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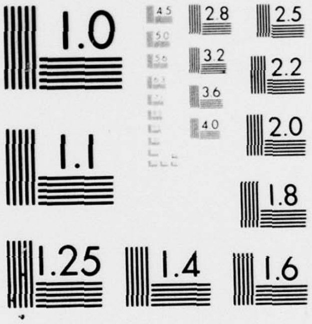

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THE EFFECTS OF PHYSICAL AND CHEMICAL PROCESSES ON TWO-PHASE DETONATIONS

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INTRODUCTION: During the past fifteen years, many studies have been conducted on the shock ignition and propagation of detonation in two-phase mixtures consisting of liquid fuel drops with a gaseous oxidizer. In most cases, oxygen-rich atmospheres and pure fuels were employed. Physical mechanisms which describe the energy transfer in a two-phase detonation were suggested and generally accepted. The sequence of processes that occur following the passage of the leading shockwave of the detonation is: (1) breakup of fuel drops via boundary layer stripping; (2) ignition of the fuel micro-mist that forms in the wake of individual drops and (3) energy transfer to the shock front via local blast waves originating from individual burning drops. However, in general practice, two-phase detonations do not occur in oxygen-rich atmospheres and often involve fuels containing compounds which modify the combustion chemistry. Lower oxygen concentration and fuel additives were expected to significantly change the physical mechanisms outlined by the work on pure fuels in oxygen-rich atmospheres.

The effects of chemical sensitizers on the ignitability and detonability of gaseous mixtures have been investigated for many years. But the effects of the additives in a two-phase mixture, where fuel-drop breakup is involved, were unknown. This study was therefore, initiated to determine the extent to which additives affect the ignitability and detonability of a two-phase mixture.

The study provides a complete examination of the role of chemical additives on fuel detonability. First, detailed laboratory

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experiments were carried out on shock ignition of individual fuel drops and on detonations propagating in monodisperse fuel sprays under controlled conditions. Then, large scale field tests of explosively-disseminated fuel aerosols were carried out, to demonstrate that the effects of additives, manifested in the laboratory, occur in the field. Each step in this sequence will be described individually.

EXPERIMENTAL PROCEDURE

A. Single Drop Studies

A combustion driver was developed and used to achieve a high enough shock strength to ignite hydrocarbons in air. The fuel drop was suspended on the horizontal section of a hypodermic needle in a shock tube test section. Shock velocities were obtained by measuring the time required for the shock to pass between two pressure transducers that were flush mounted on the inside wall of the test section. Light emission from the fuel drop was monitored by a photodiode whose output was displayed on an oscilloscope. Ignition delay was defined as the time interval between passage of the shock wave over the drop and onset of the light signal.

B. Detonation Studies

The detonation study was conducted in a vertical detonation tube apparatus consisting of drivers, a fuel drop generator, the detonation tube and dump tanks. A schematic of its layout is shown in Figure 1. The stainless steel detonation tube is 457 cm long and has an inner cross section of 4.1 x 4.1 cm. Two driver sections are mounted opposing each other at the top of the tube in such a way that detonation of the driver gas forms two blast waves which collide along the tube center line and initiate the fuel drop-air mixture. A stoichiometric hydrogen-oxygen mixture with 689 kPa initial pressure was used as the driver gas.

Two different fuel drop generators were used. One is a vibrating hypodermic needle type used to generate monodisperse aerosols of 700 micrometer or larger drops. With this generator, the fuel-air ratio was controlled by changing both the drop size and the number density of fuel drops generated in the tube. The other generator is an ultrasonic nebulizer which generated a mist of fuel drops ranging in size from 0.5 to 10 micrometers. With this generator, the fuel-air ratio was controlled by diluting the very rich fuel-air mixture from the nebulizer with various amounts of secondary air.

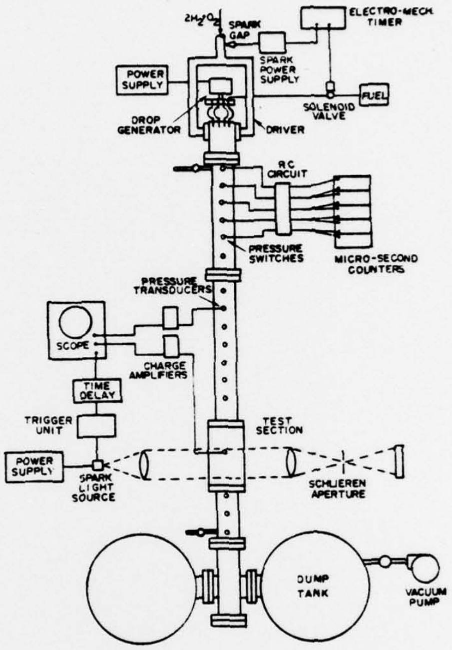


Figure 1. Schematic Diagram of Two-Phase Detonation Apparatus.

Shock velocity in the tube was obtained by measuring the time required for the shock to pass between pressure switches along the tube. Pressure-time profiles at various locations along the tube were measured by pressure transducers flush mounted in the tube wall. A spark schlieren photographic technique was used to record the detonation flow field in the tube.

C. Field Test

The field tests were conducted at the Naval Weapons Center, China Lake, California. Fuel cannisters were made of two gallon plastic jars with holes in the caps for insertion of central burster charges which disseminate the fuel. Central bursters were made from 1.27 cm internal diameter by 22.9 cm long tubes, each with a welded flange at one end which seals to the inside of the cap with an O-ring. The burster charge inserted in the burster tube was a 1.27 cm diameter by

17.8 cm long rod of PBXN-201 explosive. Initiation of a fuel-air cloud was accomplished by a small charge of N-5 explosive supported on top of a 122 cm tall wooden stand located 183 cm from a fuel cannister. All canisters were suspended 122 cm from the ground. In this study, the initiators were fired 110 milliseconds after the burster charge was fired, which was long enough to allow the fuel-air clouds to approach their maximum dimensions. Three piezoelectric pressure gages, spaced 152 cm apart, were flush mounted in the ground to measure pressure-time profiles from the detonation. The entire dissemination and detonation process was filmed using high speed cinemotography.

D. Fuels

Heptane, which has some physical properties similar to gasoline and has the poorest "knock" rating in internal combustion engines, was chosen as the basic fuel to be studied. The two additives used to alter chemical properties were butyl nitrite and normal propyl nitrate (NPN). Physical properties of each heptane and additive mixture used in this study are summarized in TAble 1. Dry air was the oxidizer used in all experiments.

Table 1

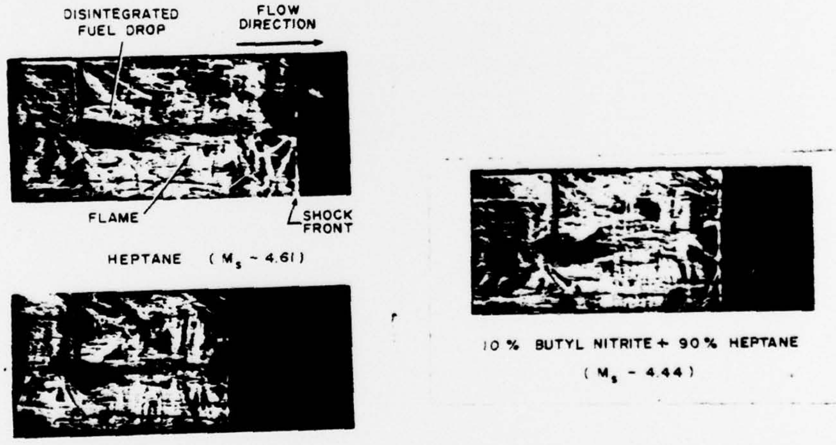
Physical Properties of Heptane/Additive Mixtures

Additive	Amount of Additive % By Weight	Mixture Density (G/CC)	Mixture Viscosity (CP)	Mixture Kinematic Viscosity (CP) (G/CC)	Mixture Surface Tension (DYNES) (CM)
None	0	.683	.429	.628	23.2
N-Propyl Nitrate (20% by volume)	29	.762	.444	.583	24.5
N-Propyl Nitrate (10% by volume)	14.5	.725	.438	.604	24.5
Butyl Nitrite (10% by volume)	12.9	.711	.448	.630	23.6

RESULTS AND DISCUSSION

A. Single Drop Studies

In Figure 2, schlieren photographs are presented of shock ignited heptane drops with various additives in air. In contrast to the previous studies of shocked fuel drops in pure oxygen by us (Ref 1,2) and by Kauffman (Ref 3), there is no local blast wave originating from the wake of each disintegrated fuel drop. This result was not too surprising since the rate of energy release from the micromist formed by mass stripping of the parent drop is expected to be a function of the oxygen concentration. With a high rate of energy release, an exploding or detonating mode of combustion is more likely and local blast waves can be generated. Since the energy generation rate is slower in air, only a deflagrating mode of combustion is apparently possible.



HEPTANE ($M_s \sim 4.61$)

10 % BUTYL NITRITE + 90 % HEPTANE (M_s - 4.44)

10% PROPYL NITRATE + 90 % HEPTANE (M_s - 4.53)

Figure 2. Schlieren Photographs of Shock Ignited Fuel Drops with Chemical Additives in Air.

Figure 3 shows measurements of ignition delay times of heptane and heptane-additive mixtures. The ignition delay time t_{ig} is plotted against the inverse of the free stream air temperature, T_2 , behind the incident shock. Least mean squares plots of the experimental data are also shown in the same figure. It is seen that both additives reduce the ignition delay time. A theoretical study by Fishburn (Ref 4) indicates that the overall breakup time (t) of a drop in a supersonic gas flow occurs on a time scale given by

$$t = \left(\frac{\rho_{gas}}{\rho_{fuel}}\right)^{\frac{1}{2}} \frac{U_{gas}}{D_{fuel}}$$

where ρ is the density, U_{gas} is the gas velocity and D_{fuel} is the drop diameter. Thus, the drop breakup rate is not very sensitive to the physical properties of the fuels. In view of the properties listed in

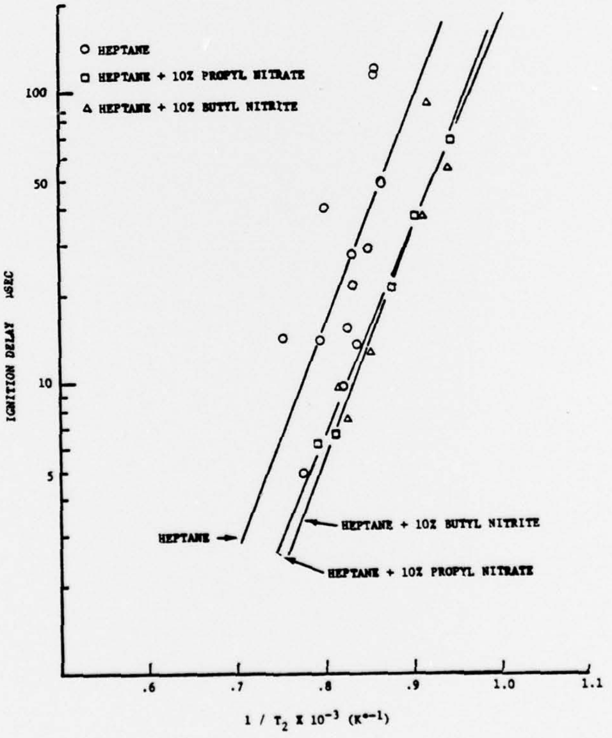


Figure 3. Ignition Delay Time of Shock Ignited Fuel Drops with Chemical Additives in Air.

Table 1 the additives are not expected to significantly effect the breakup time component of the ignition delay time. Thus, the reduction of ignition delay time by these additives must be due to chemical processes. It is known that the RO-NO and RO-NO_2 bonds in the nitrites and nitrates are much weaker than the C-C and C-H bonds in hydrocarbons (Ref 5). It is also known that additions as small as 1-2% of NO_2 can reduce the ignition delay of methane - air mixtures by 1/2-1/3 (Ref 6). Though the detailed chemical process is not known in our system, it is believed that the additives act as a source of the free radicals RO, NO NO_2, and NO, which speed initiation of chain reactions resulting in a flame and/or explosion.

B. Detonation Propagation

The effect of the propyl nitrate and butyl nitrite on the detonability of a heptane drop-air mixture can be seen in the 1400 μm drop mixture wave velocity history vs tube length shown in Figure 4. For comparison purposes, the blast wave velocity in an empty tube is also shown.

The wave speed decays in both heptane, and heptane + 10% normal propyl nitrate (NPN) air mixtures, but more slowly when NPN is present. In all other cases the wave speeds all reach a steady state after a transition region, which indicates the establishment of self-sustained detonations.

It is interesting to speculate on the cause of the differences in detonability of the mixtures mentioned above. In the case of heptane - oxygen mixtures, it is obvious that the pure oxygen atmosphere is a significant factor in the detonability. It has been r reported by Kauffman (Ref 7) that the increase of oxidizer concentration by a factor of 3 will decrease the ignition delay time of shock ignited fuel drops by a factor of 4. It is believed that due to the short ignition delay time, the energy released by the burning fuel drops is better able to couple with and support the incident shock. In the cases of 90% heptane + 10% butyl nitrite and 75% heptane + 25% NPN mixtures in air, the picture is less clear. One possibility is that only the reduction of ignition delay time caused by the addtion of nitrite and nitrate improves the coupling between the shock front and combustion zone. In addition, it is also possible the nitrite and nitrate, through the formation of the RO, NO_2 , and NO radicals, lead to new chain reaction paths which increase the overall rate of energy release from the burning drops. This would improve coupling between the shock wave and combustion zone to an even greater extent. One or both of these possibilities may be occurring.

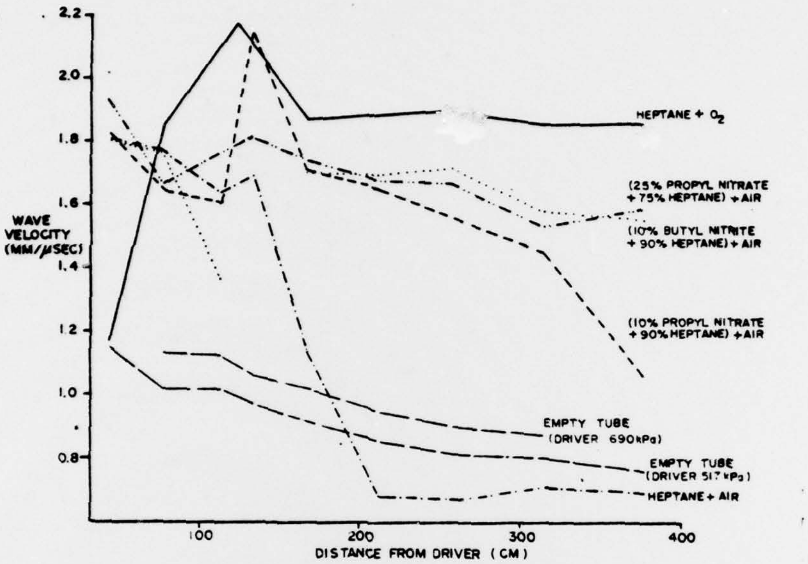


Figure 4. The Effect of Additives on the 1400 μm Heptane Drop Mixtures Wave Velocities.

The effect of the fuel drop size on the detonability of heptane - additive - air mixtures can be seen in Table 2. Because of the high vapor-pressure of heptane and its additives, most fuel drops in the fog mixture probably vaporize prior to detonation.

Table 2

Effects of Additives and Drop Sizes on the Detonability of Heptane-Air Mixtures

	Drop Size		
Fuel	1400 μm	700 μm	Fog (∿10 μm)
Heptane + 25% NPN	detonation		
Heptane + 20% NPN		detonation	detonation
Heptane + 10% NPN	no detonation	detonation	detonation
Heptane	no detonation	no detonation	detonation

These results show both the nitrate additive and small size drops enhance detonability. This is not too surprising, since both the additive and small drop size are suggestive of faster rates of chemical energy release and thus better coupling between the shock front and the combustion zone. It has been shown (Ref 8) in gaseous detonation that the quenching condition of a detonation wave depends on the coupling between shock front and combustion zone. Clearly, the hazard presented by a particular fuel-air mixture can be drastically altered by the addition of small amounts of certain additives or by decreasing the drop size. This means that the danger of any fuel-air mixture should be assessed individually.

Currently various computer codes have been developed to calculate detonation properties for any exothermic system; however, no theoretical techniques have been developed to predict the detonation limits, as kinetics and various energy coupling mechanisms will define the actual limit conditions. Figures 5 and 6 show calculated and experimental detonation wave speed vs equivalence ratio of heptane + 20% NPN and pure heptane mixtures in air. The Tiger code was used to calculate theoretical Chapman-Jouguet wave speeds. Mixture compositions where detonations cannot be sustained in the tube are also indicated in the figures. In general, the experimental wave speed data follow the calculated wave speed fairly well. In the heptane + 20% NPN mixtures, the measured wave speed of 700 μm drop mixtures show a larger decrement from the calculated curve than the measured wave speed in fog mixtures. This is due to larger energy losses to the tube wall in the thicker reaction zone produced by the larger drops. (The reaction zone structure will be described later.) It is seen from Figures 5 and 6, that both small drop size and addition of propyl nitrate expand the fuel rich detonation limit, but have essentially no effect on the fuel lean limit. The 700 μm drop mixture fuel lean limit is shown lower than that of the fog mixtures. The cause of this difference is not clear. One possible explanation is that fuel vapor originating from fuel drops falling down the tube is sufficient to make up the difference in fuel concentration. No account was taken of this vapor in calculating the fuel concentration. Another possibility is that the detonation propagation mechanism is controlled by local conditions in the reaction zone, and the local fuel concentration in the 700 μm drop mixture is quite different from the overall fuel concentration in the fog mixture.

For comparison purposes, the detonation limit of propylene oxide (Ref 9) is also shown in Figure 5. Propylene oxide is the

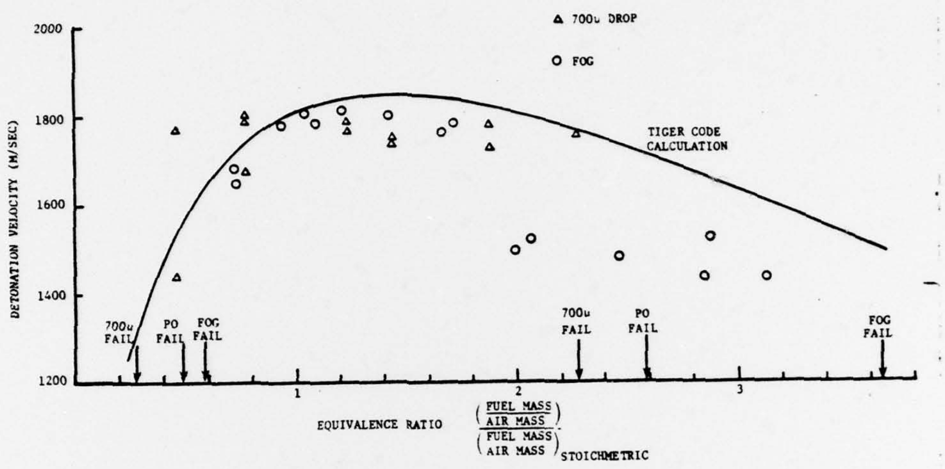


Figure 5. Comparison of Experimental and Theoretical Detonation Velocities for Various Heptane + 20% NPN/Air Mixtures.

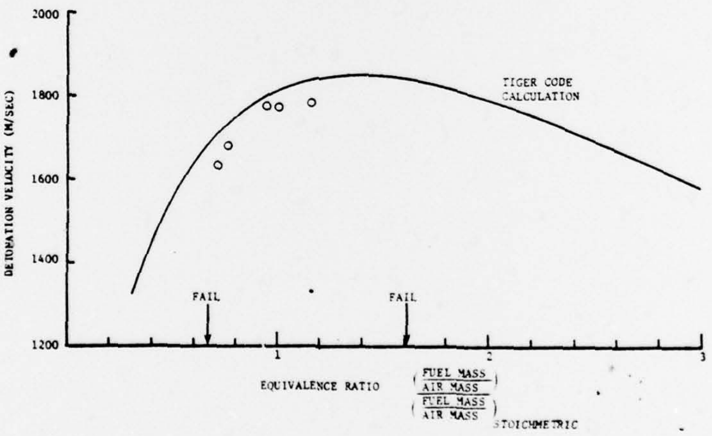


Figure 6. Comparison of Experimental and Theoretical Detonation Velocities for Various Heptane Fog/Air Mixtures.

standard fuel used in all current fuel - air explosive munitions. Note that the limits of propylene oxide are narrower than that of heptane + 20% NPN mixtures. The heptane + 20% NPN fuel should be able to perform just as well or even better than the propylene oxide in FAE munitions. This has been confirmed by field tests.

Detonations were obtained in an average 23 ft. diameter, unconfined heptane + 20% NPN cloud in air that was formed by explosive dissemination. The average wave speed was 1.58 mm/μsec. For a stoichiometric mixture, on an equal weight basis, the heptane + 20% NPN requires 27.7% more air than propylene oxide. Thus the heptane fuel has the potential of larger area coverage in FAE munitions.

Spark schlieren photographs of the detonation front in the heptane-NPN-air mixture are shown in Figure 7 to illustrate the structure of the wave front. In general, the wave is warped and apparently thick in a schlieren sense. The degree of non-planarity and the thickness of the front progressively increase as the drop size increases. Evidently, this results from poorer coupling between the shock-front and the combustion region in the long reaction zone produced by large drops. The wave front of the 1400 μm drop mixture is slanted so severely that it is actually propagating in a spinning mode as confirmed by periodically oscillating pressure traces produced by this detonation. Transverse waves are visible in all of these pictures. The number of transverse waves decreases as the drop size increases. An anology to the behavior of gaseous detonations near their detonation limits is evident.

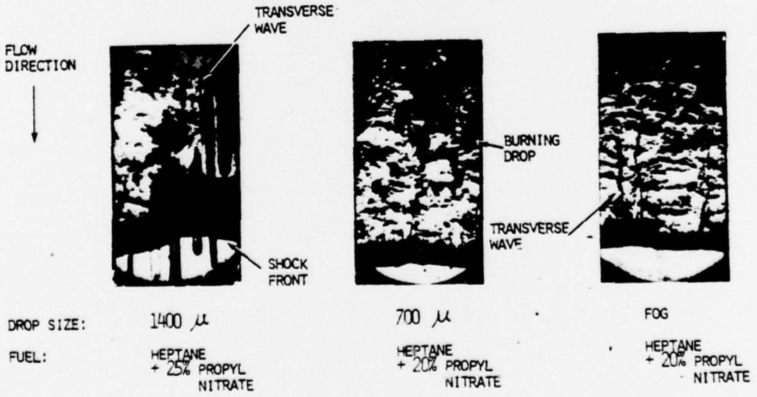


Figure 7. Schlieren Photographs of Two-Phase Detonation Fronts.

Further analogies between heterogeneous phase and gas phase are indicated. As the drop size decreases from 1400 μm to 10 μm, blast waves, generated by localized gaseous volumes behind the incident shock become more evident. Similar kinds of blast waves are observed in gaseous detonations having long reaction zones (Ref 10). These local explosions do not necessarily occur near fuel drops and are caused by fuel vaporized from falling fuel drops prior to detonation initiation. Thus the effect becomes more noticeable as the drop size decreases since greater vaporization occurs. It is interesting to note that, in spite of all indications of gas phase reactions, it has been experimentally verified that the fuel vapor alone is not sufficient to sustain a detonation in the tube.

Another interesting feature is, in contrast to studies conducted in oxygen-rich atmospheres where local blast waves from the burning micromist in the wake of individual fuel drops are observed, (Ref 11), no local blast waves originate from the wake of individual drops in air. This observation agrees with results from the single drop studies. The role of these blast waves in the two-phase detonation reaction zone has been discussed by many investigators (Ref 12). Apparently the presence of local blast waves from the fuel drops depends on the oxygen concentration and the occurrence of these blast waves is not a necessary condition for propagation of two-phase detonations.

CONCLUSIONS

Systematic studies of the effect of additives and fuel drop size on the detonability of heptane-air mixtures have been carried out under controlled laboratory conditions and in large scale field tests. It was shown in the shock tube studies that n-propyl nitrate and butyl nitrite as well as, to a lesser extent, small drop size can greatly widen the detonation limits and reduce initiation requirements of heptane-air mixtures. Large scale field tests of explosively disseminated fuel-air clouds confirm findings obtained in the laboratory tests, demonstrating that systematic laboratory tests can be used to predict detonability and performance of any new fuel system to be used in FAE munitions.

Unique schlieren photographs of the reaction zone of propagating fuel-air detonations have been successfully obtained. No blast waves are observed either in the wake of single shocked fuel drops or from drops in the reaction zones of propagating detonations with air. Apparently, the assumption which has appeared in the literature, that such blast waves are necessary to maintain a two-phase detonation, is incorrect. Furthermore, the insight into the structure of the reaction zone that these photographs have now made available can be used to suggest new fuel additives which will affect detonability, either increasing or decreasing it.

Sensitized heptane is potentially superior to fuels used in current FAE munitions, providing increased explosive performance (larger area coverage per unit weight of fuel), greater safety in transport and handling and lower procurement costs. These tests have established this system as a desirable alternative to fuels currently being used.

ACKNOWLEDGEMENTS

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