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A LITERATURE REVIEW OF SHOCK SENSITIVITY CHANGES OF TATB
DUE TO THERMAL CYCLING

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of the Requirements for the

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ABSTRACT

Insensitive high explosives (IHEs) based on 1,3,5-triamino 2,4,6-trinitro-benzene (TATB) are the IHEs of choice for use in nuclear warheads over conventional high explosives when safety is the only consideration, because they are very insensitive to thermal or mechanical initiation stimuli. It is this inherent insensitivity to high temperatures, shock, and impact, which provides detonation design challenges when designing TATB explosive systems while at the same time providing a significant level of protection against accidental initiation. Although classified as IHE, over the past few years the focus on explosive safety has demonstrated that the shock sensitivity of TATB is influenced with respect to temperature.

A number of studies have been performed on TATB and TATB formulations, plastic bonded explosives (PBX) 9502, and LX-17-01 (LX-17), which demonstrates the increase in shock sensitivity of the explosive after it has been pre-heated or thermally cycled over various temperature ranges. Many studies suggest the change in sensitivity is partly

due to the decomposition rates of the temperature elevated TATB. Others point to the coefficient of thermal expansion, the crystalline structures of TATB and/or the combination of all factors, which create voids which can become active hot spots. During thermal cycling, TATB is known to undergo an irreversible increase in specific volume called ratchet growth. This increase in specific volume correlates to a decrease in density. This decrease in density and increase in volume, demonstrate the creations of additional void spaces which could serve as potential new initiation hot spots thus, increasing the overall sensitivity of the HE. This literature review evaluates the published works to understand why the shock sensitivity of TATB-based plastic bonded explosives (PBXs) changes with temperature.

Keywords: PBX 9502; Hot Spot; TATB; shock sensitivity; LX-17; Thermal cycling; ratchet growth.

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LIST OF ABBREVIATIONS AND SYMBOLS

ATK	Alliant Tech Systems - Thiokol
CTE	Coefficient of Thermal Expansion
HE	High Explosive
IHE	Insensitive High Explosive
LX-17	92.5 wt. %, wet aminated TATB, 7.5 wt. % Kel-F 800
PBX	Plastic Bonded Explosive
PBX 9502	95 wt. %, dry aminated TATB, 5 wt. % Kel-F 800
PG	Phloroglucinola
RDX	Research Department Explosive
TATB	1,3,5-triamino 2,4,6-trinitro-benzene
TCB	1,3,5-trichlorobenzene
TCTNB	1,3,5-trichloro-2,4,6-trinitrobenzene
TNT	Trinitrotoluene
USAXS	Ultra Small Axis X-ray Scattering

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1.INTRODUCTION

1.1. Initiation of High Explosives

Maintaining stockpile weapons often requires routine handling of the high explosive components to ensure the intrinsic safety and functionality of the weapon system. While an accidental detonation of high explosives (HE) can be tragic, one involving nuclear material could be catastrophic. As the development and application of high explosives systems evolves, high explosives have also found applications off of the battlefield and further into commercial applications. Understanding the dynamics of high explosive initiation is essential to the safety of our workers and surrounding communities.

There are numerous ways that high explosives can be initiated. They can be subjected to mechanical forces (including shock loading), thermal loads, or be subjected to electrical stimuli. In all cases, enough energy must be applied to the high explosive which ultimately results in the release of enough chemical energy to sustain a detonation

wave. This energy fluence is described by the rate of work per unit area that is being done to the explosive as a shockwave passes through the explosive [33]. There is a finite amount of time in which the shockwave can do work to ensure detonation for a particular explosive. Using the energy equation and Hugoniot jump equations the critical energy fluence required to ensure detonation can be estimated for an explosive of interest. There are a number of high explosive formulations being used in industry today, the more we understand how we use them, the more we realize there are multiple avenues that could lead to an accidental detonation. The push for increased safety has led to the development and use of insensitive high explosives (IHEs). When it comes to safety considerations, IHEs based on 1,3,5-triamino 2,4,6-trinitro-benzene (TATB) are the IHEs of choice for use in nuclear warheads over conventional high explosives because they maintain excellent balance between performance and thermal resistance while remaining insensitive to initiation stimuli when compared to some common conventional high explosive formulations below as illustrated in Table 1.

Table 1. Comparison of basic explosives properties

Compound	Impact Sensitivity	Deflagration point	Density	Detonation Velocity
TATB	50 Nm	384 °C	1.93 g/cm ³	7350 m/s
RDX	7-8 Nm	204 °C	1.82 g/cm ³	8750 m/s
TNT	15 Nm	300 °C	1.65 g/cm ³	6900 m/s
Compiled from Rudolf Meyer <i>et al</i> , Explosives, 5th Edition, 2002, Wiley-VCH Publishers, Weinheim				

As the understanding of explosive initiation increased over the past decade, studies have been performed which demonstrated the shock sensitivity of TATB increases with respect to changes in temperature. There are several suspects which could be identified as the cause of the increase in sensitivity of TATB based high explosives. The increase in shock sensitivity could be due to the variance in the coefficient of thermal (CTE) expansion of TATB, the irreversible volume expansion observed due to temperature cycles called "ratchet growth," interactions with the inert binder, the manufacturing process for TATB, or a combination of these factors.

1.2. TATB (1,3,5-triamino 2,4,6-trinitro-benzene)

TATB is a high explosive that can be combined with plastic binders to produce plastic-bonded explosive (PBX) compositions, which are heat-resistant and highly insensitive. It is insoluble in organic solvents and has a melting point above 400°C. The best solvent to dissolve TATB is a heated high concentrated sulfuric acid. Cady and Larson did the first work to characterize the triclinic crystal structure of TATB [21]. It is an aromatic explosive based on a benzene ring structure with alternating NO₂ and NH₂ groups. These arrangements of the TATB molecule possesses both strong intra and inter molecular hydrogen bonds which help stabilize the molecular lattice structure.

There are various methods to create TATB. The traditional Benziger route (Fig. 1) to TATB is formulated by reacting 1, 3, 5-trichlorobenzene (TCB) with SO₃ in a 30% oleum and sodium nitrate to give a 1, 3, 5-trichloro-2, 4, 6-trinitrobenzene (TCTNB). This mixture is then reacted with ammonia and toluene to give TATB [18]. This process can produce a 99% pure TATB but creates chlorine blockage in the crystals. It results in distinct worm hole patterns, which may affect the sensitivity of the explosive.

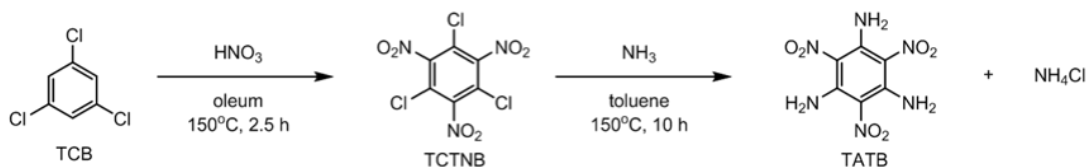


Figure 1. Tradition Benziger route

The blockage can be mitigated by using a wet amination formulation. The wet amination process requires water in the amination step and can produce a TATB crystal with less chlorine content. Alliant Tech Systems – Thiokol (ATK) Navy ManTech has been working on a different route to producing TATB. ATK's starting compound is phloroglucinola (PG), which is a synthetically accessible material unlike the TCB which is sole sourced from China. The alkylation step uses triethylorthoformate to form TETNB which is mixed with the ammonia solvent to yield TATB.

Both the wet and dry amination processes develop TATB crystals with distinct "worm hole" defects. These holes are inherit to the material and are largely influenced by the synthesis process. The wet amination process yields TATB crystals with significantly less worm hole defects [24, 30]. It has been considered by many that the worm holes are a result of ammonium chloride during the washout period. The extent at which theses holes contribute to the initiation properties of the TATB is not well understood at this time. As seen in Figure 2 [20], dry-aminated TATB had more

holes present when compared to wet aminated TATB where the worm hole defects are almost eliminated. A typical side by side comparison of the TATB formulated from both processes is shown below.

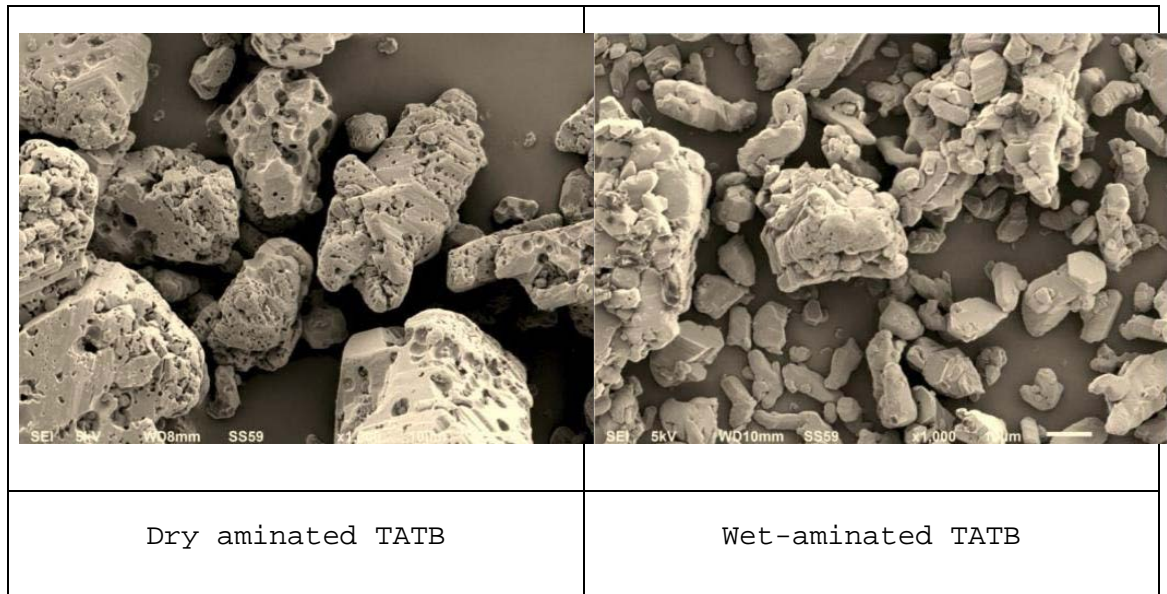


Figure 2. SEM scans of dry and wet aminated TATB

TATB is almost completely insensitive to sub-shock initiation and less sensitive to shock initiation than most other High Explosives [25].

1.3. PBX 9502

PBX 9502 consists of TATB crystals and a 3:1 chlorotrifluoroethylene vinylidene fluoride co-polymer binder (Kel-F 800). PBX 9502 is 95% TATB and 5% Kel-F 800 by

weight [3] or 95.2% TATB and 4.8% Kel-F 800 by Vol [34]. There are two commonly used formulations for PBX 9502 - Virgin PBX 9502 and recycled PBX 9502. Virgin PBX 9502 is formulated by pressing new TATB crystal that has been mixed with the Kel-F 800 binder. The crystals and binder are mixed in a solvent to produce the molding power. From there, it can be pressed in billets or other geometry to be further machined specific to the intended application. Recycled PBX 9502 makes uses of scrap PBX 9502 mixed with the virgin TATB and Kel-F 800.

PBX 9502 is very insensitive to shock initiation which makes it attractive for use from a safety standpoint. Figure 3 below is a pop plot for various explosives. It is easy to see the shock sensitivities for TATB and PBX 9502 are much less sensitive when compared to conventional HEs. Line 1 and line 4 are pop plots for commonly used HE's - PETN and HMX. The pop plots for TATB and PBX 9502 are on the far right side of the figure and represent by lines 6 and 7 [25].

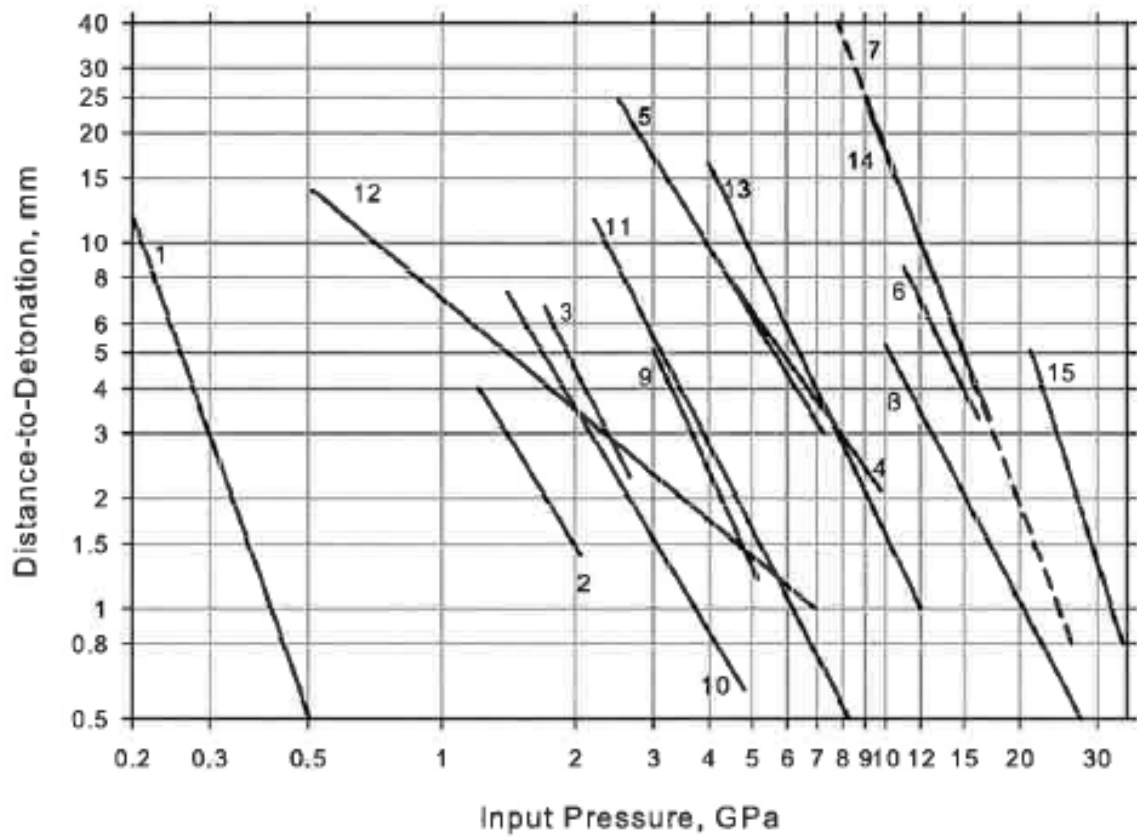


Figure 3. Pop Plot for various explosives, (1, 2, 3) PETN at various densities, (4) HMX, (5) PBX 9501, (6) TATB, (7) PBX 9502, (8) TATB Superfine, (9) XTX (10) PBX 9407, (11, 12) Tetryl, (13) pressed TNT, (14) Cast TNT, (15) NQ

2.LITERATURE REVIEW

2.1. Approach

The desire for a better understanding of the shock initiation sensitivity of temperature elevated TATB necessitated the review of past work that has been done on TATB to characterize its CTE, changes in density, and shock sensitivity. The goal of this study is to qualitatively identify and discuss the major contributors to TATB's shock sensitivity increases when the explosive is subjected to increases in temperature or various thermal cycles. The reviewed methods included a comparison of multiple author's CTE measurement, volumetric density, and shock initiation of TATB and TATB based compositions at elevated temperatures as they influence the explosives shock sensitivity.

2.2. Coefficient of Thermal Expansion (CTE)

The CTE discussion for TATB needs to start with a basic understanding of its molecular structure. In early

work Cady and Larson concluded that TATB molecules are arranged in lattice sheets parallel to the crystalline a-b plane and are held together by intra-molecular hydrogen bonding between molecular sheets [21]. Another study by Rosen and Dickson suggest that this layered hydrogen bond structure adds to the stability of TATB as a solid material. This structure is similar to that of graphite, and indicates anisotropy for all directionally dependent properties [26]. This effect is particularly obvious in thermal expansion and thermal cycling. Like graphite, TATB's anisotropic properties lead to a more complex behavior than plastic deformation or fracture [23]. Many researchers conclude as Cady did, that TATB crystals consist of molecular planes, bound to each other by weak hydrogen bonds. When pressed, the resulting compact is stronger in tension along molecular planes compared to tension normal to the planes. Conversely, the material is strong in shear normal to the planes, and weak in shear along the planes. This allows the molecular plane (a-b plane) to slide and deform to fill spaces when pressed while the c plane orients itself normal to the pressing force. This aligns the c plane with the principle stress generated from the applied pressure [21]. This dynamic molecular interactions lead to dynamic CTE values for TATB.

Olinger and Cady, used a hot stage to measure the expansion of a single crystal of TATB over a 125K temperature range and to determine the volumetric coefficient of thermal expansion, $99.5 \mu\text{m}^3/\text{m}^3\text{K}$. They noted the only noticeable growth was perpendicular to the crystals a-b plane. Many other studies have reported significant variations in the CTE for TATB. Kolb and Rizzo measured a CTE of $248 \mu\text{m}/\text{mK}$ over a higher temperature range (214-377 K), perpendicular to the a-b plane but also showed that the expansion for the single crystal was completely reversible even after thermal cycling [19]. They too attributed the enormous anisotropy to differences in bond strength: weak van der Waals forces in the c direction (between the layers) compared to the highly networked, stronger, hydrogen bonding within the a-b plane of the sheets. This agrees with conclusions made by Cady and others.

Another study performed by Rizzo on the CTE for TATB evaluated the CTE of TATB based on consolidation methods. Expanding on his previous work - Rizzo, Humphrey, Kolb [23] demonstrated the variability in the CTE for bulk TATB based on fabrication and pressing methods. See Table 2.

Table 2. Linear CTE Data

TATB Type and consolidation method	CTE ($\mu\text{m}/\text{mK}$) 223 - 263K	CTE ($\mu\text{m}/\text{mK}$) 313 - 343K
Dry aminated uniaxial	55	91
Dry aminated isostatic	43	68
Wet aminated, uniaxial	95	150
Micronized Wet-aminated uniaxial	110	142

Compiled from Rizzo and Kolb [23], "Growth of 1,3,5- Triamino-2,4,6-trinitrobenzene (TATB) II. Control of Growth by Use of High Tg Polymeric Binders"

It is easy to see the isostatically pressed samples maintained smaller CTE values for all temperature range suggesting that effects of the CTE can be reduced by uniformly pressing the compact. Looking at the uniaxial pressed samples, this data also shows that wet aminated TATB has a much higher CTE over the given temperature ranges.

In all cases evaluated above, the CTE for TATB increased with increases in temperature. The effect of which becomes more noticeable as the temperature is increased. Also in all cases, regardless of the method of consolidation, the larger value for CTE is always observed normal to the a-b crystal plane which orients itself normal to the

direction of applied force. This same property carries over to IHE formulations using TATB.

The CTE for PBX 9502 was measured by multiple researchers. Rizzo [12], Rainbolt and Hatler [27] all reported results for PBX 9502 which followed the same patterns as the TATB. They all used uniaxial pressed samples and measured significantly higher values for the CTE at various increased temperature ranges compared to the isostatically pressed samples. This reaffirms Rizzo and Klob's data above for uniaxial pressed samples CTE.

2.3. Ratchet growth and hot spots

Pressed TATB and TATB based explosives undergo a non-reversible volume expansion called ratchet growth. Ratchet growth results in a reduction of density of TATB and TATB based explosives when subjected to temperature cycles. The ratchet growth is cumulative over a set number of cycles and the irreversible growth is asymptotic. The bulk of the ratchet growth occurs during the first temperature cycles and tapers off after around 20 cycles which can lead to permanent density reductions of several percent [3]. Willey et al. [7] found that the quantity and size of the cavities of a multi crystalline TATB based PBX cylinder increased after undergoing thermal cycling. In their study, the total

void volume was derived using ultra small angle x-ray scattering (USAXS) data. They evaluated LX-17 as well as PBX 9502. Void size was from 2 nm to about 2 microns for LX-17 and PBX 9502, 1.5% and 1.6% respectively, and grows to 2.4% and 2.5% after thermal cycling. Mulford and Romero [29] concluded that the voids within TATB grains increased in both size and number. Ratchet growth continues to be the subject of multiple TATB studies and is generally associated with the graphitic crystalline structure of TATB and the directional dependence properties of the TATB coefficient of thermal expansion. As discussed above, the increase in cavities or voids is demonstrated by the reduction in density and increase in volume. These voids act as potential hot spots for ignitions sites and are capable of increasing the shock sensitivity of the TATB explosive.

Hot spots create ignition at localized regions due to elevated temperatures which result from shock interactions with the material's in-homogeneities. Hot spots form from a number of different phenomena; void collapse, plastic deformation, frictional sliding, and micro-jetting. If the hot spot can overcome the heat dissipation to its surroundings during a collapse, it will ignite and begin to consume the surrounding material. A visualization of this process is seen below in Figure 4 [28].

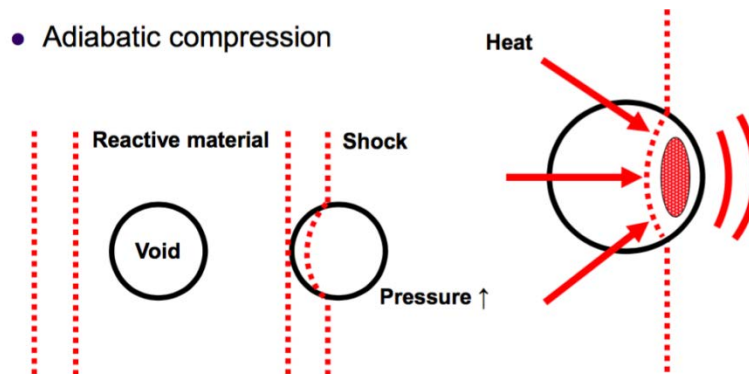


Figure 4. Illustration of a formation of a hotspot.

Consider a newly created void in a ratchet grown sample or a sample at elevated temperature undergoing adiabatic compressions due to an incoming shockwave. For simplicity, assume the void is spherical. As the shock wave (shown as dotted lines in Figure 2) passes over the void, it begins to compress the void causing an increase in local pressure. The shockwave continues to increase pressure as it moves over the void generating heat until the void collapses. The energy released during the collapse will either reinforce the propagating wave or dissipate to the surrounding material. If enough hot spots are activated and do not quench, they will coalesce lead to detonation.

Shock initiation of heterogeneous explosives requires some degree of voids to be present in the explosive. The fewer number of voids, the stronger the input shock has to

be to initiate detonation. Similarly weak input shocks require more voids to initiate detonation. Ergo, adding voids to heterogeneous explosives provides a mechanism which will allow for shock initiation at lower input energies.

2.4. Shock initiation of TATB and TATB based compositions

It is well known that it is possible to induce decomposition of heterogeneous explosive given a sufficiently strong input shock. Under the certain circumstances the decomposition of the explosive will occur rapidly enough to catch up to the incoming shockwave transforming it into a detonation wave. The time the shockwave must travel through a certain explosive before detonation is reached is referred to as its run distance and is a function of the strength of the input pressures. The run distance is unique to the particular explosive. This data has been compiled for several explosives on pop plots [25]. When the pressure vs. run distance is plotted on a log-log scale the data falls into a straight lines. This linear data can easily be used to help predict detonation under various impact conditions. For a given input pressure, the pressure pulse induced in the explosive is determined by the thickness and material of the impacting flyer. Assuming the material of

the flyer does not play a role, the thickness of the flier will dictate the width of the pulse. If the thickness of the impactor is too thin, the impact shock will reach the unconfined free surface of the flyer and reflect back into the explosive as a rarefaction wave which attenuates the peak pressure. Since the peak pressure is not maintained over the run distance, the explosive will not detonate. Run distance is just one of many factors that have to align for detonation to occur. However, assuming critical energy fluence and diameter are such that lateral rarefaction effects are not a concern, the run distance becomes a useful tool in predicting the shock sensitivity of many explosives. Dallman and Wackerle [1] expanded previous research in the shock sensitivity of TATB and TATB compositions to further investigate the sensitivity increase over an expanded temperature range (-55°C to 252°C). They used a plane wave generator with a heated pyramidal wedge configuration for PBX 9502 and LX-17. They soaked the configuration for 20 min to ensure uniform heating of the explosive prior to running the test. Streak cameras were used to capture the progression of the shockwave through the explosive. They used run distances to characterize the sensitivity of the HE at various temperatures. The samples were broken out by shots and sorted by density (See Table 3).

Table 3. Excerpt of shock to detonation data [1].

Shot Number		ρ_0 (g/cm ³)	T_0 (°C)	u (mm/us)	U (mm/us)	P (GPa)	h_d (mm)	t_d (μs)	Remarks
PBX 9520 Data									
2088	A	1.886	17	1.02	4.62	8.89	19.6	4.01	
	B			1.01	4.80	9.12	19.6	3.83	
2100	A	1.890	10	1.23	5.10	11.86	10.6	1.83	
	B			1.24	5.08	11.9	10.0	1.77	
2089	A	1.889	17	1.34	5.37	13.6	7.0	1.25	
	B			1.35	5.31	13.6	7.0	1.21	
4189	A	1.785	13	1.09	4.75	9.3	7.3	1.42	Temperature cycled;
2134	A	1.785	16	1.34	5.70	13.6	3.2	0.68	note 0.08 porosity
									on these two shots
2105	A	1.857	75	0.79	4.05	5.91	≥32.2	≥7.9	Run distance more
	B			0.80	3.93	6.13	≥31.4	≥7.5	than wedge thickness
2074	A	1.857	75	0.84	4.47	7.03	21.4	4.85	
	B			0.85	4.30	6.81	22.1	4.91	
2084	A	1.857	75	0.91	4.28	7.23	19.4	4.35	
	B			0.91	4.25	7.19	19.8	4.38	
2083	A	1.857	75	1.04	4.80	9.26	10.0	2.14	
	B			1.06	4.55	8.93	10.0	2.04	
2080	A	1.857	75	1.25	5.00	11.6	6.4	1.22	
	B			1.26	4.88	11.4	5.9	1.18	
2135	A	1.857	75	1.26	4.95	11.7	6.7	1.27	
	B			1.25	4.92	11.6	6.8	1.34	
2068	A	1.857	75	1.38	5.28	13.5	4.2	0.80	
	B			1.38	5.20	13.4	4.1	0.77	
2078	A	1.857	75	1.39	5.24	13.5	4.0	0.72	
	B			1.37	5.40	13.8	3.5	0.66	
2132	A	1.70	252	0.28	2.22	1.05	>>35	>>10	Low-pressure
	B			0.27	2.47	1.15	>>35	>>10	Hugoniot data only
2118	A	1.70	252	0.50	2.87	2.46	22.2	7.28	
	B			0.50	2.86	2.45	23.2	7.45	
2114	A	1.70	253	0.52	2.87	2.53	19.2	6.62	Pins lost; u and p
	B			0.54	2.95	2.71	19.6	6.67	from U (u) Hugoniot
2119	A	1.70	250	0.63	3.15	3.38	11.1	3.19	
	B			0.63	3.14	3.37	10.9	3.16	
2122	A	1.70	252	0.81	3.92	5.41	4.5	1.07	
	B			0.81	3.95	5.44	4.7	1.11	
2124	A	1.70	253	0.91	4.12	6.36	3.4	0.77	
	B			0.91	4.13	6.37	3.6	0.82	
2111	A	1.70	252	1.31	4.62	10.3	0.90	0.17	Short run; U from
	B			1.31	4.62	10.3	0.98	0.19	U (u) Hugoniot
2155	A	1.912	12	1.03	4.47	8.84	est. 38	est. 7.5	Slightly overran;
	B			1.03	4.51	8.88	est. 38	est. 7.5	Hugoniot data good

The data illustrates a definite trend in the overall time to detonation required as the density decreased, and then a reduction of time to detonation for the same samples as the temperature increased. When plotted (Figure 5) it is easy to see in the low input pressure range, the increased shock

sensitivity of PBX 9502 and LX-17 elevated to 252°C vs. PBX 9502 and LX-17 at ambient temperature.

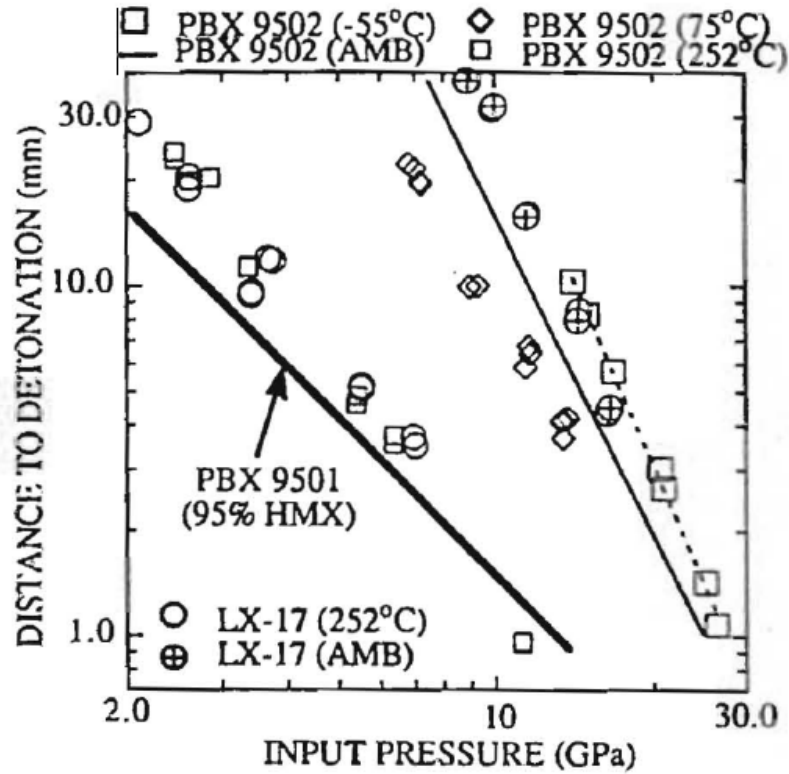


Figure 4. Pop Plot of PBX 9502 and LX-17 [1]

They suggested two main causes for the increase in TATB sensitivity; enhanced chemical reaction rates behind the shock and increased number of hot spots. These two options work well together to help explain the increase in TATB sensitivity although the main contributor of this combination is the increase in void spaces. As the hot spot are activated, they increase the temperature at the ignition site. This in turn contributes to the decomposition reaction rate.

Earlier we discussed that the CTE for TATB and TATB based explosive varies with temperature, and TATB/TATB based compositions undergo ratchet growth resulting in a permanent reduction in density which creates or rearranges intercrystalline voids in the pressing. Keeping with our basic understanding of the contributions of hot spots in shock to detonation, it is easy to conclude that TATB/TATB based explosive should show an increase in shock sensitivity with the decrease in density observed when TATB is heated or subject to ratchet growth temperature cycles.

The sensitivity of TATB and TATB based explosives continues to be studied. However, the current body of research results in similar conclusions. The CTE for TATB varies with temperature. For a single crystal of TATB, the volumetric expansion is completely reversible. Once pressed in a compact, the volumetric expansion of TATB and TATB based explosives is irreversible and the effects are cumulative over a set number of temperature cycles and ranges. This process of ratchet growth results in a decrease in density and increase in overall volume of the explosive. The volumetric expansion is anisotropic, and varies depending on the method of pressing. Uniaxial pressed samples show a greater CTE than isostatically pressed samples. This difference has been accounted for by the molecular structure

of TATB and its layering of the molecules normal to the pressing force. As Cady demonstrated the volumetric expansion is greater along the axial plane (c axis). Regardless of which direction the expansion was measured (a-b plane or along the c axis) the results were an increased number of intercrystalline voids available to act as hot spots for shock induced initiation. Characterizing the void creation and distribution resulting from ratchet grown sample will lead to a better understanding of the influence hot spots play in the increased sensitivity of TATB and TATB-based explosives at elevated temperatures.

There are also variances in CTE based on the manufacturing process (wet vs. dry aminated). The wet amination process produces TATB with significantly fewer worm holes, however the wet aminated TATB has considerably higher CTE's as seen in Rizzo and Klobe [23]. This should correlate with longer run distances for ratchet grown samples of wet aminated TATB when compared to a ratchet grown sample of identically pressed dry aminated TATB.

4.DISCUSSION

Based on all the research included in this review, there are still several questions surrounding the sensitivity changes of TATB/TATB based compositions due to thermal cycling. The mechanical mechanism that causes the ratchet growth is not well understood, but the effects are quantifiable. From the collective research presented earlier, we know that TATB will orient its a-b plane normal to the pressing force. This suggests the possibility that the void space within a sample of TATB could be re-ordered when it experiences ratchet growth temperature cycles, without ever demonstrating a volumetric growth (density reduction). It has also been demonstrated that we can stop the ratchet growth in a direction if we constrain TATB/TATB based compositions through traditional confinement [31]. If a TATB/ sample is confined in all directions during heating we would expect forces to be generated with the TATB sample. These forces would be variable compressive forces associated with the temperature. Knowing that TATB orients itself in the direction of the force being applied some reordering in the microstructure should be expected. Would the reordering effects have similar impact to void distribution as seen in ratchet growth sample? If so, a localized increase of voids could be reordered closer to a

future impact surface. The effect could be to sensitize the outside "layer" of HE enough to allow a low energy shock input to drive to detonation.

Comparisons of void size and distribution of TATB can be made based on microstructure changes associated with thermal cycling. Ultra small angle neutron scattering and x-ray microtomography has been used by other researchers to provide void distributions in a sample of TATB. If we fully constrain the ratchet growth of a sample we can maintain the density of the sample and just expose the explosive to the microstructure changes associated with the realigning of the basal planes. This data could be used to interpret sensitivity changes of TATB subjected to various temperature cycles which do not readily display any notable physical changes (no visible surface damage and no change in density). Current experimental work [35] is being performed at Los Alamos National Laboratory to explore the effects of creep in TATB which could reinforce the concept that TATB could reorder its microstructure and thus change its void space distribution. Further experimentation will be required to adequately determine the affect, if any, that this would have on the sensitivity of thermally stressed TATB.

5. CONCLUSIONS

The shock sensitivity of TATB and TATB based compositions increases with changed in temperature. The CTE for TATB and TAB based explosives has been shown to change with temperature and display anisotropic properties based on the consolidation methods used as well as being heavily influenced by the formulation method of TATB (wet or dry aminated). TATB and TATB-based compositions also demonstrate irreversible ratchet growth when thermally cycled. Although the mechanism that allows ratchet growth to occur is not understood, the effects of ratchet growth results in a reduction of density and an increase in volume, which is asymptotic over a set number of cycles. The density reduction can be attributed to the creation of void space in the microstructure of the TATB/TATB based compositions. These void spaces act as hotspots during adiabatic compression from an input shock. They are distributed such that an increase in sensitivity to low pressure shocks in TATB/TATB compositions is observed. Additional research will be required to determine what effect creep and other thermal damage within TATB samples if the density of the TATB sample is maintained.

REFERENCES

- [1] Dallman, J.C, Wackerle, J., "Temperature-Dependent Shock Initiation of TATB-Based High Explosives," Los Alamos National Lab Report, LA-UR-93-2904, submitted for 10th Annual National Detonation Symposium, 1993.
- [2] Urtiew, P.A., Cook, T.M., Maienschein, J.L, Tarver, C.M., "Shock sensitivity of IHE at Elevated Temperature," Lawrence Livermore National Lab, UCRL-JC-111337, June 1993.
- [3] Schwarz, R.B, Liu, C. Thompson, D.G., "Anisotropy in the Ratchet Growth of PBX 9502," Los Alamos National Labs, LA-UR-15-21827, 3/12/2015.
- [4] Hoffman, D.M, Martin-Williams, A., Gagliardi, F.J, Lorenz, T.K., Willey, T., Tran, T.D., "Comparison of DOTC and Legacy Benziger Dry Aminated TATBs and PBX 9502," NDIA Insensitive Munitions and Energetic Materials Technology Symposium, June 26, 2013.
- [5] Gustavensen, R.L, Thompson, D.G, Olinger, B.W, DeLuca, R., Bartram, B.D, Pierce, T.H. Sanchez, N.J. "Shock Initiation Experiments on Ratchet Grown PBX 9502, Los Alamos National Lab Report," LA-UR-10-01468, submitted for the 14th International Detonation Symposium, April 11-16, 2010.
- [6] Rae, P.J, Baca, E.V, Cartelli, A.R, Holmes, M.D, Kuiper, T.A. "The increased shock sensitivity of PBX 9502 at high temperature," 18th APS-SCCM and 24th AIRAPT, Journal of Applied Physics: Conference series 500, 2014.
- [7] Willey, T.M., Hoffman, D.M., Van Buren, T., Lauderbach, J., LLavsky, J., Gee, R.H, Maiti, A., Overturf, G., Fried, L., "In-Situ Monitoring of the Microstructure of TATB-Based Explosive Formations During Temperature Cycling using Ultra-Small Angle X-ray Scattering, Lawrence Livermore National Labs," LLNL-JRNL-401964, March 4, 2008.
- [8] Peterson, P. D., Idar, Deanne, J., "Microstructural Differences between Virgin and Recycles Lots of PBX 9502," Propellants, Explosive, Pyrotechnics, Wiley-VCH verlag GmbH & Co. KGaA, Weinheim (2005), 30, No. 2.

[9] Mulford, R.N., Swift, D.C., "*Sensitivity of PBX 9502 After Ratchet Growth*," Lawrence Livermore National Lab Report , LLNL-PROC- 515271, submitted to the American Physical Society Topical Conference on Shock Compression of Condensed Matter, June 26, 2011.

[10] Mulford, R.N, Alcon, R.R., "*Shock Initiation of PBX 9502 at Elevated Temperatures*," Los Alamos Report, LA-UR-95-2761, submitted to the 1995 APS Topical Conference on "Shock Compression of Condensed Matter, August 13-28, 1995.

[11] Paraskos, A.J., "*An Improvement Process for the Synthesis of TATB from TETNB*," presentation for 2009 Insensitive Munitions and Energetic Material Technology Symposium, Tuscon, AZ, May 2009.

[12] Thompson, D.G, Brown, G.W, Mang, J.T., DeLuca, B. Patterson, Hagelberg, S., "*Characterizing the Effects of Ratchet Growth on PBX 9502*," Los Alamos National Lab Report LA-UR-09-04402," prepared for, the 16th Topical Conference on Shock Compression of Condensed Matter, American Institute of Physics, June 28, 2009.

[13] Hill, L.G., Thompson, D.G, Cady, H.H., "*On the Ratchet Growth of TATB-Based Explosives*," Los Alamos National Lab report, LA-UR-11-02208, prepared for the 26th JANNAF Propulsion Systems Hazards Meeting Crystal City, VA, April 2011.

[14] Thompson, D.G, Brown, G.W, Mang, J.T., DeLuca, B. Patterson, Hagelberg, S. Olinger, Bart, "*Ratchet Growth in Recycles PBX 9502*," submitted to SEM Annual Conference, June 1-4, 2009.

[15] Thompson, D.G, Brown, G.W, DeLuca, R., Giambra, A.M, Sandstrom, M.M., "*Thermal Expansion of PBX 9501 and PBX 9502 Plastic-Bonded Explosives*," Los Alamos National Lab Report LA-UR-09-05002, prepared for the 37th Annual Conference of the North American Thermal Analysis Society, September 21, 2009.

[16] Chidester, S.K., Vandersall, K.S., Tarver, C.M., "*Shock Initiation of Damaged Explosives*," Lawrence Livermore National Lab report, LLNL-Conf-418560 submitted for JANNAF Interagency Propulsion Committee, December 7, 2009.

- [17] Rudolf Meyer et al, *Explosives*, 5th Edition, 2002, Wiley-VCH Publishers, Weinheim.
- [18] Zukas, Walters, 1998, "*Explosive Effects and Applications*," Springer-Verlag, New York, Chapter 2.
- [19] John R. Kolb and H. F. Rizzo, "Growth of 1,3,5-Triamino-2,4,6-trinitrobenzene (TATB) I. Anisotropic Thermal Expansion" *Propellants and Explosives* 4, 10-16 (1979).
- [20] Skidmore, Carey, Butler, Thomas, Sandoval, Cynthia, "The Elusive Coefficients of Thermal Expansion in PBX 9502" Los Alamos National Lab Report LA-14003, January 2003.
- [21] Cady, H. H. and Larson, A. c., "The Crystal Structure of 1, 3, 5-Triamino-2,4,6- trinitrobenzene," *Acta Crystallographica*, Vol. 18, p. 485, 1965.
- [22] Dobratz, B M., 1995, "The Insensitive High Explosive Triamino trinitrobenzene (TATB): Development and Characterization - 1888 to 1994", Los Alamos National Laboratory LA-3014-H.
- [23] John R. Kolb and H. F. Rizzo, "Growth of 1,3,5-Triamino-2,4,6-trinitrobenzene (TATB) Control of Growth by Use of High Tg Polymeric Binders," UCLR-52662, Lawrence Livermore National Laboratory, 1979.
- [24] Hoffman, D.M., Fontes, A.T., "Density Distributions in TATB Prepared by Various Methods," LLNL-JRNL-403880, Lawrence Livermore National Laboratory, 2008.
- [25] Horie, Y., 2009, "*Shock Wave Science and Technology Reference Library*, Vol. 3," Springer - Verlag, Berlin, Chapter 1.
- [26] Rosen, J.M. and Dickenson, J, 1969, "Vapor Pressure and Heats of Sublimation of Some High Melting Organic Explosives," *Journal of Chemical Engineering Data*, Vol. 14, pgs., 120-124.
- [27] M. Rainbolt and L. Hatler, "CTE Value for PBX 9502," Los Alamos National Laboratory memorandum ESA-WE-98-0422U (1998)
- [28] Lim, Seok Bin, Course Lecture on shockwaves, Socorro, NM, 2014.

- [29] Mulford, R.N., Romero, J.A., "*Sensitivity of the TATB-based explosives PBX 9502 after thermal expansion*," The 10th American Physical Society topical conference on shock compression of condensed matter. AIP Conference proceedings Vol. 429, pp. 723-726, 1998
- [30] Price, D, Morris, J., "*Manufacture of Wet-Aminated TATB at the Holton Army Ammunition Plant*," presentation for the 2013 Insensitive Munitions & energetic Material Technology Symposium.
- [31] Thompson, Darla, DeLuca, Racci, "*PBX 9502 Compressive Strength after Ratchet Growth: Correlation with Density and Not with Details of Thermal Profile*," LA-UR-15-23631, 5/14/2015.
- [32] Howard H. Cady, "WX-3 Monthly Report," Los Alamos Scientific Laboratory document WX-3-MR-75-4 (April 1975).
- [33] Cooper, Paul, "*Explosives Engineering*," Wiley - VCH, New York, 1996. Pg. 311.
- [34] Gibbs, T., Popolato, A, "LASL Explosive Property Data," University of California Press, Berkeley, 1980, Pg. 121.
- [35] Thompson, Darla, Personal communication, Los Alamos National Laboratory, July 06, 2016.