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TBX FORMULATIONS WITH ALTERNATIVE METAL FUELS, HIGH EXPLOSIVES AND OXIDIZERS

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***Abstract**: TKX-50 is a new and very promising secondary explosive with low sensitivity (IS = 20 J, FS = 120 N) and good calculated energetic performance parameters at its theoretical maximum density (1.877 g cm^{-3} @ 298 K) such as D = 9642 m s^{-1} and pCJ = 37 GPa. Thermobaric explosives (TBX) are a combination of high explosive (RDX, HMX, TKX-50) and pyrotechnic combustion of the (usually) metallic fuel (Al, Mg, B, Be, BeH_2, H_3N-BH_3 etc.), and in some formulations, oxidizer. In this research new TBX formulations were surveyed based on: (i) conventional (RDX) and new (TKX-50) high explosives, (ii) conventional (AP) and new (TNEF) oxidizers, and (iii) conventional (Al, Mg) and new (B, Be, BeH2, H3N-BH3 etc.) metallic and non-metallic fuels.*

***Keywords:** beryllium, high explosives, oxidizers, thermobarics*

1. INTRODUCTION

Thermobaric explosives (TBXs) derive their effectiveness not only from the initial detonation of the high explosive but also from the subsequent combustion of metallic fuels. Unlike conventional explosives, TBXs produce an extended pressure pulse and prolonged thermal output through post-detonation reactions, making them particularly effective in confined and semi-confined environments. The efficiency of these systems depends strongly on the ability of the metallic fuel to participate in both the oxygen-deficient (anaerobic) reactions immediately following detonation and the later oxygen-supported (aerobic) combustion that occurs as atmospheric air mixes with the expanding fireball [1-3].

Aluminum has traditionally been the preferred metallic fuel for thermobaric formulations because of its high energy density and relatively low cost. However, the practical utilization of aluminum is limited by the presence of a stable oxide layer and by the high melting and boiling temperatures of aluminum and alumina. These characteristics slow ignition and oxidation, reducing the fraction of aluminum that reacts during the relatively short lifetime of the expanding detonation products. Consequently, improving the reactivity of metallic fuels remains an important objective in the development of more efficient thermobaric explosives [4-6].

The present work summarizes two investigations which examined possible alternative strategies for improving TBX performance. The first study direction compares beryllium directly with the conventionally employed aluminum and magnesium as the sole metallic fuel in model thermobaric compositions. The second study direction investigates whether small additions of highly reactive metals - specifically beryllium or cerium - can act as activators that enhance the performance of aluminum without replacing it completely [6-10]. Together, these studies provide new insight into the role of metallic fuel chemistry during both the anaerobic and aerobic stages of thermobaric explosions.

This work also presents effects of introducing new oxidizer TNEF as a replacement for AP in thermobaric formulation.

2. METAL FUELS AND HIGH EXPLOSIVES

In order to consider in more detail the impact of the metal used, formulations were prepared which all employed a common energetic matrix consisting of RDX passivated with wax and ammonium perchlorate, and only the metallic component was varied. In the first approach, the metallic fuel consisted exclusively of aluminum, magnesium, or beryllium. In the second study approach, aluminum served as the principal fuel and was partially replaced by small amounts of either beryllium or cerium. Using the same formulation strategy ensured that differences in measured performance could be attributed primarily to the properties of the metallic additives rather

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than changes in the energetic matrix.

TKX-50 has recently been studied as a potential replacement for HMX in thermobaric formulations and showed extraordinary performance, introducing higher detonation properties in the observed mixtures [11-14].

3. OXIDIZERS

Tris(2,2,2-trinitroethyl) orthoformate (TNEF) (Fig. 2) is one of the most interesting examples of a purely CHNO-based oxidizer developed in recent years [13-17]. It could be shown that TNEF combines several properties that are rarely achieved simultaneously in organic oxidizers, namely a favorable oxygen balance, comparatively high density and a halogen-free composition that avoids chlorine-containing combustion products. In this respect, TNEF addresses key limitations associated with conventional oxidizers such as ammonium perchlorate. The significance of TNEF is further supported by its demonstrated applicability in practical formulations. Incorporation into nitrocellulose-, HTPB-, PDMS- and GAP-based systems has shown that TNEF is compatible with technologically relevant binders and can deliver promising thermal and combustion-related performance. Recent stability studies also indicate that TNEF possesses a more robust thermo-chemical profile than might be expected from its highly nitrated molecular structure. At the same time, the current state of research on TNEF is still at an early development stage. Comprehensive ballistic data, large-scale production routes, long-term aging studies, and full motor-level validation have so far not been realized. TNEF should therefore not be considered a replacement-ready oxidizer at present. Overall, TNEF is best regarded as a highly promising pre-technical oxidizer candidate. Its importance lies not only in its individual performance metrics, but also in demonstrating that purely organic CHNO compounds are realistic targets for use in propulsion applications. Further experimental and computational studies will determine whether this potential can be translated into application. Figure 1 shows chemical structure of TNEF molecule.

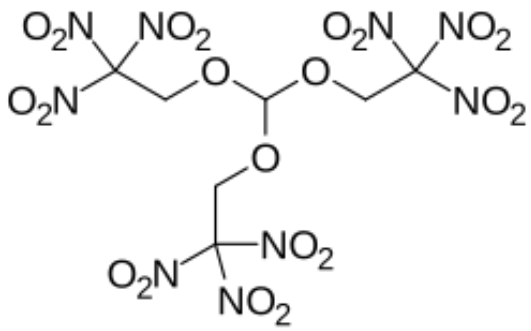


Figure 1. Structure of TNEF

The observed thermobaric composition with new oxidizer TNEF was made as cast-cured mixture with silicone binder, HMX/Al/TNEF/PDMS, and compared to a reference composition HMX/Al/AP/PDMS. They were labeled as TBX-1 (with AP) and TBX-2 (with TNEF).

4. CHARACTERIZATION OF THE THERMOBARIC FORMULATIONS

In order to characterize experimentally the explosive performance of selected thermobaric formulations, several techniques were used. For example, heat of detonation measurements were performed using bomb calorimetry under inert conditions to quantify the energy released during detonation. Quasi-static overpressure was measured inside a nitrogen-filled explosion chamber, allowing evaluation of energy release during the anaerobic combustion stage without interference from atmospheric oxygen. Finally, 500 g pressed charges were detonated in a semi-confined bunker where detonation velocity, peak blast pressure, and blast impulse were determined, thereby assessing the combined effects of anaerobic and aerobic combustion under realistic conditions. The experimental measurements were complemented by thermochemical calculations using the EXPLO5 code with the BKWs equation of state to compare measured behavior with equilibrium predictions.

5. RESULTS AND DISCUSSION

Calculated and measured heats of detonation for TBX formulations containing 60% RDX, 20% AP and 20% fuel (metal) are compared in Figure 2. LiF was included as an inert reference material. Here we may observe the effects of individual metal fuels incorporated in the reference thermobaric composition.

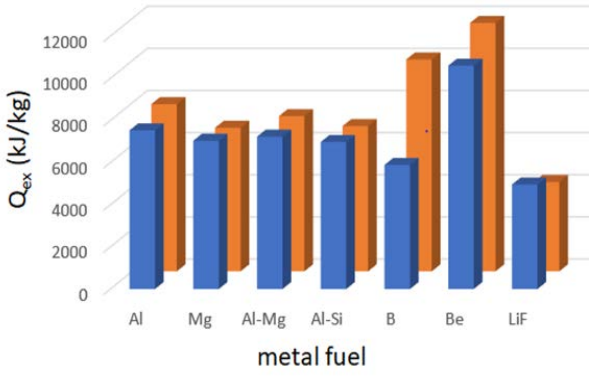


Figure 2. Calculated (orange) and measured (blue) heats of detonation for TBX formulations.

Direct comparison of the results obtained using aluminum, magnesium, and beryllium demonstrated that beryllium possesses a substantially greater ability to contribute energy during both stages of the thermobaric process. The beryllium-containing formulation produced the highest experimentally measured heat of detonation, exceeding the corresponding aluminum and magnesium formulations by more than forty and fifty percent, respectively.

Although equilibrium calculations predicted even greater energy release, the measured values indicate that reaction kinetics and incomplete oxidation limit full utilization of

beryllium under experimental conditions. Nevertheless, the energy contribution of beryllium remained significantly greater than that of conventional metallic fuels (Fig. 2).

Measurements in the nitrogen-filled chamber further demonstrated the exceptional activity of beryllium during anaerobic combustion. The composition containing beryllium generated the highest quasi-static overpressure and the largest TNT equivalent among the formulations investigated. These results show that beryllium reacts efficiently with the gaseous products formed immediately after detonation, even before atmospheric oxygen becomes available. Subsequent bunker experiments confirmed that this enhanced reactivity also translates into superior blast-wave characteristics under practical conditions, including increased peak overpressure and blast impulse. Overall, the data consistently indicate that beryllium is considerably more effective than either aluminum or magnesium in promoting energy release throughout the thermobaric event.

Building upon these findings, the second investigation explored whether smaller quantities of highly reactive metals could improve the thermobaric performance of aluminum-based formulations. Partial replacement of aluminum by only 4 wt% beryllium or cerium produced measurable improvements in explosive performance despite the comparatively small concentration added. Both modified formulations generated approximately ten percent higher quasi-static overpressures than the aluminum reference composition, while corresponding TNT equivalents derived from chamber measurements and blast-wave impulses also increased noticeably. These observations indicate that both additives (Be or Ce) accelerate or promote aluminum participation during the early stages of combustion, thereby improving overall energy utilization.

The behavior of beryllium and cerium, however, differs in important respects. Beryllium possesses an exceptionally high heat of combustion and therefore contributes both chemical activation and substantial additional energy release. Cerium, in contrast, has a considerably lower calorific value but exhibits high chemical reactivity toward oxidizing species generated during detonation. Consequently, cerium appears to function primarily as an ignition promoter that facilitates earlier aluminum oxidation rather than serving as a major energy source itself. Despite these different mechanisms, both additives successfully enhance the effectiveness of aluminum-containing thermobaric formulations.

Thermochemical calculations further support the experimental observations while also highlighting the importance of reaction kinetics. Equilibrium calculations generally predict greater energy release than is measured experimentally, indicating that complete oxidation of metallic particles is not achieved during the rapid expansion of detonation products. This discrepancy is particularly significant for beryllium because of its high oxygen demand and the limited time available for complete combustion. Nevertheless, the experimental results demonstrate that even partial reaction of beryllium provides substantial performance benefits owing to its high intrinsic energy content and rapid participation in post-detonation chemistry.

Regarding the thermobaric output of the formulations with new oxidizer, TNEF, the observed outputs are given graphically in Figures 3 and 4. It may be noted that TNEF provides equal to somewhat higher thermobaric output compared to AP. Being an eco-friendly, chlorine-free oxidizer, TNEF is a promising replacement for AP and other chlorinated oxidizers.

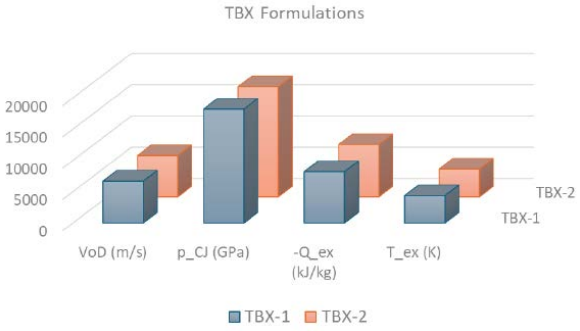


Figure 3. Graphical representation of the performance parameters of the TBX formulations TBX-1 (containing AP) and TBX-2 (containing TNEF instead of AP).

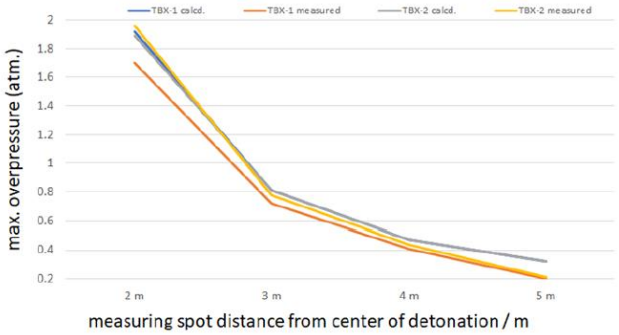


Figure 4. The maximum overpressures at different distances for TBX-1 (with AP) and TBX-2 (with TNEF) as a function of the distance

Replacing RDX in model thermobaric formulations by the highly promising secondary explosive TKX-50 was of particular interest since TKX-50 is a nitrogen-rich secondary explosive with the empirical formula $C_2H_8N_{10}O_4$ and therefore raised the question as to whether using a nitrogen-rich secondary explosive would reduce the quantity of oxidizer required in the TBX formulation, with the metal fuel potentially forming a metal nitride e.g. AlN (aluminum nitride) in the post-detonation products [11-12]. However, it was found that the heat of detonation of a 90/10 TKX-50/Al formulation was 90 J/g lower than the value for 100% TKX-50. It was found that in the post-detonation stage, Al reacts with the detonation products of TKX-50 contributing in this process 375 J/g. In an air-filled detonation chamber adding Al to TKX-50 results in a higher observed maximum temperature of the explosion products by 700 K, while this difference is reduced to 370 K in an argon-filled chamber. It was also found that the addition of Al under air-filled chamber conditions resulted in a much longer duration of time during which a temperature of at least 1600 K is observed. Interestingly

however, X-ray powder diffraction identified solid residue from the detonations performed under an Ar atmosphere as being predominantly $Al_{2.811}N_{0.435}O_{3.565}$ and not pure aluminum nitride, and under air-filled chamber conditions, essentially no aluminum oxynitride phase was observed. It should also be mentioned that TKX-50/ph/Al (70/3/27) shows a maximum overpressure value which is 30% higher than that of TKX-50ph (TKX-50/paraffin 97/3) in air atmosphere chamber conditions, which suggests that Al reacts with both oxygen from the air as well as the detonation products of nitrogen-rich TKX-50.

Based on these experimental observations, it was concluded that in this case, despite the higher concentration of nitrogen in the post-detonation products of nitrogen-rich TKX-50 in comparison with less nitrogen-rich secondary explosives, the burning of Al in nitrogen does not provide vast quantities of energy and aluminum oxides appear to be preferentially formed, even when the concentration of nitrogen in post-detonation products is considerably higher than that of oxygen.

6. CONCLUSION

Two promising approaches for improving thermobaric explosives have been described. Complete replacement of conventional metallic fuels by beryllium or, potentially, a beryllium-aluminum alloy, produces the greatest overall enhancement in detonation energy, quasi-static overpressure, and blast-wave performance. Alternatively, small additions of either beryllium or cerium to conventional aluminum formulations provide significant improvements while requiring only limited modification of existing compositions. The results show that careful selection and optimization of metallic fuel chemistry can substantially improve the efficiency of energy release during both the anaerobic and aerobic stages of thermobaric explosions. These findings provide valuable guidance for the future design of advanced thermobaric formulations in which both the energetic properties and the reaction kinetics of metallic additives are considered simultaneously. TKX-50 as a nitrogen-rich secondary explosive also significantly enhances thermobaric output of aluminized formulation in controlled conditions.
New oxidizer TNEF has shown potential as a chlorine-free replacement for AP on TBX formulations, providing even higher thermobaric output compared to reference AP-based TBX.

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