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ABSTRACT

Two newly synthesized versions of the insensitive high explosive (IHE) 1,3,5-triamino-2,4,6-trinitrobenzenes (TATBs) were compared to two legacy explosives currently used by the Department of Energy. Except for thermal analysis, small scale safety tests could not distinguish between the different synthetic routes. Morphologies of new TATBs were less faceted and more spherical. The particle size distribution of one new material was similar to legacy TATBs, but the other was very fine. Densities and submicron structure of the new TATBs were also significantly different from the legacy explosives. Pressed pellets of the new explosives were less dense. New FK-800 binder was used to prepare LX-17-like plastic bonded explosives (PBXs) from new and wet aminated TATB. Some mechanical, thermal and performance characterization of the new binder and LX-17-like PBXs was done. Significant differences were found. The reason for a number of these differences is not well understood.

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Two newly synthesized versions of the insensitive high explosive (IHE) 1,3,5-triamino-2,4,6-trinitrobenzenes (TATBs) were compared to two legacy explosives currently used by the Department of Energy. Except for thermal analysis, small scale safety tests could not distinguish between the different synthetic routes. Morphologies of new TATBs were less faceted and more spherical. The particle size distribution of one new material was similar to legacy TATBs, but the other was very fine. Densities and submicron structure of the new TATBs were also significantly different from the legacy explosives. Pressed pellets of the new explosives were less dense. New FK-800 binder was used to prepare LX-17-like plastic bonded explosives (PBXs) from new and wet aminated TATB. Some mechanical, thermal and performance characterization of the new binder and LX-17-like PBXs was done. Significant differences were found. The reason for a number of these differences is not well understood.

INTRODUCTION

TATB and Kel-F 800 are the explosive and binder for LX-17 and PBX 9502 used in all DOE IHE systems. Two new commercial versions of TATB synthesized by Thiokol (ATK) and Holston (BAE) have been developed as a result of a DOD mantech to support production of PBX-N7. Kel-F 800 was discontinued by 3M because an environmentally persistent emulsifier was used in its polymerization. A new copolymer similar to Kel-F 800, FK 800 was introduced as a possible substitute in 2006. It seemed prudent to evaluate LX-17-like formulations using these new explosives and binder and compare the results with legacy LX-17-1 to assess the viability of their use for DOE applications. Based on the results discussed below, the replacement binder seems viable, but the new TATBs are sufficiently different that they cannot be considered drop in replacements for legacy TATBs. We hope to evaluate these new TATBs and LX-17-like PBXs further to identify root causes of the differences observed in these tests.

KF 800 CHARACTERIZATION

There is always disagreement about what the pertinent properties of a binder are. Among the most important characteristics are molecular weight distribution and copolymer content. Kel-F 800 is nominally a 75/25 mole% chlorotrifluoroethylene (CTFE)/ vinylidene fluoride (VF2) copolymer about 200-400 monomers long. Table 1 compares molecular weight and copolymer content of previous lots of Kel-F 800 to new FK 800. As can be seen from the table, the CTFE content is high, but not outside the range of values produced in the past and the molecular weight is also comparable to previous polymer. Unfortunately, the sequence distribution and tacticity of the CTFE are not known but expected to be random and mostly syndiotactic, respectively.

Next in importance are the thermal and mechanical properties of Kel-F 800. These are dependent on the glass transition, Tg, and the melting point, Tm. Tg depends weakly on copolymer content, method and rate of measurement. Values of Tg for FK 800 by Dynamic Mechanical Analysis at 1 Hz were 32.8°C compared to 31± 1.5°C for different lots of Kel-F 800. The melting point depends on crystallization time and temperature,

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copolymercomposition, and annealing conditions. The melting point varies from 80 to 104 °C for isothermal crystallization over 90 days at temperatures from 30 to 70°C. Other properties like viscosity at processing temperatures, modulus at use temperatures, thermal expansion coefficient and strength are also dependent on composition and rate. Many of these properties have been measured and reported in the literature. [1,2] In general properties of the new FK 800 are nearly identical to Kel F 800 samples used in formulating LX-17.

Table 1. Some properties of Kel-F 800 lots compared with new lot 1 FK 800 binder.

	Mn*	Mw	Mw/Mn	ρ(a)	VF2	CTFE
Lot	kDa	kDa		g/cc	Mole %	Mole %
1	43	93	2.16		19.87	80.13
500 -700	37.5 ± 5	76.0 ± 12	2.03	1.9880	24.6±7.0	75.4±7.0
30000	35.8± 5.5	76.8± 9.6	2.20	1.9880	23.7	76.3

*Mn- number average molecular weight; Mw –Weight average molecular weight; ρ(a) – amorphous density; VF2 – mole % vinylidine fluoride monomer; CTFE – mole % chlorotrifluoroethylene monomer determined by NMR.

NEW TATBS

The current specifications for TATB explosive crystals (13Y-188025) requires very low levels of impurities and particle size depending on the type, wet aminated (WA), dry aminated (DA) or ultra fine (UF), but was written for TATB made by the Benziger synthesis. Because WA and DA TATB were synthesized from trichloro benzene, they contain 0.1 and 0.5 % residual chloride, respectively. Since the new TATBs are synthesized from 3,5-bromoanisole (BAE) [3] or phloroglucinol (ATK) [4] no chlorine containing contaminents will show up in HPLC analysis. Instead because of the oxygens on the benzene ring both processes generate ammonium diaminopicrate (ADAP) during aminolysis at about 1% levels and dibromo-trinitroanisole or 1-ethoxy-3,5-diamino-2,4,6-trinitrobenzene , the nitrated starting material. Both companies claim 98-99% TATB, but our analyses were closer to 96-97%, whereas legacy TATBs are 99+%.

Five small scale safety tests are performed on all LLNL explosives and formulations. These tests are Drop Hammer (DH 50), BAM friction, spark, differential scanning calorimetry (DSC) and chemical reactivity tests (CRT). These tests are described elsewhere. [5] As can be seen in Table 2, TATB is off scale in drop hammer, friction and spark (not shown) tests. Both new TATBs had 15-20C lower decomposition onset and peak temperatures in the DSC and 3-10 times more off gassing than legacy TATBs.

Table2. Small scale safety test results show all synthetic routes produce insensitive HE.*

TATB	DH 50	Friction	CRT/g	DSC (Ton)	Tpk
WA	>177.4 cm	>36.0 Kg	0.01-0.03	353	386.9
DA	>177.4 cm	>36.0 Kg	0.01-0.03	348	378.3
ATK	>177.4 cm	>36.0 Kg	0.20	285	352.7; 368.4
BAE	>177.4 cm	>36.0 Kg	0.10	310	367.3

*None of the TATBs was spark sensitivity in our test.

Morphology (crystal habit) and particle size are important for good formulation and processing characteristics as well as mechanical and initiation behavior. Figure 1 shows scanning electron micrographs of the new and legacy TATBs. As can be seen in the figure, the classic Swiss cheese holes in DA TATB and the polycrystalline habit of WA TATB are very different from the cauliflower structure found in the ATK TATB or the ultrafine particles of the BAE TATB. Particle size distributions were analyzed by light scattering rather than sieving (called out in the specification) because a much better indication of the size distribution is obtained. Figure 2 shows the particle size distributions of the 4 TATBs. The distributions are nearly monomodal for WA and DA legacy TATBs. The new ATK TATB has a mean particle size similar that of the legacy TATBs, but has a significant small diameter tail. The BAE TATB is finer than ultrafine (UF) TATB. Mean particle sizes are given in the column in the upper left of the figure.

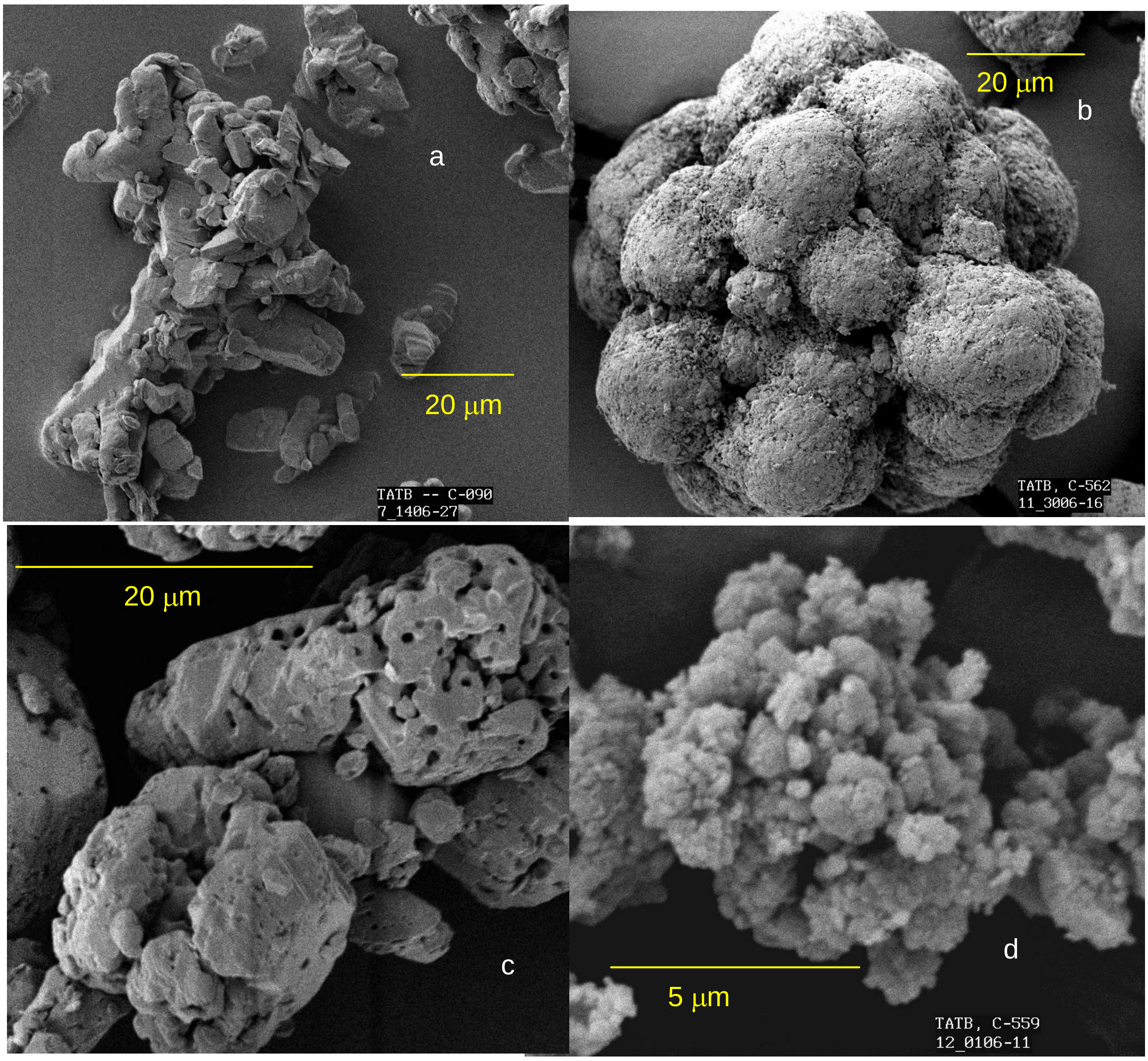

Figure 1. SEMs of (a)Wet aminated TATB; (b) ATK Thiokol TATB (c) Dry aminated TATB and (d) BAE Holston TATB.

A wide variety of techniques have been used to evaluate “crystal quality” with an eye toward reducing the sensitivity of conventional explosives. [6] Using a density gradient column with calibrated density floats, the density distribution of legacy TATBs were compared to the new TATBs. Theoretical maximum density (TMD) of TATB is 1.937 g/cc at room temperature. From Figure 3, the average density of WA and DA TATB were 1.9173 and 1.9181 g/cc , respectively. This is about 98.98% and 99.02% TMD. The new ATK TATB had much lower average crystal density, (1.8355 g/cc or only 94.75% TMD). The BAE TATB crystal density distribution was very broad with a mean density of 1.8010 g/cc. Disks about 1 mm thick by 12.7 mm diameter of each TATB were compression molded at increasing pressure from 35 to 200 MPa and the density was calculated from weight and dimensional measurements. Table 3 shows the density as a function of pressure and the average crystal density from the density gradient measurement. The results at the highest pressing pressure approach those of the crystal seeming to imply that a major contributor to the density of the PBX would be the mean density of the explosive crystal.

Submicron structure was analyzed by ultra-small angle x-ray scattering on the pellets pressed at 200 MPa in Table 3. Scattering occurs due to electron density differences, and thus cannot distinguish between scattering from particles or voids. In these cases, the volume contributing to the scattering calculated using the invariant is about 5% and 4% for wet and dry aminated, 13% for the Holsten and 4% for the Thiokol TATB. With the exception of the Thiokol, these are much higher than the void volume calculated by density, so we must assume the observed scattering occurs from both voids and particles. The clearest scattering difference between the Thiokol and the other TATB samples is the power-law exponent annotated in Fig. 4. For an ideal, two phase system (i.e. TATB and air) with three-dimensional scatterers, the exponent approaches -4. Wet-aminated (3.89 – 3.94) dry-aminated (3.85-3.90) and even the Holsten (3.97) are very close to this value, indicating an abrupt interface between TATB and air, consistent with crystalline facets at the interface. Thiokol TATB, however, has an exponent of -3.42. Although different power-law exponents are associated with reduced dimensionality, the exponent seen in the Thiokol case most likely arises from a diffuse or rough fractal-like surface interface.

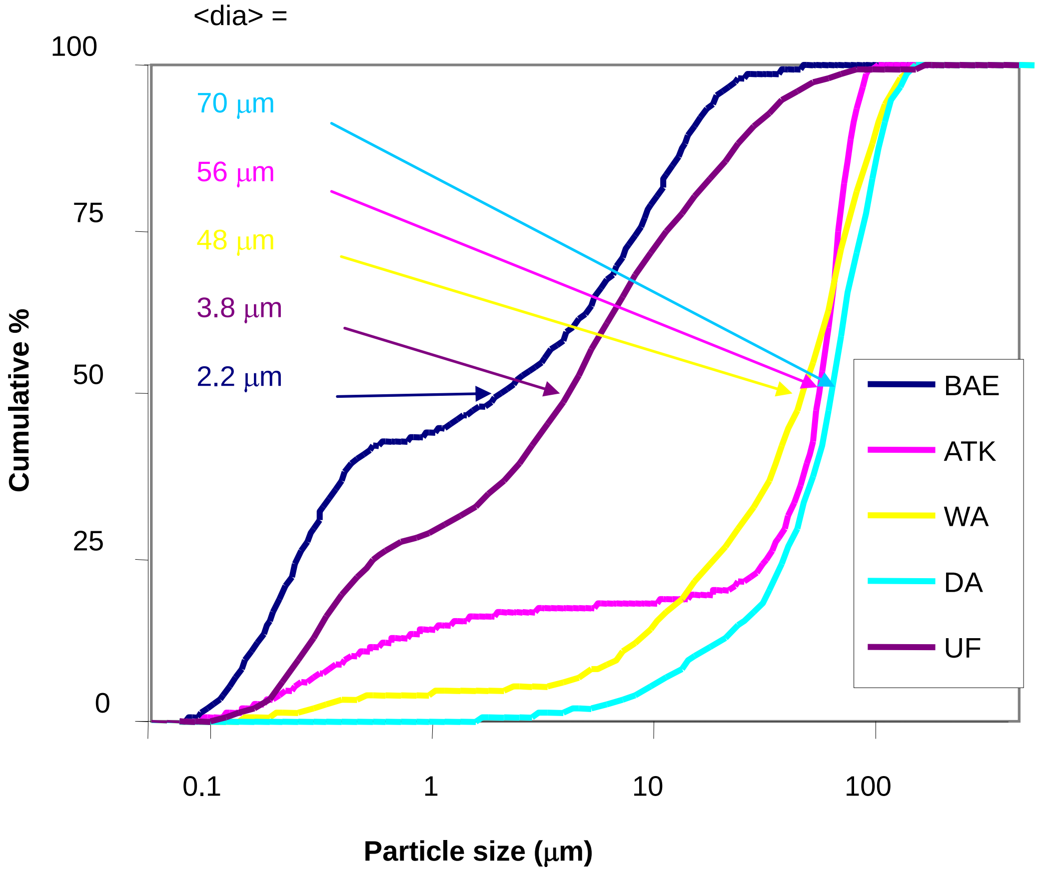

Figure 2. ATK, wet and dry aminated TATB particle size distribution were fairly similar, but BAE TATB was finer than ultrafine TATB made in a Sturtevant mill.

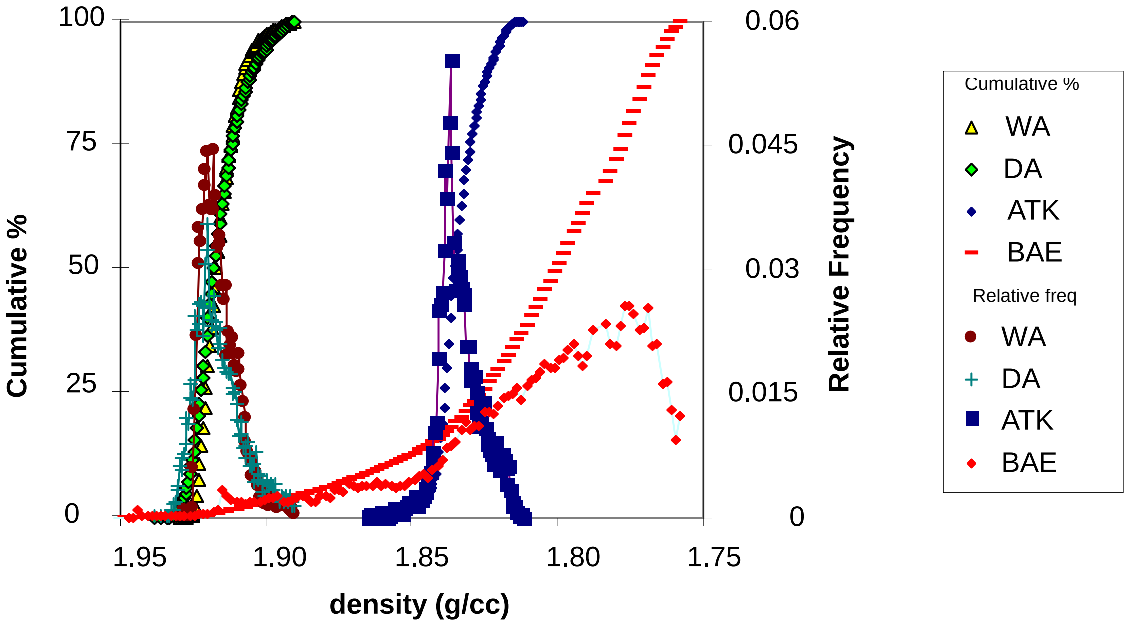

Figure 3. Comparison of density distributions for new and legacy TATBs shows much lower density of new TATB crystals compared to WA and DA TATB.

Table 3. Density, ρ and void volume, ϕ(v), of 0.2-g disks of TATB as a function of pressing pressure compare well with average crystal density from the gradient column measurements.

P / TATB	ρ(DA)	ϕ(v) %	ρ(WA)	ϕ(v) %	ρ(ATK)	ϕ(v)%	ρ(BAE)	ϕ(v) %
0 MPa	0.973	50	0.773	60	0.968	50	0.472	76
35.2	1.629	16	1.473	24	1.617	17	1.475	24
66.9	1.799	7.1	1.524	21	1.662	14	1.634	16
137.2	1.886	2.6	1.772	8.5	1.793	7.4	1.706	12
106.2	1.888	2.5	1.824	5.8	1.832	5.4	1.743	10
208.2	1.933	0.21	1.924	0.67	1.842	5.1	1.761	9.1
crystal	1.9181	0.98	1.9173	1.02	1.8355	5.24	1.8010	7.02

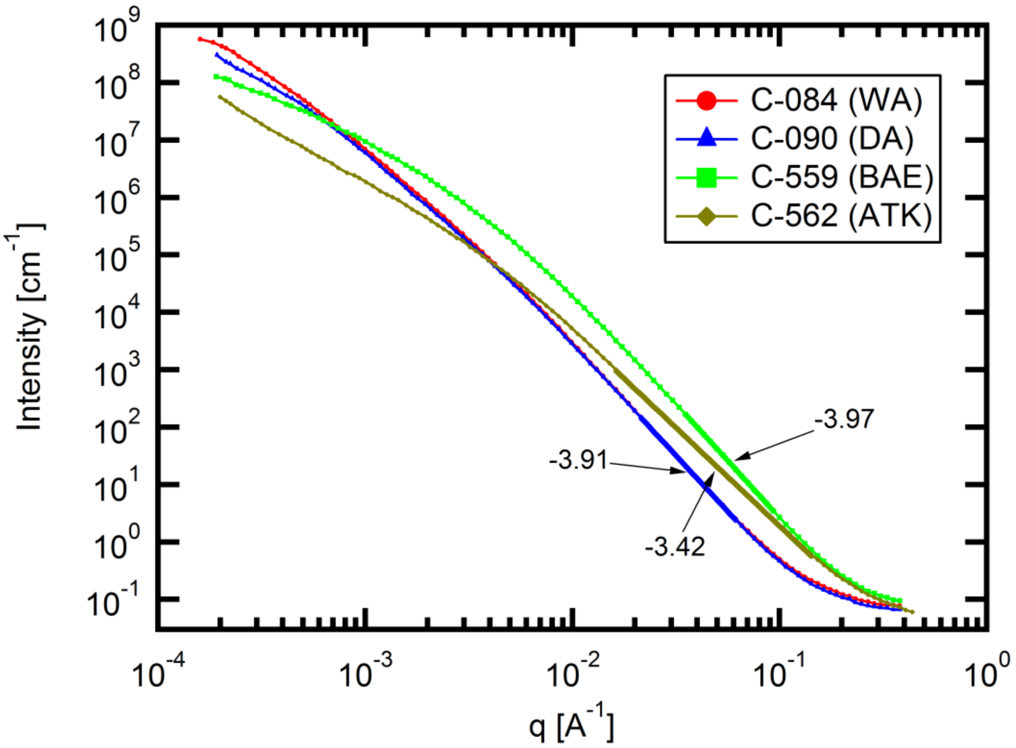

Figure 4. Comparison of ultra small angle x-ray scattering of WA (red), DA (blue), BAE (green) and ATK (yellow) TATBs from pressed disks shows substantial differences between manufacturers

LX-17 like formulations from new FK-800 binder with new & legacy TATBs

It should be obvious that only limited information can be gathered about new explosives and binders without actually attempting to formulate them into the plastic bonded explosive (PBS) of interest. LX-17-0 and LX-17-1 were developed from wet and dry aminated TATB formulated in a Holston slurry coater with Kel-F 800 lacquers. Ethyl acetate was used to dissolve Kel-F 800 and coat TATB in a water slurry to produce 50 grams of LX-17-like PBX. Details of the coating operation are given elsewhere. [7, 8] The results of small scale safety tests on the LX-17-like molding powders are compared to LX-17-1 in Table 4. As can be seen in the table, the results are similar except for the DSC onset temperature which is approximately 15-21°C lower for LX-17-like beads made from ATK or BAE TATB, consistent with what was observed in thermal analysis of these TATBs.

A brief pressing study in a mechanical press produced 12.7 mm dia. x 24.5 mm long cylinders with maximum density of 1.840 (94.7 %TMD), 1.876 (95.9% TMD) and 1.889 (97.2% TMD) for LX-17-like formulations from ATK, BAK, and WA TATB, respectively. There is much less difference in the pressed density of the LX-17-like samples than those found for TATB alone and the order of density increase in reversed, ie, BAE pressed to slightly higher density than ATK formulations. The reason for this is not known.

Table 4. Small-scale safety data for LX-17-2 molding powder

ID	DH50 (cm)	Friction @ 36 kg	Spark (1 J)	CRT@ 120°C (g/cc)	DSC Onset Temp (°C)
Typical LX-17-1	>177.4	0/10	0/10	0.20	377
LX-17-2-ATK	>177.4	0/10	0/10	0.15	362
LX-17-2-BAE	>177.4	0/10	0/10	0.18	361
LX-17-2-WA1	>177.4	0/10	0/10	0.11	375
LX-17-2-WA2	>177.4	0/10	0/10	0.07	380
LX-17-2-WA3	>177.4	0/10	0/10	0.12	382

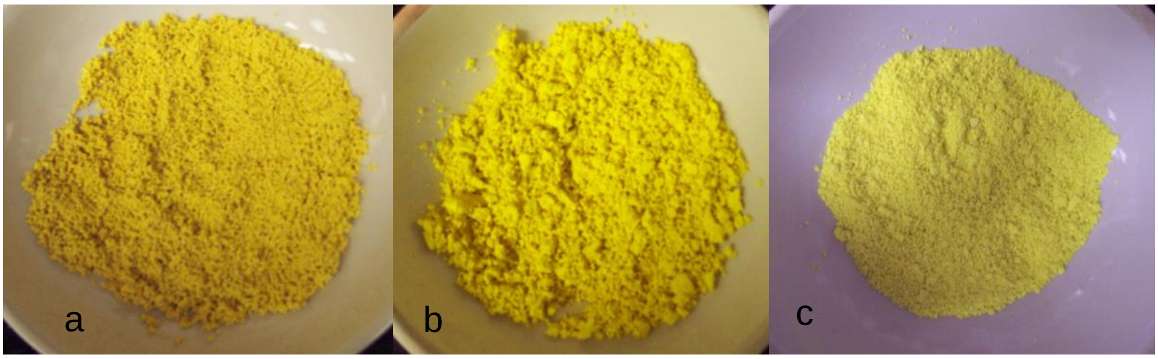

Figure 5. a) LX-17-ATK (made with ATK Thiokol TATB); b) LX-17-BAE (made with BAE Holston TATB); c) LX-17-1-WA1 (made with Wet-aminated TATB lot C-061). All formulations used lot 1 FK 800 binder.

Compressive stress-strain measurements of the LX-17-like parts from the pressing study were made at constant strain rate (0.0001 s^{-1}) and at 3 temperatures, 74, 23 and -50°C. The stress strain curves for different samples at -54, 23 and 74°C are shown in Figure 6 with results from LX-17-1 used for comparison. In all cases the BAE formulation had the highest strength. LX-17-BAE was always at least a factor of 2 stronger than any other formulation. The LX-17-WA formulation did not press well and consistently gave the lowest strength though at elevated temperatures had high elongation. For parts with good densities, the modulus under cold and ambient conditions was fairly constant. In all cases, the lower stress-strain curve from the same LX-17-like formulation was the lower density pressing.

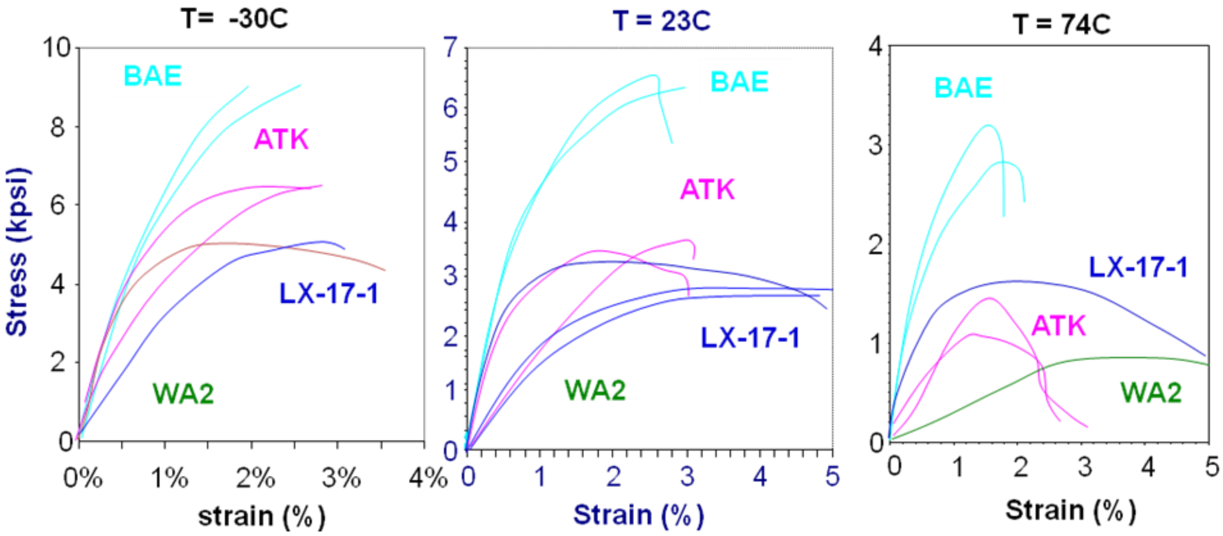

Figure 6. Compression tests on LX-17-like explosives show the effect of particle size and different pressing densities.

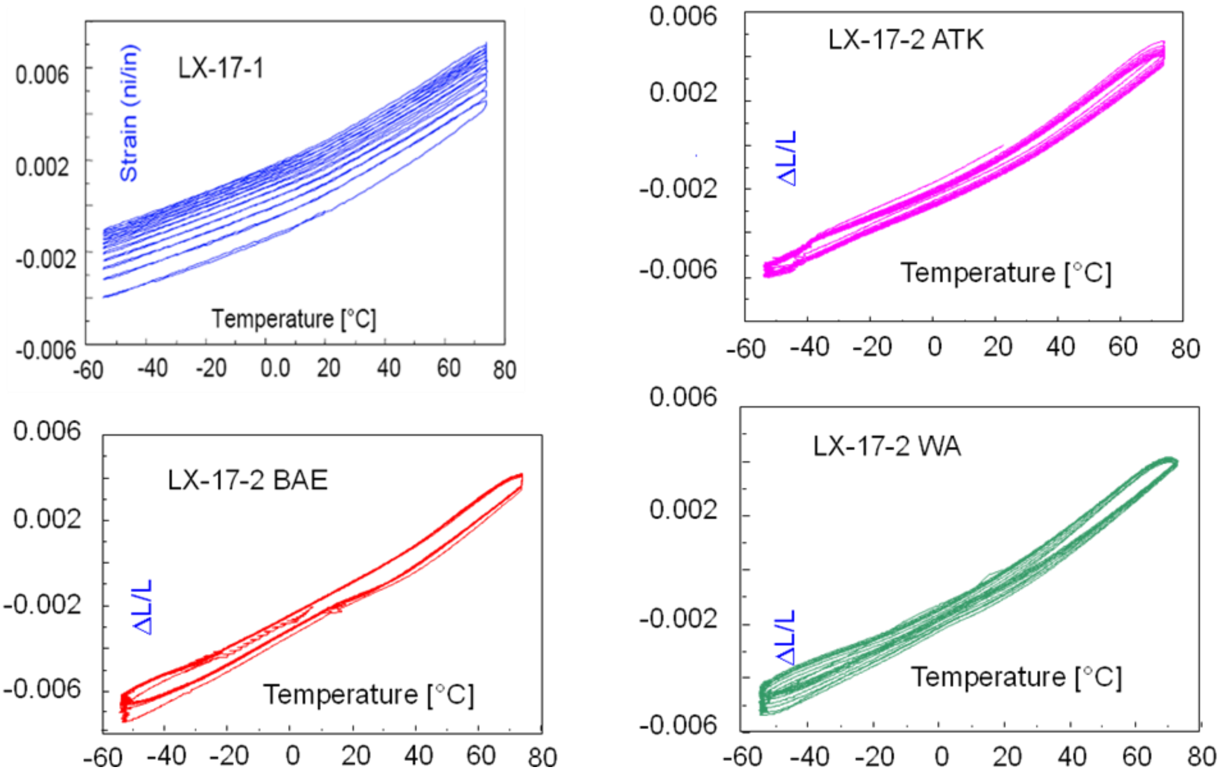

Figure 7. Thermal expansion measurements cycled approximately 10 times over the STS temperature range show almost no growth in BAE and ATK LX-17-like formulations compared to typical LX-17-1 ratchet growth.

Thermal expansion of new LX-17-like formulations was compared to LX-17-1 to determine the ratchet growth behavior of the new TATBs and whether or not new FK 800 binder inhibited ratchet growth. Figure 7 shows the strain (ΔL/L) versus temperature behavior of the 3 new formulations compared to classic LX-17-1 behavior in the upper left hand corner. As can be seen in the figure, lower irreversible growth was observed in all of the LX-17-like formulations compared to LX-17-1. The typical linear growth estimated from the initial length cold divided by the difference in length after 10 cycles is about 0.3%. New LX-17-1-like PBXs grew only about half this value. The reason for this is not known, but may be associated with the inability to achieve high density in the new explosive formulations.

Preliminary performance of new LX-17-like formulations was evaluated from their detonation velocity as measured by the embedded fiber test. A schematic of the test is shown in the upper half of Figure 8. A fiber optic probe was embedded in the center of six 25 x 25 mm right circular cylinders of explosive. The test consisted of an RP1 detonator lighting a PBX 9501 booster which drives a linear array of two LX-17-1 cylinders, 2 LX-17-like cylinders and 1 LX-17-1 cylinder. An in depth description of the EFT is given elsewhere. [9] The densities of the LX-17-like pellets were 1.8497± 0.0005, 1.8863 ± 0.0001; and 1.9112± 0.0002 gm/cc for ATK, BAE and WA formulations, respectively. The average detonation velocity for the 2 LX-17-like pellets was 7.33, 7.50 and 7.52 for ATK, BAE and WA formulations, respectively.

CONCLUSIONS

Preliminary data on new TATBs from ATK and BAE have shown that they are significantly different from legacy WA and DA TATB. This would seem to eliminate them as candidates for replacement of legacy TATBs in LLNL applications. On the other hand, there are fewer differences in the new FK 800 binder compared to Kel-F 800, so that with sufficient characterization and further evaluation of this binder in LX-17, it seems to be a very feasible candidate for 1:1 replacement as the binder in current IHE formulations like LX-17-1 and PBX 9502.

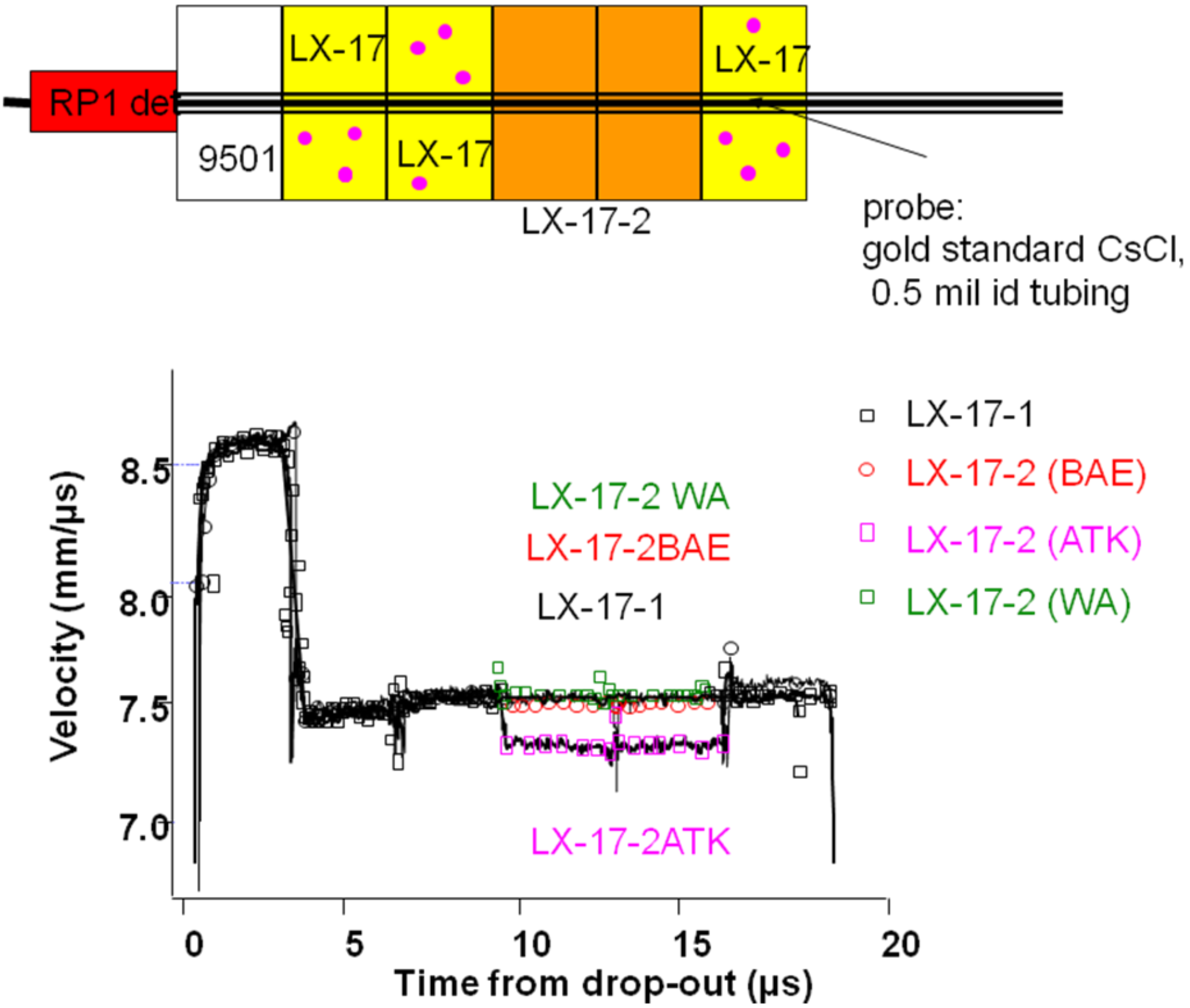

Figure 8. Embedded fiber test (EFT) comparison of LX-17-like formulations showed LX-17-ATK detonation velocity at 7.33 mm/ms compared to about 7.5 for LX-17-1 and the other new formulations.

REFERENCES

1. D.M. Hoffman and S.C. DePiero, “Characterization and Qualification of new TATB and Kel-F 800 for LX-17” UCRL-TA-228-232, Lawrence Livermore National Laboratory, Livermore, CA 94550 (Feb. 21, 2007).
2. D. Funk, et al “Kel-F 800 Experimental Characterization and Model Development” LA-UR-07-6404, Los Alamos National Laboratory, Los Alamos, NM (Oct 1, 2007).
3. Sleadd, B. “Synthesis and Scale-up of sym-triaminotrinitrobenzene at Holston Army Ammunition Plant”, Presented at IM&EM Technology Symposium; NDIA, Bristol, UK.: 2006.
4. Velarde, S. ”Pilot Plant Synthesis of Triaminotrinitrobenzene (TATB)“Presented at IM/EM Technical Symposium; NDIA, Bristol, UK: April 24-28, 2006,.
5. Hoffman, D. M.; Willey, T. M.; Mitchell, A. R.; DePiero, S. C., “Comparison of New and Legacy TATBs”, Journal of Energetic Materials 26, 139 2008.
6. . D. M. Hoffman, "Voids and Density Distributions in 2,4,6,8,10,12-Hexanitro-2,4,6,8,10,12-Hexaazaisowurtzitane (CL-20) Prepared Under Various Conditions." Propellants, Explosives, Pyrotechnics **28**(4) (2003).
7. Operating Procedure, Formulation of PBX-9502 or LX-17,” Index No. P6-5636-17, BWTX Pantex (January 2006).
8. Sabrina C. DePiero, D. Mark Hoffman, “Formulation and Characterization of LX-17-2 from new FK 800 binder and WA, ATK, and BAE TATBs” unpublished report (July 30, 2007).
9. Hare, D. E.; Goosman, D. R.; Lorenz, K. T.; Lee, E. L. “Application of the Embedded Fiber Optic Probe in High Explosive Detonation Studies: PBX 9502 and LX-17.“ in 13th International Detonation Symposium, Norfolk, VA,: 2006.