

Further Studies of the High Rate
Decomposition of High Energy Materials

J. M. Rosen and J. R. Holden

U. S. Naval Ordnance Laboratory
White Oak, Silver Spring, Maryland

INTRODUCTION

Recent studies at the Naval Ordnance Laboratory have been carried out to gain additional information on the sensitivity of high energy materials. A unique thermal sensitivity method has been devised by Wenograd (1) in which small (3 to 4 mg) samples are very rapidly heated to temperatures in the range of 300 to 1000°C. The delay time to explosion is measured as a function of sample temperature.

This present report contains additional thermal sensitivity data on high energy liquid compositions using Wenograd's method. The work was performed primarily to demonstrate the capability of the thermal sensitivity method in following changes in the sensitivity of high energy systems.

In the thermal sensitivity determination a 2.1 microliter sample is enclosed in a $2\frac{1}{2}$ inch length of stainless steel hypodermic needle tubing. The tubing is then heated very rapidly by discharging a capacitor through it, and its resistance is measured as a function of time. The temperature to which the tubing has been raised by the capacitor discharge can be calculated from the ratio of its hot resistance to its room temperature resistance. When the sample within the tube explodes, it bursts the tube wall causing an abrupt change in the resistance of the tube. Therefore, both the temperature of the sample container and the delay time before the sample explodes can be determined by measuring the resistance of the hypodermic needle tube as a function of time. In the sensitivity apparatus, this is done by making the tube one arm of a Wheatstone bridge circuit and displaying the unbalance voltage of the bridge on an oscilloscope. The delay time is also measured with an electronic timer which is started by a signal from the capacitor discharge and stopped by a signal from a microphone located near the bursting sample tube.

EXPERIMENTAL

No basic change has been made in the original circuit designed by Wenograd (1). The fundamental part of the circuit is shown schematically in Figure 1. The high voltage pulser consists of a high voltage power supply, which charges a $2 \mu F$ capacitor to voltages ranging to about 7 kV, and 5C22 thyatron for switching this charge. The capacitor discharges its energy through all three branches of the circuit, but because of the lower resistance of $R_1 + R_2$, the bulk of the current flows through this path. When the capacitor has finished discharging, the high-voltage pulser represents an open circuit and only the simple Wheatstone bridge powered by E_B through R_A remains.

The sample tubes are easily filled with a liquid by placing the open ends in the liquid as shown in Figure 2. Air is removed from the tubing by evacuation. When the atmosphere is readmitted, the liquid sample is forced into the tubing. About 0.1 cc of sample is required for a series of measurements.

It is possible to work with volatile liquids if the sample is cooled to reduce the vapor pressure. In this way the sample may be loaded by evacuation without permitting a significant loss of the sample.

A program for the IBM 7090 digital computer is used to treat the thermal sensitivity experimental data. In addition to computing temperatures from the unbalance voltages, the program yields a least square fit of the data to the straight line defined by

$$\log_{10} \text{ delay time in milliseconds} = A + \frac{1000B}{T, ^\circ K}.$$

All of the data shown represent the results of the least square fit described above.

RESULTS AND DISCUSSION

The employment of improved experimental techniques has reduced the amount of scatter of the data compared to that previously reported (1). Figure 3 is representative of the measurements at the present time. The dashed lines represent the limits of one standard deviation of \log_{10} delay time. Three replicate measurements of nitroglycerine made at intervals of about one month are shown in Table 1.

TABLE 1

THERMAL SENSITIVITY OF NITROGLYCERINE

Sample	Temp., °C at 250 microsec. delay	Slope, B / Δ	Stand. dev. of log ₁₀ delay time	No. of trials	Range, millisec.
1	395	7.7	0.21	17	0.03 to 8.27
2	392	8.3	0.22	13	0.02 to 6.05
3	397	8.1	0.19	20	0.04 to 27.50

$$\Delta \log_{10} \text{ delay time in milliseconds} = A + \frac{1000 B}{T, ^\circ K}$$

Most of the experimental error at the present time can be attributed to oscilloscope drift and uncertainty in the resistance measurements. It is not expected that a further improvement in the quality of data can be achieved with the apparatus in use.

Tetranitromethane (TNM) with two added fuels, toluene and nitromethane, was studied in an attempt to follow changes in sensitivity as a function of composition. The data obtained were extrapolated to the 10 microsecond delay times and the temperatures corresponding to these times were plotted as a function of composition, Figures 4 and 5. For purposes of comparison with booster sensitivity data, the 10 microsecond time seemed reasonable as that is the approximate time an explosive is heated to a high temperature by the shock wave in the booster type test.

A very sharp drop in temperature is obtained with the addition of 6% toluene, Figure 4, which is interpreted as a marked increase in sensitivity. The rise in temperature obtained with larger amounts of toluene is believed to represent a decrease in sensitivity.

The TNM-nitromethane system was briefly investigated, Figure 5. The temperature drop did not appear to be as sharp as that obtained with added toluene. Further measurements will be made to complete the TNM-nitromethane study.

Tschinkel and Morrison investigated the sensitivity of TNM with added benzene and nitromethane (2). They found the addition of 5% benzene increased the "card gap" value for TNM from 25 to greater than 300. TNM with 25% benzene also had a "card gap" value greater than 300. However, only a relatively small increase in sensitivity occurred with added nitromethane. The maximum "card gap" value was 80 at 70% TNM.

Tschinkel and Morrison point out the large difference between the shock sensitivities of TNM with added benzene and nitromethane. This large difference is not indicated by the thermal sensitivity method where the minimum temperatures required for thermal initiation differ by only about 100°C. The greatest sensitivity of TNM containing toluene occurs in the range of maximum energy as computed by Tschinkel and Morrison. In the TNM-hydrocarbon system, there is a general agreement between shock sensitivity and thermal sensitivity data as both show a marked increase in sensitivity with the addition of a small percentage of hydrocarbon.

It seemed worthwhile to examine the sensitivity of nitroglycerine with added dimethyl phthalate as this compound has been used as a desensitizer for nitroglycerine. Data obtained on a number of compositions are shown in Figure 6. Progressive increases in dimethyl phthalate content also increase the temperature required for thermal initiation. The decrease in sensitivity with the addition of 9.3% and 18.7% dimethyl phthalate appear to be rather small. It is believed this is a real effect although it could not be defended by a statistical proof. A very large difference is noted between 30% and 40% dimethyl phthalate, particularly at short delay times.

Although the hot-tube thermal sensitivity information is believed to provide a good characterization for high energy materials, it cannot be considered trustworthy in determining handling hazards. Certainly there are many properties that affect the sensitivity characteristics of a liquid such as vapor pressure, viscosity, and chemical reactivity.

Further studies of high energy systems will be carried out to gain insight into the parameters that affect the thermal sensitivity.

REFERENCES

- (1) J. Wenograd, *Trans. Faraday Soc.*, 57, 1612 (1961).
- (2) J. G. Tschinkel and C. R. Morrison, *J. of Chem. and Eng. Data*, 2, 350 (1958).

$R_3 = R_4 = 25$ OHM NON-INDUCTIVE RESISTOR; $R_A = 10$ OHM NON-INDUCTIVE RESISTOR;
 $R_2 =$ CONSTANTAN RESISTOR; $R_1 =$ TUBE UNDER TEST; $E_B = 24$ V STORAGE BATTERY;
 $E =$ OSCILLOSCOPE

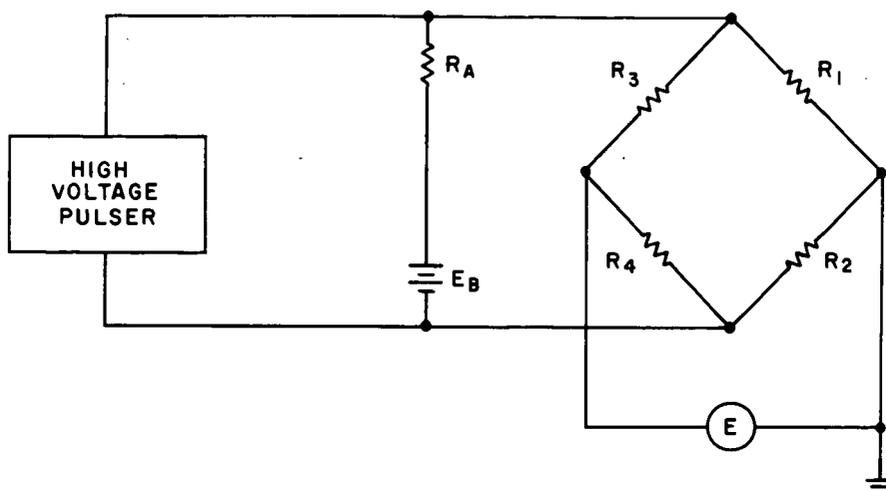
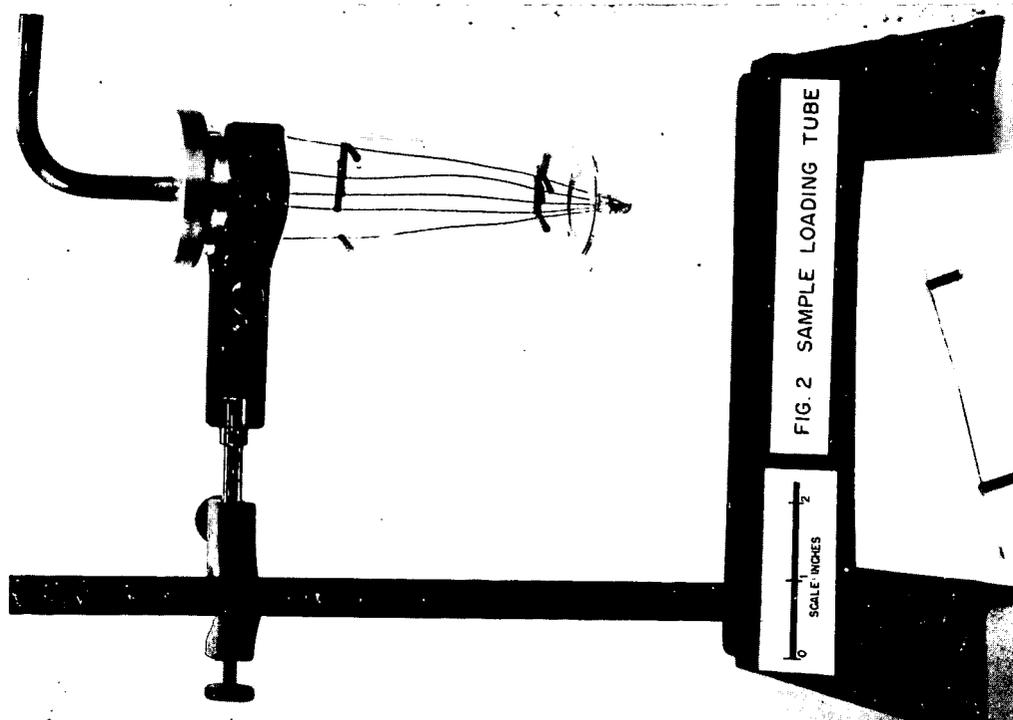


FIG. 1 CIRCUIT OF THERMAL SENSITIVITY APPARATUS



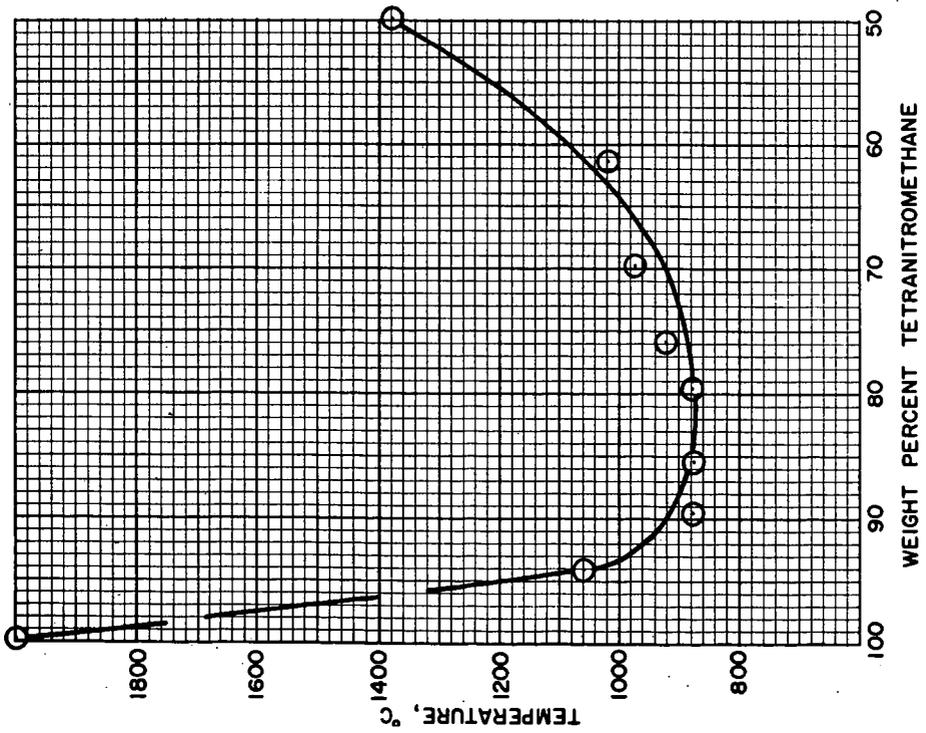
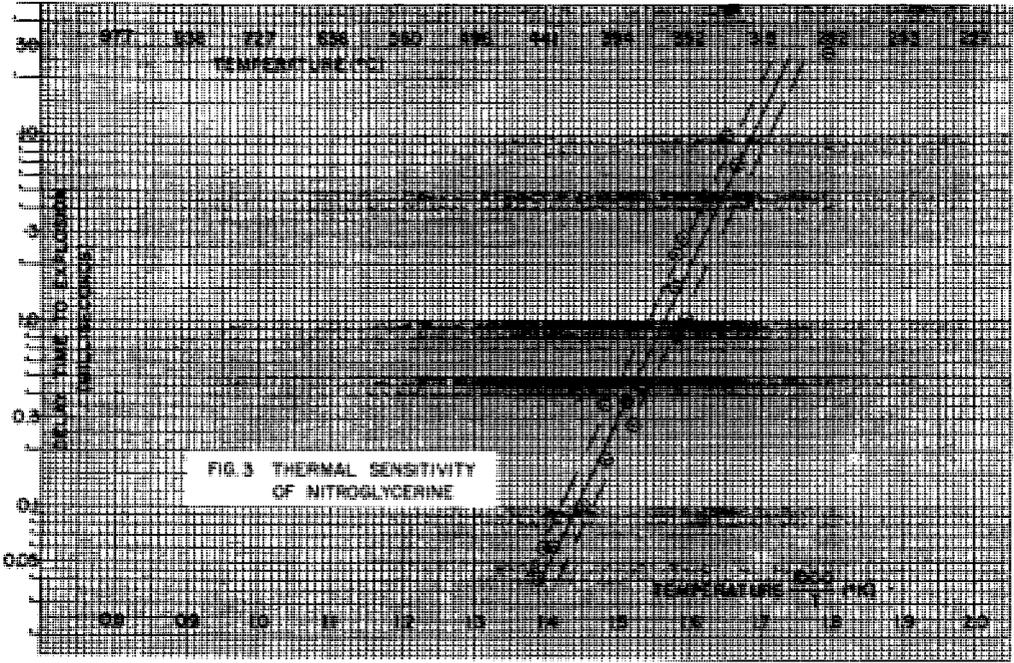


FIG. 4 TNM-TOLUENE COMPOSITIONS; TEMPERATURE AT THE 10 MICROSECOND DELAY TIME

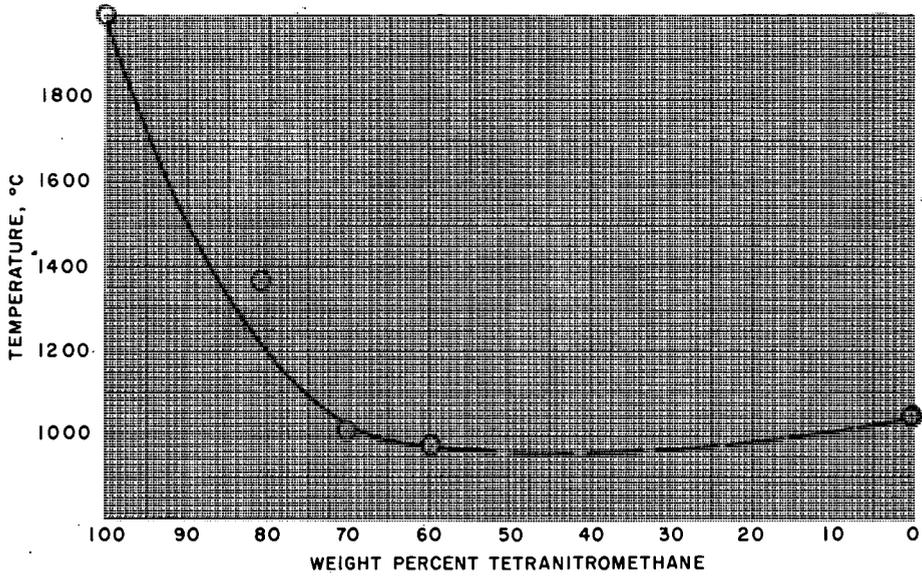


FIG. 5 TNM - NITROMETHANE COMPOSITIONS; TEMPERATURE AT THE 10 MICROSECOND DELAY TIME

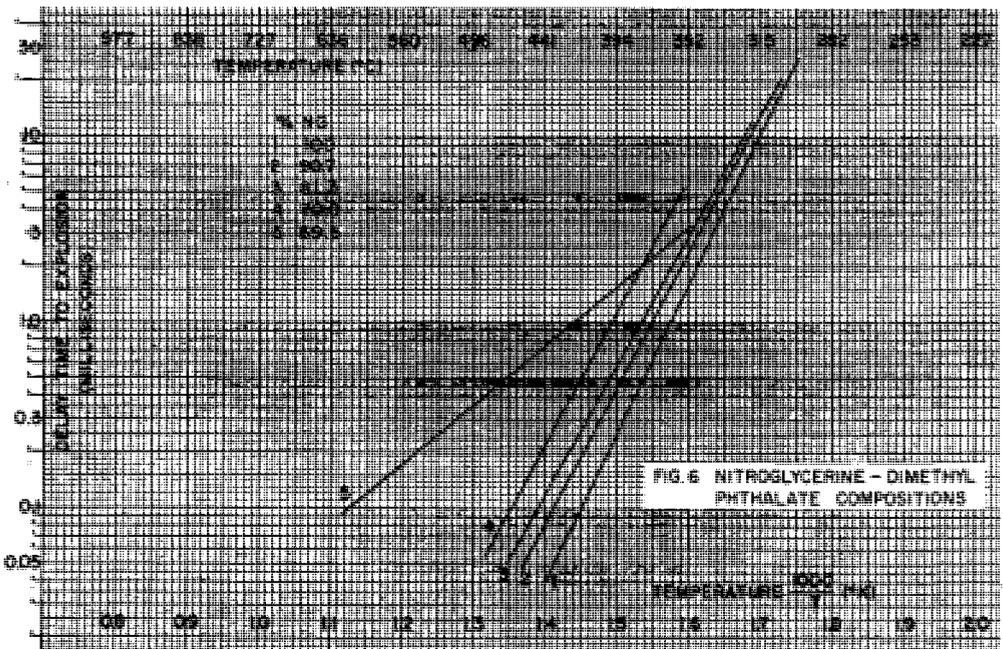


FIG. 6 NITROGLYCERINE - DIMETHYL PHTHALATE COMPOSITIONS