

SHORT COMMUNICATION

Thermal Stability and Shelf-life of High Energy Fuel for Torpedoes

K.C. Raha, S.S. Adhav, N.M. Bhide, A.D. Yewale, G.K. Gupta and J.S. Karir

High Energy Materials Research Laboratory, Pune – 411 021

ABSTRACT

1,2-Dinitroxy propane-based liquid fuel is an advanced high energy fuel for torpedoes. The high energy fuel is used with an oxidiser, viz., hydroxyl ammonium perchlorate as a bi-propellant system for torpedo propulsion. Thermal stability of high energy fuel has been arrived at by differential thermal analysis and also by following the depletion in stabiliser content as well as increase in acidity with ageing. Rate constant for decomposition, activation energy for depletion of 2-nitro diphenylamine (2-NDPA) and shelf-life of high energy fuel have been determined. Due to the high vapour pressure of high energy fuel (because of 1,2-dinitroxy propane), usual experimental set up could not be used and the sample was conditioned in sealed tubes. The shelf-life of high energy fuel is arrived at using Woolwich, Berthelot and Arrhenius equations and the results obtained are 100 years, 125 years and 276 years, respectively. Considering the safety aspect, the lowest value, viz., 100 years is recommended as safe life of high energy fuel. This work confirms the reported estimates of the good storage stability of high energy fuel.

Keywords: High energy fuel, torpedoes, shelf-life, explosives, liquid fuel, 2-nitro diphenylamine, thermal stability, torpedo propulsion, bi-propellant system, 1,2-dinitroxy propane

INTRODUCTION

1,2-Dinitroxy propane-based high energy fuel is one of the irreplaceable liquid fuel used since sixties, mainly for heavy weight torpedoes^{1,2}. The decomposition of a nitric ester on ageing is its inherent property. It is slow at the start and becomes fast with the passing of time, due to the catalytic effect of the decomposition products, viz, oxides of nitrogen. The nitric ester is stabilised by 2-nitro diphenylamine (2-NDPA) and desensitised by di-*n*-butyl sebacate (DBS). The nominal composition of high energy fuel³ is 1,2-dinitroxy propane 76.0 per cent, 2-NDPA 1.5 per cent and DBS 22.5 per cent.

The high energy fuel is dark orange liquid at room temperature. The vapour pressure⁴ of

1,2-dinitroxy propane is 0.098 mm of mercury at 25 °C and is 400 times higher than that of commonly used NG (2.475×10^{-4} mm of mercury at 20 °C)⁵. High vapour pressure of high energy fuel poses problem in undertaking its thermal analysis and in determining its shelf-life by accelerated ageing at higher temperature in contrast to conventional double and triple-base propellants. 1,2-Dinitroxy propane-based high energy fuel has been reported physically and chemically stable when kept at 50 °C for three years³. In another work⁶, the shelf-life of high energy fuel has been reported to be 102 years at 50 °C. In both the cases only the life in years has been reported and no method of life assessment is given. According to Urbanski⁷, this particular alkyl ester is insufficiently stable even in the purest form. Therefore, the method to assess the shelf-life of high energy fuel

has been developed by High Energy Materials Research Laboratory (HEMRL), Pune.

The life assessment of high energy fuel has been carried out by conducting various stability tests at elevated temperatures and extrapolating the results to ambient temperature. In practice, the time required for depletion of half of the initial stabiliser content of propellant under storage condition, is taken as the shelf-life of the propellant. The high energy fuel is subjected to storage at elevated temperature and depletion in stabiliser content is followed with time. Rate of depletion of stabiliser⁸⁻¹⁰ is used to calculate the shelf-life at ambient temperature using various equations, viz., Woolwich, Berthelot and Arrhenius equations. The generation of data on the stability and shelf-life of high energy fuel is of utmost importance for its safe storage and handling.

2. EXPERIMENTAL PROCEDURE

Differential thermal analysis (DTA) of high energy fuel was carried out and the profile was recorded as a function of temperature on a two pen strip chart recorder.

In accelerated ageing of high energy fuel, the major problem encountered was that of the vapour pressure of nitric ester component of high energy fuel. Thus, usual method of ageing caused preferential loss of nitric ester at elevated temperature, resulting in apparent increase in stabiliser content in initial stages. Hence, high energy fuel required some special technique to be used for keeping the sample at elevated temperature during ageing. Various methods were tried to prevent the loss of sample due to evaporation. In one set up, the arrangement was made in such a way that the sample in the container was kept in a high temperature water bath and the capillary attached to lid was kept out of the bath in open, to allow condensation. It was found that there was no condensation of vapours even though the length of the capillary tube was increased to about 50 cm but there was clear evidence of loss of high energy fuel.

The boiling point of both DBS and 1, 2 dinitroxy propane is 90-92 °C at 5 mm of pressure. Thus, the boiling point of the liquid, viz., high energy fuel will be very high at atmospheric pressure and there is no chance of building up of pressure when high energy fuel is heated in a sealed cell at 90 °C. Therefore, it was decided to take high energy fuel in a sealed container for conditioning at 60 °C, 70 °C, 80 °C, and 90 °C and the fall in stabiliser was estimated by withdrawing the sample at different time intervals. The separation and estimation of stabiliser was carried out by high pressure liquid chromatography (HPLC) using reverse phase technique on Zorbax C-18 column using methanol:water (70:30) as mobile phase and UV detector at 232 nm. It is well known¹¹ that the DBS will hydrolyse with the residual moisture present in the high energy fuel to generate acid, which in turn will catalyse the decomposition of nitric ester. In Bergmann and Junk test (B&J test)¹², stability of the propellant is monitored by the quantity of oxides of nitrogen in the evolved gases or acidity due to these. Therefore, the acidity developed in the conditioned sample was estimated by memotitrator. The assessment of shelf-life was carried out using the three equations⁸⁻¹⁰. In all these equations, the depletion of 2-NDPA has been considered as first-order reaction. Abel heat test was carried out to determine the stability of high energy fuel at different stages of ageing.

2.1 Woolwich Equation

$$\text{Shelf-life } (t_1 \text{ years}) = \frac{t_2 \times \log(A + 2)}{\log[A(1 + x)/(A - x)]} \times 1.8^Y$$

- t_2 = Time of test in years
- A = Initial concentration of stabiliser (1.5 per cent),
- x = Fall in stabiliser
- Y = (Test temperature °F – Ambient temperature °F)/10.

2.2 Berthelot Equation

Berthelot equation is applied to develop curves reflecting the variation in rate of reaction

with temperature and is written as

$\log K = aT + b$, where K is the rate constant, T is the temperature in Kelvin and a and b are constants.

For reaction rate constants at two different temperatures, the rate constants are related as

$$\log k_2 - \log k_1 = a (T_2 - T_1)$$

$$t_1 = t_2 \times \delta_{10}^{(T_2 - T_1)/10}$$

$$D_x = (a_x/365) \times \delta_{10}^{(T_2 - T_1)/10}$$

considering $t_1 = D_x$ and $t_2 = a_x$, where a_x is the time in days necessary to obtain a 50 per cent decrease in stabiliser content at T_2 , δ_{10} is the increase in rate of reaction for 10 °C rise and D_x is the prediction of the safe life to obtain a 50 per cent decrease in stabiliser content at T_1 . In these studies, the shelf-life has been determined at 20 °C and the extent of decomposition considered is 50 per cent.

2.3 Arrhenius Equation

Arrhenius equation for rate constant of reaction is given as $k = Ae^{-E/RT}$, where k is the rate constant for depletion of stabiliser, A is frequency factor, E is activation energy for depletion in stabiliser, R is gas constant and T is temperature in Kelvin. At the stage of 50 per cent depletion after time period t , $\log (c/2) = k \times t$, where t is half-life, and c is the original concentration. Thus, when one compares at two different temperatures, the half-life can be compared as

$$t_1/t_2 = k_2/k_1 = e^{E/R \times (1/T_1 - 1/T_2)}$$

$$t_1 = t_2 \times e^{E/R (1/T_1 - 1/T_2)}$$

where t_1 is the half-life at T_1 K, and t_2 is the half-life at T_2 K, and E is the activation energy for depletion of 2-NDPA.

3. RESULTS & DISCUSSION

Various DTA experiments were carried out using different heating rates, where ΔT , viz.,

difference in temperature of the sample wrt the neutral (Al_2O_3) has been recorded as a function of temperature. It was observed that because of high vapour pressure, high energy fuel sample up to 15 mg just evaporates before any thermal change occurs, with the heating rates within 2 °C/min to 20 °C/min. Thus, the DTA does not record any peak up to 400 °C, except endothermic base line shift up to 200 °C. Efforts were made to optimise the heating rate and sample quantity to reduce the time of experiment leading to minimum vaporisation. At the high heating rate of 20 °C/min with 20 mg sample, small endotherm was observed at 185 °C followed by exotherm at 190 °C. Secondly, to minimise the loss due to evaporation, the sample and the reference cups were covered lightly with thin aluminium foil, to ensure that sample remains in equilibrium with its vapours throughout the temperature range till it starts decomposing and it does not produce excess pressure in the cup.

The representative thermogram is shown in Fig. 1. It was observed that initially up to around 180 °C, there is slight endothermic shift in baseline showing evaporation of liquid. After 180 °C, there is inflection in the baseline with exothermal peak at 190 °C, followed by complex overlapping exotherms up to 400 °C, thereby revealing that the fast decomposition can be at about 180 °C and proceeds through stages of exotherms to completion.

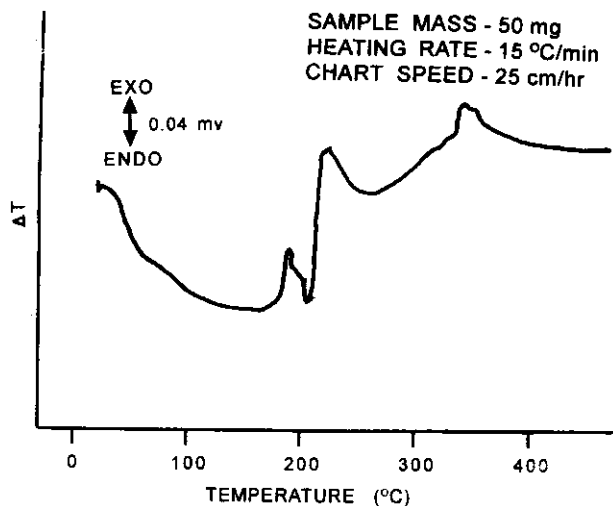


Figure 1. Differential thermal analysis of high energy fuel

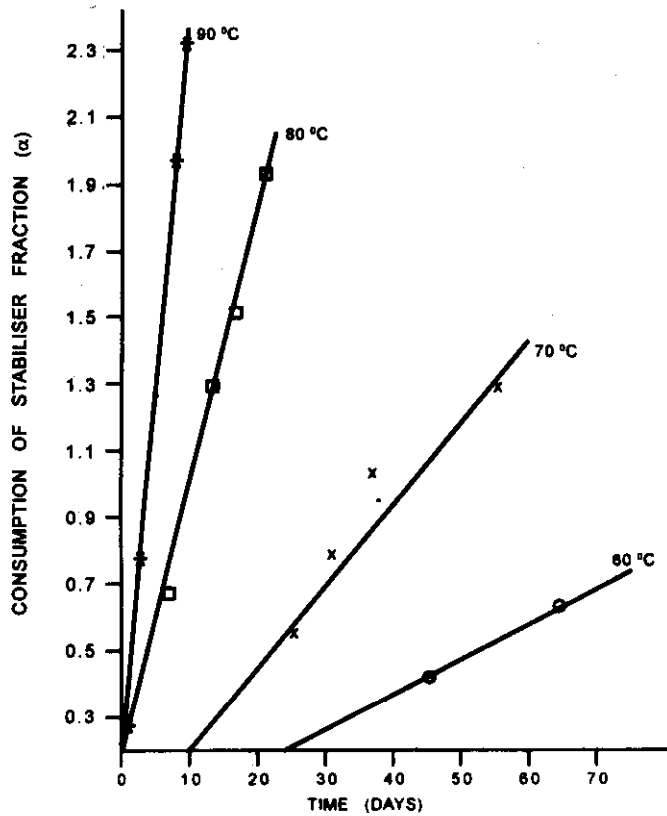


Figure 2. Fraction of stabiliser depleted with time at 60 °C, 70 °C, 80 °C and 90 °C.

The accelerated ageing was carried out to monitor depletion of 2-NDPA till about 30 per cent loss at 80 °C and 90 °C, and 20 per cent loss at 60 °C and 70 °C. The samples were withdrawn at regular time intervals, and heat test values and stabiliser contents were determined. Heat test values gradually decrease with ageing as expected. Thus an ageing at 80 °C, the heat test values decreased from 26 min to 24 min, 17 min, 16 min and 15 min after 4 days, 8 days, 12 days and 20 days, respectively. In the chromatogram for the separation of stabiliser by HPLC, the area under the peak is proportional to the quantity of 2-NDPA. The fraction of stabiliser decrease as a function of time ($\alpha-t$ curve) at 60 °C, 70 °C, 80 °C and 90 °C has been calculated and reproduced in Fig. 2. From the $\alpha-t$ curve, the rate constant of decomposition at different temperatures has been evaluated assuming first-order reaction. Figure 3 gives the $\log k$ versus $1/T$ plot and the slope gives the value of

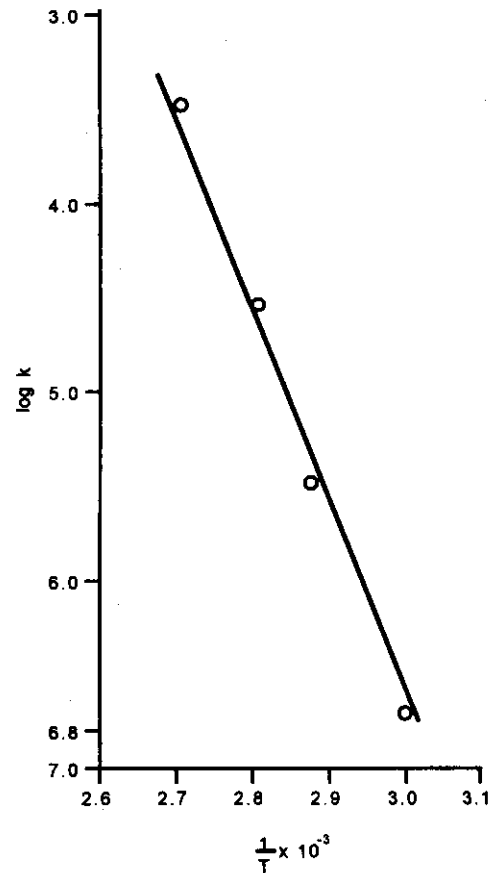


Figure 3. Arrhenius plot for rate of depletion of stabiliser

activation energy as 23 kcal/mole. The slope of $\alpha-t$ curve was used to calculate the time of depletion of 2-NDPA to the extent of 10 per cent, 20 per cent, 30 per cent, 40 per cent and 50 per cent at the temperatures of experiments by

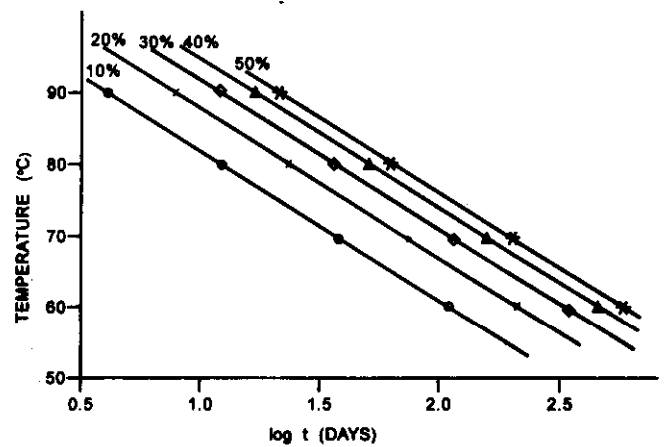


Figure 4. Berthelot plot of $\log t$ (time) and temperature

Table 1. Experimental data

Temp (°C)	Time interval (days)	Stabiliser content (x = %)	Abel heat test (min)	Acidity (sebacic acid) (%)
60	00	1.05	28,29	—
60	45	1.44	26,25	—
60	65	1.41	26,25	—
70	00	1.05	28,29	—
70	25	1.41	26,25	—
70	30	1.37	25,25	—
70	35	1.35	25,25	—
70	50	1.31	24,24	—
80	00	1.05	28,29	—
80	08	1.40	25,25	0.086
80	15	1.31	24,24	0.095
80	18	1.27	16,16	0.111
80	23	1.21	15,15	0.170
90	00	1.05	28,29	—
90	01	1.46	26,26	—
90	03	1.39	23,23	—
90	08	1.20	15,15	—
90	10	1.15	13,13	—

extrapolation (Fig. 4). The calculation of slope was done by least square method.

Table 1 presents the experimental data. The α - t curves in Fig. 2 have been used to compute the value of shelf-life of high energy fuel by

Woolwich equation that gives the average value of shelf-life as 100 years.

Figure 4 gives the increase in rate of reaction for 10° rise in temperature, viz., δ_{10} (average) as 3.007. The average value of shelf-life has been computed by Berthelot equation as 125 years.

The value of E/R being known from Fig. 3 as 1.176×10^4 , the shelf-life has been calculated by Arrhenius equation. The average shelf-life works out to be 276 years. The computation of shelf-life varies widely on small variation of activation energy. So, least square method was used. The results of calculation of shelf-life are presented in Table 2.

The average values of shelf-life determined by Woolwich, Berthelot and Arrhenius equations are 100 years, 125 years and 276 years, respectively. This trend has also been observed by Garman,¹⁰ *et al.* for double-base propellants. The acidity developed on ageing at 80 °C has been determined (Fig. 5). It has been found that acidity increases to 0.17 per cent after 15 days of ageing, as expected.

4. CONCLUSION

Calculation of shelf-life of high energy fuel by Arrhenius equation gives shelf-life of 276 years, as compared to 100 years and 125 years by Woolwich and Berthelot equations, respectively. Considering

Table 2. Results of calculation of shelf-life

Temp (°C)	Time for 50 % depletion of stabiliser (days)		$\delta_{10} = t_r/t_{T+10}$	Shelf-life at 20 °C (years)		
	$\log t$	t		Woolwich test	Berthelot equation $t/365 \times \delta_{10}^{(T_2-T_1)/10}$	Arrhenius equation $e^{E/R(1/T_1-1/T_2)} \times t_r/365$
60	2.750	562	2.942	106	125	287
70	2.281	191	3.183	104	128	297
80	1.778	060	2.857	95	121	268
90	1.328	021	—	96	127	253
Average shelf-life (years)				100	125	276

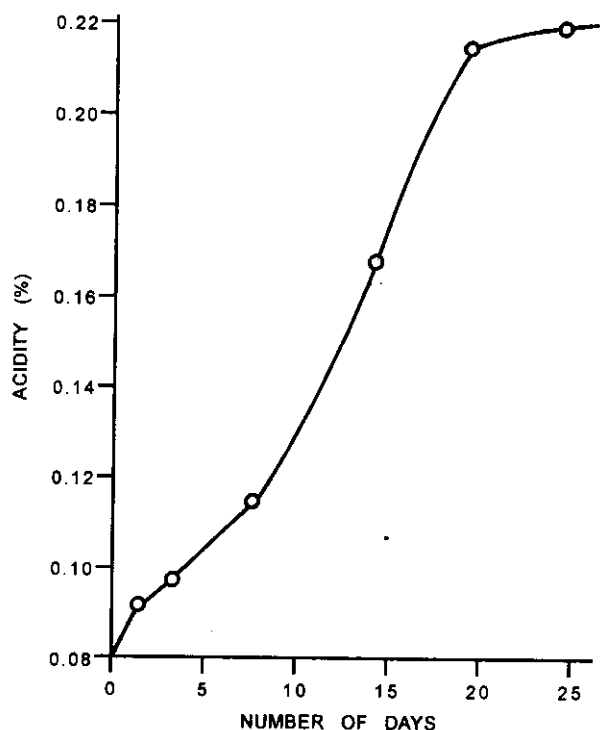


Figure 5. Percentage of acidity (calculated as sebacic acid) developed with time at 80 °C.

the safety aspect, it is recommended that the safe life of high energy fuel may be considered as 100 years at 20 °C.

The decomposition mechanism of propellant is very complex and even the derivatives of the stabiliser formed after reaction with the oxides of nitrogen act as stabilisers. Thus, it is very difficult to separate the rate determining reaction from the total complex reaction. The long shelf-life of high energy fuel compared to conventional gun propellants cannot be explained on the basis of chemical mechanism of stabilisation and requires additional studies.

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