Shock Sensitivity of Tetranitromethane and Some of Its Mixtures with Fuels

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In a previous paper (*4*), the possibility of composing monopropellants from tetranitromethane and fuels was discussed. The objective of this investigation is to provide more data on the explosive safety of such monopropellants.

CARD GAP TEST

The "card gap test" (*1*) was used to assess explosive safety in terms of "shock sensitivity."

In essence, the test setup consists, in vertical upward sequence, of a blasting cap (a 50-gram tetryl pellet), separated by a stack of plastic disks ("cards") from a sample of 35 to 40 ml. contained in a steel cylinder 1 inch in diameter. On top of the sample cylinder is placed a steel "target" plate $^3/_8$ inch in thickness.

The number of cards that attenuates the shock of the detonating tetryl pellet just enough to allow the sample to detonate with 50% probability is the measure of sensitivity. Detonation of the sample is indicated by puncture or fracture of the target plate.

Because the method involves some uncontrollable variables, a statistical procedure must be followed, firing about 20 shots. Results are given as the number of cards at 50% probability of detonation of the sample.

Maintaining the sample temperature within ± 1° C., a precision of ± 1 card can be obtained in the range 0 to 50 cards.

As to the meaning of the results, the test simulates only one of the possible causes of detonation, namely a hydrodynamic shock. In particular, results are not indicative of the tendency toward thermal explosions.

CHEMICALS USED

The following chemicals were used in composing the tested mixtures.

Tetranitromethane, 99.5% pure, Polynitro Chemical Co.

Nitromethane, 99.5% pure, Commercial Solvents Corp.

Monomethyl glycol, source unknown, distilled, met refractive index specification

Benzene, 99 to 100% pure, General Chemical Division, Allied Chemical & Dye Corp.

TEST RESULTS

The experimental data are listed in Table I. Sample temperature was 20° ± 1° C. throughout.

The same data are plotted as Figure 1. A theoretically more significant plot is obtained by expressing the mixture ratios in terms of fuel equivalence fraction, *q*. This is simply obtained by calculating an average molecular formula of the mixture containing *C* carbon atoms, *H* hydrogen atoms, and *X* oxygen atoms. Then

$$q = \frac{4C + H}{4C + H + 2X}$$

Thus, $q = 0.5$ signifies equivalent, $q < 0.5$ fuel lean, $q > 0.5$ fuel rich.

In Figure 3 is given a plot of enthalpy of explosion *vs.*

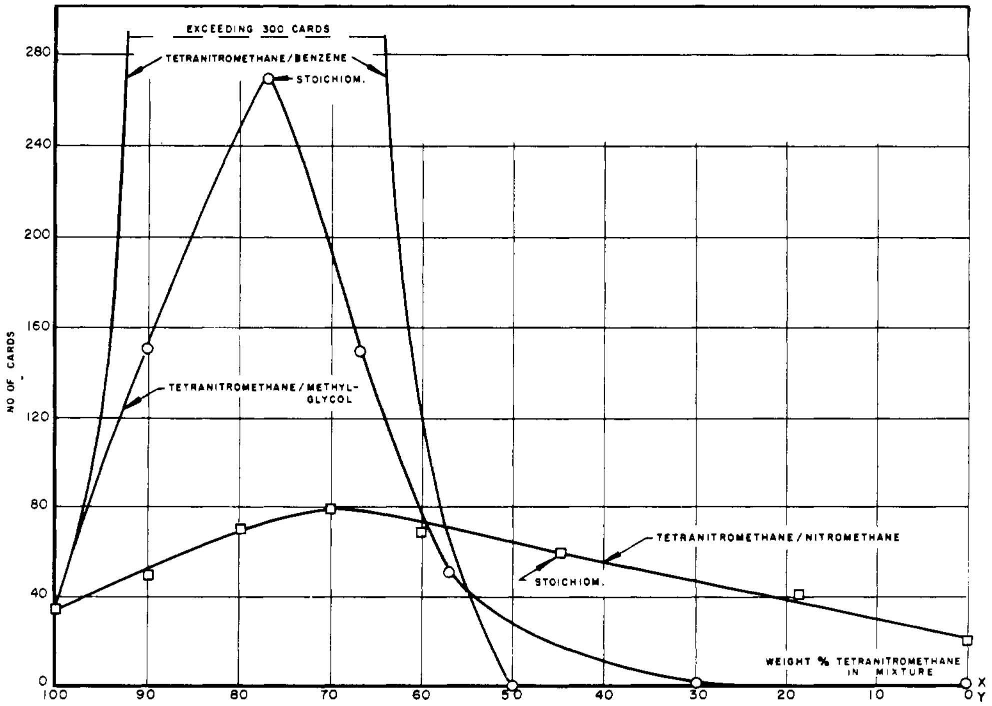

Figure 1. Card gap value *vs.* weight composition of mixtures

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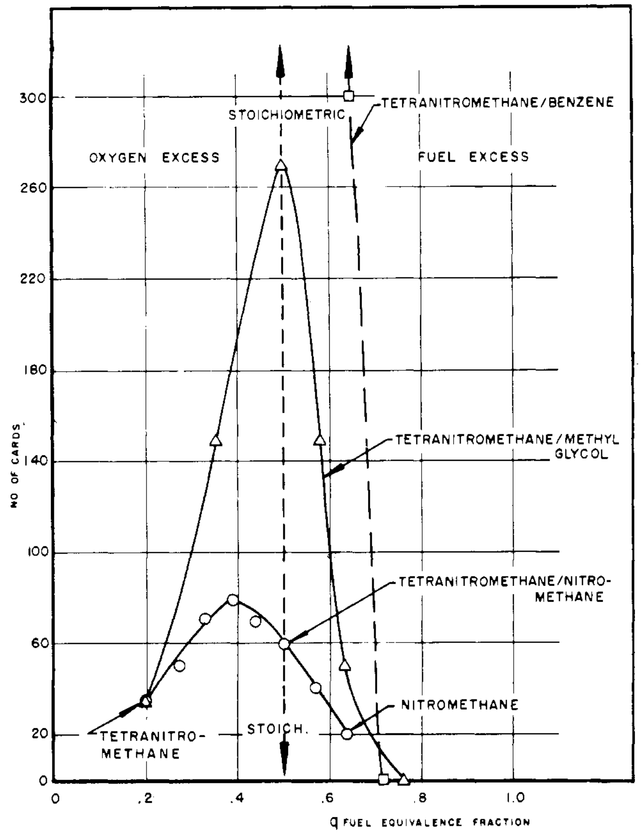

Figure 2. Card gap value vs. fuel equivalence fraction

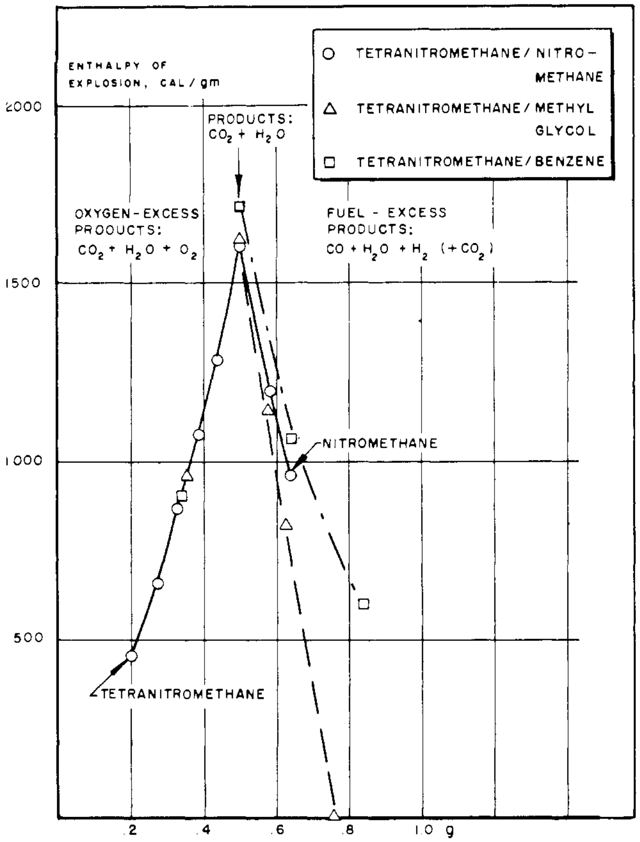

Figure 3. Enthalpy of explosion vs. fuel equivalence fraction

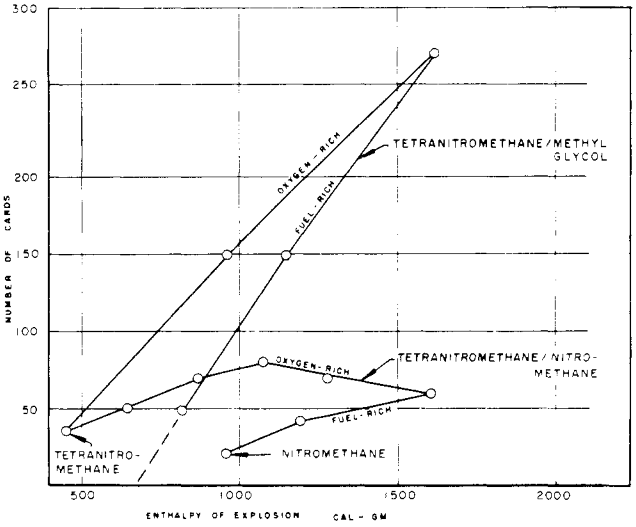

Figure 4. Card gap value vs. enthalpy of explosion

fuel equivalence fraction. In calculating this enthalpy, products of explosion were assumed to be CO_2, H_2O, and O_2 at $q < 0.5$; CO_2 and H_2O at $q = 0.5$; and CO_2, CO, H_2O, H_2 according to the water gas equilibrium at an estimated flame temperature at $q > 0.5$.

When Figures 2 and 3 were cross-plotted, Figure 4 was obtained, showing the card number vs. enthalpy of explosion.

DISCUSSION OF RESULTS

Data confirm earlier indication (*3*) that tetranitromethane-nitromethane mixtures are safer than stoichiometrically equivalent mixtures of tetranitromethane and hydrocarbons. Tetranitromethane-benzene mixtures are extremely sensitive, as one would expect from other tests using a graded scale of blasting caps (2, *4*).

The tetranitromethane–methyl glycol mixture ranges in sensitivity between the nitromethane mixtures and benzene mixtures. On the fuel-rich branch, the sensitivity of the methyl glycol mixture exceeds the sensitivity of pure nitromethane by a factor of 2.5.

This means that composing a monopropellant of higher density (*4*) than and approximately equal performance to nitromethane by mixing tetranitromethane and methyl glycol would lead to increased sensitivity.

Table I. Experimental Data

Propellant				
Tetranitromethane, Wt. %	Fuel	Fuel Equiv. Fraction, q	Enthalpy of Explosion, Cal./Gram	50% Probability of Detonation at Number of Cards
100	Nitromethane	0.20	455	35
90		0.27	660	50
80		0.33	870	70
70		0.39	1080	80
60		0.44	1285	69
44.5		0.50	1600	59
18.8		0.59	1195	41
0		0.64	960	20
90	Methyl glycol	0.36	960	150
77		0.50	1625	270
67		0.58	1145	150
57		0.63	820	50
30		0.76	7	0
95	Benzene	0.33	905	In excess of 300 cards
86		0.50	1720	
75		0.64	1070	
50		0.83	600	0

Another remarkable observation on Figure 2 is the shift of the maximum of sensitivity to the oxygen-rich side with the tetranitromethane-nitromethane mixtures. If the card number is plotted as a function of enthalpy of explosion in Figure 4, it is seen that peak sensitivity appears at peak enthalpy (1600 cal. per gram) except with the oxygen-rich branch of tetranitromethane-nitromethane, where a somewhat higher sensitivity is reached at 1100 cal. per gram. Note that the sensitivity increase at the enthalpy of nitromethane (960 cal. per gram) is more than fourfold.

In general, the chemical constitution has a great influence on shock sensitivity in accord with experience at other places. Tests on more types of mixtures appear to be worth while.

LITERATURE CITED

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Volume Changes in Petroleum Waxes as Determined from Refractive Index Measurements

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Solid transitions take place in commercial paraffin waxes as well as in pure *n*-paraffin hydrocarbons, and these changes can be detected in a variety of ways (*13*, *14*, *20*, *21*, *25*, *26*). The changes in translucency, mottling, and formation of bubbles that occur in masses of paraffin wax during storage are evidences that basic changes in structure are taking place.

The volume changes accompanying such transitions are of considerable importance in commercial applications for waxes. For example, in the molding of candles, contraction must be carefully controlled, if the candles are to release from the mold properly, and yet not contain stresses which will make them unduly fragile in handling. The cracking of wax films on paper food cups and milk containers as a result of thermal shocks which accompany the processing of the containers is a further example of the practical importance of volume changes in solid waxes.

Therefore, in the formulation of waxes for specific end uses a convenient method is needed for measuring volume changes with respect to temperature.

The direct method is to measure changes in volume as they occur with variations in temperature, using apparatus such as the dilatometer (*24*). The chief difficulties in using the dilatometer lie in the need for completely removing and excluding gases from the solid sample and in the lengthy periods of time needed to bring the system to equilibrium. Certain other methods, such as those involving measurement of dielectric constant, or x-ray diffraction, permit the calculation of wax volume, but are too complex for everyday use.

Described here is a method by which volume changes in petroleum waxes may be estimated over a range of temperatures with sufficient ease and accuracy to warrant its use in the development of wax products. The method uses a density determination in the liquid state together with measurements of refractive index in both liquid and solid states, to provide the data needed to calculate density or specific volume at other temperatures.

METHOD OF CALCULATION

The fact that a relationship exists between density and refractive index of a material permits calculation of density and of specific volume at any temperature from easily obtained measurements of the refractive index at that temperature and of the density and refractive index at one temperature in the liquid state. Johnson (*13*) has successfully used this relationship to measure transition temperature ranges in paraffin waxes, and to determine densities of liquid and solid dotriacontane.

The expression of this relationship showing closest agreement with observation over the range of temperatures considered here is given by the formula of Lorentz and Lorenz:

$$r = \frac{n^2 - 1}{n^2 + 2} \times \frac{1}{d} \qquad (1)$$

where r is the specific refractivity in terms of n, the refractive index, and d, the density at the same temperature.

The specific refractivity has been shown to be considered substantially independent of the state of aggregation and relatively invariant to change in temperature (*10*, *11*, *16*). Thus, the density at any temperature may be calculated from the refractive index at that temperature and the specific refractivity. The specific refractivity is most easily calculated from refractive index and density at a temperature where the wax is liquid.

By equating the expressions for specific refractivity at the two temperatures, the density at the second temperature can be calculated. It is given by

$$d_2 = d_1 \left(\frac{n_1^2 + 2}{n_1^2 - 1}\right)\left(\frac{n_2^2 - 1}{n_2^2 + 2}\right) \qquad (2)$$

where d_1 and d_2 are the densities at the two temperatures, and n_1 and n_2 are the refractive indices at the same two temperatures.

In practical application it is usually more convenient to speak in terms of volume rather than of density changes taking place in a wax. Accordingly in the cases which follow, specific volume, the reciprocal of the density, has been shown in addition to or instead of density.

As solid petroleum wax is known to be birefringent, a mean value for refractive index must be calculated for use in Equation 2. Although strict adherence to the theory requires the use of a geometric mean, in practice the approximation given by Pope (*18*)

$$n = \frac{2\,n_o + n_e}{3} \qquad (3)$$

is sufficiently accurate for most work. Here n_o and n_e represent the refractive indices as given by the ordinary and extraordinary rays, respectively.

In this work no correction of the observed refractive indices was made, as the main interest was comparison and not absolute values.