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SHORT COMMUNICATION

Tagging of Explosives for Detection

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ABSTRACT

This paper gives the results of a study on estimation of shelf life of 2,3-dimethyl 2,3-dinitrobutane (DMNB)-tagged RDX and PETN explosives by monitoring DMNB depletion by high performance liquid chromatography and simultaneously recording the detectability of the tagged explosive composition using explosive vapour detector Model-97 HS. DMNB was incorporated in the explosive using methanol as solvent for DMNB and the explosive compositions were stored at 35, 55 and 75 °C over a long period. Methods developed for preparing the homogeneously tagged composition with DMNB at 0.5 per cent level and for the analysis of DMNB for ensuring homogeneity of DMNB in the composition are described. The results show no change in compatibility and sensitivity on the incorporation of DMNB in the explosive. Estimation of shelf life of DMNB in the explosive was done for a period of storage of 202-304 days at different temperatures.

1. INTRODUCTION

Plastic bonded explosives (PBXs) based on cyclotrimethylene trinitramine (RDX) and penta erythritol tetranitrate (PETN) are not easily detectable by any explosive vapour detector (EVD) due to low vapour pressure values, especially when the quantity is minute and they are kept under concealed condition. For detection of explosives in concealed form, taggants or detection agents which have high vapour pressure, and are compatible with the basic explosive ingredients have been used[1]. These taggants are incorporated into the explosives at the time of manufacture, as a measure to control illegal/secret transport of explosives.

Several taggants have been reported in literature[2]. Although several of these taggants have good detectability, most of them have low storage life due to their high rate of evaporation. One particular detection agent, 2,3-dimethyl 2,3-dinitrobutane (DMNB), has been identified as the most promising taggant. This paper describes the results of a study on the effect of tagging on the explosive and the life of RDX/PETN-based compositions using DMNB as the tagging agent.

2. EXPERIMENTAL WORK

DMNB was synthesised in the laboratory by a method reported in literature[3,4] using ammonium persulphate and 2-nitropropane. The recrystallised product was then characterised[1,5] by infrared spectroscopy, ultraviolet spectroscopy, high performance liquid chromatography (HPLC) and DTA and melting point determination. DMNB with 99 per cent purity, as estimated by HPLC, was used in the preparation of the compositions. Two types of compositions were prepared: (i) RDX/DMNB (99.5/0.5), and (ii) PETN/DMNB (99.5/0.5), using methanol (*MeOH*) as the solvent. These compositions were then kept under different temperature conditions, i.e. at 35, 55 and 75 °C. A 50 mg sample

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Table 1. Compatibility, impact & friction test results

Explosive composition	Compatibility test: Vol. of gas evolved 120 °C, 48 hr (ml)	Impact sensitivity: (50% Ht. of explosion) (cm)	Friction sensitivity (kg)
Pure RDX	0.36	54	19.2
RDX + 0.5% DMNB	0.37	55	19.2
Pure PETN	1.39	35	12.0
PETN + 0.5% DMNB	1.41	34	12.0

Table 2. Detectability test results

Explosive composition	Distance between probe and explosive (cm)	After 4 months (cm)	After 6 months (cm)	After 10 months (cm)
Pure RDX	2.0	2.0	2.0	2.0
RDX + 0.5% DMNB	7.5	7.0	6.0	5.0
Pure PETN	2.5	2.5	2.5	2.5
PETN +0.5% DMNB	8.5	8.0	7.0	6.0
Pure DMNB	15.0	15.0	15.0	15.0

of each composition was then analysed by HPLC at an interval of 7 days (168 hr). A mobile phase of 35:60:5 ($MeOH$: H_2O: AcN), C_{18} reverse phase Zorbax ODS column with a flow rate of 1 ml/min was used in the HPLC studies. Detectability of the composition was simultaneously studied using explosive vapour detector Model-97 HS manufactured by Ai Cambridge Ltd., UK.

Impact and friction sensitivities of the compositions were determined by standard methods and the values are give in Table 1. Compatibility of DMNB with RDX and PETN was assessed by standard vacuum stability test and the values (Table 1) were found to be within the compatibility limit. The results of the detectability test using the explosive detector are given in Table 2.

The percentage of DMNB present in the tagged explosives was determined immediately after mixing; the DMNB content was found to be the same as incorporated. For life assessment, samples were withdrawn from the tagged explosives kept at different temperatures and the percentage of residual DMNB was determined through HPLC analysis. The data obtained were computed as a function of time and percentage of residual DMNB in the sample. The following Arrhenius equation was used to calculate the life of DMNB in the tagged explosives.

$$E \quad \frac{4.576(\log K_2 - \log K_1) \times T_2\, T_1}{T_2 - T_1}$$

where E is the activation energy (21,326.45 cal/mol) for RDX/DMNB (99.5/0.5 per cent) in the temperature range 55-75 °C, E is the activation energy (25,029.71 cal/mol) for PETN/DMNB (99.5/0.5 per cent) in the temperature range 55-75 °C, and K_1, K_2 are the reciprocal of evaporation time at absolute temperatures T_1 and T_2, respectively.

HPLC studies on RDX and PETN compositions tagged with DMNB indicated that at ambient temperature, the loss of DMNB after 245 and 200 days, respectively was marginal. However, in the case of conditioned samples, there was substantial loss of DMNB in tagged RDX and PETN compositions. At 75 °C, the percentage of DMNB in RDX/DMNB (99.5/0.5) composition was reduced from 0.50 per cent to 0.01 per cent in 111 days. At 55 °C, DMNB level was reduced from 0.50 per cent to 0.31 per cent in 202 days, and at 35 °C, DMNB level was reduced from 0.50 per cent to 0.38 per cent in 202 days. The percentages of residual DMNB in the compositions conditioned at different temperatures are given in Table 3. At 75 °C, the percentage of DMNB in PETN/DMNB (99.5/0.5) composition was reduced from 0.50 per cent to 0.01 per cent in 65 days. At 55 °C, DMNB level was reduced from 0.50 per cent to 0.20 per cent in 304 days. At 35 °C, DMNB level was reduced from 0.50 per cent to 0.22 per cent in 304 days. The percentages of residual DMNB in the compositions conditioned at various temperatures are given in Table 4.

3. RESULTS & DISCUSSION

The characteristics of synthesised DMNB have been found to be comparable with the reported values. The impact and friction sensitivity values indicate that there is not much change in the sensitivities of the tagged compositions wrt the base compositions. The compatibility test values indicate that DMNB is compatible with the explosive, since the gases

Table 3. HPLC test results of RDX/DMNB compositions per cent of residual DMNB

Period of storage (days)	Storage Temperature		
	35 °C	55 °C	75 °C
6	0.5000	0.4993	0.4103
14	0.4998	0.4991	0.3951
22	0.4988	0.4979	0.3646
30	0.4920	0.4890	0.3001
45	0.4884	0.4862	0.2432
59	0.4803	0.4775	0.2019
66	0.4780	0.4721	0.1597
74	0.4731	0.4653	0.1202
82	0.4692	0.4570	0.0802
93	0.4570	0.4311	0.0389
111	0.4500	0.4250	0.0140
120	0.4412	0.4220	
128	0.4320	0.4078	
143	0.4250	0.3992	
158	0.4101	0.3756	
172	0.4025	0.3520	
187	0.3920	0.3255	
202	0.3821	0.3102	

Table 4. HPLC test results of PETN/DMNB compositions per cent of residual DMNB

Period of storage (days)	Storage temperature		
	35 °C	55 °C	75 °C
7	0.4902	0.4739	0.3214
11	0.4863	0.4689	0.2704
18	0.4703	0.4494	0.2168
24	0.4612	0.4382	0.1814
27	0.4572	0.4314	0.1502
35	0.4528	0.4204	0.1121
39	0.4493	0.4140	0.0873
46	0.4416	0.4136	0.0583
53	0.4397	0.4114	0.0210
65	0.4302	0.4095	0.0112
71	0.4285	0.4033	
80	0.4214	0.3960	
88	0.4187	0.3924	
96	0.4115	0.3852	
104	0.4090	0.3818	
112	0.4016	0.3720	
127	0.4000	0.3638	
141	0.3915	0.3515	
149	0.3901	0.3488	
157	0.3877	0.3390	
165	0.3801	0.3215	

evolved do not exceed 2.0 ml/5 g of the composition.

The RDX/DMNB composition gives instant response to the detector at 7.5 cm from the probe, while pure RDX gives instant response only up to 2.0 cm from the probe of the detector, for the same quantity of the explosive, indicating that the response for detection of the explosives tagged with DMNB is better than for untagged explosives. PETN/DMNB composition also gives the same response.

For RDX/DMNB system at 75 °C, the percentage of DMNB was reduced from 0.50 per cent to 0.01 per cent in 111 days. The data obtained on conditioning the composition at 55 and 35 °C reveal that DMNB is quite stable at these temperatures.

The activation energy values for RDX/DMNB and PETN/DMNB (99.5/0.5) were found to be 21,326.45 and 25,029.71 cal/mol, respectively. The assumption is made that heating the components to a high temperature for a relatively short period is equivalent to storing them for a much longer time at a lower temperature[6]

If the evaporation time at a particular temperature is known, the same at any other temperature can be calculated, since the activation energy is known[7]. Based on the weight loss data for DMNB obtained by HPLC at different temperatures, the activation energy was calculated. For assessing the life, 0.1 per cent DMNB content was taken as the cut off line, since at this concentration of DMNB, the detector was able to detect the tagged explosive composition properly. However, detectability of the composition with the explosive vapour detector model-97 HS becomes weak only after 0.01per cent. By using the activation energy value, the life of DMNB has been calculated[8].

Using the activation energy and the weight loss data, the storage life of DMNB in RDX/DMNB composition has been evaluated to be 32.1 and 8.0 years at 27 and 40 °C, respectively. Similarly, in

PETN/DMNB composition, the storage life of DMNB at 27 and 40 °C has been evaluated to be 31 and 7 years, respectively.

4. CONCLUSION

DMNB has no adverse effect on the basic explosive properties of the parent compound. Addition of DMNB increases detectability of the explosives. The shelf life of DMNB in the compositions is found to be satisfactory.

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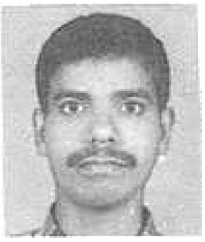

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