IHE candidate 3-picrylamino-1,2,4-triazole: Synthesis, Properties, and Testing

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Abstract:
3-Picrylamino-1,2,4-triazole (PATO) was invented at Los Alamos National Laboratory (LANL) almost half a century ago. This thermally stable explosive is insensitive to handling insults such as impact and friction, and decomposes over 300 ºC. The synthesis of this molecule is rapid and high yielding, however performance data for this promising explosive were scant before our recent reporting. We prepared material using Coburn's synthesis methodology and have reported low particle size distribution and needle-like morphology. Although these properties lead to difficulties in pressing to high density, we have prepared multiple formulations with fluorocarbon, polyester, and energetic binders. The maximum pressed density of these formulations was 90% of theoretical maximum density (TMD). Detonation velocity and detonation pressure was determined and IHE testing pursued through impactor shock to detonation transition (SDT) and large scale thermal testing. The performance of PATO is similar to TATB at equivalent density while PATO has a critical diameter below 10 mm and can initiate at low (61%) TMD.

Background:

Warheads and munitions are exposed to various threats as a result of their manufacture, transport, hostile environments, and ultimate deployment. In the late 1960s the United States was confronted with two unfortunate events: the accidental release of weapons during an aircraft accident over Palomares Spain, and a catastrophic fire onboard the USS Forrestal.

Picture 1. HE accidents that furthered IHE development..
Above left: a MK 28 bomb recovered during naval operations offshore Palomares Spain, 1966.
Above right: Still from footage from the deck of USS Forrestal, 1967.

As a direct result of these incidents a number of preventative measures were taken to improve the safety of munitions. Particular interest was devoted to the exposure of HE-bearing weapons to fire, impact, and other insults.[1]

Interest in Insensitive High Explosives (IHE) had existed at LANL since the receipt of samples of TATB from the Naval Ordnance Laboratory (NOL) during the 1950s in an effort to assist the

[1] The USS FORRESTAL (CVA-59) fire and munition explosions, http://www.insensitivemunitions.org, recovered 9/28/2019.

Plowshare project to utilize atomic energy for civilian purposes.[2] During research into the synthesis of novel explosives, the material 3-picrylamino-1,2,4-triazole (PATO) was synthesized and characterized by Michael Coburn.[3] PATO presents several positive attributes including good handling safety, high density, high thermal stability, and low cost of manufacture. At the time picryl chloride was readily available. At present, conversion of picric acid to picryl chloride is the most facile route to the desired starting material. However even with this impediment the synthesis is still facile.

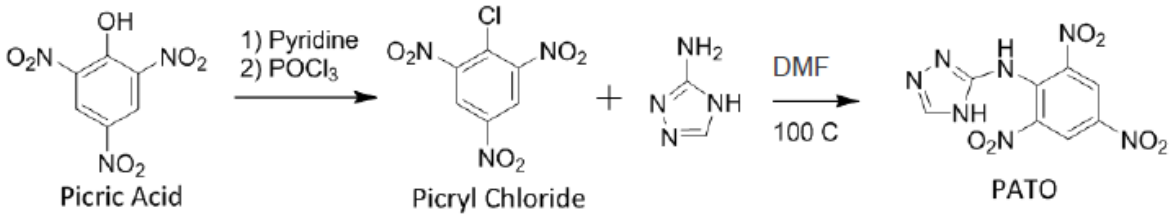

Figure 1. Overall synthetic route to PATO.

Interest in PATO was rekindled as a result of the publication of the new IHE qualification standard by DOE.[4] This standard imposes four tests in place of its more lengthy predecessor. These four tests include:

1) Deflagration to Detonation Transition (DDT) through destructive heating
2) Shock to Detonation Transition (SDT) through gas gun experiments
3) Bullet Impact (BI) testing using 50 BMG ammunition
4) Skid testing

For the purpose of evaluating these tests PATO was considered a convenient test explosive due to its facile synthesis and small scale safety properties.

Synthesis and Formualtion:

Picryl chloride was synthesized by the method of O'Keefe utilizing the Vilsmeyer reagent to dehydrate and chlorinate picric acid.[5] For each batch 7-8 kilograms of picric acid were combined with pyridine to afford the pyridinium salt as large yellow crystals upon filtration. Once this material had dried, the pyridinum salt was dissolved in 20 liters of DMF and phosphorous oxychloride was added over an hour to achieve a target temperature of 50 ºC. After one hour the contents were pumped into a receiving vessel which had been charged with HCl solution and the reaction digested to give picryl chloride as a light beige powder in 85% yield.

In order to manufacture enough PATO to accomplish the first two tests listed above the method of Coburn was followed at scales up to a maximum 10 kg yield. 3-Amino-1,2,4-triazole in two-fold excess is dissolved in N,N-dimethylformamide. Picryl chloride is slowly added to the mixture. The resulting mixture is heated to 100 °C for 4-5 hours, then allowed to cool before being quenched with water added in stages. A yellow precipitate forms which is filtered and dried. Oven drying at 60 ºC was found to be expedient. We found FTIR and NMR spectra to be consistent with literature values.

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[2] Executive Summary: Plowshare Program, US Department of Energy, Office of Science and Technical Information.

[3] M. D. Coburn, 3-Picrylamino-1,2,4-triazole and its preparation. US 3,483,211, LASL, Los Alamos, NM, USA, **1969**.

[4] L. D. Leininger, J. L. Maienschein, D. E. Hooks, DOE/NNSA Insensitive High Explosive (IHE) Qualification and Testing, **2018**, LLNL-PRES-755265.

[5] D. M. O'Keefe, HNAB: Synthesis and Characterization, **1976**, SAND-0239.

1H NMR (DMSO-d_6): 8.40 (1), 8.93 (2), 10.48 (1), 13.87 (1) 13C{1H} NMR (DMSO-d_6): 126.12, 135.93, 137.50, 139.88, 143.47, 157.21. FTIR (KBr): 700, 782, 1027, 1176, 1221, 1322, 1445, 1569, 1616, 3216, 3317 cm^{-1}.

In eight batches we were able to produce 35 kilograms of PATO by this method and proceeded to formulation. To accelerate formulation development we utilized contact angle measurement on pressed PATO parts to approximate surface energy. As expected for an amine with an active hydrogen the total surface energy is substantial at 59 dynes/cm compared to that of many common polymeric binders as shown in Table 1 below.

Table 1. Total surface energies of PATO and selected polymers.

Material	Surface energy
FK-800	30.9
Estane	46.0
Viton A	31.6
Phenoxy	33.6
PPA	46.5
PATO	59.2

For this project Viton A was selected as binder. Viton A has high thermal stability, is produced consistently on large scale, and is facile to prepare as an organic lacquer.

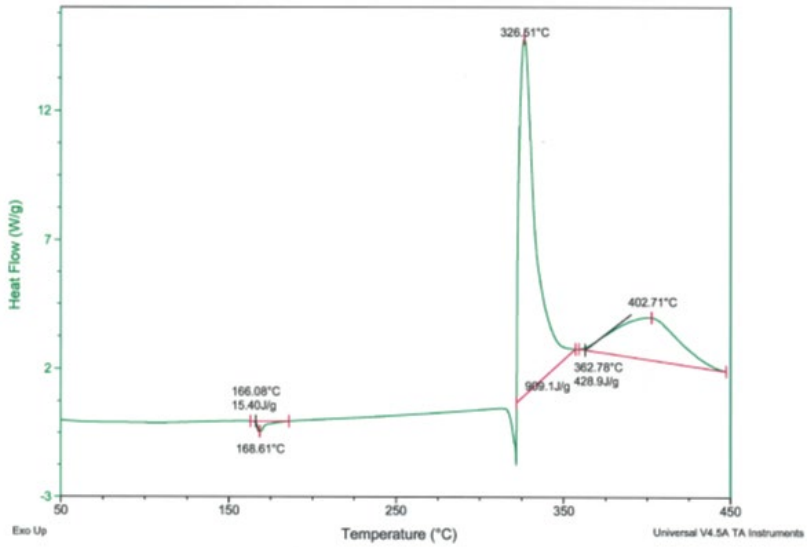

Figure 2. Differntial Scanning Calorimetry of PATO/Viton A mixture, TA Instruments DSC, 0.9 mg sample.

PATO was found to be compatible with Viton A as can be seen in the DSC in Figure 2, showing no reduction in the DSC exotherm of 326 ºC. Formulation was accomplished by the wet slurry method as published by Kasprzyk.[6] The binder is dissolved in ethyl acetate at 10 wt%.

[6] D. J. Kasprzyk, D. A. Bell, R. L. Flesner, S. A. Larson, Characterization of a Slurry Process Used to Make a Plastic-Bonded Explosive, Propellants, Explos., Pyrotech., **1999**, *24*, 333-338

The explosive PATO is agitated in water at a ratio of 10 wt%. As the binder is added to the stirred suspension a bilayer forms. The suspension is heated with stirring. As the organic layer evaporates the PATO prills form and are harvested through gravity filtration.

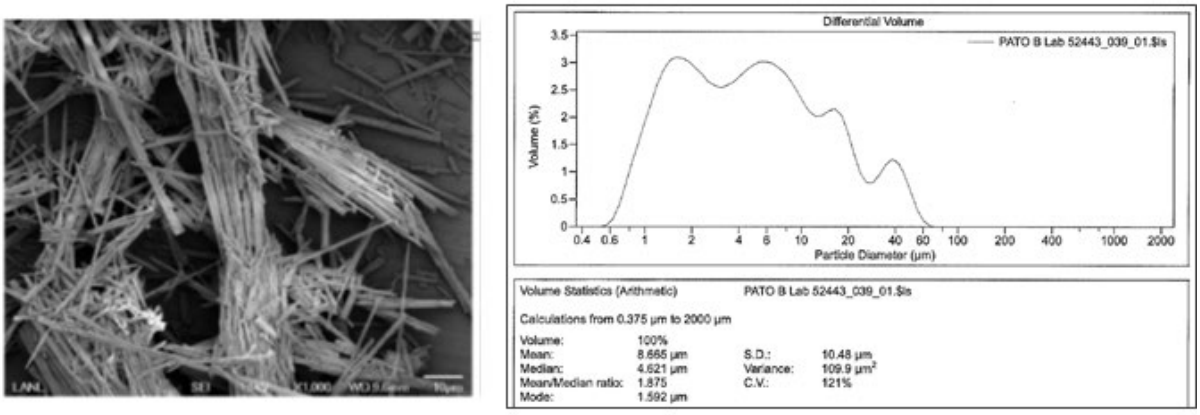

Figure 3. Left: SEM image of PATO crystals. Right: Particle size distribution of PATO as measured by Coulter light scattering.

Pressing and Performance Testing:

As discussed in our previous publication and shown in Figure 3, the morphology and particle size distribution (PSD) of PATO, presents a particular disadvantage in pressing as the needle like morphology does not press to theoretical maximum density (TMD) in our experience.[7] Thus for formulation made with Viton A we achieved a pressed density no higher than 1.72 g/cc, which is below 90% of TMD for this formulation. A 12.7 mm diameter cylinder shot experiment demonstrated a detonation velocity of 7.04 km/s and four PDV probes measured wall velocities which were used to extract JWL parameters.

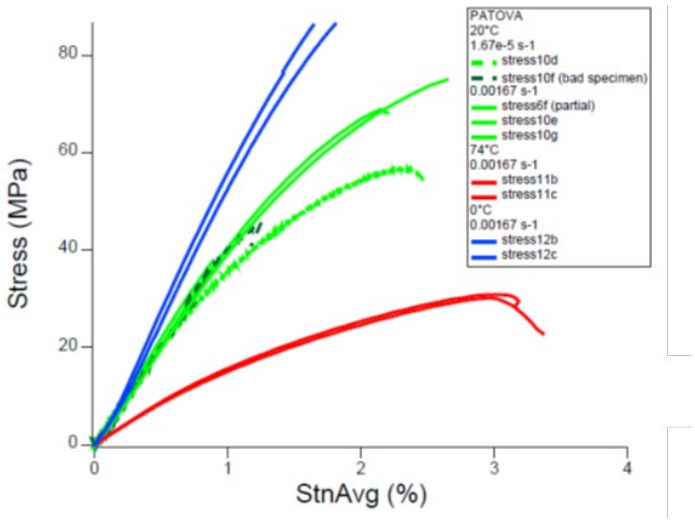

Figure 4. Stress and strain curves of PATO/Viton A tested at 0 (blue), 20 (green), and 74 ºC (red).

[7] P. Leonard, P. Bowden, M. Shorty, M. Schmitt, Propellants Explos. Pyrotech. **2019**, *44*, 203–206.

Mechanical Testing:
Compression testing using Instron load frames at several temperatures showed that the PATO/Viton A formulation withstood high stress but only up to relatively low average strain.[8] Images of the failed parts confirmed that the material was prone to brittle fracture under high load as would eb expected given the plots shown in Figure 4.

DDT testing:
The test articles for DDT testing are steel tubes of seven inch outside diameter, three inch inner diameter, and 40 inch length. The fill for the initial cookoff test is solid pressed pucks. In this case, 36 pressed parts of 3 inch diameter and one inch height were assembled and heated at a rate of 20 ºC/hr until a reaction occurred at 205 ºC. The following two tests involved rapid heating (100 ºC/hr) to 155 ºC followed by slow heating (20 ºC/hr) to a final temperature of 195 ºC. At this temperature thermite in the top of the column was ignited in an attempt to prompt a rapid thermal response. In one test solid explosive parts were used whereas molding powder was used in the second assembly.[9]

Figure 5. Steel test article before and after firing

In all cases the material inside the assembly was at least partially consumed by the ignition event. The tubes were then “baked out” by heating up to 400 ºC to decompose the remaining explosive. Proof that a detonation event did not occur is provided by the condition of the steel tubes. These test articles remained intact with their metal end-plates in position and there was no evidence of rupture or shatter as can be seen in Figure 5. Video of the event shows a rapid deflagration of the mass of explosive however no transition to detonation was detected in any case.

SDT Testing:
Shock to detonation testing involved three impact conditions:

- 5.3 GPa for 0.5 μs

[8] Experiments performed by the M-7 Thermal/Mechanical Team: D. Thompson, C. Woznick, R. Deluca.
[9] PATO IHE DDT Test Series, W. Perry, B.Broilo, P.Bowden, I. Lopez-Pulliam, P. Leonard, LA-UR-19-28935.

- 3.5 GPa for 3.0 μs
- 1.5 GPa for 3.0 μs at 195 ºC

The general design of experiment called for the explosive part to be sandwiched between a mounting tunnel, through which the flyer would impact the HE, and a lithium fluoride window which allowed PDV measurement of the backside of the part. For the short-shock experiment of 5.3 GPa over 500 ns a composite flyer of Kel-F81 and foam was driven into the 25.4 mm diameter puck using a two-stage gas gun. The longer shock at 3.5 GPa employed a copper impactor into a 71 mm diameter target. For the final test, the target chamber was heated to 195 ºC and an aluminum impactor was driven into a 25.4 mm diameter PATO/Viton A target. As described for this test methodology the absence of a shock response in the PDV trace is diagnostic of a successful test (no go).

No detonation was detected in any of the experiments as evidenced by the flat-topped profile of the PDV trace and the remnants of the HE part coating the inside of the firing vessel.[10]

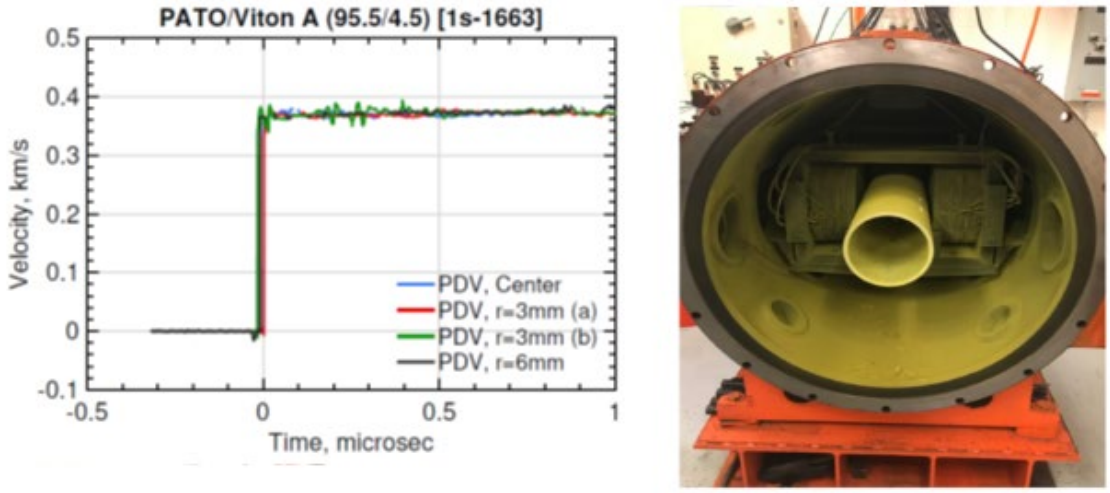

Figure 6. Left: PDV profile of impact on PATO/Viton A target. Right: PATO contamination inside firing vessel.

Conclusion:

The DOE differentiates itself from other users of HE by our suite of IHE testing performed directly on explosives. More effort will be required to show that PATO and its formulations satisfy the current IHE qualification standard. This will involve synthesis and formulation of adequate material to complete the tests required by the standard including BI and skid testing. Experience gained during this project will be applied to this, and future candidate materials.

Acknowledgements:

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[10] Preliminary IHE Qualication of a PATO/Viton-A Formulation: Shock-to-Detonation Experiments, F. Svingala, P. Leonard, B. Bartram, L. Gibson, J. Jones, A. Houlton, LA-UR-19-29823.