording plate.

The small critical thickness of the TBP/FNA mixture is about the same order as that of the liquid explosives[5], high explosives[6], and emulsion explosives containing glass microballoon (0.2-0.7

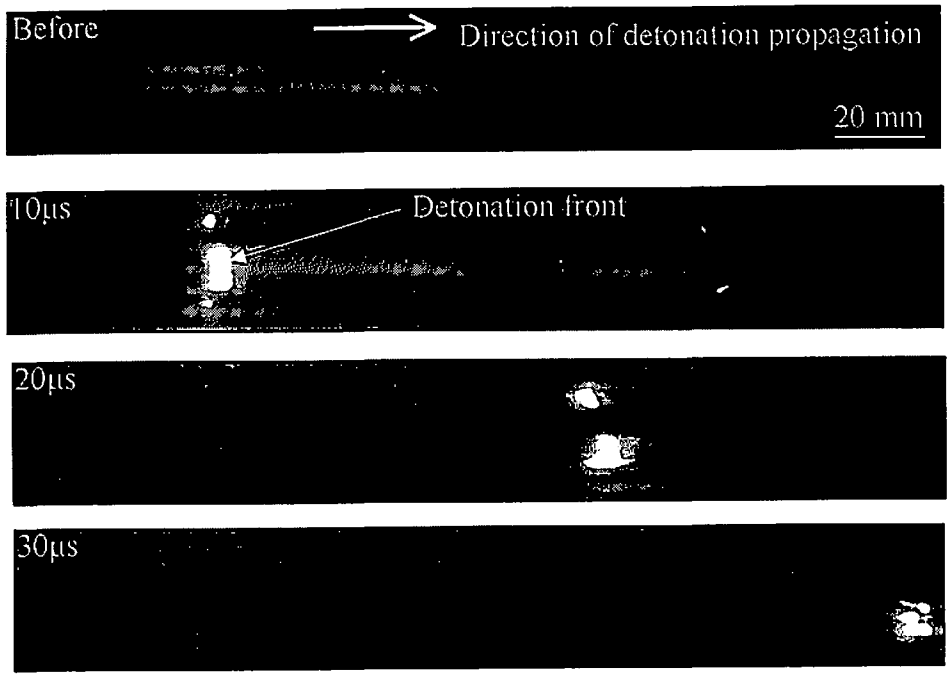

Fig. 6 Photographs of detonation propagation in the wedge of the TBP/FNA mixture taken by framing camera before and 10, 20 and 30μs after firing. The photographs have been taken from the side view of the wedge explosive with 2μs/frame

vol. fraction)[7]. This suggests that the reaction zone length of the TBP/FNA mixture was very small, since it was considered to be approximately proportional to the reaction zone length[7].

Short of the failure point, a few finely slanted lines in the propagation direction were recorded on the recording plate (Fig. 3 (b)-(d)). These fine lines are probably similar to those seen in the NM/acetone [5] and other liquid explosives[13]. They are concluded to be dark waves, which are thought to be associated with hydrodynamic rarefactions originating at the sample boundary. Due to high confinement of the Al plate, the traces of dark waves were observed just short of the failure point in very small numbers[13].

3.3 Photography with ultra high-speed camera

Fig. 6 shows the representative photographs of detonation propagation in the TBP/FNA mixture taken by a framing camera before and at 10, 20 and 30 μs after firing. The detonation propagation in the wedge charge can be observed. The propagation until the thin charge (approximately 1 mm thickness) was confirmed at 30 μs. Some luminousness above and at the bottom of the wedge explosive was considered to be reflections from the Al plates.

From the photograph, the propagation distance and time were plotted. The data was fitted approximately as linear. The average detonation velocity was obtained from the gradient of a linear, which was determined as 6.24±0.24 km/s. This value was slightly smaller than the previous study, which was obtained as 6.45 km/s in a PVC cylinder with 20 mm i.d.[3]. This was considered to be an acceptable error range of the measurement. To obtain a detonation velocity with high accuracy, and evaluate the effect of the decrease of the wedge thickness on the detonation velocity, continuous photography by streak camera should be employed.

4. Conclusions

The TBP/FNA mixture within the first 2 hours of being mixed showed no significant chemical changes. The critical thickness of the TBP/FNA mixture within the first 2 hours was evaluated. The critical thickness of the TBP/FNA mixture was very small, determined as 0.5-0.6 mm. The detonation propagation in the wedge charge was confirmed by framing camera photography and the

average detonation velocity was 6.24±0.24 km/s.

The TBP/FNA mixture has a similar order of critical thickness to that of the liquid explosives, high explosives and some emulsion explosives. Handling the TBP/FNA mixture requires a lot of attention because of its ability to propagate the detonation in small thickness of mm order.

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