DEVELOPMENT OF A CONUS MANUFACTURING CAPABILITY FOR FOX-7

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Abstract

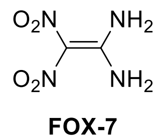
1,1-diamino-2,2-dinitroethene, or FOX-7, is an insensitive energetic material originally developed by FOI Sweden. Theoretical thermochemical calculations indicate that FOX-7 should exhibit nearly equivalent performance with that of RDX, while being considerably less sensitive to unplanned stimuli. Much like TATB, FOX-7 contains amino and nitro groups which can participate in intra and intermolecular hydrogen bonding. This phenomenon is believed to provide both materials with their unusual stability.

FOX-7 has been evaluated in both propellant and explosive applications with very promising results. As such, a domestic source of FOX-7 is highly desirable since the only current commercial supplier is the European conglomerate, Eurenco.

As part of a JIMTP program, NSWC IHEODTD has been tasked with developing a domestic manufacturing capability for FOX-7, as well as providing the four classes of material currently available from Eurenco. FOX-7 has been synthesized at NSWC IHEODTD at the 5, 20, 100 gram and kilogram scales, and there is currently an active SOP for the manufacture of FOX-7 at the multi-kilogram scale with yields typically in the 65-70% range. We have also produced all four classes/particle size distributions of FOX-7; Class 1 (20-40 µm), Class 2 (50-100 µm), Class 3 (100-200 µm) and Class 4 (250-350 µm) via recrystallization, and have produced Class 1 and Class 4 via recrystallization at the multi-kilogram scale.

Introduction

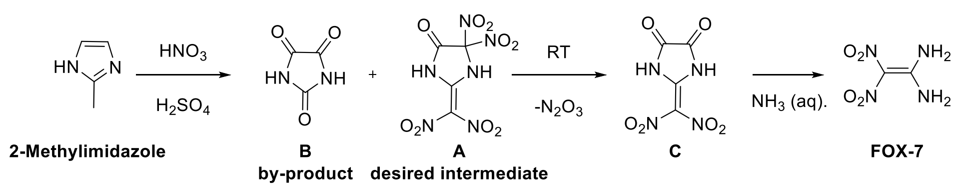
The objective of this effort was to develop a scalable process which would produce R&D quantities of 1,1-diamino-2,2-dinitroethene (aka FOX-7 or DADNE, Figure 1). The Chemical Scale-up Group at NSWC IHEODTD was selected for this process R&D effort to act as a continental United States (CONUS) source of R&D quantities of FOX-7 for JIMTP Task 14-2-68. Developing this capability would in turn provide the ability to support future programs requiring R&D quantities of FOX-7 synthesized in the CONUS.



1,1-diamino-2,2-dinitroethene (FOX-7)

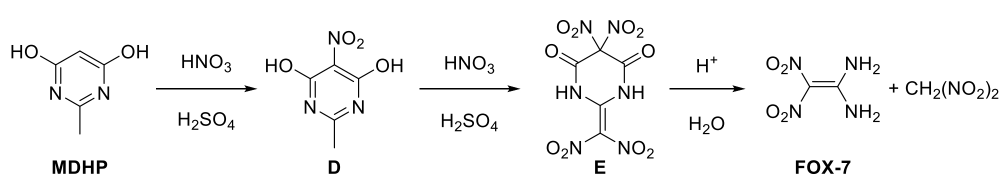
FOX-7 was first synthesized and reported by Latypov, Langlet, and Wellmar of the Swedish Defense Research Agency (FOI).[1] Currently, EURENCO Bofors AB is licensed by the Swedish government to synthesize pilot and production scale quantities of FOX-7.

As shown in Figure 2, FOI's first generation synthesis of FOX-7 proceeded from 2-methylimidazole in mixed acid containing up to 20% water to afford the desired intermediate, 2-dinitromethylene-4,4-dinitroimidazolidin-5-one (A), along with parabanic acid (B) as a by-product. Use of oleum afforded none of the desired intermediate, but rather 2-methyl-4-nitro-imidazole and parabanic acid (B). The desired intermediate would then hydrolyze at ambient temperature to form 2-dinitromethyleneimidazolidine-4,5-dione (C), which would then be exposed to aqueous ammonia to afford FOX-7.



FOI's first generation synthesis of FOX-7

An improved process to FOX-7 was also developed at FOI.[2] As shown in Figure 3, exposing 2-methyl-3,5-dihydroxypyrimidine (MDHP) to mixed acid proceeds through two stages of nitration. The first nitration is reported to be fast,[3] which affords 4,6-dihydroxy-2-methyl-5-nitropyrimidine (D). The second nitration is the slow step,[3] which gives access to 2-dinitromethylene-5,5-dinitrodihydropyrimidine-4,6(1H,5H)-dione (E). Intermediate E can either be isolated and hydrolyzed after separation from the mixed acid,[4] or an *in-situ* quench can be performed to directly afford FOX-7 and dinitromethane,[2] which typically undergoes further hydrolytic decomposition.



FOI's second generation synthesis of FOX-7

FOX-7 has been reported to have a crystal density[5] of 1.88 g/cm^3. It has been reported to be significantly less sensitive than RDX with respect to impact[6] and friction while maintaining RDX-like performance properties.[7] EURENCO Bofors has produced FOX-7 in different particle sizes: Class I (20 – 40 μm), Class II (50 – 100 μm), Class III (100 – 200 μm), and Class IV (250 – 350 μm).[3] Unlike typical energetic molecules, FOX-7 has been observed to have increased shock sensitivity as particle size decreases. This phenomenon is still not well understood.[9,10]

Results and Discussion

The NSWC IHEODTD Chemical Scale-up Group chose the MDHP process as a starting point for this effort. From a cost-savings perspective, this process would be an ideal starting point; the starting materials were readily available in bulk, and the process would be less labor intensive. An *in-situ* ice quench would avoid the need for a separate hydrolysis step and would eliminate the need to deal with the major by-product of the reaction, dinitromethane.

Scale-up from the 1 gram to 20 gram scale

Initial investigations into reproducing the conditions described by Latypov and Bellamy in the literature[2,4] were performed at the 1g, 5g, and 20g scales in laboratory glassware. The reaction proceeded as described in the literature, and the exothermic behavior of the reaction was controlled using an ice water bath and by controlling the dose rate of the white fuming nitric acid. The *in-situ* ice quench often produced yellow NO_x fumes, heat, and moderate amounts of foam. The heat generated was largely was due to acid-base chemistry occurring between the ice water and mixed acid, while the foam was generated from hydrolytic decomposition to NO_x and CO_2 by-products in addition to rapid precipitation of FOX-7 out of solution. The samples of FOX-7 were analyzed by NMR and DSC and were compared with an authentic sample and checked against data published in the open literature. The ^{1}H and ^{13}C NMR data for FOX-7 were consistent with those previously reported.

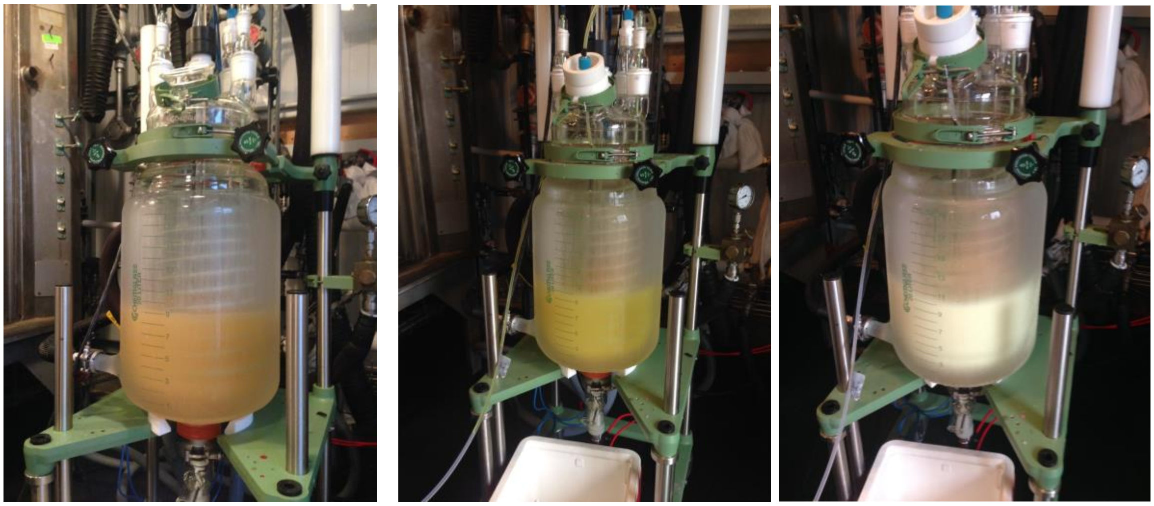
2-Liter RC-1 Scale-up to 100 grams

At the 100 gram scale, an initial thermal profile was developed using a Mettler Toledo RC1e reaction calorimeter. When the first 100 gram batch was performed, T_R-T_J was observed to peak around 10K and began to fall off immediately after the dose stopped. The second 100 gram batch was used to obtain heat flow data on the reaction. The reaction typically behaved similarly to the smaller scale batches. Again, the *in-situ* ice quench often produced yellow NO_x fumes, heat, and foam. The Chemical Scale-up Group's evaluation of the amount NO_x, heat, and foam produced during the quench warranted a more delicate approach to quenching at larger scale, where the crude mixture in mixed acid would be dosed into a stirred quench reactor containing water while maintaining a desired temperature.

Scale-up synthesis to the 1 kilogram batch in the 20-liter reactor

The 1 kilogram batch synthesis of FOX-7 was performed in a Chemglass 20-liter reactor with Teflon-coated temperature controlling coils. The kilogram batch synthesis of FOX-7 began by dissolving MDHP in sulfuric acid in the 20-liter reactor. Temperature control was maintained through the use of a combination of the 20-liter reactor jacket along with the internal cooling coils, which were controlled by a separate, external chiller.

The dose rate and coolant feed to the reactor jacket and coils were continuously adjusted to maintain the desired nitration temperature. During the dose, the color of the material changed from a light brown, to a transparent yellow, and finally to a transparent white. The agitation was stopped to observe the material and the solids looked suspended in the liquid.



A *B* *C*

20-Liter reactor contents during nitration: A) MDHP dissolved in sulfuric acid; homogeneous. B) Reactor contents during nitric acid dose; homogeneous. C) Reactor contents near completion of nitric acid dose; color change, fine suspension, no longer homogenous.

The slurry containing E from the 20 L reactor was then pumped into warm water in a 50 L reactor for the quench decomposition to form FOX-7.

A *B* *C*

50-liter reactor during quench: A) Reactor at beginning of quench. B) Reactor 30 minutes into quench, particles suspended, color change, mostly translucent. C) Reactor 1 hour into quench, contents opaque.

The contents of the 50-liter reactor were then drained into a 1 micron filter bag. The solids were washed with water and air dried to give a 72% overall crude yield.

Recrystallization Method Development and Recrystallization of Kilogram Batches

Crystallization conditions used to obtain particle sizes and morphologies consistent with material produced by Eurenco Bofors was proprietary information given to Joseph Clubb, NAWC WD, and later shared with us with permission by Eurenco.[8] Consequently, it will not be presented in this paper.

Safety and Thermal Characterization

In order to assess the CONUS material and compare against OCONUS source a series of round-robin safety and thermal evaluations were conducted by NSWC IHEODTD, NAWC China Lake, and ARDEC Picatinny. Each participant was shipped up to 1-kg batch of both the Class I and Class IV recrystallized CONUS FOX-7 from NSWC Indian Head. In order to avoid method or machine bias the round-robin participants made 'best attempt' to standardize the test protocol and stipulations were agreed upon prior to testing. The testing followed the Allied Ordinance Publication (AOP-7) 2nd edition MANUAL OF DATA REQUIREMENTS AND TESTS FOR THE QUALIFICATION OF EXPLOSIVE MATERIALS FOR MILITARY USE that calls out accepted methods via associated STANAGs for friction (4487), impact (4489), electrostatic discharge (4490), and thermal stability (4515). Where methods or testing equipment differed in the slightest, stipulations were agreed upon with respect to mass of testing samples, testing environment, data analysis and reporting. The testing equipment and stipulations are as follows:

<u>Equipment</u>

Impact – ERL

- Type 12 Tooling
- Mass of drop weight: 2.5 kg
- Mass of Striker: 520-540 gm
- 180A Garnet Paper

Friction – Safety Management System (SMS) supplied Alleghany Ballistics Laboratory (ABL) and BAM

- Wheels and Plates – verify hardness finish use hardened steel ≅ 60 microinch
- Pressure Gauge Calibration – verify calibration is valid

Electrostatic Discharge – SMS and ABL

- Verify Ohm value of in-line resistor
- Needle distance-position approximate 0.0020" Hold voltage at 5.785 Kv
- Run using IH intervals – start at 0.326 joules

Differential Scanning Calorimetry – TA Instruments or Mettler Toledo models

- DSC to be run at 5°C/min per ASTM E3537

<u>Additional Stipulations</u>

- All test masses will be 35mgs ± 2
- All tests to proceed with 'lights off' for observational effect
- Testing to proceed at 45-55% relative humidity or as close to it as possible - note Hr and T
- All sites used the older hemetic aluminum pans, closed pan vented

Test Results and Discussion

Each site conducted impact, friction via ABL and BAM, electrostatic discharge, and differential scanning calorimetry. Data analysis was to include a 50% failure point, low fire, and threshold initiation limit (TIL). Results were collated and compared to each other and to an 'as received' OCONUS source provided by Eurenco Bofors at the time. Test results from round-robin effort are shown below in Table 1. Table 2 shows the comparison with the OCONUS FOX-7 material.

Table 1: Round-Robin Safety and Thermal Test Results

Site	Sample Lot# Class	Impact (cm)			Friction		ESD (joules)			DSC (°C)
		50%	Low	TiL	ABL (lbf)	BAM (N)	50%	Low	TiL	
Indian Head	IHM170FX7-076 I	*55	51	32	708 (50%)	10/10 NF 216	TBD	0.095	0.037	Doublet 231,282
	IHM17FFX7-104 IV	*46	41	26	20/20 NF 1000	10/10 NF 216	TBD	0.095	0.037	Doublet 228, 282
Picatinny	IHM170FX7-076 I	**79	79	63	20/20 NF @ 1800	10/10 NF 324	TBD	0.095	0.037	Doublet 232, 261
	IHM17FFX7-104 IV	*71	63	32	20/20 NF @ 1800	10/10 NF 360	TBD	0.095	0.037	Doublet 232, 260
China Lake	IHM170FX7-076 I	**71	63	50	20/20 NF @ 1000	10/10 NF 360	8.37	3.80	1.50	Doublet 231, 289
	IHM17FFX7-104 IV	**51	40	32	20/20 NF @ 1000	10/10 NF 360	20/20 NF @ 8.0			Doublet 228, 288

*50% point determined by Bruceton Method
** 50% point determined by either Probit or Modified Bruceton Method

Table 2. Comparison of OCONUS and CONUS FOX-7 Material

Test	Class I		Class IV	
	OCONUS	CONUS	OCONUS	CONUS
ERL Impact (cm) (50%/LF/TiL)	60/40/20	71/63/50	34/32/13	51/40/32
ABL Friction (lbf)	20/20 NF 1000	20/20 NF 1000	20/20 NF 1000	20/20 NF 1000
BAM Friction (N)	10/10 NF 360	10/10 NF 360	288	10/10 NF 360
*ESD (joules) (50%/LF/TiL)	> 8.0/3.80/1.50	8.37/3.80/1.50	> 8.0	> 8.0
DSC (°C)	228, 286	231, 289	228, 286	228, 288

In general, the testing results from each round-robin site are similar with respect to impact and friction. Some small differences were noted on impact and friction values specifically with the test results between Indian Head and the other two sites Picatinny and China Lake. Indian Head observed impact 50% values of 55 and 46 centimeters (cm) for the two classes (I and IV), whereas, Picatinny and China Lake were in very close agreement with the Class I material (79 and 71cm) and Indian Head and China Lake were in better agreement for the Class IV material (51 to 46cm). Additionally, Indian Head found the BAM friction values to be lower than both Picatinny and China Lake (216 to 324/360 newtons). The ESD results from both Picatinny and Indian Head were in good agreement with respect to the low fire (0.095 j) and the Til (0.037 j), no 50% values were determined. On the other hand China Lake observed a significant difference in the ESD values (order of magnitude) where both classes of material 50% initiation values were above 8.0 joules. At first glance, this would appear to be of great concern in the data, but closer inspection suggests the difference is based on the 'interpretation' of the data. China Lake follows the method protocol called out in AOP-7 2nd edition under the US Mil-Std-1751A category 201.03.002 entitled 'Electrostatic Discharge Sensitivity – NAWC Method'. Under that method the description for a fire is outlined as 'a test sample has a positive result, i.e., flash, spark, burn, odor, or noise other than instrument noise'. Upon discussion with the other sites it was found that they consider a 'hot spot' or 'localized glow' a positive result whereas NAWC does not consider that to be positive.

In comparing the CONUS material to OCONUS the data set used was conducted specifically by NAWC China Lake. For the CONUS material the data set from the round robin was used. For the OCONUS material prior safety and thermal testing data was used. Differences seen in the number of ESD testing shots was a result of using the prior safety data for in-house use. Only the minimum of 0.25 joules is reported as the OCONUS material was not tested beyond that value. As can be seen both FOX-7 material showed no initiation at 0.25 joules and interestingly, the high values reported by China Lake during the round-robin study coincide with the literature value reported by FOI at > 8.0 joules. The impact data suggests that the CONUS material appears to show somewhat better results in sensitivity with 50% values of 71 and 51 for class I and IV compared to 60 and 34 for the OCONUS material. Both materials are insensitive to friction at 1000 pounds of applied force. Overall, the CONUS material is as good or better with respect to safety testing as the OCONUS material. The thermal profiles, measured by DSC, show no anomalies displaying well known decomposition peaks approximately 228 and 288°C.

Conclusion

In summary, the synthesis and scale-up of FOX-7 was performed by the Chemical Scale-up group at NSWC IHEODTD. FOX-7 was successfully scaled up to the kilogram batch. The crude material was successfully recrystallized to access the Class I and Class IV particle sizes. Characterization and safety data acquired at all three sites including NSWC IHEODTD was found to be either in agreement or exceeded that of authentic samples of FOX-7.

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