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Explosive Characteristics and Shaped Charge Applications of Nitromethane (NM): A Review

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Abstract: Nitromethane (NM or CH₃NO₂) has a wide range of applications as a detonating homogeneous liquid explosive. Although, its use as a liquid propellant is more pronounced, the determination and characterization of NM and its mixtures for their various detonation properties has gained in importance. Various researchers have performed initiation studies of NM by shock and jet, and the presence of a superdetonation zone has also been debated. The opacity or otherwise of the reaction and detonation zones has been investigated experimentally. Sensitization or dilution of NM by various additives and the effect on the detonation behavior has also been investigated. In recent times, the use of NM as a field-filled homogeneous filling in shaped charges for the disposal of unexploded ordnance has gained in importance. The experimental observations and related theoretical aspects for the use of NM as a filling for shaped charges are illustrated in this article. Overall, NM can be thought suitable as a viable future alternative for both commercial and military applications.

Keywords: liquid explosive, nitromethane, detonation, shaped charge, sensitization

Abbreviations

NM : nitromethane

DETA: diethylenetriamine (NH₂C₂H₄NHC₂H₄NH₂)

VOD : velocity of detonation

EDA : ethylenediamine (NH₂C₂H₄NH₂) DDT : deflagration to detonation transition

TNT : trinitrotoluene

Introduction

Nitromethane (NM or CH₃NO₂) is a chemical reagent which cannot be detonated on its own even after receiving a very high shock from a detonator. However it can be used as a propellant and its combustion behaviour has been investigated [1, 2]. The integration of the kinetics of the C-N bond scission of nitromethane has allowed an elementary reaction scheme to be established. The reduction to a very simplified mechanism gives the reactions for a transient combustion calculation. The theoretical results obtained for the profiles of temperature, species and burning rates agree roughly with the experimental data of strand burner measurements. Only when NM is sensitized by the addition of other chemicals, can it be used as an explosive. NM sensitized with ammonia (5-6%) can detonate with standard blasting caps and delivers around 24% more power as compared to conventional TNT (trinitrotoluene). There are several other sensitizers for NM such as aniline, ethylenediamine (EDA), diethylenetriamine (DETA) etc., which have successfully given detonation of sufficient strength. Many detonating compositions containing nitromethane as the major ingredient are reported [3-13]. NM is a liquid at room temperature (melting point -29 °C), with a density of 1.138 g/cm³ at 20 °C and has a boiling point of 101.2 °C. It has a lower explosive limit of 7.3% volume by volume in air and a molecular weight of 61.04 [14]. NM has an oxygen balance of -39.3%, The velocity of detonation is 6300 m/s under confinement and the volume of the gaseous products of detonation is 1060 litres per kg. The current review paper discusses the explosive characterization of nitromethane and its mixtures. The use of nitromethane along with some additives in shaped charges is discussed. However, the general theoretical developments and advanced experimental techniques related to other common solid or liquid explosives are excluded.

Explosive characteristics of nitromethane

In one of the early reports on the explosive characteristics of nitromethane [15], the experimentally observed shock initiation of homogeneous explosives was quantitatively reproduced using one-dimensional, numerical, reactive hydrodynamics, and realistic equations of state. A shock travels into the explosive, causing shock heating. A detonation develops and overtakes the shock wave. The hydrodynamic hot spot is reasonably successful as a model for computing the critical sizes of hot spots in shocked nitromethane. A hydrodynamic hot spot may fail to explode if the rarefaction reaches its center before it can explode

adiabatically. If the hot spot explodes, it sends a shock wave into the undetonated explosive, which heats the explosive. Whether or not it propagates depends upon the initial strength of the shock wave and how well it is supported from the rear. As an extension to this work, work done prior to 1976 is compiled as a report and certain major findings for detonation of nitromethane as an homogeneous explosive is enumerated [16]. The small (2500 Angstrom thick) and pulsating reaction zone leads to difficulty in evaluating the effect of the reaction zone on flow. Although the head of the rarefaction goes into the reaction zone at the same speed regardless of the reaction zone thickness, the wave curvature depends on how much the confining surface or wall moves out during passage of the reaction zone. Because lower density walls permit more outward motion than higher density walls, the lower density walls result in more curved fronts. Shortening the reaction zone keeps the wall from moving outwards as much during transit, which results in less shock curvature. The two critical parameters are the rarefaction speed and the reaction zone length. It is also observed that thin metal foils are as effective as thick cylinders of the same metal in confining the nitromethane detonation wave.

The detonation reaction-zone length in neat, denatured, and chemically sensitized nitromethane (NM) has been measured by using several different, laserbased velocity interferometry techniques. The experiments involved measuring the particle velocity history at a NM/PMMA (polymethylmethacrylate) window interface during the time a detonation in the NM interacted with the interface. Profiles measured at the NM/PMMA interface agreed with the ZND theory, in that a spike (~2.45 mm/µs) is measured that is consistent with an extrapolated reactant NM Hugoniot matched to the PMMA window. The spike is rather sharp, followed by a rapid drop in particle velocity over a time of 5 to 10 ns; this is evidence of early fast reactions. Over about 50 ns, a much slower particle velocity decrease occurs to the assumed CJ condition, indicating a total reaction zone length of ~300 μm. When the NM is chemically modified, such as replacing the hydrogen atoms with deuterium or chemically sensitizing with a base, some differences are observed in the early part of the reaction [17]. NM behaves as a wide-bandgap insulator and it undergoes chemical decomposition and transformation into a semi-metallic state for a limited distance behind the detonation front. The transformation is found to be associated with the production of charged decomposition species. The shock front of NM is found to be optically absorbing and thick. The formation of charged CO, NCO and CNO on the 10-100 ps timescale provides a possible mechanism for such optical behaviour. However elsewhere the reaction zone of NM is stated to be transparent. It is also concluded that the lowering of the bandgap or electronic excited states is not

required to sustain chemical reactions under the conditions of higher pressure detonation in NM [18].

Shock initiation of nitromethane has been investigated [19] and impedance mismatches are considered as sources of hot spots for heterogeneous NM (NM gelled with 6% by wt of silica beads of discrete sizes). The smaller beads, which are at a higher number density and closer interparticle spacing, were found to be more sensitizing than the larger beads. For the samples containing 6 wt% 40 μ m beads in gelled nitromethane, a range of initiation behaviours was observed for the first time. As the initial shock strength was varied, the behavior transitioned from "heterogeneous"-like, with growth in the front at low shock input pressures, to initiation via thermal explosion, and build-up of a reactive wave more characteristic of homogeneous explosives, at high pressures.

Jet initiation of nitromethane and its mixtures was studied and the governing criteria were established in terms of jet velocity and jet diameter [20, 21]. The paper provides findings for the four different materials, namely nitromethane (NM), diethylenetriamine (DETA), boron carbide (B₄C), and Cab-O-sil TS-720 fumed silica (TS720), and control parameters included the failure diameter (d_f), the shaped-charge jet velocity (v) and the jet diameter (d_i). Plate dent and temperature measurements have been obtained to determine the failure diameter for neat NM, NM/DETA, and NM/B₄C/TS720 mixtures as a function of temperature and/or additive concentration. For equivalent wt% concentrations, DETA was found to be more effective than B₄C at reducing the failure diameter of nitromethane. It was also demonstrated that the B₄C additive has a larger effect on the failure diameter of nitromethane, probably due to the increased number density of particles or a difference in particle impedances. Measurements of the radiographic jet-diameter by utilising a microdensitometer scanning technique gave a refined threshold criterion. The d_f curve fits were subsequently used to determine failure diameters for threshold experiments, and for comparison of homogeneous- and heterogeneous-sensitization. Hypervelocity jet initiation threshold criteria were established over a broad range of jet velocities and diameters, and the initiation criteria for the individual NM data sets were calculated in the $v^2/d_i = k$ form for comparison to the literature threshold criteria values for other explosives. These values were then normalized with the respective HE failure diameters, and displayed a strong correlation (with the exception of two points) to the linear relationship $v^2 d_i/d_f = 4.7$. This correlation suggests that a universal form can be established for different explosives responding to similar threats and under similar experimental conditions using the failure diameter as a normalization factor between explosives.

The presence of curved shock and non-constant amplitude was confirmed in

another paper [22] by using the gap test. It was stated that multiple mechanisms for initiation of liquid explosives act simultaneously at small scales, but these disappears at large scales (100 mm). The type of sensitivity being tested was difficult to finalize. However, the result was said to be valid specifically for the mixture of nitromethane and 5% DETA. The critical radius of initiation was also found to be in good agreement with the measurements of the shock overtake distance in planar shock initiation experiments by Sheffield et al. [23].

The detonation wave structure in homogenous liquid explosives indicates both sharply rising and smoothly growing pressure [24]. NM is taken as a sample liquid explosive and theoretical modeling for its detonation was proposed [25]. Its reaction rates obey Arrhenius kinetics and the phenomena needs many collisions before equilibrium of vibrational, rotational and translational energies are achieved behind the shock front. Homogenous liquid explosives show longer induction times and the leading shock is often multi-dimensional cellular in nature. Ignition and growth models were experimentally validated for NM.

For the explosive characterization of NM, the equation of state for unreacted, shocked NM was established [26]. The Monte Carlo Technique was used to develop the equation, which is able to predict primary properties like pressure-specific volume curves, shock velocity-particle velocity relations, shock temperature etc. Certain derived explosive properties like the Grüneisen parameter, the heat capacity at constant volume, the sound velocity and others, were established and a comparison has been made with two well-known EOS in the literature. Velocity of sound, isothermal compressibility and coefficient of thermal expansion were computed by the two EOS and the Monte Carlo simulations, and the results agree with each other.

Reactive flow modeling and numerical simulation results using the CHEETAH code have been presented for NM [27] and it was observed that the failure diameter is highly sensitive to the reaction rate. The detonation velocity was found to depend on the charge size and linear dependence between velocity of detonation and shock front curvature was also established both practically and by simulation.

In one of the earlier studies [28], by means of Perot Fabry Velocimetry (PFV), material velocities generated by an intense shock wave (P > 70 kbar) in pure nitromethane showed that nitromethane does not behave according to the Campbell-Travis model for detonation in liquid explosives. No evidence of a so-called super-detonation, which would start behind and overtake the pressure shock wave, was observed. The liquid explosive behaves very similarly to that of solid polycrystalline explosives and is compatible with the heterogeneous decomposition scheme. However, with more advanced techniques,

superdetonation was subsequently observed by spectroscopic measurements during the deflagration to detonation transition of nitromethane [29]. The time-resolved radiant spectra showed that the detonation front, the reaction products produced during the superdetonation, and the detonation products are semitransparent. For shocked NM, the minimum temperature reaches 2500 K and during the superdetonation and detonation propagations, it reaches 3200 K and 3600 K respectively . NM has a slow reaction stage and the detonation structure is characterized by a fast reaction stage behind the detonation shock, followed by a slow reaction stage, which tends to be destabilizing.

Experimental and theoretical studies were conducted with mixture of nitromethane with other diluents [30, 31]. Binary mixtures of nitromethane and non-explosive liquids (like methanol and nitrobenzene) were investigated using an electromagnetic method for measurement of the particle velocity. The detonation limit on concentration (DLC) was experimentally evaluated. As the concentration of nitromethane in the nitromethane-methanol mixture increases, the density of the mixture, the velocity of detonation, the particle velocity, and the detonation pressure, all increase. Some disagreement with one-dimensional hydrodynamic theory was also observed. It was stated that the detonation front of pure nitromethane is not smooth and addition of a non-explosive liquid leads to a further increase in irregularities. According to the hydrodynamic Zel'dovich-Neumann-Doering (ZND) theory a detonation wave's forepart represents a smooth shock front that is propagating with detonation velocity. Dilution of liquid explosives by non-explosive liquids inevitably results in pulsations at the front. It gives rise to unstable and a non-one-dimensional (non-smooth) detonation front. The NM/M mixtures under study were not limiting. It needs to be ascertained to what extent this situation can cause the "discrepancy" between the values of the detonation front and the particle velocities. It was observed that the detonation velocity decreases with increase in non-explosive liquid component and methanol is more effective in reducing the velocity of detonation than nitrobenzene. The variation of the velocity of detonation with degree of dilution is found to be linear but the detonation pressure has a quadratic variation with degree of dilution. Some of the results were also inconclusive, and need further investigation.

Shaped charge applications

Shaped charges are commonly filled with solid explosives having high density and high velocity of detonation (VOD) in order to penetrate very hard and thick targets. They are utilized against tanks, bunkers, armoured or fortified installations, soil (oil-well fracturing) and unexploded ordnance. They exhibit deteriorated performance due to non-homogeneous fillings. Out of various applications, disposal of unserviceable and unexploded ordnance has a peculiar requirement of limited penetration and deflagration of the explosive filling in the ordnance by external devices. The size, explosive filling, liner, stand-off etc. of the shaped charges are tailored to obtain the desired performance. In fact, conventional solid explosive systems are more energetic than desirable for the intended use and invariably reduced performance is attempted by other means. Wasting the explosive energy of solid explosives by other mechanisms can be replaced by the use of relatively less energetic liquid explosives. In this context, the use of liquid explosives like nitromethane (NM) is pertinent.

The main advantage of using NM is proven homogeneity of filling. Since NM is liquid at room temperature, it can be filled without any density variation in the prepared charges. The conventional melt-cast solid explosives are filled at high temperature in liquid form and allowed to solidify. Instead, simple pouring at room temperature can acheive the filling of NM. This makes the device suitable for filling under field-conditions. An empty charge container can become a shaped charge if filled with NM. The lower density of NM (1.12 g/cm³) as compared to conventional solid explosives (1.75 g/cm³) can be offset by incorporating suitable gelling agents. The NM filling is relatively safe to handle and in fact addition of the sensitizing agents is done to initiate the charges. Performance parameters of sensitized NM as an explosive have been investigated by many researchers [32]. In that paper, sensitization was achieved using polymer foam and glass micro-balloons suspended in polymer-thickened NM.

In another paper, the advantages of field-filled shaped charge using liquid explosives are listed as minimized toxic and explosive hazards, consistent performance, rapid filling, safe transportation, easy decommissioning and cheap [33]. Sensitization of NM by adding amine in small percentages is implemented for shaped charge applications. The superiority of diethylenetriamine (DETA) and ethylenediamine (EDA) over others was mentioned. However the disadvantages of increased toxicity and transient time dependent variation in sensitivity have to be considered by the users. Another method for sensitization is by using expanded polymer foams and hollow glass microballoons. These refer to physical sensitization and the mechanism is dependent on entrapment of gas bubbles, which cannot be displaced by NM in the sensitizer. Since glass microballoons are light in weight, dispersion in NM is realized by either increasing the viscosity of NM by addition of polymeric polyetheneoxide or by trapping microballoons in polymer foams. NM gelled with a gelling agent and micro-balloons was used

and the VOD was found to increase with gel density. The density of NM with 5% polyox (gelling agent) and 5% micro-balloons was found to be 1.04 g/cm³ with a VOD of 5300 m/s. NM based shaped charges were successfully used for disposal of bombs and the TNT-based explosive fillings of the bombs deflagrated without any obvious sign of detonation.

As an extension to this work, a 4 mm thick plastic tube was filled with gelled NM, attached with a 1.25 mm thick copper cone with cone angle of 60° [34] and tested against MS target positioned at an optimum standoff distance of 5 cone diameters. NM sensitized with DETA resulted in the formation of a copper jet of adequate strength and a penetration of 52 mm was realized. In the explosive filling, gelling by addition of microballoons and polyox resulted in reduction of the VOD and penetration of the charge. For 5% each of microballoons and polyox, a VOD of 4880 m/s was realized and penetration of only 30 mm was achieved. It was also shown that with 10% concentration of both, the copper liner spatter on the plate and penetration of the order of 15mm only was achieved because the VOD was reduced to 4292 m/s.

The criterion of a certain minimum critical energy needed for penetration is proposed and confirmed by further experiments in another article [35]. The critical energy, defined as proportional to the square of the velocity and the jet diameter (V²d), was explained. On a conceptual front, it was proposed that to dispose of a munition by deflagration of its filling, it is desirable to produce just sufficient energy by the NM charge to penetrate the casing and to induce a burning reaction in the charge under disposal. It is also demonstarted that explosives can withstand very high pressures, if it is applied very slowly, and the rate of pressure rise is more important than actual pressure levels. So, an alternate critical power density criteria is proposed, where rate of energy deposition per unit mass (in W/kg) has been postulated as an important criterion. This critical power input per unit mass is equivalent to V³/d. For non-initiation of deflagration DDT, an energy density of 108 W/kg is sufficient, while with 1011 W/kg energy, initiation to deflagration is likely to lead to DDT. In contrast to this, if an energy density of 10¹⁴ W/kg is applied, detonation is very likely to occur. Compared to conventional explosive formulations like PE4, NM filled shaped charges have lower jet tip velocity and bigger jet diameter. So, it reduces the chances of the occurrence of DDT. This was also practically demonstrated The heat dose from 1000-lb bombs is observed to cause second degree burns for personnel less than 30 m upwind from the event. The blast overpressure can cause injury to personnel standing within the 23-m circle. Decommissioning of unused NM filled warheads by simply washing with warm water is also reported.

Conclusion

Nitromethane (NM), a commercial chemical and liquid propellant has been investigated as a detonating explosive. The mechanism of shock heating, reaction zone creation, hot-spot creation, semi-metallic layer formation and jet initiation are discussed for the initiation of NM. The optical characteristics of the reaction zone, curvature of the shock, the variable amplitude of the shock, the effect of sensitizers on detonating NM is also elaborated. Mixtures of NM with various additives like DETA, EDA, methanol, trinitrobenzene, ammonia, silica, boron carbide etc. were investigated and the phenomena of superdetonation, detonation limits, parametric studies on the detonation characteristics are also presented. The article establishes the fact that NM can be used as an explosive without completely understanding the governing mechanisms. One of the potential applications of NM is in shaped charges, which has been investigated and the feasibility of its use is established via the literature. NM with suitable additives, either as diluents or as sensitizers, can pave the way for future field filled demolition devices.

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