**Research paper**

# Thermal hazard evaluation of ammonium nitrate emulsions by DSC and 1.5 L pressure vessel test

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## Abstract

Bulk emulsion explosives have been generally used for blasting systems in many countries but not in Japan. As ammonium nitrate emulsion (ANE) is sensitized as an explosive precursor only at the time of use, its thermal hazard evaluation during the storage and the transportation is essentially important ; ANE is composed of ammonium nitrate, water, oil and emulsifier. For evaluation of its thermal stability, 1.5 L pressure vessel tests (1.5L-PVT) have been newly developed in the present work as a testing method on an intermediate scale. The vessel of the 1.5L-PVT is composed of a thermocouple, a pressure sensor, an orifice plate and a bursting disk. Some kinds of ANEs with different water contents have been prepared. The ANEs of 100 g order have been heated by gas burners, and the temperature and the pressure have been measured simultaneously. The bursting disk is adjusted to relieve the pressure above 2MPa. In the case of 1.5 L-PVT, orifice blocking is fully expected not to occur so readily as in the current Koenen test. The DSC before 1.5L-PVT has also supplied useful information as a screening test. The water contents of the ANEs are found to be one of the key factors for reducing a probability of thermal hazard.

***Keywords*** : ammonium nitrate emulsion, thermal hazard evaluation, DSC, 1.5 L-pressure vessel test

## Introduction

In many countries, site mixing technique of bulk emulsion is a new trend for mining and tunneling ; bulk emulsion, which itself is nonexplosive, is mixed with bubbles, sensitized and charged to the bore hole with pumping. The emulsion matrix, which has nonexplosive property, can be transported and stored with a tank lorry. Thus, by keeping the safety at the transportation and the storage, the cost can be brought down. The bulk emulsion is appropriate for charging by using a machine on the spot. Thus, a method of using bulk emulsions must be suitable for large scale blasting.

The United Nations Sub-Committee of Experts on the Transport of Dangerous Goods (UN-SCETDG) has so far made a large scale test of whether ANE is suitable for transport in bulk. The test code name is UN series 8 (d) tests. The Modified Vent Pipe Test (MVPT) is testing among UN series 8 (d)[1), 2)] ; however, the MVPT is a test on a large scale and may presumably contaminate the environment. Therefore, development of experimental methods on a smaller scale is needed as an alternative one. A number of research work on thermal behavior of emulsion explosives and ANEs using DTA, ARC, and DSC has so far been performed[3)-8)].

Oxiey et al[3), 4)]. have studied the thermal stability of ANE. The effect of thermal stability of various contaminants such as metal ions was examined by DSC. Iron ions ((II) and (III)) severely destabilize ANE.

For the sake of safe transportation of emulsions with a pump, the Minimum Burning Pressure (MBP) test has been established ; for example, under various pressures, the sample of ANE is fired with a Nichrome wire, and, from these experiments, the minimum pressure above which burning continues is defined as the MBP of ANE.

For the commercial explosives industry in Canada, the MBP for ANE supplies a good knowledge to estimate safe

**Table 1** Comparison of some pressure-vessel-tests in terms of ANE.

| Type of PVT | MCPVT | Koenen Test | D-PVT | USA-PVT | 1.5L-PVT |
|---|---|---|---|---|---|
| Orifice position | Top | Top | Side | Side | Side |
| Vessel volume [$cm^3$] | 6 | 27 | ~190 | ~230 | ~1500 |
| Diameter [mm] | 16 | 24 | 50 | 47 | 100 |
| Height [mm] | 48 | 60 | 95 | 133 | 190 |
| Sample amount | 1 g | 27 $cm^3$ | 10, 50 g [a)] | 5 g | 100 g |
| Filling ratio [%] | 17 | 100 | 5.3, 26 | 2.2 | 6.7 |
| Heating method | Electricity | Gas | Gas | Electricity | Gas |
| Heating rate [$K\ min^{-1}$] | 10 | 198 | 210 | 30 | 10 |
| Bursting pressure [MPa] | 35 | 30 | 0.62 | 0.62 | 2 |
| Thermal hazard evaluation for ANE | Not suitable [b)] | Not suitable [c)] | Applicable | Not suitable [b)] | Suitable |
| Reference | [13)] | [1)] | [1)] | [1)] | This work |

[a)] For a normal test, 10.0 g of the substance should be place in the vessel. In case where no disk rupture is observed with an orifice of 1.0 mm, the next test with an orifice of 1.0 mm is carried out with 50.0 g of the substance instead of 10.0 g.

[b)] Sample amount is too small.

[c)] The orifice position is not appropriate ; Orifice blocking by ANE occurred.

operating pressure for manufacturing, and handling processes ; The MBPs have extensively been studied for a lot of chemicals by Turcotte et al[9)-12)].

On the other hand, the pressure vessel test (PVT) has been conducted for safety in anticipation of a possible fire during the transportation caused externally, for example, by a fire of a tank truck. Thus, PVT tests and MBP ones are different in their purposes, and therefore, these could not be directly compared ; further, the MBP tests have not been officially recognized internationally.

As pressure vessel tests, Dutch Pressure Vessel[1)] Test (Dutch PVT)[1)], USA PVT[1)], MCPVT[13)] and Koenen test[1)] are available. Since ANE is a fairly viscous substance at room temperature, a certain amount of ANE is needed for examining the effect by convection under heating. As the testing method simulating the firing condition, electrical heating is too mild, and the evaluation by the MCPVT or the USA PVT employing electric heating may be inappropriate.

Thus, we have developed a 1.5L-PVT which requires only about 100 g of ANE and uses a gas heating method ($10\ K\cdot min^{-1}$ by water calibration). In the present work, we have prepared three kinds of ANEs, performed DSC and 1.5L-PVT for them, and compared the experimental results with each other. One of the aims of the present work was to evaluate the thermal hazard of ANE using DSC and 1.5L-PVT.

In Table 1, the main available testing methods are briefly compared with the present one in terms of thermal hazard evaluation of ANE.

## 1. Experimental procedure

### 2.1 Preparation of ANEs and DSC measurements

The following chemicals were used in the preparation of the ANEs : $NH_4NO_3$ (Wako Pure Chemicals Industries Ltd, purity 99.0%), diesel fuel oil (DFO No.2, CAS No. 68476-30-2, Imperial Oil, Canada), and emulsifier, i.e., a mixture of polyolefin aminoester (2824S, Lubrizol, Co., USA) and sorbitan monooleate (Sigma-Aldrich Canada, Ltd).

The oil and the emulsifier contained in a glass beaker was stirred by a ramond stirrer (ϕ89 mm, ST5, Environmental Science Technology Corp., Japan) in a silicone oil bath at 100°C. An aqueous ammonium nitrate was gradually added into the beaker, and then the mixture of the oil solution and the aqueous one was emulsified further by mixing for 6 min. The contents of the starting materials are given in Table 2 together with the rotation speed of the stirrer ; the rotation speed was set at 1250 rpm or 1500 rpm ; these will be referred to as "-L" and "-H", respectively. Thus, three kinds of ANEs regarding compositions were prepared, that is, ANE-#1, ANE-#2 and ANE-#3 ; the former two had lower water contents -Δ6% and -Δ4%, respectively, with respect to ANE#3 which had a reference water content (17 mass%).

**Table 2** The content of the investigated samples.

| Name | $NH_4NO_3$ | $H_2O$ | Oil | Emulsifier | Remarks[b)] |
|---|---|---|---|---|---|
| | Mass% | | | | |
| ANE#1-L, -H[a)] | 83.3 | 11 | 4.0 | 1.7 | deficient (-6%) |
| ANE#2-L, -H | 81.5 | 13 | 3.8 | 1.7 | deficient (-4%) |
| ANE#3-L, -H | 77.8 | 17 | 3.5 | 1.7 | standard |

[a)] -L (rotation speed : 1250 rpm) and -H (2000 rpm)

[b)] "Deficient (-6% and -4%)" : the water contents in comparison with that of "the standard sample (17%)".

As each ANE was emulsified with the 2 different rotation speeds, totally 6 kinds of ANEs were prepared. The viscosity of the ANEs was measured mainly at room temperature by a Brookfield RVT viscometer (spindle#7 ; speed 20 rpm) ; some were measured also at 60°C.

DSC measurements were carried out using DSC2920 (TA Instruments) in a Hastelloy pressure cell (NEZSCH). The cell was 5 mm in diameter, and the sample drop was ~ 1.5 mm in diameter. The sample of about 1 mg was heated from room temperature to 500°C at a rate of 5°C·min$^{-1}$.

### 2.2 1.5 L-PVT

In order to evaluate the thermal hazard of ANE on a 100 gram scale, we prepared a pressure vessel of SUS 304 having an inner volume of 1.5 L (1.5L-PV (see Figure 1)) ; this had outer and inner diameters of 130 mm (OD) and 100 mm (ID), respectively, and the inner height of 190 mm. The total weight of the vessel was 15.8 kg (vessel : 11.3 kg, inner cover : 1.5 kg, and screw : 3.0 kg). The PV had an Al rupture disk, which was designed to function at 2MPa and placed on the top of the PV. The aluminum rupture disk of 0.2 mm in thickness was held in place with a retaining plug having a 20 mm bore on the top. The orifice was mounted on the side part of the vessel. The Koenen tests have so far been conducted to determine the sensitivity of solid and liquid substances to the effect of intense heat under high confinement.

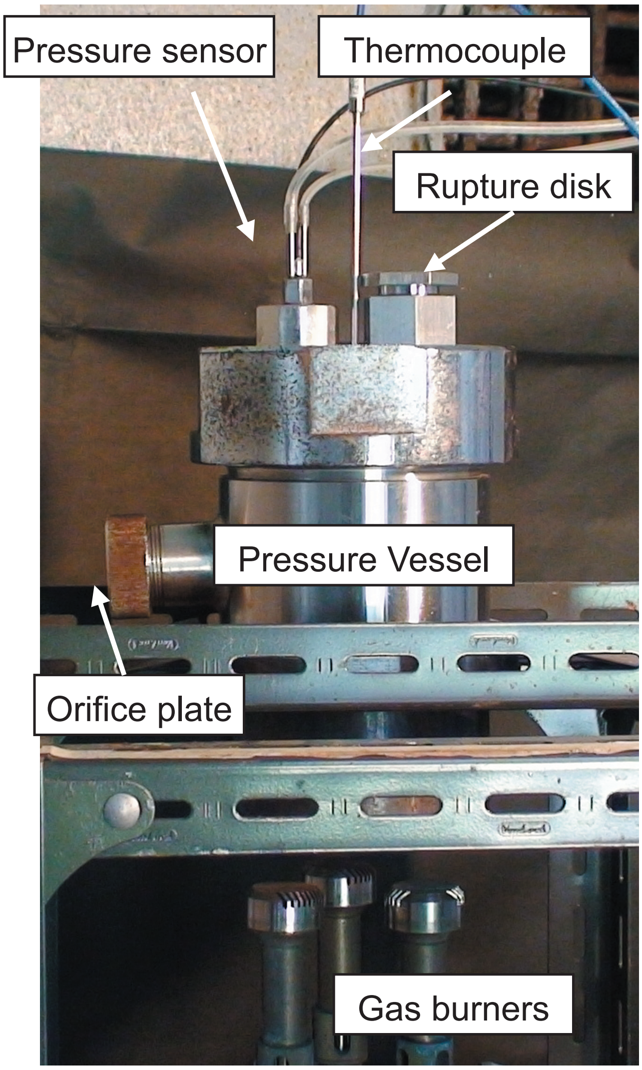

**Figure 1** Photo of 1.5 L-pressure vessel (1.5L-PV).

The top part is not a suitable position for the orifice in the ANE testing ; because, ANE would block the orifice hole. Thus, the side part of orifice is more suitable for ANE testing. Various kinds of orifice plates were prepared. The orifice diameter, ϕ, ranged from 0.7 mm to 5.0 mm (ϕ : 0.7, 1.0, 1.5, 2, 2.5, 2.9, 3.0, 3.4, 4.0, 4.2, and 5.0 mm), and the thickness was 3 mm. The temperature of the sample (ANE) was measured with K-type thermocouples (3.2 mm in diameter). The inner pressure was measured with a pressure sensor (PEF-S-20MPSA1, Kyowa Co.) The pressure sensor was a water cooling type one, and functioned up to 300°C. The heating process of the PV is as follows. The PV was heated by LNG gas burners ; the heating rate was calibrated by water. From 60°C to 80°C, the heating rate was 10°C·min$^{-1}$. The gas flow rate could be changed to adjust the heating rate. One hundred grams of ANE was introduced into the inner vessel. This amount may be appropriate for an indoor explosion facility. The volume of the inner vessel was 85 (ϕ) mm x 102 mm (=580 cm$^3$). Employment of an inner vessel is convenient for the maintenance, as the outer vessel can be cleaned more easily after each explosion test.

## 2. Results and discussion

### 3.1 ANE characteristics

Figure 2 shows optical microscope images of ANEs at the 2 different rotation speeds. The emulsion diameter is smaller at the higher rotation speed (1500 rpm) than at the lower rotation speed (1250 rpm).

Figure 3 shows the droplet size distribution for formula ANE#3-L and ANE#3-H. Figure 4 shows the relation between rotation speed and viscosity. Some samples were measured at 60°C ; the viscosity at 60°C indicates about 85% of the ones at room temperature (RT). The viscosity is highly dependent on the diameter of emulsion. The target viscosity of ANE ranges from 20 to 70 Pa·s ; this value corresponds to the one of generally used bulk emulsion systems.

### 3.2 DSC

Figure 5 shows the DSC curves of ANE#3. We measured at least twice for each sample to check the reproducibility. The averaged $T_a$ (detected onset temperature), $T_o$ (extrapolated onset temperature) and $Q_{DSC}$ are summarized in Table 3. We have assumed $T_o$ equal to $T_{DSC}$, which is generally regarded as the onset temperature in Yoshida's plot[14]. The relation between $Q_{DSC}$ and $T_{DSC}$ obtained from DSC analysis is given in Figure 5.

In Figure 6, the values of $\log(Q_{DSC}/\mathrm{kJ \cdot g^{-1}})$ are plotted against the ones of $\log(T_{DSC}/°\mathrm{C}-25)$ for ANE#1, ANE#2, and ANE#3. As 2,4-dinitro-toluene (DNT) and dibenzoyl-peroxide (BPO) are regarded as the standard chemicals, their values are also plotted in Figure 6 for comparison ; then, these two points are connected with a straight line[13]. If the data point is located above this straight line, the sample may be considered to have propagational qualities.

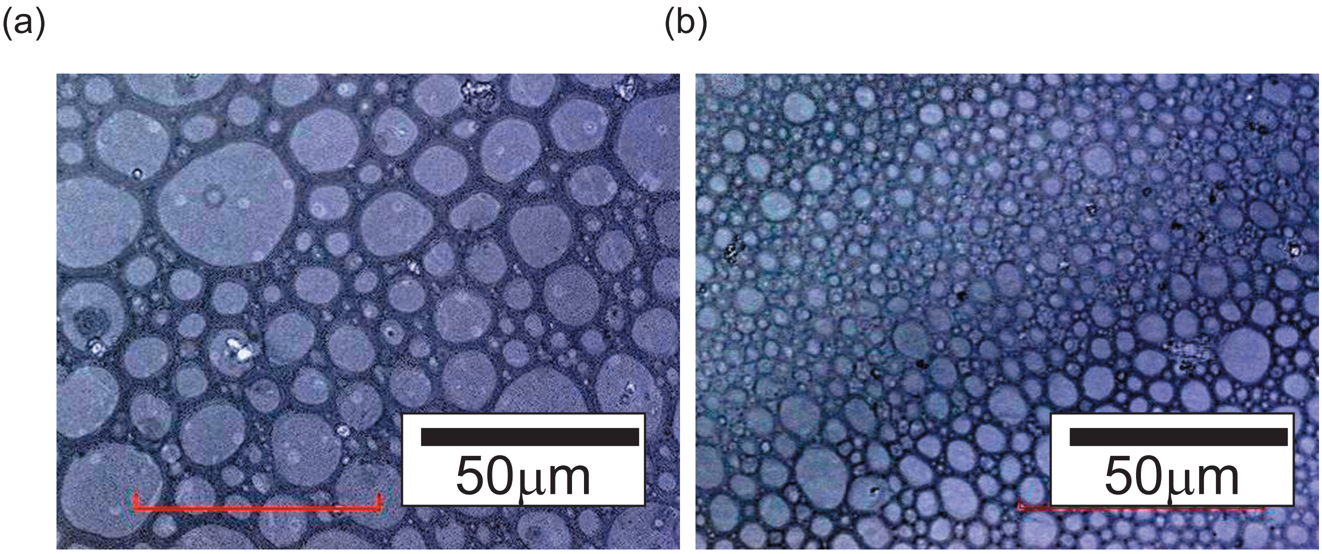

**Figure 2** Laser microscopy of ANE (a) ANE#3-L (b) ANE#3-H.

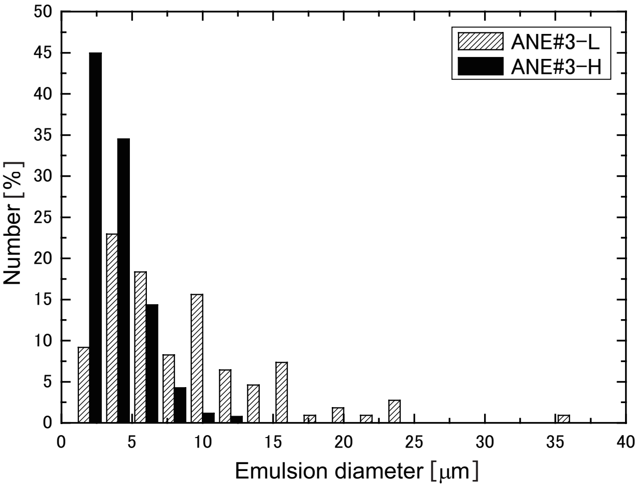

**Figure 3** Droplet size distribution for formula ANE#3-L and ANE#3-H.

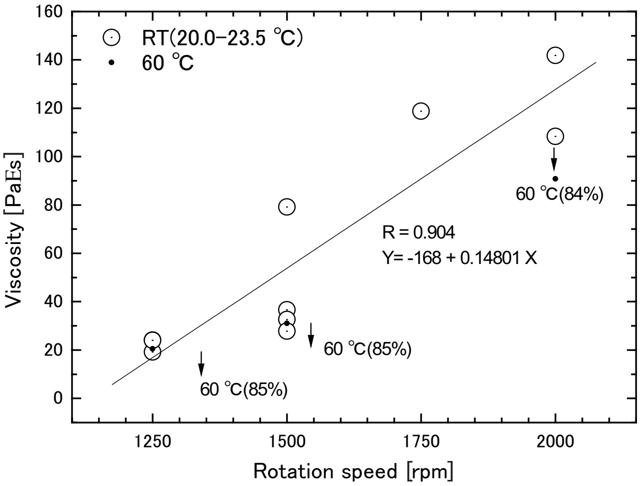

**Figure 4** Relation between rotation speed and viscosity of ANEs.

Figure 6 reveals that ANE#3-L has non-propagational quality and that the others have propagational one.

While ANE#3-L is assumed to be most thermally stable among the samples examined in the present work, the $Q_{DSC}$ of ANE#3-H is considerably higher than that of ANE #3-L. This is presumably because the interface area between oil and aqueous phases is larger in the former, which, in turn, increases the reactivity. Meanwhile the onset temperatures of the reaction are practically equal for both samples.

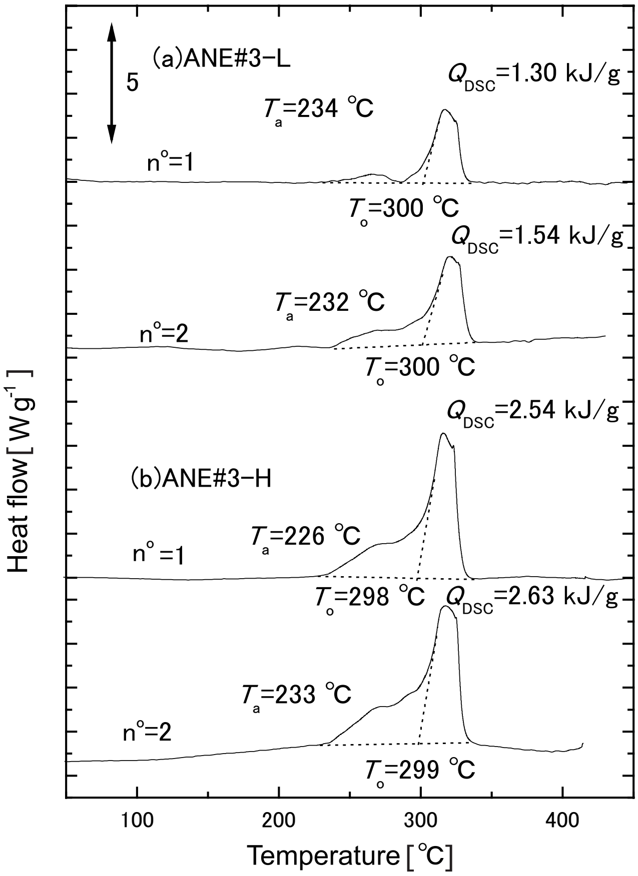

**Figure 5** DSC curves of ANE#3, the rotation speed of (a)1250 rpm (ANE#3-L) (b)1500 rpm (ANE#3-H).

As the samples are of the order of less than 1g, the effect by convection may be neglected. Table 3 reveals that, as the values of $Q_{DSC}$ are not related with the viscosities, the thermal stability is not explicitly affected by the viscosity.

**Table 3** The viscosity, the emulsion diameter, and the data obtained from DSC.

| Name | | Rotation speed[rpm] | Viscosity [Pa s] | Emulsion diameter [μm] | $T_a$ a) [℃] | $T_o$ a) [℃] | $Q_{DSC}$ a) [kJ·g$^{-1}$] |
|---|---|---|---|---|---|---|---|
| ANE#1 | -L | 1250 | 13.0 | 10~50 | 214 | 298 | 3.6 |
| | -H | 1500 | 17.7 | 5~20 | 214 | 298 | 3.6 |
| ANE#2 | -L | 1250 | 27.5 | 5~20 | 230 | 294 | 3.2 |
| | -H | 1500 | 45.7 | 2~10 | 233 | 291 | 3.3 |
| ANE#3 | -L | 1250 | 19.2 | 2~25 | 233 | 300 | 1.4 |
| | -H | 1500 | 33.2 | 1~12 | 230 | 298 | 2.6 |

a) For the values for ANE#3, the ones given in Figure 5 are the averaged ones. As for $T_a$, $T_o$ and $Q_{DSC}$, see the text.

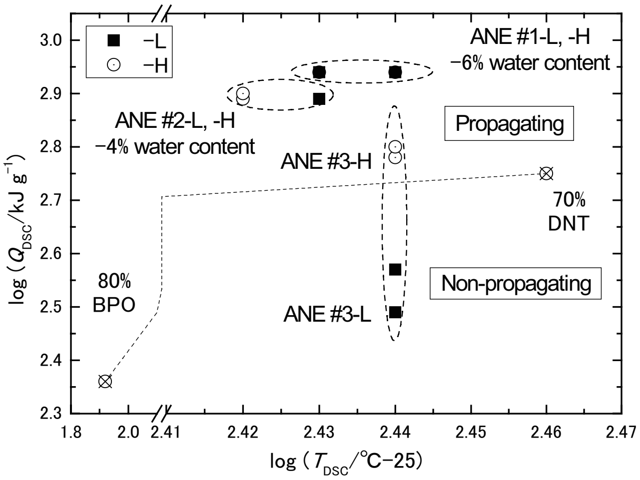

**Figure 6** Logarithmic plot of DSC parameters (Yoshida's plot).

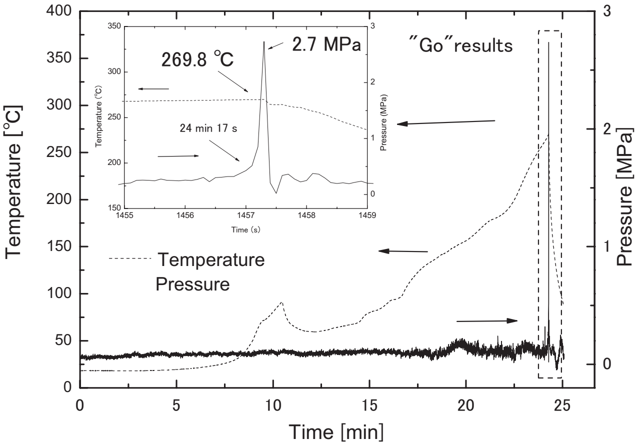

**Figure 7** Temperature and pressure record for ANE#2-H with orifice diam. Of 4.2 mm, "Go results" of 1.5L-PVT.

### 3.3 1.5L-PVT

Figure 7 shows the test results on the change in the temperature and pressure obtained from the 1.5L-PVT. After 24 min 17 s from the start of testing, the sample was decomposed at 269.8°C, and the inside pressure drastically increased. The temperature and the time at the decomposition of samples are defined as "decomposition temperature" and "decomposition time", respectively. The inside pressure attained to 2.7 MPa, and the bursting disk was ruptured. The inside temperature drastically decreased. The test result is defined as "Go" result. If the inside pressure does not attain to 2 MPa, the rupture disk is not broken. This result is regarded as "Nogo" result. The "Go" or "Nogo" is judged according to rupture or non-rupture of the rupture disk.

Figure 8 shows the decomposition time and the decomposition temperature at different water contents. The decomposition time of ANE#3 is longer than that of ANE#1 and ANE#2 by 8.2 and 11.2 min, respectively. The decomposition temperature of ANE#3 is higher than that of ANE#1 and ANE#2 by 14.8 and 17.6°C, respectively. In case of ANE#1 and ANE#2, neither the decomposition time nor the decomposition temperature is explicitly affected by the rotation speed in the preparation process. The decomposition time is longer for ANE#3-H than for ANE#3-L, and the decomposition temperature is higher for the former than for the latter.

Thus, ANE#3-H has the longest decomposition time and the highest decomposition temperature. These findings signify that ANE#3-H is safest among the investigated samples; the smaller diameter of the emulsion is assumed to make its water evaporation more difficult.

When it comes to larger samples of ~100 g, the effect by convection could not be neglected. Since ANE#3-H is more viscous than ANE#3-L, it will take more time for the former to be heated uniformly than for the latter. Therefore, with increasing scale, the advantage of ANE#3-H in the decomposition time and the temperature could be enhanced.

Figure 9 shows the functional range of the orifice diameter for each sample. In case of ANE#3, Go/Nogo criteria are at about 3.0 mm. On the other hand, in case of ANE#1 and ANE#2 Go/Nogo criteria are at 4.0-4.2 mm. Therefore, in case of ANE#3, the internal pressure could be kept to be in the safe range, when the orifice diameter is over 3 mm. Also in this respect, the ANE#3-H (rotation speed : 1500 rpm) is found to be most stable.

As ANE#3-H is more viscous than ANE#3-L, the former may be more difficult to be uniformly heated than the latter. Therefore, even if thermal hazard is locally

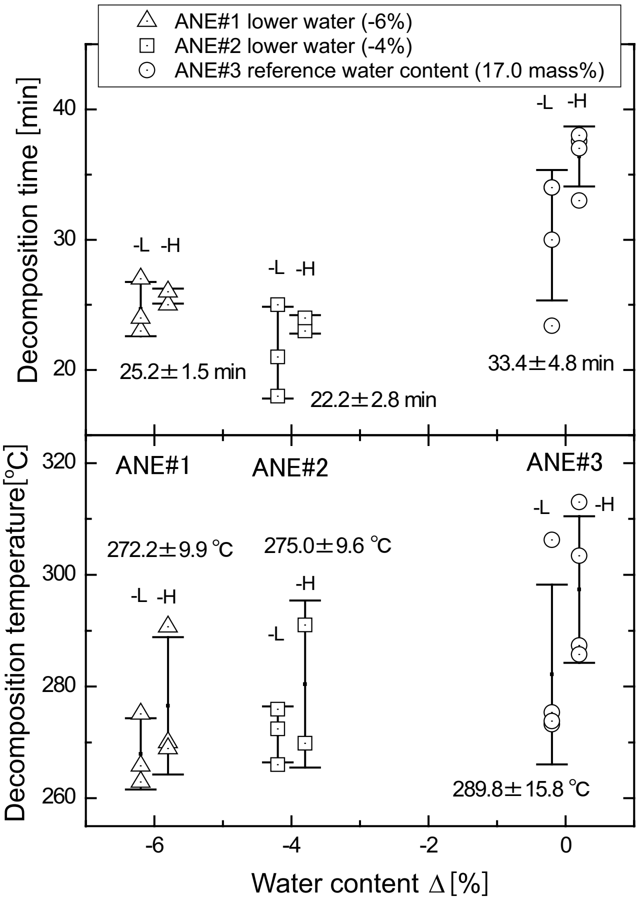

**Figure 8** Decomposition time and temperature of 1.5L-PVT at different water contents. (The values given on the time and temperature are the averaged ones for the ANEs prepared at the high and low rotation speeds.)

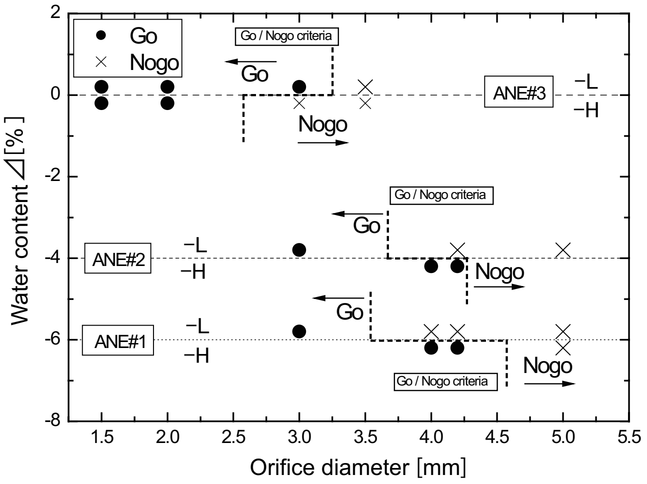

**Figure 9** Go/Nogo results at various orifice diameters and water contents of 1.5L-PVT.

generated, there will be higher probabilities for the former that, owing to temperature gradient and shortening of the orifice diameter limit, the thermal hazard could be prevented from propagating over the whole of the chemicals. At any rate, it should be recommended that the thermal characteristics of the chemicals are examined by DSC in advance before an investigation of the thermal hazard on a large scale.

The 1.5L-PVT possesses the following characteristics : (1) a trial examination of rapid heating simulating an occurrence of a fire can be performed without choking the orifice, (2) as the amount of the used chemicals is of the order of ~100 g, the effect by convection, which is an important factor for the practical use, can be examined, and (3) as the main apparatus is non-destructive by the test and the time needed for one experiment is about 30 min, several trials can be done in a short period.

In the present method, the samples having high viscosity are in fairly large quantities (~100 g). The samples, which are heated by gas burners, are not isotropic as regards transfer of heat. The thermal decomposition involves combustion and oxidation. Consequently the supply feature of oxygen gas is expected to be different from test to test.

## 3. Conclusion

Three kinds of ANEs with different moisture contents were prepared at first ; then, the starting materials for the ANEs were mixed at two different stirring speeds (1250 rpm and 2500 rpm). Thus, six kinds of ANEs were prepared finally. With an increase in the stirring speed, the particle size decreases, and the viscosity, in turn, increases.

Measurement of $T_{DSC}$ and $Q_{DSC}$ of ANEs by sealed-cell DSC (SC-DSC) is effective as a screening test. The results of SC-DSC of these ANEs have been analyzed according to Yoshida's plot. Only ANE#3-L having higher water content and larger emulsion diameter is located below Yoshida's plot. From the DSC result, ANE#3-L appears to be safest among the investigated ANEs. In the measurement by SC-DSC, however, in which the sample scale is small, convection effect is practically neglected. On the other hand, the 1.5L-PVT, which has been developed in the present work, could supply additional information on ANEs as bulk emulsion explosives.

From a viewpoint of transportation of bulk amounts of ANE, ANE#3-H is likely to be most appropriate. Thus, while SC-DSC is effective for a screening test, the information given only by this method could not necessarily lead to a synthetic conclusion concerning transportation of the bulk. Probability of thermal hazard of ANE could be decreased with increasing water content. Therefore, evaporation of the water content during preparation, storage and transportation should be prevented as entirely as possible. Although the variance in the measured properties is inevitably larger in the 1.5L-PVT than in the DSC. the present test method could be considered to meet the demand as a testing method.

## Acknowledgements

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# DSCおよび1.5L圧力容器試験を用いた硝酸アンモニウムエマルションの熱的危険性評価

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バルクエマルションを用いた発破システムは，海外で多く使われている。硝酸アンモニウムエマルション（ANE）は，爆薬の前駆体で，使用の直前に鋭敏化し爆薬となる。ANEの熱的危険性評価は，貯蔵や移動の際に火災になった場合に重要である。ANEの熱的危険性評価を実施するために，1.5 Lの圧力容器試験（1.5L-PVT）とDSC測定を実施した。ANEは，硝酸アンモニウム，水，油，乳化剤が混ぜられてエマルションとなっている。1.5L-PVTの容器は熱電対，圧力センサー，オリフィス板，破裂板を有している。100 gのANEをガスバーナーで加熱し，温度と圧力の同時測定を行った。破裂板は2 MPaを超えると破裂する。現行のケーネンテストに比べ，1.5L-PVTはオリフィス閉塞が少ない。DSCを実施することで1.5L-PVTのスクリーニングテストとなることも判った。最終的には，ANEの水分含有量が熱的危険性評価の1つのポイントとなることが判った。

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