Defence Science Journal, Vol. 57, No. 6, November 2007, pp. 811-815

SHORT COMMUNICATION

Modelling of DMNB Content for Marked Plastic Explosives

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ABSTRACT

2,3-dimethyl-2,3-dinitrobutane (DMNB) has been internationally accepted as an additive for the purpose of marking, as it has desired vapour pressure for reliable detection. It is reported to be compatible with known explosive formulations and has a good shelf life. Explosive compositions with DMNB as marking agent can be detected in the temperature range –20 ºC to + 50 ºC. This paper describes modelling for quantifying activation energy for depletion of DMNB in the marked explosives, period for definite detection of the marked explosives and optimum initial concentration needed for the detection of DMNB content in the marked plastic explosives.

Keywords: Cyclonite, RDX, low-temperature plastic explosive, LTPE, plastic explosive Kirkee, PEK, DMNB, marked plastic explosive

1. INTRODUCTION

Explosives formulations based on cyclonite (RDX), pentaerythritol tetranitrate (PETN) and tetralite ceriam [$(NO_2)_3\ C_6H_2N(NO_2)CH_3.Ce$] are not easily detectable by the explosive vapour detectors (EVDs) due to low-vapour pressure values of these explosive compounds. Detection becomes more difficult when these explosive ingredients are used to make plastic explosives based on binders or when the quantity is minute and also when they are kept under concealed condition. For detection of explosives in concealed form, marking agents, which have high-vapour pressure, and are compatible with the basic explosive ingredients, have been used[1]. These agents are incorporated into the explosives at the time of manufacture to facilitate their monitoring during illegal/secret transport of explosives. 2,3-dimethyl-2,3-dinitrobutane (DMNB) has been extensively evaluated in various plastic and sheet explosives by many countries, because it enhances the detection without adversely affecting the performance of explosives. Experimental work was conducted to ascertain compatibility, stability and determination of 2,3-dimethyl-2,3-dinitrobutane (DMNB) depletion rate for the two plastic explosives, namely LTPE (low-temperature plastic explosive) and PEK (plastic explosive Kirkee) being manufactured in the Indian ordnance factories. For reliable detection throughout the life of the explosives, it is necessary to optimise the initial concentration of DMNB incorporated into the plastic explosives. The results of the abovesaid study on modelling on depleting characteristics of DMNB in these two marked explosives are reported in this paper.

2. EXPERIMENTAL PROCEDURE

DMNB was synthesised by minor modifications of the reported methods by Shechter[2] and Guicheney[3].

Received 25 January 2006, revised 23 March 2007

The product was recrystallised from ethanol. Plastic explosives, PEK and LTPE were prepared on a laboratory-scale limited to a 10 kg per batch simulating the conditions used for the large-scale manufacture. PEK is based on cerium (Ce), in which different percentages of DMNB was incorporated before addition of the binder. The explosive was mixed for three-and-half-hours at room temperature in sigma mixer with 10 rpm speed. It was a dry process and the EVD detected loss of about 10 per cent of DMNB in the final product using gas chromatography technique of analysis. RDX- based plastic explosive, LTPE was manufactured by a water-based process, which involved mixing at an elevated temperature for seven-and-half-hours and removal of water by heating under vacuum. Here, DMNB was incorporated at the end of drying stage and the marked explosive was mixed for another one-and-half-hours at about 40 - 45 °C. Addition at this stage resulted in the marked LTPE with a loss of about 10 per cent of DMNB originally added. In both the cases, the marked explosives of 100 g cartridge (ϕ 25 mm x length: 100 mm) were wrapped in a polythene/wax paper. These cartridges were used for all the experiments.

Compatibility of DMNB with both the plastic explosives was assessed by standard vacuum stability test and the values were found to be within the acceptable limits. Detectability of the explosives was studied using the EVD Model-97 HS manufactured by the Ai Cambridge Ltd (now, Ion Track Instruments Ltd), UK. The instrument detects DMNB in vapour state. Methods for the estimation of DMNB content in marked explosives were established by gas chromatography using electron capture detector.

3. MODELLING

Plastic explosive Kirkee and LTPE samples were prepared with initial DMNB concentrations of 0.5 per cent. They were subjected to heating at three different temperatures i.e, 35 °C, 55 °C and 75 °C. The variation of residual DMNB content in the respective marked explosive with storage time at different temperatures are presented in Figs 1 and 2.

The rate of depletion of DMNB concentration is assumed to take place in accordance with the Arrhenius equation[4], $k = A\, e^{-E/RT}$. Using the concentration depletion data for both the compositions, the value of activation energy is calculated as 20.78 kcal/mol in the temperature range 55-75 °C. At 75 °C, DMNB depletes in LTPE to 0.1 per cent concentration in 41 days while in PEK, it takes about 80 days for similar decrease in concentration. This is due to change in binder systems, actual particle size and particle size distribution used for manufacturing the two marked explosives. With these data, storage

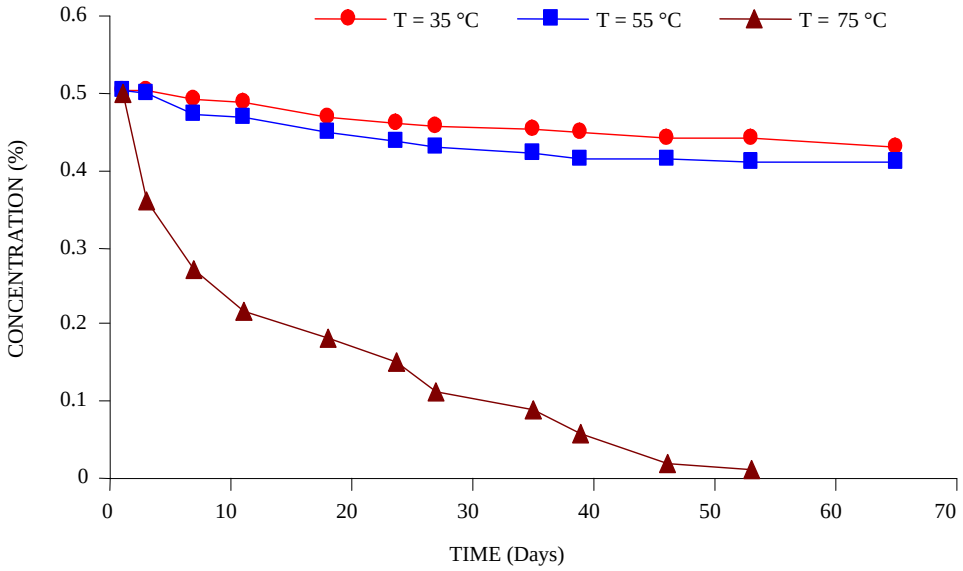

Figure 1. Degradation of DMNB in marked PEK at different temperatures.

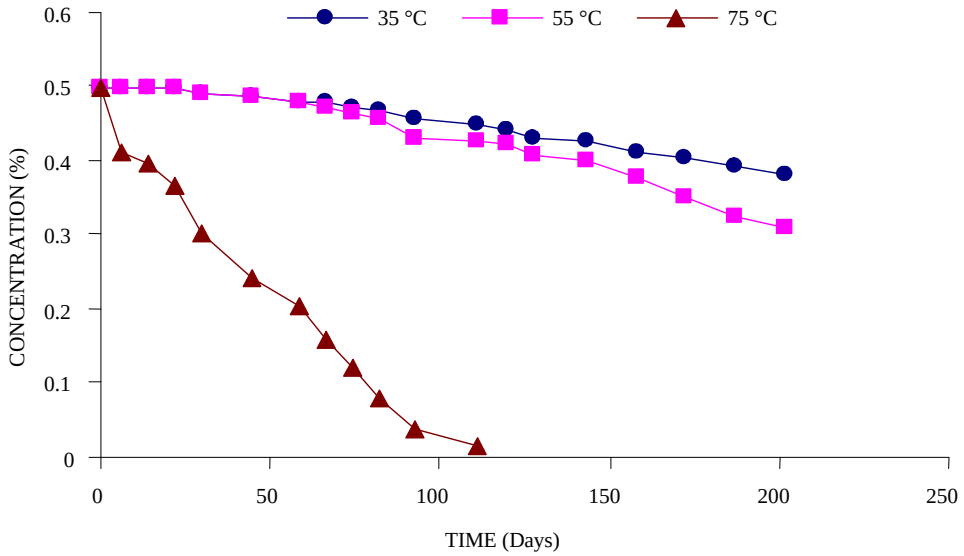

Figure 2. Degradation of DMNB in marked LTPE at different temperatures.

life of the two formulations where the concentration of DMNB is at detectable level was calculated at 27 °C and 40 °C, using Eqn (1):

$$\ln (k_r/k_1) = -E/R\ (1/T_r - 1/T_1) \qquad (1)$$

where, k is the velocity constant of chemical process, E is the activation energy, and T is the temperature. Subscripts r and 1 are used to denote reference and desired temperature conditions respectively.

If minimum detection limit for DMNB in the composition is 0.1 per cent and initial DMNB concentration is maintained at 0.5 per cent, the level of DMNB in PEK and LTPE can be monitored definitely upto 26.8 years and 11.2 years respectively at storage temperature of 27 °C. However, at 40 °C, the period for which DMNB can be detected successfully in PEK and LTPE, marked initially with 0.5 per cent DMNB is 6.3 years and 2.6 years respectively. If the concentration required for definite detection is raised from 0.1 per cent to 0.3 per cent, the life for sure detection at 27 °C will reduce considerably. Enhancing the detection limit of DMNB in PEK to 0.3 per cent reduces period of detection at 27 °C to 13.4 years. For LTPE, similar change will reduce definite detection period to 5.6 years. For assigning a positive detection life of 15 years at 27 °C with minimum detection limit of DMNB as 0.3 per cent for marked PEK and LTPE compositions, the initial DMNB concentration must be more than 0.525 per cent for PEK and 0.8375 per cent for LTPE.

The marked PEK samples with 0.5 per cent and 1.0 per cent initial concentration of DMNB were subjected to ISAT-A and ISAT-B (intensified standard alternating trials) environmental conditions. During both the trials, samples are subjected to thermal shocks for predefined durations in succession. In ISAT-A peak temperature is 60 ^{0}C, while in ISAT-B, peak temperature is 75 ^{0}C. Duration for holding sample at peak temperature in ISAT-B is higher than that in ISAT-A. Due to more severity of ISAT-B conditions, the rate of depletion of DMNB was found to be higher. In general, one-month storage at ISAT-A and ISAT-B conditions is equivalent to 6 months and 9 months, respectively of actual detection life. Although the rate of depletion is not constant throughout the period, but an average rate of depletion of DMNB is found to be between 0.015 per cent per month and 0.02 per cent per month for ISAT-A and ISAT-B, respectively.

Under ISAT-A conditions, a safe detection life of 12.6 months was observed for the marked LTPE with 0.5 per cent initial concentration of DMNB, which is equivalent to 6.3 years storage at ambient conditions (27 °C). For attaining minimum detection limit of 0.3 per cent after 15 years, ISAT-A conditions predict that the initial concentration of DMNB should be 0.78 per cent or more. ISAT-

B trials give a definite detection period of 10.8 months, which is equivalent to 5.4 years. The minimum initial concentration of DMNB needed for definite detection after 15 years works out to be 0.67 per cent.

For PEK, ISAT-A predicts a safe detection life of 13.2 months corresponding to storage life of 9.8 years at ambient conditions could be assigned for samples with 0.5 per cent initial concentration of DMNB. For attaining minimum detection limit of 0.3 per cent after 15 years, ISAT-A conditions predict initial concentration of DMNB should be 0.76 per cent or more. ISAT-B trials give a safe detection life of 12.7 months, which is equivalent to 9.5 years. The minimum initial concentration of DMNB needed for safe detection after 15 years is about 0.62 per cent.

The marked LTPE with 0.7 per cent DMNB was processed and kept in normal ambient condition, where temperature was varying from 10 ^{o}C in winter to about 40 ^{o}C in summer. Under such circumstances, after 6 years the DMNB content was found to be 0.5 per cent, which gives an average rate of depletion of 0.0027 per cent per month. This is much lower than the depletion of DMNB in ISAT, conditions.

4. CONCLUSIONS

Although value of depletion rate is found varying in different explosives, LTPE needs more DMNB doping as compared to PEK for positive detection life of 15 years. For ensuring a concentration of 0.3 per cent of DMNB after 15 years storage, it is necessary to incorporate 0.8 per cent DMNB at the time of manufacture in both the marked explosives, PEK and LTPE. A similar trend is depicted in ISAT-A, ISAT-B and depletion trials at different temperature conditions. Calculation of initial concentration based on ISAT-A results are more conservative and compositions fulfilling ISAT-A conditions will automatically fulfil ISAT-B condition for detection. Experimental trial under ambient storage condition for the marked LTPE showed much lower depletion rate of DMNB, indicating conservative estimates, obtained through ISAT conditions. Relaxing the detection criteria in terms of detectable concentration of DMNB or time for safe detection will correspondingly reduce the concentration of DMNB doped at the time of manufacturing these explosives.

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