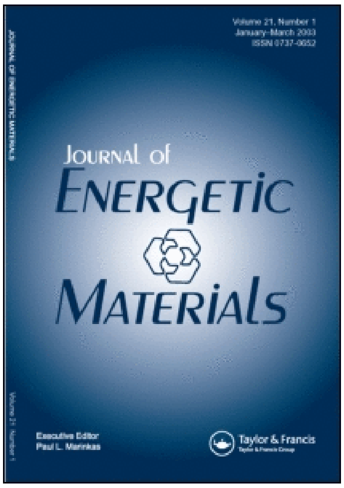

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Non-Solid Explosives for Shaped Charges I: Explosive Parameters Measurements for Sensitized Liquid Explosives

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The disposal of time-expired and unexploded ordnance is a major problem for the NATO countries. Simple functioning of the device, either in its design mode or by attachment of additional explosive and firing, requires extended safety zones. Inducing deflagration could reduce co-lateral damage within the safety zone. One solution to the problem, with current explosive fillings, of producing predictable performance devices for EOD work is to use liquid explosives in shaped charges. This article reports measurement of explosive performance of sensitized nitromethane, a cheap, non-detonator-sensitive liquid. Sensitization was achieved either by adiabatic gas compression, using microballoon collapse, or by a combination of trapped air bubbles in a porous polymer foam, and the chemical nature of the foam. Nitrogen-containing polyurethane foams were superior to oxygen-containing polyester foams. The results show the velocity of detonation of

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nitromethane is proportional to the nitromethane density in the sample rather than sample density; i.e., type I behavior. Results are promising in terms of reliability, reproducibility, and performance to encourage further investigation against EOD targets.

Keywords: nitromethane, sensitivity

Introduction

Military use of shaped charges concentrates on the attack of armor obtaining maximum target penetration for a given charge geometry with the minimum of explosive material. Normally these devices are filled with solid explosives possessing high velocity of detonation. Consistent performance depends on homogeneity of the filling and is vital to ensure correct functioning of the device [1]. Air gaps in the filling distort the detonation wave and produce an off-axis jet, which exhibits reduced or, in the worst case, no penetration. Shaped charges filled with PE4 explosive, a mixture of 88% RDX and 12% wax, normally used in EOD work, can give variable performance [2]. In a series of firings with a metal-cased, 60° copper cone shaped charges, filled by the same highly experienced operator from the same batch of PE4, the following data were produced:

Mean penetration	185 mm
Standard deviation	±29.3 mm
Penetration range	151–251 mm

If such variability is attained under carefully controlled conditions, then field filling cannot give desired consistency. Consistent device filling is difficult even for melt-cast TNT fillings, where shrinkage and cracking are particularly significant. Liquid explosives are easy to fill consistently but have poor performance compared to solid explosives due to low relative density (1.1–1.3 g cm^{-3} compared to a typical 1.7 g cm^{-3} for solids). As a result, the jet velocities and hence armor-penetration performance from liquid-filled shaped charges are lower than for solid explosive-filled devices. Tasks such as explosive ordnance disposal and demolition may not require the same performance but may require operator safety with high reliability and consistent performance. Liquid explosives should give good filling integrity with consistent performance. Ideally, for ordnance disposal the device should penetrate the munitions case and initiate the filling in a burning mode with deflagration being the final objective and detonation being the least desirable result. Since PE4-filled shaped charges currently require performance degradation either by increased stand-off or reduced explosive content, liquid explosives becomes an attractive option. Even with the degradation procedures applied, detonations or misfires have occurred when PE4-filled devices were used.

Nitromethane, a cheap industrial solvent, is a potential liquid explosive that could meet many of these requirements, with a number of additional advantages. The liquid is a not detonator sensitive, requiring a minimum of 30 g of a tetryl booster for detonation and can be transported in light walled containers as a combustible liquid rather than an explosive [3]. Since it is a liquid, it can be readily poured into a device and should give very consistent fillings. Data shown in Fig. 1

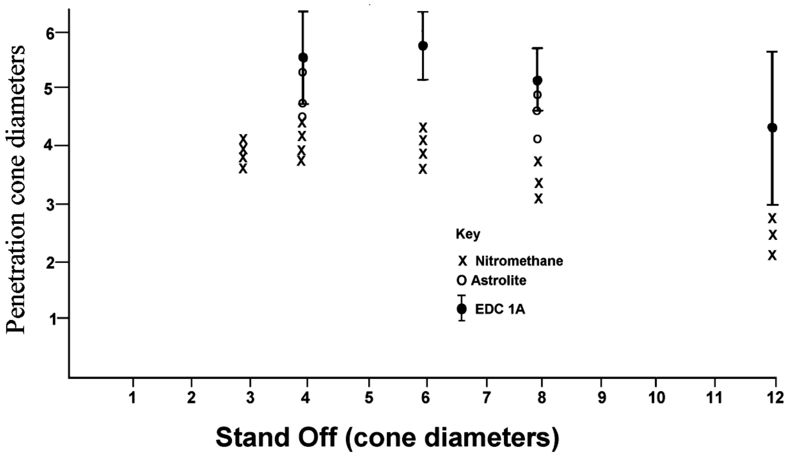

Figure 1. Comparison of variation of target penetration with stand-off distance for K4, 60-mm-diameter 60° copper cone devices filled with different explosive compositions.

indicate that shaped charges filled with sensitized liquid NM are more consistent than typical EDC 1A (75% RDX, 25% TNT)-filled devices [4]. Nitromethane can be made detonator sensitive by a number of chemical and physical methods [5,6] that could be performed immediately prior to operating the device and, in some cases, are easily reversed if the device is to be decommissioned. Nitromethane is less toxic than many conventional explosives; e.g., TNT [7].

Sensitization of Nitromethane

Chemical

Chemical reagents containing donor nitrogen atoms increase sensitivity while maintaining the density and producing higher performance. Optimum sensitization occurs with the amines ethylenediamine, EDA, $NH_2C_2H_4NH_2$ [8] and diethylenetriamine, DETA, and $NH_2C_2H_4NHC_2H_4NH_2$. Unfortunately, their high toxicity increases the hazards for the operator. Twenty-our hours after mixing the liquids, the solution turns dark yellow, showing reduced sensitivity and performance. Sensitivity can disappear completely after two days, leaving a dark solid at the bottom. It is also difficult to desensitize and decommission the chemically treated NM in the event of non-use of the device. Less toxic oxygen donor molecules do not show the same level of sensitization as the nitrogen donor molecules. DETA-sensitized NM and PE4-filled devices provide a comparison with physical forms of sensitization.

Physical

Physical sensitization of NM represents a reduced chemical hazard and a more easily decommissioned system. Simple passage of a continuous stream of fine gas bubbles up through the NM can be used, but this requires additional apparati and is not very convenient. Two other methods have been tried, expanded polymer foams and hollow glass microballoons. Both depend on the entrapment of gas bubbles within the liquid that cannot be displaced by the NM, The sensitization mechanism has been attributed to a number of different processes [9], of which adiabatic gas compression is important.

Polymer Foams

The wide varieties of polymer foams available increase the options for tailor-making the device. By analogy with simple molecular chemical sensitizers, foams containing N donor atoms, i.e., polyurethane and polyamide, should be better sensitizers than oxygen-containing polyester and polyether foams. The physical properties of the foam play a significant role in the sensitization of the NM. The proportion of open and closed cells and their size and distribution determines how much NM can be absorbed onto the foam and the quantity of air available for the sensitization.

Hollow Glass Microballoons

Hollow, lowdensity glass microballoons float on the surface and there is insufficient NM trapped between the microballoons for the NM to pick up from the detonator. Sensitization requires constant extremely vigorous stirring, an impossible operation. Incorporation of microballoons [10] into a polymer matrix during the foam manufacture ensures a uniform dispersion of the spheres but is not ideal. Increasing the viscosity of the liquid NM with polymeric thickening agents, such as gums, nitrocellulose, and polyethylene oxide, can stabilize the dispersion of microballoons for a sufficient period of time to enable the NM to respond to the detonator [11]. Nitrocellulose and polyethylene oxide provided additional sensitization due to their chemical composition. This study measures explosive performance and sensitivity parameters of treated nitromethane. Results obtained, when used in field-filled shaped charge devices as part of EOD operations for munitions attack, will be described in later reports. Other liquid explosives are the subject of ongoing investigations and will be reported in due course.

Experimental

Materials

Nitromethane, 95% pure; polyethylene oxide, mean molecular weight 300,000; and surface-modified guar gum were supplied by Aldrich Chemical Company (Gillingham, Dorset, UK). Nitrocellulose was manufactured from cotton fibers by nitration with mixed acid by literature methods [12]. Three different types of glass microballoons, supplied by 3 M Ltd (Harlow, Essex, UK), all with the same particle size distribution but requiring different collapse pressures, were investigated. Different specification polymer foams, ranging from polyether to polyurethane, supplied by Caligen Foams (Accrington, Lancashire. UK), were tested. The properties of the foams tested are given in Table 1. The first five foams in the table were polyurethane and the second five were polyester. Identifying codes represent the manufacturer's data based on properties such as mechanical strength, compressibility, and proportion of open to closed pockets. This ratio was carefully controlled by the supplier during the foam manufacture. Reticulated foams have less than 2% of closed cells by design, so the NM should completely fill all the voids, leaving no air-filled cells to sensitize the filling. Cylindrical samples of the foams were taken from suitable 30-mm-thick sheets of the foam by section with a cork borer of suitable dimensions to match the charge diameter. The cut surface of the samples was microscopically examined to ensure that the number and size distribution of the cells matched the manufacturer's specification. A number of these sections could be stacked inside the charge tube to alter the depth of the foam sensitizer within the charge.

Gel Preparation

To a measured volume of the NM in a beaker was slowly added, with vigorous stirring, a weighed quantity of the gelling agent, sufficient to give agent concentrations in the range of 2–10%. Nitrocellulose was pretreated with "Analar" acetone to gel the fibers to reduce the mixing time with the NM. When the

Table 1
Properties of polymer foams tested and measured velocities of detonation

Foam type	Density ($g\ cm^{-3}$)	Solid as %vol	% Air in soaked foam	Density of NM soaked foam ($g\ cm^{-3}$)	VOD ($m\ sec^{-1}$)
SF6577	0.033	3.4	13.85	0.936	5800
X6276 AC	0.032	3.1	12.63	1.062	6000
X8173 LP	0.040	3.9	15.89	0.927	5700
XE2873 FRL	0.027	4.6	18.74	0.916	5600
X4272	0.016	4.8	19.55	0.912	5590
X7200 AF	0.018	4.5	18.33	0.917	5610
Reticulated	0.03	3.17	0.42	1.104	0
5200F	0.033	13.9	10.8	0.98	
4200C	0.028	30.98	28.4	0.79	
E1800	0.019	12.39	11.2	0.99	0
5% DETA					6800

addition was complete, the stirring was continued for a minimum of one hour until any solid lumps had been dispersed and the gel showed a uniform transparency. Gelled NM was sensitized by incorporation of a weighed quantity of the microballoons, previously wetted with a small amount of NM to reduce dusting problems, with vigorous stirring using a wooden tool for 2 min before pouring into the charge device immediately prior to use. The range of compositions varying the proportion of gelling agent and sensitizer prepared are detailed in Table 1.

Density Measurements

Densities of sensitized NM gels were determined by standard density bottle techniques. Foam density was determined by weighing sheets of measured dimensions supplied by the manufacturer (typically 400 mm square by 30 mm deep). Density of the NM in the foam was determined by weighing a measuring cylinder with and without a column of the foam then reweighing when foam was covered with NM and filled to the mark. Filling the measuring cylinder with neat NM to the same mark provided a system check.

Measurement Systems

Velocities of detonations were measured for samples contained in plastic tubes of 21 or 37 mm o.d. Two 2-mm holes were drilled into the side of the tube 100 mm apart and 20 mm from the bottom. The tubes were glued to a 120-mm-square by 10-mm-deep mild steel witness plate. Twisted wire pair ionization probes were sealed into the side holes as shown in Fig. 2 using epoxy resin adhesives. The charge tubes were filled with the gelled NM to different heights ranging from 25 to 75 mm above the first ionization probe. When using polymer foam sensitization, the foam was placed into the firing tube before sealing in the ionization probes in order to prevent damage to the probes and to limit the distortion of the foam in the region around the probes. Signals from the

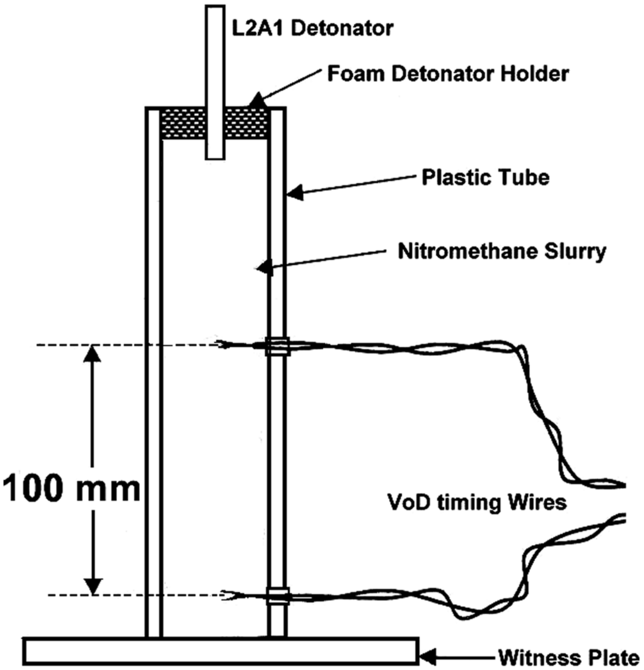

Figure 2. Equipment used for velocity of detonation measurements.

probes were used to trigger the timing circuit (Gould advance timer/counter type TC314, Gould Electronics, Chandler, AZ, USA) connected through an in-house assembled impedance matching circuit. The length of foam below the detonator was varied from 50 mm to a full charge length in order to determine if the output from the foam-sensitized material would provide sufficient pressure boost to initiate pure NM and maintain the final performance from the denser NM.

The dent volume on the witness plate was measured by filling with water from a graduated burette. When the indent did not have a clear edge, a glass tube of known volume was sealed to the witness plate and the volume required to fill to the top of the added tube determined. Correction for the volume in the tube yielded the dent volume.

Results and Discussion

The surface-modified guar gum, while offering a good gel, was comparatively expensive, with only limited sources of supply, and was discarded after preliminary trials. Since nitrocellulose required prior treatment with acetone before it would readily incorporate into the nitromethane and the mixture was sometimes detonator sensitive, before addition of the microballoons, NC was discarded after preliminary trials even though it had good performance. Polyethylene oxide, a cheap material readily available in a range of molecular weight specifications, could easily be incorporated into the NM and produced a non-detonator sensitive gel that was easily sensitized by the addition of the microballoons. The levels of gelling agent and microballoons were varied to optimize the performance and reliability while retaining the dispersed nature of the microballoons. Three samples of microballoons with different collapse strengths as detailed below were tested, but this parameter appeared to be unimportant in the sensitizing action since the detonator output was greater than the maximum collapse pressure of the microballoons.

Although some of the polyester and polyether foams investigated produced sensitization, their performance was inconsistent, and only one in five of the trials with 4200F foam resulted in a detonation. Incorporation of a small booster, 5 g plastic explosive (PE No. 4), overcame this problem but defeated the purpose of the method, which was to reduce the amount of vulnerable material carried. There were no obvious differences in the air pocket distribution between the sample that detonated and those which did not. These foams were discarded after preliminary trials. Polyurethane foams, as predicted from their known nitrogen donor properties, behaved consistently. This indicates that the sensitization with the foams is a combination of the adiabatic compression of the air trapped in the foam with a contribution from chemical sensitization from the nitrogen donor atoms in the polyurethane. Fully protonated nitrogen in primary amines is the best chemical sensitizer. None of the reticulated foams, even the polyurethane-based samples, detonated. This was unsurprising since they have the minimum closed cells ($<2\%$) containing trapped air to act as a sensitizer. The partial chemical sensitization from the nitrogen atoms could not compensate for the lack of adiabatic air heating. The conclusion is that the sensitization mechanism is a combination of the adiabatic gas compression of the air in the closed cells and the chemical sensitization of the lone pair of nitrogen atoms in the polyurethane polymer. Reticulated foams produced the highest density fillings but they were not detonator sensitive.

Results from the VOD measurements are summarized in Table 1 for the foam-sensitized NM and in Table 2 for the gelled NM samples. Notice that the error in the plotted values for VOD averaged over five measurements was less than 5%. The plot of VOD against density for the foam-sensitized samples is given in Fig. 3. The measurements are plotted as density of nitromethane in the foam and not just density of the system. Some foam-sensitized samples gave VODs less than that predicted by the theory for their measured density. This may be because the foam itself was quite dense and the number of open pores, which could be filled by the NM, was low so that the density of the NM explosive was low. The foam itself is quite oxygen deficient and so is almost an inert diluent in the system. When these results are plotted as density of NM present, the deviation is greatly reduced. The resulting detonation velocity is higher than the low-order detonation mentioned by Usselstein [13] for NM initiated by an insufficient shock wave stimulus. A linear regression curve is a good fit to the data, indicating that the explosives conform to the type I class of explosives [14].

The data for the gelled nitromethane fillings are plotted in Fig. 4 as a function of nitromethane density rather than simple gel density. This reduced the deviation from linearity for the higher polyox concentrations. In Fig. 4 the measurements fall onto three, almost parallel, linear relationships. Notice that in both figures the data fit between the two theoretical prediction lines from Kamlet and Jacobs' [15] and Marshall's [16] formulae, which are empirical formulae based on simple thermodynamic properties and density. Those with the highest

Table 2
Variation of VOD with gel composition

Gel composition				
			VOD@diameter	
% Polyox	% Microspheres	Density g cm^{-3}	20 mm	37 mm
2	1	1.14		6500
2	5	1.049		6390
2	10	0.973		6150
5	1	1.114	6369	6350
5	5	1.017	5880	6060
5	10	0.911	5550	5550
10	1	1.051	5376	5370
10	5	0.958	4785	4900
10	10	0.805	4292	4348

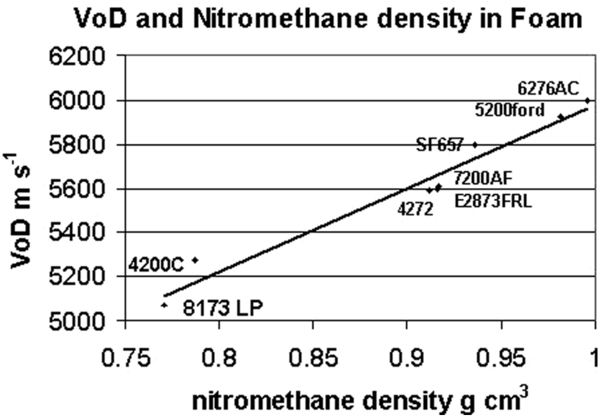

Figure 3. Plot of velocity of detonation as function of nitromethane density in foam-sensitized samples.

concentration of polyox show the lowest VOD and also the maximum deviation from the predicted lines. Since polyox formula $[(CH_2)_2O]_n$ has a lower oxygen balance, Ω, defined as the percentage deficiency positive or negative to give carbon

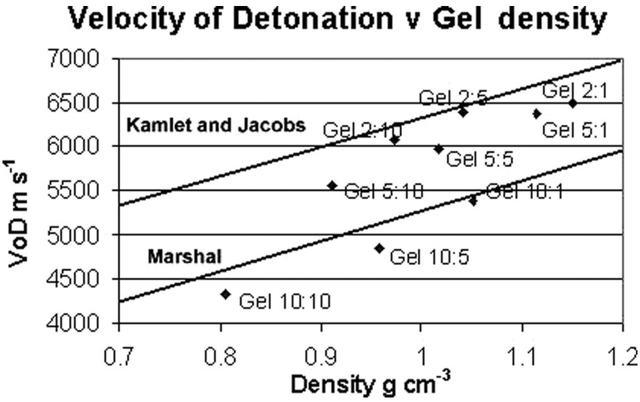

Figure 4. Plot of velocity of detonation against density of nitromethane in gelled fillings.

dioxide and water as the only oxygen products, −180, than NM, −39 (see below), there will be a reduction in the Q value and hence the VOD of the explosive composition as the polyox proportion increases.

$$(\mathrm{CH_2})_2\mathrm{O} = 2\ \mathrm{CO_2} + 2\ \mathrm{H_2O} - 5' O' \Omega = -5 \times 1600/44 = -180$$

$$\mathrm{CH_3NO_2} = \mathrm{CO_2} + 3/2\mathrm{H_2O} - 1.5' O' \Omega = -1.5 \times 1600/63 = -39$$

The high polyox concentration, 10%, results indicate that there may be a change in the behavior of the shock wave chemistry in these mixtures, which have an oxygen balance of $\Omega = -54$. These changes will alter the products of the explosion and the thermochemistry driving the shock wave; hence the reduced VOD. Also, there may be an increase in the thickness of the reaction zone at the higher polyox concentration, which would reduce the VOD. Further work is in progress to assess the products of the explosion process from the polyox-sensitised explosives.

Reduction in the polyox concentration increased the VOD, but experimentally the lower limit was 2%, since most samples with 1% polyox failed to detonate. Although the top ionization probe fired, the lower one did not and the witness plate was unaffected, indicating that the detonation was not sustained in the lower part of the charge. Failure may be due to sensitizer separation, and further work on this aspect will be described in later work. Changes in the average polymer molecular weight could improve the stability at low polymer content, and this is currently being investigated. Similar considerations apply to the microballoons but with the additional difficulty of the large volume occupied by the low-density microballoons; hence the effect of microballoon concentration on performance is greater then for the polyox, but this is corrected when the density of nitromethane is plotted. The microballoons are effectively an inert diluant. When the higher microballoon concentrations are used, the mixture is sensitive to the smallest available detonator (No. 6).

When the foam-sensitized data and the gel/microballoon-sensitized data are plotted on one graph, the data for the gel

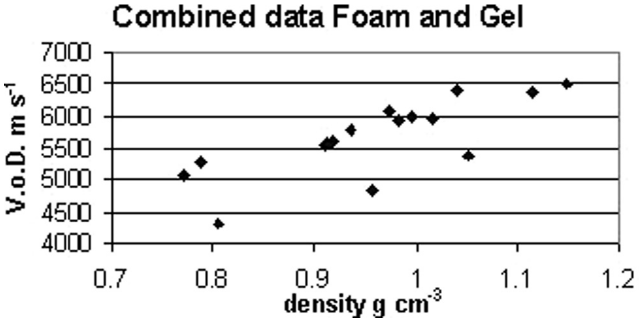

Figure 5. Combined velocity of detonation against nitromethane density data for foam-sensitized and gelled nitromethane fillings.

with the highest polyox concentration show the largest deviation; see Fig. 5. If these three data points are omitted, there is good correlation between density and VOD of the shock wave; see Fig. 6.

VOD measurements from charges with differing depths of explosive between the bottom of the detonator and the first timing probe indicate that, for all of the gels trialed, run-up distances appeared to be 25 mm for the 20-mm-diameter charges. These results were consistent with the normal behavior of type 1 explosives. In experiments with the top half of the

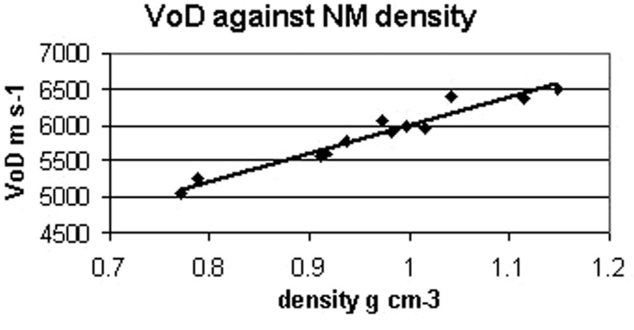

Figure 6. As in Fig. 5 but with 10% polyox data removed. Note the linear trend line fit.

device containing 5/5 sensitized NM gel with pure NM in the lower half, the lower timing device did not function and no indentation was produced on the witness block, indicating that the detonation had not been sustained. Hence the shock wave intensity from the most sensitive NM was insufficient to initiate pure NM. A more gradual change in the polyox and microballoon concentrations may enable a higher VOD to be achieved. These results mean that for both gelled and foam-sensitized NM, the sensitizer must be present throughout the charge from the bottom of the detonator to the witness plate. Since there was no observed difference between VOD of the 20- and 37-mm-diameter charges, critical charge diameter must be less than 20 mm for the plastic pipe confined charges.

Conclusion

Liquid nitromethane can be rendered detonator sensitive either by the inclusion of a sample of a polyurethane foam containing closed, air-filled cells or by the incorporation of microballoons into polymer (polyethylene oxide)-thickened samples. With both methods of sensitization the sensitized composition must occupy the complete dimensions of the charge extending from around the detonator to the metal witness plate. The shock wave from the sensitized nitromethane cannot initiate unsensitized NM.

The velocity of detonation of these mixtures is proportional to the density of the nitromethane present in accordance with typical type 1 explosive behavior as predicted by Kamlett and Jacobs.

The variation in VOD for any formulation, based on five repeat determinations, was less than 5%, ensuring predictable performance when used in shaped charge devices.

Velocity of detonation for the higher polyox concentration trialed (10%) was lower than expected from the basic type I behavior. Foam-sensitized material can be rapidly desensitized if necessary by simply removing the foam and squeezing out the nitomethane liquid from the foam, ideal for EOD applications.

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