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Trinitromethyl Heterocyclic Oxidizers as a Solid Propellant Ingredient Final Report CRADA No TC02146.0

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Disclaimer

This work performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract DE-AC52-07NA27344.

Trinitromethyl Heterocyclic Oxidizers as a Solid Propellant Ingredient

Final Report
CRADA No. TC02146.0
Date Technical Work Ended: June 30, 2010

Date: January 18, 2011 Revision: 1

A. Parties

This project was a relationship between Lawrence Livermore National Laboratory (LLNL) and Physical Sciences, Inc.

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B. Project Scope

This was a collaborative effort between Lawrence Livermore National Security, LLC as manager and operator of Lawrence Livermore National Laboratory (LLNL) and Physical Sciences, Inc. (PSI), to develop a synthesis of two novel energetic heterocyclic oxidizers as possible replacements for ammonium perchlorate (AP) in rocket propellant formulations. This CRADA resulted from the award of the Phase I Small Business Technology Transfer (STTR) from DOD.

The CRADA consisted of two phases. The goal for Phase 1 was to produce a new oxidizer called TNMDNP. Phase 2 is optional (based on the success of Phase 1) and the goal of Phase 2 (optional) was to produce a new oxidizer called TNMDNT. Phase 2 tasks would be performed based on the successful results of Phase 1. The project consisted of the following tasks and deliverables:

Task 1 (Phase 1): Synthesis of 4 grams of precursor compounds (PSI) (Months 1-3)
PSI will prepare 4 grams of precursor compounds (for both Phase 1 and Phase 2) and fully characterize the compounds.

Task 2 (Phase 1): Synthesis of 2 grams of target compound, TNMDNP (LLNL) (Months 4-6)
LLNL will synthesize two grams of TNMDNP, using 2 grams of precursor from Task 1.

Task 3 (Phase 1): Testing of TNMDNP (LLNL) Months 6-7
LLNL will perform testing on a 2 gram sample of the target oxidizer material. The results of safety, physical property, and thermal testing as laid out below will be provided to PSI in a written report. Testing will include:

- Safety testing – Friction, ESD, Impact sensitivity
- Density – Density will be assessed by x-ray crystallography or helium pycnometry, as appropriate
- Thermal characteristics – Phase transitions, melting point, and decomposition energy will be assessed by Differential Scanning Calorimetry (DSC)

Task 4 (Phase 2): Synthesis of second target molecule, TNMDNT (LLNL) Months 5-7
Synthesize two grams of TNMDNT from a precursor compound shipped from PSI, using 2 grams of precursor prepared during Task 1.

Task 5 (Phase 2): Testing of TNMDNT (LLNL) Months 6-8
LLNL will perform testing on a 2 gram sample of the second oxidizer material. Tests performed will be identical to those described above for the first oxidizer material. The results of safety, physical property, and thermal testing as laid out below will be provided to PSI in a written report.

Task 6 (Phase 1 and Phase 2): Management and Reporting (LLNL/PSI) Months 7-10
LLNL and PSI will manage the project and write reports for DOE and the sponsor.

Deliverables:

Deliverable 1: PSI will synthesize precursor compounds and ship the precursor compounds to LLNL. (Task 1) Month 4

Deliverable 2: LLNL will test compounds. A report containing characterization data for the 2 gram sample of the target molecule(s) TNMDNP will be prepared for PSI. Testing results reported are to include: (Task 3) Month 8

- Thermal stability (DSC at 1,5,10, and 20^{o}C/min with decomposition analysis)
- Density
- Sensitivity (Friction, Impact, ESD)

Deliverable 3 (Phase 2): LLNL will test compounds. A report containing characterization data for the 2 gram sample of the target molecule(s) TNMDNT will be prepared for PSI. Testing results reported are to include (Task 5) Month 9:

- Thermal stability (DSC at 1,5,10, and 20^{o}C/min with decomposition analysis)
- Density
- Sensitivity (Friction, Impact, ESD)

Deliverable 4: Final Report and Abstract due within thirty (30) days of completion or termination of the project, as required under Article XI of the CRADA (Task 6) (LLNL/PSI).

This CRADA was designated as a twelve (12) month project. All of the Phase 1 tasks were not successfully completed. PSI successfully synthesized the precursor compounds and delivered them to LLNL. LLNL was not able to synthesize the target compound, TMNDNP, using the precursor supplied by PSI. Because the target was not isolated no follow up small-scale safety tests could be measured. Therefore only task and deliverable 1 was successfully accomplished. No Phase 2 was awarded. With a greater funding level the task and deliverables could have been completed.

C. Technical Accomplishments

The specific technical accomplishments of this project were the synthesis of the precursor compounds by PSI. Several attempts at the synthesis of the target compound, TNMDNP were performed without success. If the funding level allowed greater effort, it is believed the target compounds could have been synthesized, isolated and tested. This was a research project and the synthesis of the target compounds proved to be more difficult than anticipated. Further funding probably would have resulted in the success of this project but none was available.

D. Expected Economic Impact

No economic impact was generated under this CRADA because the target compound was not synthesized. In addition a Phase 2 was not awarded.

D.1 Specific Benefits

Benefits to DOE
This CRADA broadened the expertise of the LLNL chemists. If it had been successful it would have brought additional funding and national recognition to the LLNL synthesis chemists.

Benefits to Industry
The benefit to industry if this CRADA was successful was the possibility that new oxidizers could be synthesized that would replace AP in solid propellants. This could have alleviated the known environmental issues of AP from the U.S. stockpile.

E. Partner Contribution

The Partner, PSI, was successful in synthesizing 4 grams of the two precursor materials. No subject inventions were made under this CRADA as the precursor compounds are known compounds and the target compounds were not synthesized.

F. Documents/Reference List

Reports
A report was submitted by PSI to the funding agency summarizing our results. PSI has the reporting responsibility for this CRADA.

Copyright Activity
None

Subject Inventions
No subject inventions were submitted under this CRADA.

Background Intellectual Property

No Background Intellectual Property was disclosed by either party for this CRADA.

G. Acknowledgement

Industrial Participant's signature of the final report indicates the following:

1) The Participant has reviewed the final report and concurs with the statements made therein.
2) The Participant agrees that any modifications or changes from the initial proposal were discussed and agreed to during the term of the project.
3) The Participant certifies that all reports either completed or in process are listed and all subject inventions and the associated intellectual property protection measures generated by his/her respective company and attributable to the project have been disclosed and included in Section E or are included on a list attached to this report.
4) The Participant certifies that if tangible personal property was exchanged during the agreement, all has either been returned to the initial custodian or transferred permanently.
5) The Participant certifies that proprietary information has been returned or destroyed by LLNL.

A Racoveanu 06/06/2011

Ana Racoveanu, Principal Research Scientist — Date
Physical Sciences Inc.

Philip F Pagoria 6/3/11

Philip F. Pagoria, LLNL Principal Investigator — Date
Lawrence Livermore National Laboratory

for Veronica Lozier 6/9/11

Erik J. Stenehjem, Industrial Partnerships Director — Date
Lawrence Livermore National Laboratory

Attachment I – Final Abstract

Trinitromethyl Heterocyclic Oxidizers as a Solid Propellant Ingredient

Final Abstract (Attachment I)
CRADA No. TC02146.0
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A. Parties

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B. Purpose and Description

The Navy requires higher performing propellants and explosives for use in small rocket motors and ordnance applications. These formulations must simultaneously possess higher energy and density while maintaining acceptable hazard, mechanical, and processing properties. For over 50 years, ammonium perchlorate (AP) has been the most commonly used oxidizer for solid propellants and explosives (particularly metallized systems). It has substantial advantages in terms of cost and familiarity that have maintained it in an entrenched position. At the current time, no oxidizers exist that are capable of broadly replacing AP. We proposed to synthesize trinitromethyl derivatives of known highly nitrated heterocycles such as 3,4-dinitropyrazole and 3,5-dinitro-1,2,4-triazole as AP replacements. These highly oxidized organic compounds should be effective oxidizers in a manner similar to AP. The main issue with these organic oxidizers will be whether they will be thermally stable enough for use in future weapon systems.

This CRADA resulted from the award of a Phase I STTR proposal number N09A-017-0537 ("STTR") from DOD. The purpose of the STTR is to team a small business with a National

Laboratory and a commercial company to take advantage of the expertise of each member of the team. The success of this CRADA could have led to a Phase II STTR from DOD.

The project was on time, but only one deliverable was met. LLNL was not able to effect the conversion of the precursor molecules to the target molecules. LLNL believes that with a higher funding level the deliverables could have been met. The project ran out of funding before it was completed. As this was a research effort, the conversion of the precursor compounds to the target compounds proved to be more difficult than anticipated.

Because the target compounds were not synthesized, no Phase 2 of the CRADA was awarded or further funding was supplied to complete the deliverables.

C. Benefit to Industry

The benefit to industry if this CRADA was successful was the possibility that new oxidizers could be synthesized that would replace AP in solid propellants. This could have alleviated the known environmental issues of AP from the U.S. stockpile.

D. Benefit to DOE/LLNL

This CRADA broadened the expertise of the LLNL chemists. If it had been successful it would have brought additional funding and national recognition to the LLNL synthesis chemists.

E. Project Dates

January 6, 2010 to June 30, 2010