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COMMITTEE OF EXPERTS ON THE TRANSPORT OF DANGEROUS GOODS AND ON THE GLOBALLY HARMONIZED SYSTEM OF CLASSIFICATION AND LABELLING OF CHEMICALS <u>Sub-Committee of Experts on the</u> <u>Transport of Dangerous Goods</u> (Twenty-first session, 1-10 July 2002, agenda item 3 (b))

EXPLOSIVES, SELF-REACTIVE SUBSTANCES AND ORGANIC PEROXIDES

Classification of ammonium nitrate emulsions, suspensions and gels

Minimum burning pressure of commercial explosives

Transmitted by the expert from Canada

Background

During the twenty-first session of the Committee of Experts on the Transport of Dangerous Goods, December 2000, it was decided to create a new entry for AMMONIUM NITRATE EMULSION or SUSPENSION or GEL, intermediate for blasting explosives (ANEs), in Division 5.1 (UN No. 3375). To determine whether a substance may be classified under this new entry, a new Test series 8 was also included in the Manual of Tests and Criteria. This new test series is presently being evaluated by various regulatory and industry groups. These ANEs are commonly transported in bulk in tanker trailers in many parts of the world, so it is important to be able to predict their behaviour when involved in an intense fire such as that produced by burning tires or diesel fuel. One test which might be suitable for this purpose is the Vented Vessel Test (test 8d) which is being evaluated by the explosives industries of Norway, Sweden and Finland. Another is the Minimum Burning Pressure Test (MBP) which is being examined by the Canadian Explosives Research Laboratory (CERL.) This paper briefly describes the MBP test and some preliminary results: a more detailed paper will be presented to the ANE Working Group.

Introduction

It is well accepted that modern water-based commercial explosives are intrinsically much less sensitive than traditional products such as dynamites or black powder. However, they have still been involved in a significant number of accidental explosions.

Accidental initiations of these explosives are all thermal in origin, and two broad categories can be defined. When the temperature of a sizable mass of explosive is globally elevated above a critical value, a runaway decomposition reaction may result. This is usually termed 'thermal explosion (or cook-off)'. A different scenario results when mechanical or thermal energy is deposited locally into the explosive. In this case, a localized high temperature region, usually called 'hot spot', results. Depending on the size and the heat flux delivered by this hot spot, and on the initial physical conditions, initiation of a combustion reaction may result at the hot spot/explosive interface. The latter may propagate into a deflagration and even into a detonation, depending on the pressure and confinement conditions.

While several quantitative tests have been developed to investigate thermal explosion hazards (e.g. DSC, ARC, adiabatic Dewar), very few tests have been put forward to quantify hazards originating from localized energy deposition into commercial explosives. It has been found that, at atmospheric pressure, such local ignitions do not lead to self-sustained reactions in water-based explosives. This is because the initial stage of combustion is endothermic and, therefore, not self-propagating. Thus, for all water-based explosives, there

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is a minimum pressure required for combustion to take place. The latter is usually referred to as the 'Minimum Burning Pressure (MBP)' of the explosive. Below this pressure, the explosive cannot sustain combustion even if ignited by a strong hot spot. However, above the MBP, the explosive undergoes a normal combustion with a measurable burn rate. In evaluating the hazards associated with water-based explosives operations, the MBP is an important parameter to determine. For candidates for the ANE category, the test could be used to determine the likelihood of deflagration or detonation during transportation if an accident involving fire occurred. A significant advantage of this test is that it does not require an extensive test facility. Nevertheless, in spite of its small scale it should predict well the behaviour of a much larger quantity of material.

Description of the apparatus

The main part of the apparatus consists of a 4 litre high-pressure vessel. The explosive sample is contained in an aluminum oxide crucible (48 mm i.d. at the top, 25 mm i.d. at the bottom, 61 mm depth), which is suspended in the high-pressure vessel (Fig. 2). The ignition source consists of a 1 nichrome wire coil imbedded 10 mm under the surface of the sample. This coil is heated by an electric current. Two thermocouples are also mounted for diagnostic purposes.

The procedure consists of:

- Loading the sample
- Purging the high-pressure vessel with nitrogen and pressurizing the system to a pre-determined initial pressure
- Igniting the sample by means of a hot wire
- Controlling the vessel's internal pressure to a given level while the explosive sample is burning
- Remotely venting the combustion gases into the containment chamber

While the sample is burning, gas is generated at high rates. The vessel would therefore pressurize itself very rapidly if the pressure were not regulated. The vessel pressure is therefore regulated to an approximate constant level.

Preliminary results

The first system to be studied using the MBP apparatus was a commercially available detonator-sensitive emulsion explosive. A total of nine experiments were completed at various initial pressures. For each one, the quantity of material initially in the crucible was kept constant (89 ± 1 g). For this product, a MBP = 136 \pm 12 psig (0.94 \pm 0.08 MPa) was determined.

The information computed using the pressure and temperature traces, combined with the proportion of sample material burned, can be used to extract approximate information on the linear burn rate of the explosive. This also constitutes useful information since the combustion rate of an explosive determines the ease with which it can undergo a violent explosive reaction if it is ignited locally.

At least near the MBP, the linear burn rate was found to be a linear function of the pressure. This is consistent with previous observations on other water-based commercial explosives. A linear regression of results gave a value of about 2 mm/s at 500 psig, consistent with these earlier findings. In practical terms, this result demonstrates how an accidental ignition of an emulsion explosive above its MBP in a closed system will lead to a rapidly accelerating reaction as pressure builds up. Ultimately, detonation may result.

Conclusions

- An apparatus has been designed and commissioned to measure the MBP of water-based commercial explosives in the range from 0 to 2000 psi (0 to 14 MPa).
- The present apparatus has been successfully used to investigate the MBP of an emulsion explosive at room temperature.
- For such an explosive, the MBP was demonstrated to constitute a sharp threshold under which thermal ignition by a strong localized heat source does not lead to a self-propagating combustion reaction.
- Extrapolation of the measured average linear burn rates to pressures well above the MBP leads to combustion rates consistent with previously reported values.

Recommendations

- that the present apparatus be used to investigate the MBP of emulsion explosives as a function of water content (8 to 18% w/w)
- that the present apparatus and procedure be used to investigate the MBP of emulsion explosives at elevated temperatures representative of the corresponding maximum process or transportation temperatures.
- that, at some point in the future, MBP measurements be considered as part of the testing requirements for TDG classification of ANEs and other water-based explosives or precursors.